# Jana2006 Cookbook

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**Solved examples on various topics covered by crystallographic computing system Jana2006. The cookbook cumulates examples from all Jana workshops. The program Jana2006, the latest cookbook and data for examples are available in jana.fzu.cz.**

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# Contents

# Installation notes

**For the workshop, following programs are necessary:**

- **Jana2006 for most tasks**
- **Diamond for plotting crystal structures**
- **Superflip (part of Jana2006 distribution) for solution of phase problem**
- **Vesta for visualization of electron density with isosurfaces and for magnetic structures**
- **PETS for data processing of electron diffraction patterns**
- **ImageJ for viewing graphical output from PETS**

Diamond can be replaced by any other plotting software capable to read CIF in command line. For the workshop we recommend Diamond because the connection with Jana2006 is very well tested.

## Installation of Diamond

Install demo version of Diamond from the directory Setup\Diamond installation in the flash disk.

Copy the licence file "yourlicence.lic" to the same directory where Diamond.exe has been installed. Usually it will be c:\Program files\Diamond 4
*This time limited license has been kindly provided by Crystal Impact for this workshop.*

*Note: Diamond started from Jana2006 may behave differently than when started separately. For instance, it doesn't offer automatic wizards.*

## Installation of Vesta

Unpack the archive "Vesta_2.1.2.zip" from the directory Setup\Vesta to a directory of your choice

## Installation of Jana2006

Execute janainst.msi from the directory Setup\Jana2006 and follow instructions.
*The installation creates shortcut to Jana2006 in the desktop and in Start $\rightarrow$ Programs*

Start Jana2006, go to "Tools $\rightarrow$ About Jana2006" and verify the version string.
*The version date should be close to the workshop date*

- Don't use your "old" preinstalled versions of Jana2006

- Don't use flash disk for calculation. Copy the example files to hard disk.

- Don't install Jana2006 to desktop or flash disk

## Configuration of Jana2006

Start Jana2006
Go to "Tools $\rightarrow$ Preferences", **adjust size of the window** (for instance 60% of the screen height) and font height (about 11 points)
Go to "Tools $\rightarrow$ Programs"; focus with mouse the textbox "Graphic viewer"; press "Browse" and localize Diamond.exe (usually in Program Files x86)
Focus "3d visualization of maps"; press "Browse" and localize VESTA.exe
*(VESTA is needed for examples 9.x, 10.x, 12.x and 13.x)*
For using a different text editor than Notepad define its pathname in the textbox "Editor name".

## Installation of ImageJ (only for electron diffraction)

Install ImageJ from the installer in the directory Setup\ImageJ to a directory of your choice. Use ij148-jdk6-64bit-setup.exe, if you have a 64-bit system. Use ij148-jdk6-setup.exe for a 32-bit system, or if you are not sure.

## Installation of PETS (only for electron diffraction)

Copy the file pets.exe from the directory Setup\PETS to a directory of your choice.

## Add ImageJ and PETS in the system variable PATH:

*Under Windows XP:*

Go to "Start → Settings → Control Panel"

Double click "System"

Go to "Advanced → Environment variables"

In the list "System variables" find and double click "Path"

In the small window that opens, add the full paths to the files ImageJ.exe and pets.exe (without the file names), separated by a semicolon

*Under Windows 7:*

Right click on the Computer icon on your Desktop and choose "Properties → Advanced system settings → Environment variables

In the list "System variables" find and double click "Path"

In the small window that opens, add the full paths to the files ImageJ.exe and pets.exe (without the file names), separated by a semicolon

## Launching PETS:

*PETS must be called with the input file as a command-line argument. There are several ways of launching PETS:*

*Method 1 – the most convenient:*

Locate the file .pts (input to PETS) on your system

Right-click to open context menu

 "Open → Select program from a list → Browse…"

Locate the file pets.exe on your system; Open

Make sure the checkbox next to "Always use the selected program to open this kind of file" is checked

OK

*PETS starts. Next time you want to run PETS, it is sufficient to double click the icon of the pts file you want to run. Unfortunately, this method fails on some systems, notably if the extension pts is already associated with another software.*

*Method 2:*

*Place the shortcut to PETS on Desktop:*

Locate the file pets.exe on your system

Select it and copy it to clipboard (Ctrl+C)

Place cursor on the place on the desktop where you want to place the icon of PETS

Right-click → Paste shortcut

*Now you can run PETS by drag-and-dropping the file .pts on the icon on the desktop. Unfortunately, even this method does not work on all systems.*

*Method 3 – works always:*

Open DOS terminal (Start → All programs → Accessories → Command Prompt)

Move to the directory with the file .pts you want to use (use command cd)

Run PETS by typing "pets filename.pts", where filename.pts is the file you want to use.

## Upgrade of Jana2006 installed from janainst.msi (new way of installation)

Execute janainst.msi and follow instructions. Make sure the installation directory is the same like for the previous version.
*The installation wizard will reinstall Jana2006. For the same version it will offer "Modify – Repair – Remove".*

## Upgrade of Jana2006 installed from janainst.exe (old way of installation)

Previously Jana2006 was installed from the self extracting archive janainst.exe. The user had to define "by hand" the system environment variable JANA2006DIR. The installation from janainst.msi in some cases cannot reinstall Jana2006 installed from janainst.exe.

Start Jana2006 (old installation)
Go to "Tools → About Jana2006" and note the version string.

Start janainst.msi and follow instructions. Make sure the installation directory is the same like for the old version.

Start Jana2006 (new installation)
Go to "Tools → About Jana2006" and verify the version string is new.

### Troubleshooting (for upgrade of Jana2006 installed from janainst.exe)

### 1. Installation from janainst.msi was running without warnings but the version string of Jana2006 remains old

Start janainst.msi again. It will offer "Modify – Repair – Remove". Used "Remove" and uninstall old version of Jana2006.

Start janainst.msi (the third time) and follow instructions. Make sure the installation directory is the same like for the old version.

Start Jana2006 (new installation)
Go to "Tools → About Jana2006" and verify the version string is new.

### 2. Another issues or when method 1 fails

Localize installation directory of Jana2006 and make backup copy of jana2006.ini and jana2006.hst

Delete installation directory of Jana2006

Go to "Start → Settings → Control Panel → System"
Go to page "Advanced"
Press "Environment variables"
Delete all instances of JANA2006DIR in User variables as well as in System variables

Start janainst.msi and follow instructions.

Return files jana2006.hst and jana2006.ini to the installation directory (where jana2006.exe is located)

Start Jana2006 (new installation)
Go to "Tools → About Jana2006" and verify the version string is new.

# Example 1.1: Zn

**Application of Jana2006 to simple 3d structure. Creating jobname, reading input files, determination of symmetry, solving structure with charge flipping, editing of atomic parameters, refinement, hydrogen assignment.**

**Revised: 4 October 2015**

## Chemical formula: $(NH_3CH_2CH_2NH_3)_2ZnCl_6$

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: Zn.hkl, Zn_red.sum
Frame scaling, absorption correction: done with software of diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click Zn
   *Right pane detects possible Jana files and shows one jobname for each group of files*

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction $\rightarrow$ CCD"; NEXT
   Select "Input from "sum" file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   *The program reads 24240 reflections from hkl file*
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *Each line in data repository window corresponds to one data set converted to Jana format.*
   *In our case we use only one data set. Data repository is saved in file Zn.m95.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   *[On the screen: "Tolerances for crystal system recognition".]*
   *Symmetry Wizard can be started separately by "File $\rightarrow$ Reflection file $\rightarrow$ Make space group test.*
   Leave all settings default; NEXT
   *[On the screen: Select Laue symmetry]*
   Select Orthorhombic Laue symmetry; NEXT
   Select primitive unit cell; NEXT
   *[On the screen: Select space group]*
   *The window shows possible space groups.*
   *"Obs/all" column shows for each space group number of reflections which should be*

*systematically extinct. For instance Pbnm has "Obs/all"=2/1677, which means that total number of forbidden reflections is 1677 and two of them violate the extinction rules because they are above the 3σ limit.*

*"Ave(I/sig(I)" lists average ratio I/σ (I) for columns "Obs/all". For Pbnm this means that 1677 forbidden reflections have average I/σ (I) 0.153 and two of them, which violate extinction rules, have average I/σ (I) 4.783.*

*The limits for average ratio I/σ (I) have been defined previously in "Tolerances" window. Space groups exceeding the limits are not shown.*

*For selecting a space group we should look for a case with the highest number of unobserved forbidden reflections having at the same time reasonably low average I/σ (I) for reflections violating the extinction rules. The reason why in our example Pbnm is more likely than Pbmm is that the number of reflections affected by the extinction rules is for the first space group larger by 608 reflections and only two of them have intensity larger than 3 σ (I). The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.*

*Jana2006 does not test data for centre of symmetry. At this point centrosymmetric space group should be preferred unless we would have a strong reason for not using center of symmetry. Thus we select Pbnm and not Pbn21. Centrosymmetry is usually confirmed or denied in following steps by the symmetry analysis of Superflip (see Step 6).*

Select Pbnm; NEXT
Accept the space group in the standard setting, i.e. like Pnma; NEXT
*Symmetry is saved in file Zn.M50.*

5. ***Creating refinement reflection file***
   *In this step program creates file Zn.M90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*
   NEXT to confirm threshold 3sigma; OK; OK (to confirm Informations)
   *[On the screen: settings for merging of reflections]*
   Leave all settings default; NEXT
   *The program reports Rint 3.97% for 1259 observed reflections merged from 12466 observed reflections.*
   Select "Accept the new DatBlock and calculate coverage"; FINISH

6. ***Structure Solution Wizard***
   *[On the screen: Structure solution]*
   *Structure solution wizard can be executed separately through "Run → Solution" or by double clicking the icon Structure solution in the main window.*
   *Jana2006 does not contain solution procedures, it calls external programs. The program used in most our examples is Superflip (using the charge flipping algorithm) because it is automatically installed together with jana2006.*

In "Formula" textbox type list of chemical elements: Zn Cl C N H

*Superflip does not need information about chemical elements but they will be required for peak assignment based on electron density map calculated by Superflip. If Jana2006 is used for peak assignment, a list of expected chemical elements is sufficient information. For other evaluation methods or for the solution using SIR you may need to enter the correct formula and number of formula units.*

Select "Use Superflip"; leave other settings default; press "Run solution"

*[On the screen: window of Superflip replaced after reaching the convergence with listing of Superflip]*

*Superflip converges (after noise suppression) with R value ~15%. This is very good result. The space group suggested from the symmetry search in the direct space electron density map is Pnma, i.e. the same like obtained previously in Jana2006. The low agreement factors at the bottom of the listing indicate good fit of the user-defined symmetry elements (here Pnma) with the resulting electron density map.*

Press CLOSE to leave the listing


7. ***Verification of the structure solution from the structure solution wizard***

   *[On the screen: Structure solution]*

   Press "Draw structure"

   Press "Draw + continue"

   *[On the screen: window of Diamond]*

   Start "Build → Get molecules" or use ⬡ on the bottom toolbar

   Rotate the molecule (⊕ and ↻ on the bottom toolbar) to get an optimal view

   Move mouse pointer over the terminal carbon atoms. Diamond will show the atomic labels.

   Note labels (probably C1,C2) of the terminal carbons.

   *[On the screen: plot of the structure in Diamond]*
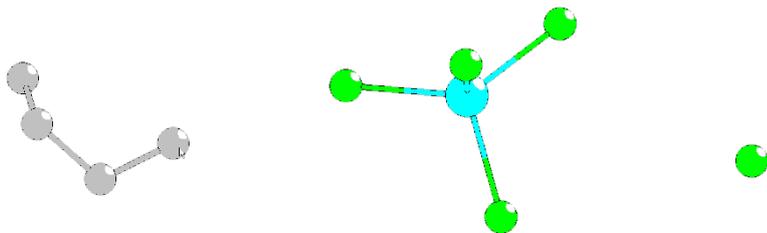
Quit Diamond (without saving changes)

*[On the screen: Structure solution]*

Press "Draw 3d map"

*This button starts Vesta (requires path to Vesta set in Tools → Programs), which plots the electron density found by Superflip*
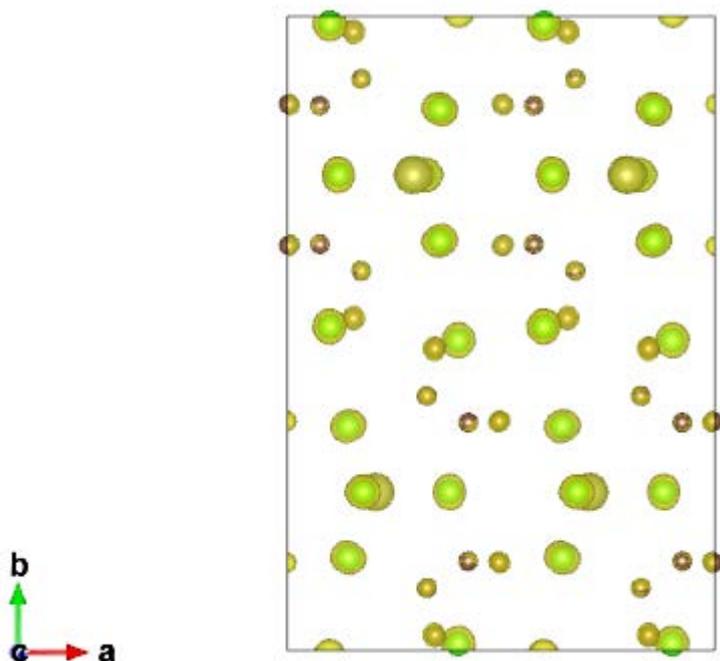


Quit VESTA without saving the plot

Press "Accept last solution". This action will also close the structure solution wizard

8. **Assignment of correct chemical types**

   *[On the screen: basic Jana window]*

   Start EditM50; go to page Composition; enter 4 for "Formula units", press "Formula from M40"

   *It displays formula Zn Cl6 C8 (for Z=4). However, the expected composition (without hydrogens) is Zn Cl6 C4 N4. This means that some nitrogens have been falsely assigned as carbons.The expected chemical formula also suggests that nitrogens should be at the terminal positions of the organic part.*

   *[On the screen: Information about formula]*

   OK; YES for updating the formula.

   *Numbers of elements in the formula are not important for refinement. This information is useful only for interpretation of difference Fourier maps and for creating the final CIF. The chemical types in M40 are defined by their sequence numbers in the chemical formula. Nevertheless, the order of atoms in the formula can be arbitrarily changed if it is done through EditM50. Also new chemical elements can be included in arbitrary position of the*

*formula.*
OK; YES to rewrite M50

Start "Edit atoms"
*[On the screen: list of atoms]*
Select (with Ctrl-left mouse button) the previously noted terminal carbon atoms
*Plotting of the structure can be repeated by "Plot structure" icon*
Start "Action → Edit/define"
Choose "Type" nitrogen; OK
*[On the screen: list of atoms. The labels are still the original ones but the chemical type of two selected atoms is nitrogen]*
Press "Select All"
Press "Action" or right-click on one of the selected atoms
Choose "Rename selected atoms to atom_type + number"
*[On the screen: list of atoms with labels corresponding to chemical types]*
*You should see one zinc, four chlorines, two nitrogens and two carbons.*
Press "Select All"
Press "Action" or right-click on one of the selected atoms
Choose "Make symmetrically contiguous motifs"
*This makes happy editors of Acta E and it is also necessary for using rigid body (later in this Cookbook). The distances between atoms in a motif, typically molecules, can be calculated without applying any symmetry operation except identity.*
OK; YES to save the changes

9. **Refinement**
   *[On the screen: basic window of Jana]*
   Right-click the icon of Refine.
   *[On the screen: refinement options]*
   Define 100 of cycles; OK
   Choose "YES+START"
   *Refinement converges with R value about 6%*
   Start "Edit atoms"
   *[On the screen: list of atoms]*
   Press "Select all" and "Action → Edit/define"
   Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms.* OK, OK, Yes *to save changes*
   Double-click the icon Refine.
   *Refinement converges with R value about 4 % for 73 refined parameters*.

10. **Adding of hydrogen atoms**
    *[On the screen: basic window of Jana]*
    Start "Edit atoms"
    Select carbons and nitrogens
    Start "Action → Adding of hydrogen atoms"
    *[On the screen: Adding of hydrogen atoms dialogue]*
    Leave all settings default; OK
    *The procedure adds automatically C-H hydrogen atoms, while for adding hydrogens to the terminal $NH_3$ groups it goes to the manual mode.*

*[On the screen: Adding of hydrogen atoms to N1]*
For the type of coordination select "Tetrahedral", change number of neighbors to 1
*Using tetrahedral instead of trigonal geometry around nitrogen follows from chemistry. The terminal groups are expected as NH3 because of the charge balance (unlike NH2, they have positive charge).*
*The only neighbor of N1 is C1 (or C2 depending how the maxima were assigned after running Superflip). You can verify this by focusing the textbox with C1(or C2) and starting "Select neighbors"*
Define names of hydrogens, for instance H1N1, H2N1 and H3N1
Start "Locate position in the map"
In the Fourier section window which follows press "Optimal" and "Apply"
*Locating position in the map is not necessary. In most cases, the rotation of $NH_3$ or $CH_3$ group can be refined correctly from the initial positions. However, in our case we want to confirm that there are really NH3 groups and not NH2.*
*[On the screen: Adding of hydrogen atoms to N1]*
"Apply → Go to next"
Repeat the procedure for N2
*[On the screen: list of atoms]*
*Total number of atoms should be 19 (can be verified with Select All).*
*The hydrogens keep in ideal geometry by commands, which can be viewed or edited in*
*"Refinement commands → Various → Keep commands".*
OK to close Atoms-Edit; Yes to save changes
"Plot structure" to check results of hydrogen assignment
*[On the screen: window of Diamond]*
Start "Build → Connectivity" or press button 
*[On the screen: Connectivity dialogue]*
Press "Evaluate" to see which bonds will be used by Diamond
Plot the structure with 
Use  at the bottom toolbar of Diamond to see temperature ellipsoids.
Quit Diamond

*[On the screen: basic window of Jana2006]*
Double-click Refine and refine the final structure
*Refinement converges with R factor 2.5%, goodness of fit 1.9. Number of refined parameters is still 73because the positions of hydrogen atoms are defined geometrically.*

## 11. *Extinction correction*
*The results seem to be very nice, but:*
*[On the screen: basic window of Jana2006]*
Open listing of Refine (by "Edit/View → View of Refine")
Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement"
*R value should decrease with increasing intensity or with lowering the diffraction angle. Here the R value for strongest reflections as well as for the low angle reflections is higher than in the neighboring shell. This suggests that extinction correction is required.*

```
Statistics as a function of sin(th)/lambda and structure factors
sin(th)/lambda
              limits     0.291439  0.368932  0.427538  0.475982  0.512727  0.554318  0.594972  0.658297
              number +         72        85        73        72        68        54        58        47
                     -         85        73        84        86        89       103       100       110
              together        157       158       157       158       157       157       158       157
              av. wd F     7.8512    3.2241    4.6751    5.7601    2.5786    1.1541    0.5997    0.4633
              numerator +    29.5      25.2      28.5      45.9      26.2      13.8      11.7      11.5
                     -      -79.2     -17.9     -20.8     -19.3     -23.6     -28.6     -26.4     -37.2
              together      108.7      43.0      49.4      65.2      49.7      42.5      38.1      48.7
              denominator  4222.5    2785.9    2290.5    1997.1    1815.2    1713.9    1455.6    1453.6
              R factor       2.57      1.54      2.16      3.27      2.74      2.48      2.62      3.35
struct. factors
              limits          5.4       6.9       8.4      10.4      13.0      17.2      25.1     125.1     unobs
              number +         50        55        48        48        62        75       103        88       232
                     -        108       103       109       109        95        82        55        69       367
              together        158       158       157       157       157       157       158       157       599
              av. wd F     3.7948    4.3205    3.2673    1.6940    3.7324    2.0309    2.0832    5.3792    0.2187
              numerator +    28.6      28.4      17.3      10.2      17.5      17.5      30.5      42.2     134.1
                     -      -30.6     -30.1     -34.6     -30.6     -20.2     -20.7     -10.6     -75.7    -195.6
              together       59.2      58.5      52.0      40.7      37.6      38.2      41.2     117.9     329.8
              denominator   692.3     963.0    1202.6    1484.5    1824.6    2353.1    3282.4    5931.9    1465.3
              R factor       8.55      6.07      4.32      2.74      2.06      1.63      1.25      1.99     22.50
```

Close the refinement listing
"Parameters → Extinction"
Select "Isotropic" "Type 1" "Gaussion"; OK
*Refinement of extinction coefficient is enabled by default*

## 12. Final refinement

*[On the screen: basic window of Jana2006]*
Double-click Refine and refine the final structure
*Refinement converges with R factor 2.24%, goodness of fit 1.77, 74 parameters.*
Check the extinction coefficient through "Parameters → Extinction"
View listing of Refine; Go to "Statistics"; check improved R value for strongest reflections.
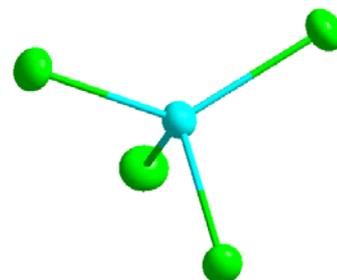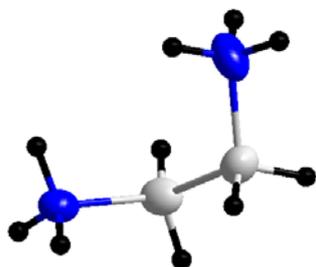


*The resulting structure*

# Example 2.1: PbSO₄

**Simple structure from powder data**

*Revised: 4 October 2015*

## PbSO₄

Powder data measured with laboratory diffractometer
Input files:     PbSO4.mac (powder profile data)
                 PbSO4.txt (additional information)

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click PbSO4

2. *Import Wizard*
   Select "Various CW formats", NEXT
   CW stands for constant wavelength
   Select "MAC format" and "Another/unknown method"; NEXT
   File name is automatically set to"PbSO4.mac".
   Fill cell parameters 8.48 5.4 6.96 90 90 90
   For wavelength type first select Kalpha1/Kalpha2 doublet and then select X-ray tube Cu
   Select "Parallel setting", "Glancing angle" 13.28815, "Perfectness 0.5"; NEXT; FINISH
   Accept the data in Data repository
   Select "Yes, I would like to continue with the wizard"; OK
   At this point Jana2006 offers wizard for determining powder profile parameters, space group and structure. We shall use the wizard but all its tools could be also started separately.

3. *Refinement of the powder profile*
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *Profile viewer shows experimental powder profile*
   Leave profile viewer
   "Edit refinement commands"; set 0 cycles; leave other settings default; OK
   "Run Refine"
   "Show powder profile"
   *Now the profile viewer shows experimental and calculated powder profile.*
   *The calculated profile is based on default profile parameters.*
   *The calculated profile is stored in PbSO4.prf*
   Leave profile viewer
   "Edit profile parameters"
   *[On the screen: Powder options]*
   In "Cell" page select refinement of a, b and c
   In "Profile" page select Cutoff to 12*FWHM; activate refinement of GW;
   In "Corrections" page activate refinement of "shift";

In "Corrections" page select "Legendre polynomials" with 5 terms for background calculation
*Refinement of background terms is enabled by default*
Leave Powder options, save changes
"Edit refinement commands"; set 10 refinement cycles; OK
"Run Refine"
*After 10 refinement cycles Rp~11.4%.*
"Show powder profile"
In Powder profile viewer press "Default" and move close to theta 20°
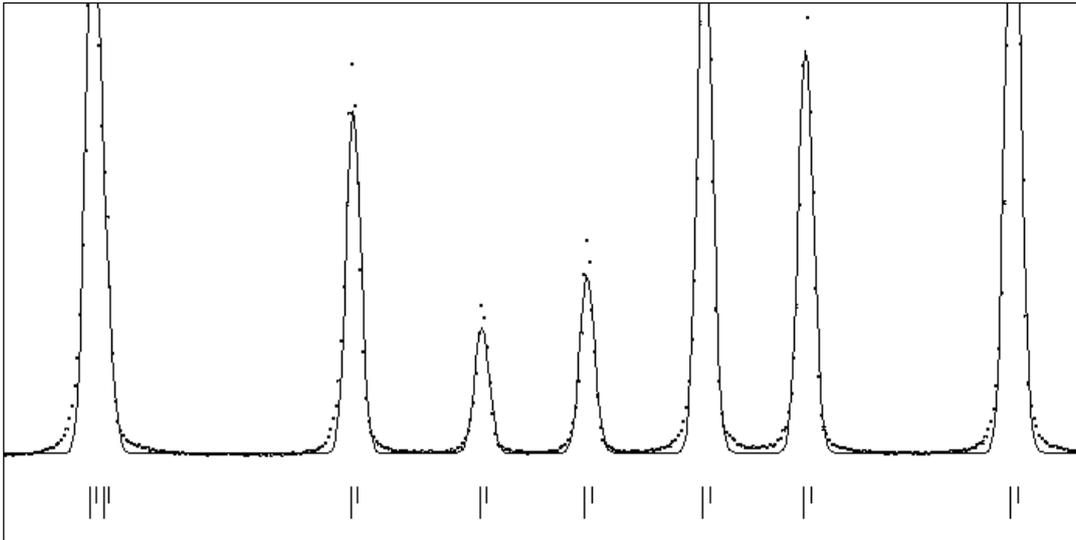


*The observed peaks are systematically broader which may indicate that Lorentzian broadening is to be combined with the Gaussian profiles.*
"Edit profile parameters"
*[On the screen: Powder options]*
In page "Profile" select Pseudo-Voigt and activate refinement of LY;
"Run Refine"
*After10 refinement cycles Rp~8%*
"Show powder profile"
"Edit profile parameters"
*[On the screen: Powder options]*
In page "Profile" activate refinement of LX.
"Run Refine"
*After 10 refinement cycles Rp~6.2%*
"Show powder profile"
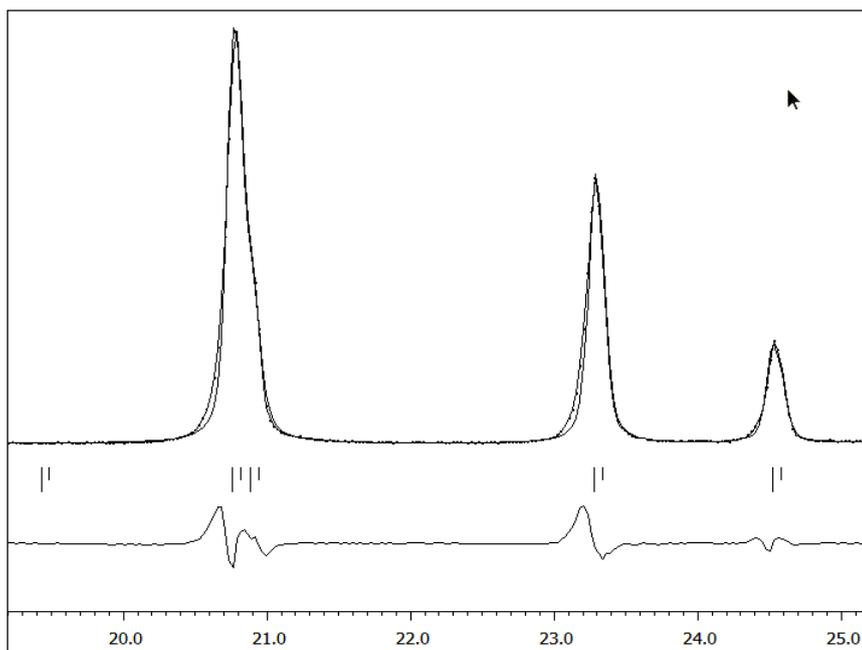
The observed peaks at low angles still have some asymmetry. (Use "X+" and "X-" buttons to see it better)
"Edit profile parameters"
[On the screen: Powder options]
In page "Asymmetry" select the Berar-Baldinozzi correction and activate refinement of asym1, asym2, asym3, asym4;
"Run Refine"
After 10 refinement cycles Rp~5.4%
FINISH; Yes to close the refinement tool; Next


4. *Space group determination*
[On the screen: Tolerances for crystal system recognition]
Use default; NEXT
[On the screen: Select Laue symmetry]
Select the highest one – orthorhombic; NEXT
[On the screen: Select cell centering]
The table shows Rp values calculated for various centering vectors. For instance, when we introduce A centering and discard corresponding extinct Bragg positions, Rp becomes about 30% . This indicates we don't have A centering. In our case no centering is indicated.
Select P centering as it gives much better profile fit; NEXT
[On the screen: Information about progress of space group tests. It takes some time…]
[On the screen: Select space group];
Among the space groups with good profile fit we are looking – in analogy with a single-crystal experiment – for a space group with maximum number of extinct reflections consistent with the experiment. The space groups Pnma and $Pn2_1a$ have good profile fit ($R_p$~5.4%) and the largest ratio of systematically extinct reflections (about 13%). We shall select the centrosymmetric one.
Select space group *Pnma*; NEXT
[On the screen: Final step of the space group test];

Accept the space group transformed into the original cell; FINISH
NO to refine profile parameters once more.

5. **Structure solution**

   *[On the screen: Structure solution]*
   *This part of wizard can be also started separately by  "Run → Solution"*
   Type formula Pb S O4; Formula units 4
   Select "Use Superflip"
   Check "Repeat Superflip until the convergence is detected"
   Set "Maxcycles" to 1000



Press "Run solution" to start Superflip
*Jana makes LeBail decomposition and then it starts Superflip.*
*Superflip confirms space group Pnma*
Close listing of Superflip; "Draw structure"; "Draw+continue".

*For plotting with Diamond use button* ⊕ *at the bottom toolbar and plot only Pb and S. In Build → Connectivity adjust limits for S-O distances. The complete  coordination of Pb and S with* ◉ *.*
*The sulphur atom should be coordinated by four oxygen atoms. But as the structure contains one very heavy atom it may happen that some of O atoms are missing or that the solution contains some spurious peaks or that SO$_4$ tetrahedron is incomplete.*
**If the structure model looks strange you may repeat the solution step with "Run → Structure solution".** *Superflip starts from random phases and its results can be different.*

Press "Accept last solution". This action will also close the structure solution wizard.

6. **Refinement of the structure**

*[On the screen: basic window of Jana]*
Open refinement options (by the right-click on the icon of Refine).
*[On the screen: refinement options]*
Uncheck "Make only profile matching", OK, Yes+start
Wait for convergence and open the listing. (You can access the listing of Refine also by "Edit/View → View of Refine")
*It may happen that Refinement fails. In such case use "Tools → Recover files" and repeat Structure solution. Superflip starts from random phases and may return better result in the next attempt.*
Press "Go to" and select "Changes overview":



*At the beginning of "Changes overview" there will be probably list of spurious atoms automatically excluded from the refinement as their ADP is larger than the allowed limit. In this example this is O4. The excluded atoms are still present in M40 file with zero occupation. In order to delete them:*
Run "Edit atoms", press "Select rejected"
Press the button Action and delete them; OK
Start EditM50, select page "Composition" and press "Formula from M40". It should display "Pb S O4".

7. ***Completing the structure***
*In the case that some of oxygen atoms are still missing they can be localized from the difference Fourier.*
*If your structure is complete (EditM50 displays correct formula) but you would like to try this part, please start "Edit Atoms", delete some oxygen and repeat refinement to prepare proper input for Fourier calculation)*
Right-click on the Fourier icon opens the command editing procedure for Fourier.
Select "F(obs)-F(calc) – difference Fourier"; OK; Start the program;
Answer "Yes" to start the procedure for including atoms.
*[On the screen: Inserting/replacing atoms]*
*The program transforms each found maximum to various symmetry equivalent positions where it is close to some already existing atoms. In this dialogue we choose that the right panel will show only atoms with distance to some (transformed) Fourier maximum between 1 and 3 Å. By selecting such line we select the maximum and it corresponding symmetry transformation.*

**Inserting/replacing of atoms**

☑ Skip peaks being too close to existing atoms

Minimal distance     [ 1 ]   Angs.

Show distances up to   [ 3 ]   Angs.

Include all missing atoms, i.e. the maxima with large enough charge and reasonable distance to some of already existing atoms; FINISH

*It may happen there are no such maxima*

Verify the added maxima with plotting tool.

Verify the formula with "Editm50 → Composition → Formula from M40"

Repeat refinement (in case of changes)

*Refinement should converge with Rp around 6.7%, GOF 1.8 and structure R factor around 3.5%.*

"Edit/View → View of Refine"; GoTo; List of serious warnings

*This list should be empty. This means for instance that ADP are positive definite.*
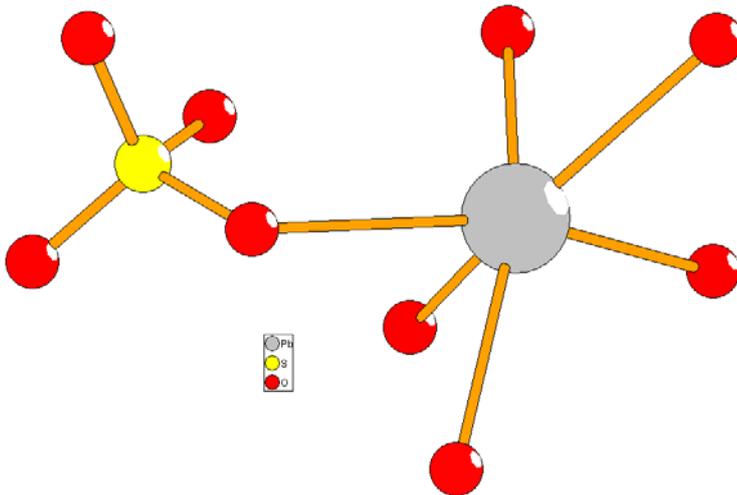


*The resulting structure*

```
R factors : [384=381+3/17]
R(obs)=   3.49    wR(obs)=   4.04    R(all)=   3.54    wR(all)=   4.05
==============================================
Profile R factors :[5769/16+17],   Damping factor:  1.0000
GOF  = 1.79 Rp  = 6.69 wRp   = 8.83
Last wRp: 8.83
Maximum change/s.u. :  -0.0070 for b
```

*The resulting R values*

# Example 2.2: Y₂O₃

**Le Bail refinement against powder data with strong asymmetry of peaks**
**Revised: 4 October 2015**

Powder data measured with laboratory diffractometer experimental setup with Johannson-type monochromator and transmission mode in asymmetric Guinier type arrangement.

Input files:  Y2O3-icsd.cif (crystal structure from data base)
Y2O3.dat (powder diffraction data)

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click Y2O3

2. *Import procedure*
   Select "Structure: from CIF"; NEXT
   *[On the screen: Select input CIF file]*
   Select "Y2O3-icsd.cif"; OK
   *[On the screen: "CIF file does not contain any reflection block"]*
   Answer "Yes" to the question: "Do you want to import data from file?"
   *[On the screen: Specify type of the file to be imported]*
   Select "Powder data: various CW formats" (CW = constant wavelength); NEXT
   *[On the screen: Powder data from:]*
   Select "Riet7 formats"; NEXT
   *[On the screen: Complete/correct experimental parameters]*
   For wavelength type use "X-ray tube" Cu, Kalpha1/Kalpha2 doublet deselected and wavelength 1.54051
   Select "Parallel setting", "Glancing angle" 13.6409 (CuK$_\alpha$, Ge[111]) "Perfectness 1"; NEXT; FINISH
   Accept the data in Data repository

3. *Refinement of the powder profile*
   *[On the screen: Basic Jana window]*
   Start "Edit profile"
   *[On the screen: Powder options]*
   In "Cell" page select refinement of the parameter a
   In "Profile" page select Cutoff to 12*FWHM; activate refinement of GW
   In "Corrections" page activate refinement of "shift"
   In "Corrections" page select "Legendre polynomials" with 5 terms for background calculation
   *Refinement of background terms is enabled by default*
   Leave Powder options, save changes
   *[On the screen: Basic Jana window]*
   Right click on the Refine icon;

Check "Make only profile matching";
Keep default values for another parameters; OK;
*[On the screen: Do you want to save new command?]*
Select Yes+start
*Refinement converges in 10 cycles to Rp~7.7%*
Start "Profile viewer"
*[On the screen: Jana 2006 profile viewer]*
Press "X exactly" and select the 2θ interval from 19 to 35.
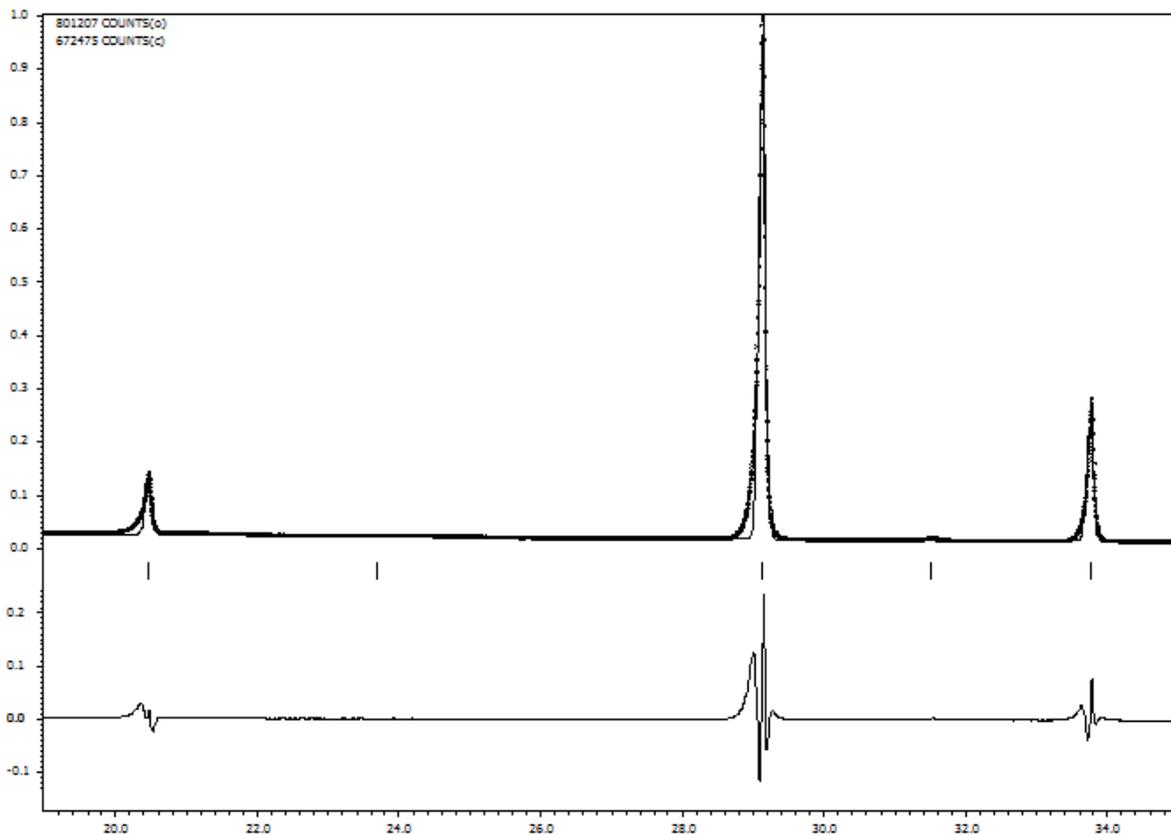


*The observed peaks are systematically broader which can indicate that Lorentzian broadening is to be combined with the Gaussian profiles.*
Start "Edit profile"
*[On the screen: Powder options]*
In page "Profile" select Pseudo-Voigt and activate refinement of LY; OK
Yes to rewrite changes
Start refinement (icon Refine)
*Refinement converges in 10 cycles to Rp=7.1%*
Start "Edit profile"
*[On the screen: Powder options]*
In page "Profile" activate refinement of GU; OK
Yes to rewrite changes
Start refinement (icon Refine)
*Refinement converges in 10 cycles to Rp~7.0%*
Start "Profile viewer"
*[On the screen: Jana 2006 profile viewer]*
Press "X exactly" and select the 2θ interval from 19 to 35.
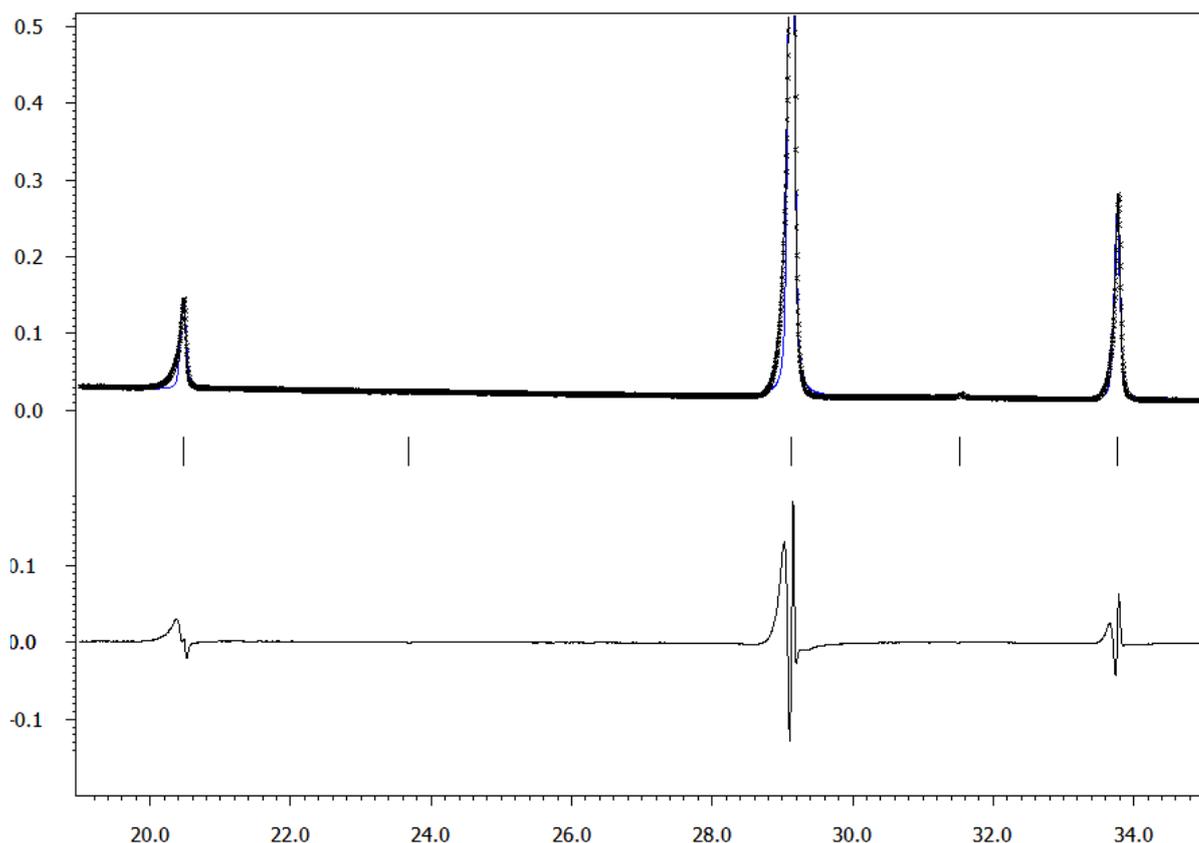
The experimental peaks have very strong asymmetry which is not explained by the profile model.

4. **Asymmetry correction by the Simpson's model**

*[On the screen: Basic Jana window]*

*In order to save the basic refinement result for testing of all different asymmetry models a new structure will be opened:*

Start "File → Structure → Save As"

*[On the screen: File manager for saving structure]*

In File manager focus the right-bottom textbox and define a name for testing of the Simpson's model, for instance "Y2O3-Simpson"; OK

Yes to continue with the new structure

*[On the screen: Basic Jana window]*

Start "Edit profile"

*[On the screen: Powder options]*

In page "Asymmetry" select "Simpson", use the default value and activate refinement of the "asym1" parameter; OK;

Yes to rewrite changed files

*[On the screen: Basic Jana window]*

Double-click the icon Refine.

*Refinement converges in 10 cycles to Rp~6.1%*

Start "Profile viewer"

*[On the screen: Jana 2006 profile viewer]*

Press "X exactly" and select the 2θ interval from 19 to 35.
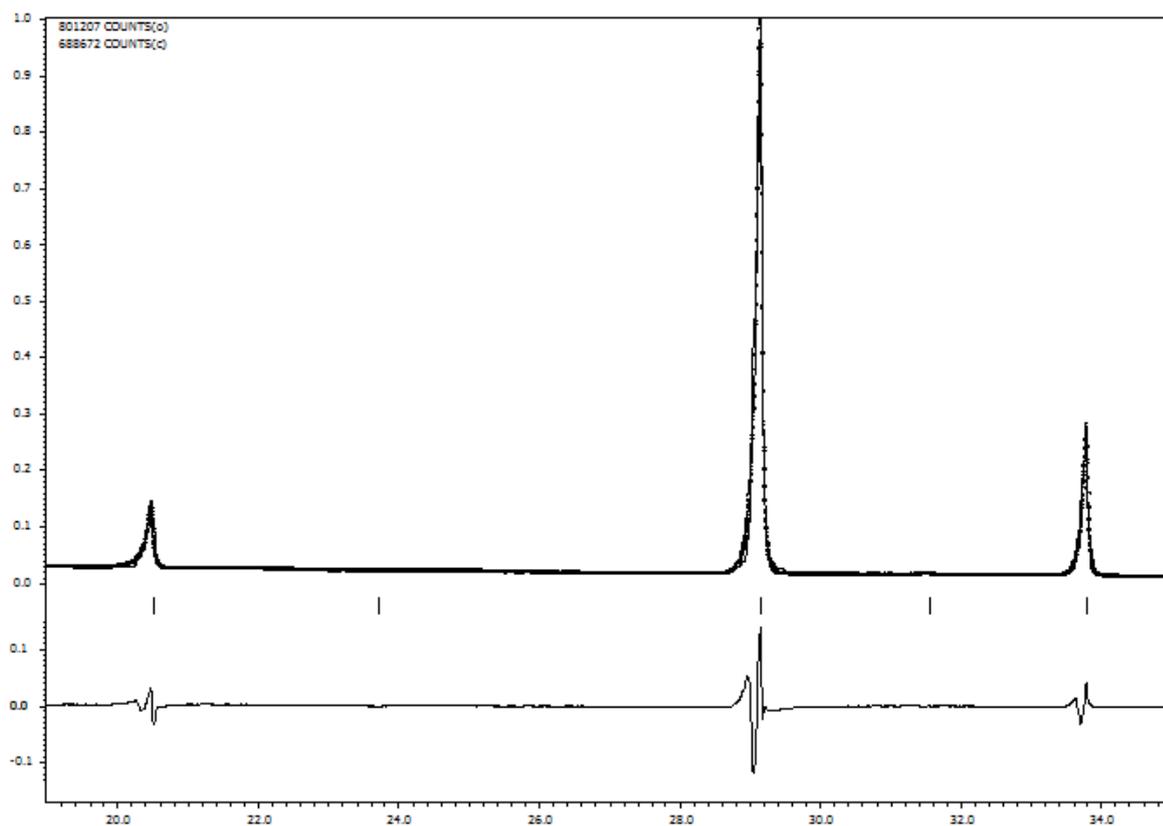
*The Simpson's model improves considerably the profile fit. But some discrepancies due to asymmetry are still visible.*

5. **Asymmetry by Berar-Baldinozzi**
   *[On the screen: Basic Jana window]*
   Start "File → Structure → History"
   *[On the screen: History]*
   Select the original structure Y2O3; OK
   *[On the screen: Basic Jana window]*
   Start "File → Structure → Save As"
   *[On the screen: File manager for saving structure]*
   In File manager focus the right-bottom textbox and define a name for testing of the Berar-Baldinozzi model i.e. "Y2O3-BB"; OK
   Yes to continue with the new structure
   *[On the screen: Basic Jana window]*
   Start "Edit profile"
   *[On the screen: Powder options]*
   In page "Asymmetry" select "Berar-Baldinozzi", use the default value and activate refinement of the asym1, asym2, asym3 and asym4 parameters; OK;
   Yes to rewrite changed files
   *[On the screen: Basic Jana window]*
   Start "Refine commands" (right-click on the icon "Refine")
   In page "Basic" set 100 refinement cycles and Damping factor 0.3
   OK; YES+START to save commands and start refinement.
   *Refinement converges after many cycles to Rp~5.8%*
   Start "Profile viewer"

*[On the screen: Jana 2006 profile viewer]*
Press "X exactly" and select the 2θ interval from 19 to 35.
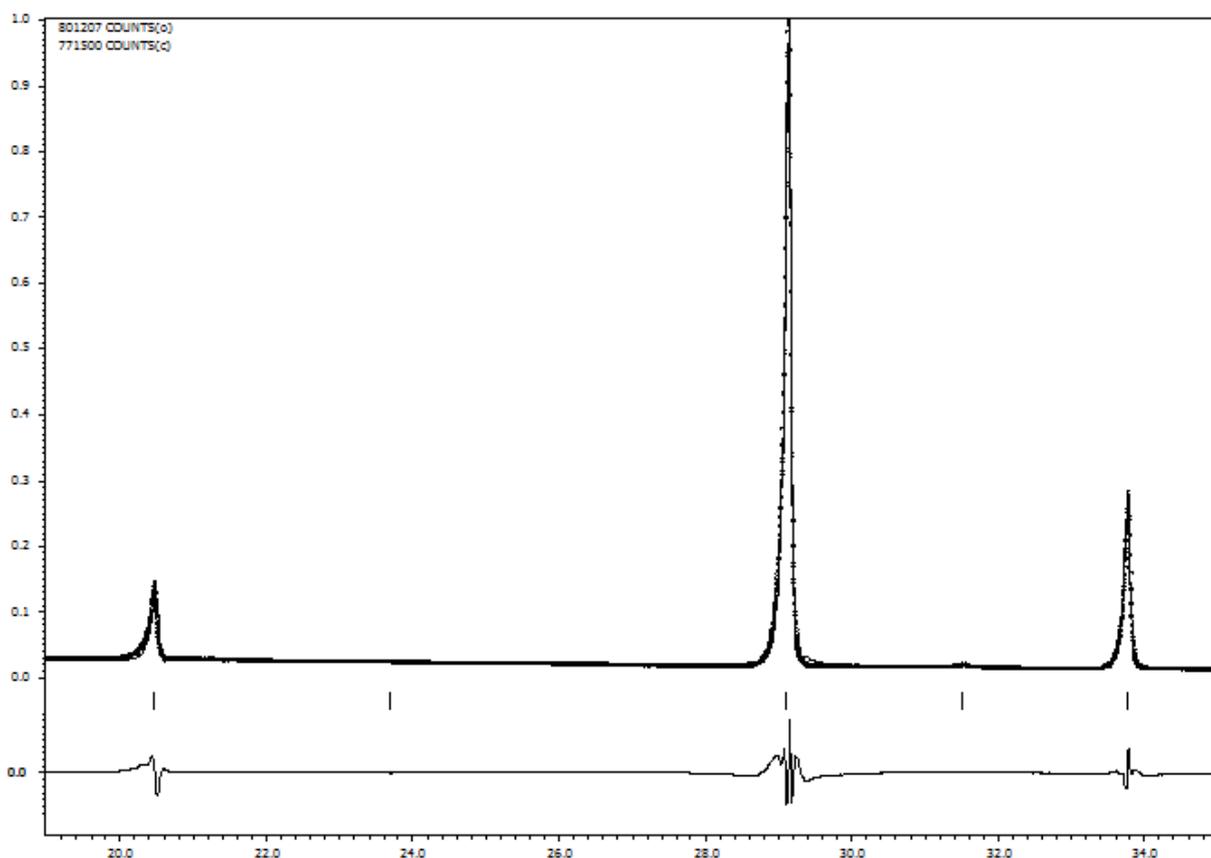


*The fit is even better than for the previous method but the number of asymmetry parameters is now four.*

6. ***Asymmetry by axial divergence***
   ***(Finger, Cox, Jephcoat, J.Appl.Cryst.(1994). 24, 892-900)***
   *[On the screen: Basic Jana window]*
   Start "File → Structure → History"
   *[On the screen: History]*
   Select the original structure Y2O3; OK
   *[On the screen: Basic Jana window]*
   Start "File → Structure → Save As"
   *[On the screen: File manager for saving structure]*
   In File manager focus the right-bottom textbox and define a name for testing of the axial divergence correction i.e. "Y2O3-FCJ"; OK
   Yes to continue with the new structure
   *[On the screen: Basic Jana window]*
   Start "Edit profile"
   *[On the screen: Powder options]*
   In page "Asymmetry" select "correction by divergence", use the default value and activate refinement of the HpS/L and HmS/L parameters; OK;
   Yes to rewrite changed files
   *[On the screen: Basic Jana window]*
   Right-click the icon Refine

*[On the screen: Refine commands]*

In page "Basic" set 30 refinement cycles and Damping factor 0.5

OK; Yes+start to save the changes and start refinement

*Refinement reaches after 20 cycles  Rp~4.8%*

*Open the refinement listing. (You can access the listing of Refine also by "Edit/View → View of Refine")*.

*Press "Go to" and select "Changes overview":*
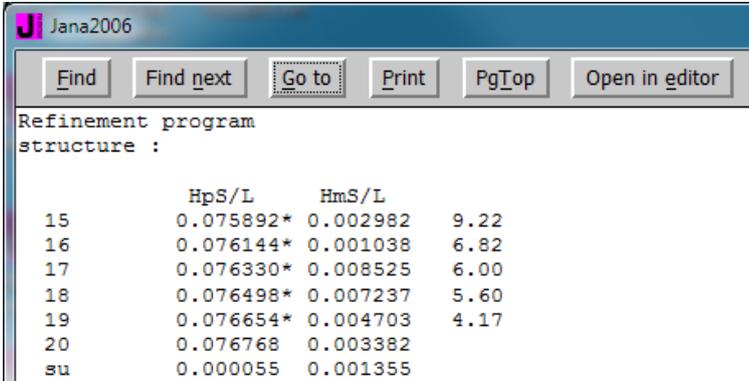


| | HpS/L | HmS/L | |
|----|----------|----------|------|
| 15 | 0.075892* | 0.002982 | 9.22 |
| 16 | 0.076144* | 0.001038 | 6.82 |
| 17 | 0.076330* | 0.008525 | 6.00 |
| 18 | 0.076498* | 0.007237 | 5.60 |
| 19 | 0.076654* | 0.004703 | 4.17 |
| 20 | 0.076768 | 0.003382 | |
| su | 0.000055 | 0.001355 | |

*The parameter HmS/L oscillates , within three times the standard uncertainty, about zero which induces instability in the refinement. For this reason, we can change it to zero and keep it fixed.*

Start "Edit profile"

In page "Asymmetry" set HmS/L to zero and unselect it; OK;

*Refinement reaches after 20 cycles  Rp~4.9%*

Start "Profile viewer"

*[On the screen: Jana 2006 profile viewer]*

Press "X exactly" and select the 2θ interval from 19 to 35.
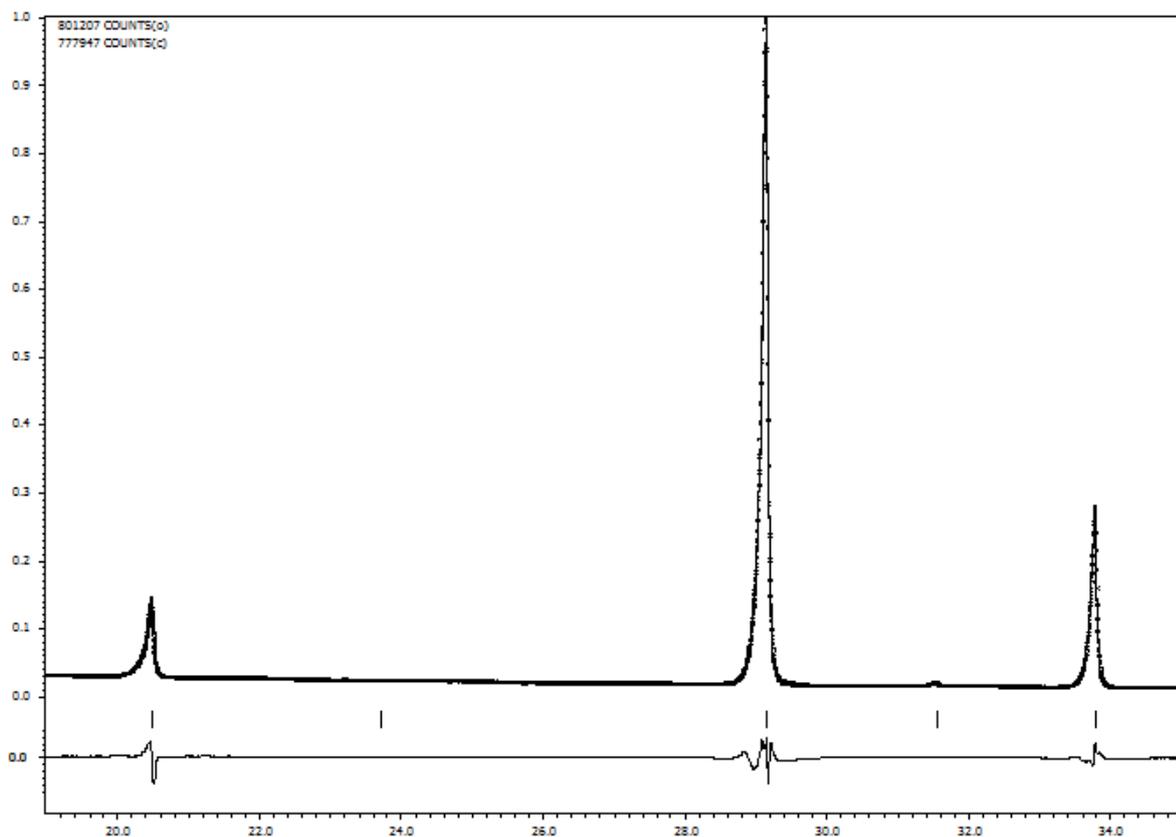
*With only one additional free parameter the fit is significantly better than for the previous methods.*

*In Jana2006 there is also implemented the fundamental approach following closely the approach described by Cheary and Coelho [J. Appl. Cryst. (1998). 31, 851-861; J. Appl. Cryst. (1998). 31, 862-868]. This method was not applied in our example because it was developed for Bragg-Brentano geometry.*

# Example 2.3.1: MagCag

**Solution of simple organometallic structure from powder data**

**Revised: 4 October 2015**

Powder data measured with diffractometer Empyrean (PANalytical) using CuKα radiation, focusing mirror and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

Input files: magcag.xrdml with powder profile
Additional information:
unit cell 9.19 21.38 8.12 90 113.78 90
composition $Mg_2\ O_{20}\ H_{80}\ Br_4\ N_{16}\ C_{28}$
Expected chemical scheme:
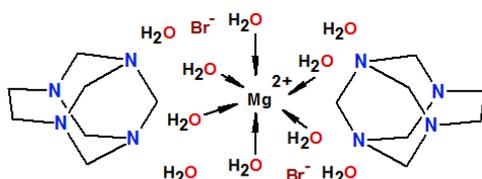


1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click magcag

2. *Import procedure*
   Select "Powder data – various CW formats"; NEXT
   *[On the screen: Powder data form]*
   Select "PANalytical XRDML"
   For method select "Debye-Scherrer"
   *[On the screen: Complete/correct experimental parameters]*
   Fill cell parameters 9.19 21.38 8.12 90 113.78 90
   Check the radiation (should be interpreted from the xrdml file as Copper with doublet):

NEXT; FINISH; OK to close data repository; YES to accept the data set

*[On the screen: question how to continue]*

Select "Yes, I would like to continue with the wizard"; OK

*The typical steps for refinement of powder profile will be offered in the wizard. However, all steps can be also done separately from the basic window of Jana2006.*

3. **Refinement of the powder profile**

   *[On the screen: refinement of the powder profile by the le Bail algorithm]*

   Press "Show powder profile" – just to see how it looks like

   Press "Default" to see more details

   Quit powder viewer

   Press "Edit profile parameters"

   *Unlike for structure parameters, refinement keys of profile parameters are not set automatically*

   In page "Cell" activate refinement of a,b,c,beta

   In page "Profile" activate refinement of GW

   In page "Corrections" activate refinement of "shift";

   Change number of Legendre terms for background to 30;

   OK; Yes to rewrite

   Press "Edit refinement commands"

   Set 100 refinement cycles and Damping factor

   OK

   Press "Run Refine"

   *Refinement of profile slowly converges to the profile R value Rp~3.4% and GOF ~ 7.5. Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile viewer.*

   In page "Profile" activate refinement of GV

   OK, YES to save changes

   Run several cycles of Refine

   *Refinement of profile slowly converges to the profile R value Rp~3.0% and GOF ~ 7.0*

   *For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*

   "Show Powder profile"

   *The calculated profile fits quite well with the experimental one but some profiles are too narrow, especially for low angles*

   Quit profile viewer

   "Edit profile parameters"

   In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt" , activate refinement of LX and LY

   OK, YES to save changes

   "Run Refine"

   *Refinement of profile slowly converges to the profile R value Rp~1.6% and GOF ~4.2.*

   "Show Powder profile"

   Enlarge the profile and investigate details of the fit between the calculated and experimental profile*.*

   *We are especially interesting whether asymmetry of peaks has been correctly described. Not*

*correctly described asymmetry can be found for low angle reflections:*
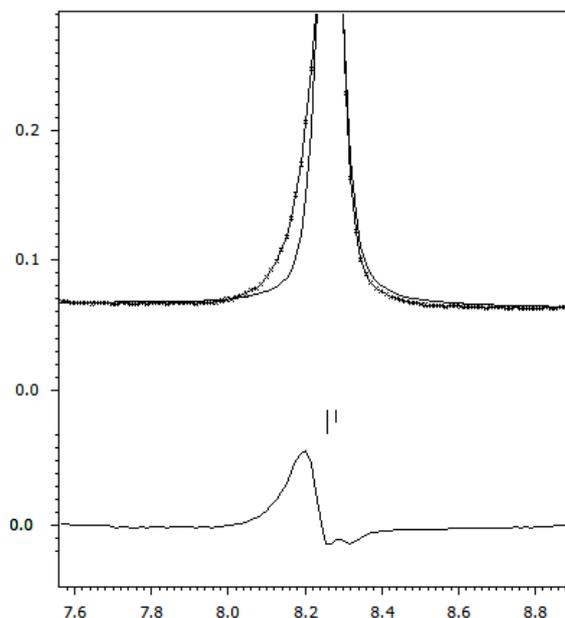


"Edit profile parameters"
In page "Asymmetry/Diffractometer" select "correction by divergence"
Activate refinement of "HpS/L", set HmS/L to zero and do not refine it
OK; YES to save changes

"Run Refine"
*Refinement of profile slowly converges to the profile R value Rp=1.4 and GOF ~3.0.*
"Show Powder profile"
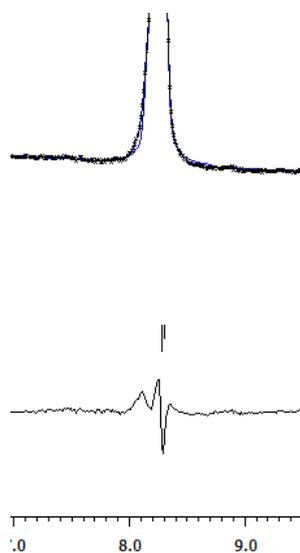


*Description of asymmetry seems to be better than before*
Quit the profile viewer
Press "Save As" and **make a backup copy** of the structure
FINISH to close the Powder wizard

### 4. Space group determination

*[On the screen: Tolerances for crystal system recognition]*
Use default; NEXT
*[On the screen: Select Laue symmetry]*
Select the highest one – monoclinic; NEXT
*[On the screen: Select cell centering]*
Select P centering as it gives the best profile fit; NEXT
*[On the screen: Select space group]*
Select space group *P21/a*; NEXT
*[On the screen: Final step of the space group test]*;
Accept the space group transformed into the original cell; FINISH
YES to refine profile parameters once more.
*This new profile refinement uses only independent Bragg reflections compatible with P21/a. The results are almost the same like for P-1 but calculation taking into the account the symmetry is faster.*

### 5. Structure solution

*[On the screen: information that the solution wizard will start]*
*OK*
*Type formula* Mg O10 H40 Br2 N8 C14; *Formula units 2*
*Select "Use Superflip"*
*Check "Repeat Superflip: Number of runs" and choose 10 runs*
*With this setting Superflip will run ten times and a solution with the best fit will be used*
*OK*
*The agreement factors of the symmetry printed at the bottom of the Superflip listing will be between 10-20, indicating rather worse fit for the screw axis.*
Press the button "Draw structure"
*The initial structure model should display octahedrally coordinated Mg located in one of inversion centers, isolated Br, two oxygens of the water molecules, a fragment of the $N_4C_7$ cage and probably some false maxima. For instance:*
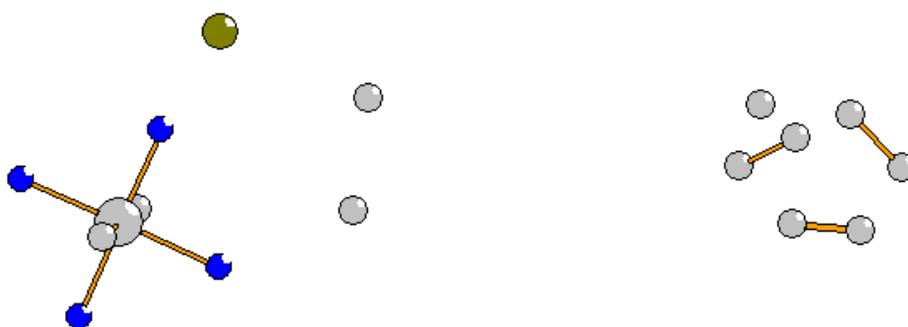


Press button "Accept last solution"
Start File → Structure → Save as and make a backup copy

### 6. Completing structure without hydrogen atoms

*In this part the task is to finalize the $N_4C_7$ cage from the difference Fourier.*

*Rietveld refinement with initial structure model could destroy profile parameters:*
Start Parameters → Powder
Clear refinement keys for all refined powder parameters in page "Cell", "Profile", "Asymmetry/Diffractometer" and "Corrections"

*The stability of the structure model refined with powder data requires binding together ADP parameters of some atoms and keeping them isotropic. For instance, carbon and nitrogen atoms will all have the same isotropic ADP.*
Plot the structure and note atoms around Mg
Start "Edit atoms";
change the atoms around Mg to oxygen O1, O2, O3;
change all other atoms except Br and Mg to carbon.
Start Refinement options, page "Various"
Start "Restrictions" and define:
The same ADP for O*
The same ADP for C*

*Be careful not to make by mistake identical their coordinates*

restric O* 12
restric C* 12
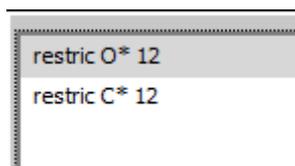
OK;

In page Basic change number of refinement cycles to 100 and damping factor to 0.5
Clear "Disable atoms having too large isotropic ADP parameter"
Clear "Make only profile matching"
OK; Yes+Start
*Rietveld refinement slowly converges with Robs=9%, Rp=6%, and GOF=13.*
***The numbers are only indicative!***
*In case of oscillations, note the label of the oscillating atom. Plot the structure and try to identify and delete false maxima. In case of troubles, repeat charge flipping.*
Change ADP of Br to anisotropic and repeat refinement
*Br is slightly disordered and it can be described with an ellipsoid even from powder data*
For isolated carbon atoms out of the fragment of the cage change their chemical type to oxygen
Repeat refinement
*Two of the isolated positions will be oxygens of water. The others will probably move to the cage during the refinement.*
Start Fourier option
In the page "Basic" define "F(obs)-F(calc) – difference Fourier)
OK; YES+START
OK to start procedure for including new atoms
*The charge of difference maxima will be extremely low comparing with single crystal*

*diffraction, however some of them will be carbon or nitrogen atoms. It is advisable to plot the maxima before refinement and to delete any strange position as false maxima.*

Repeat refinement

Repeat plotting and deleting false maxima

Repeat difference Fourier

Repeat adding of atoms

*Finally, the structure will be completed like this:*
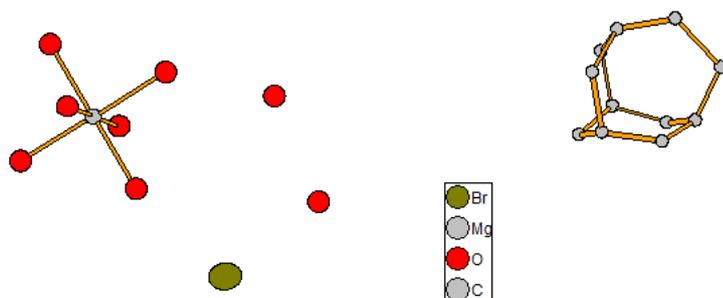


*Rietveld refinement converges with Robs~3.6%, Rp~2.8%, and GOF~6.3.*

*ADP of carbon atoms of the cage may be negative at this stage*

*In the cage the atoms with three bonds are nitrogens.*

Start "Edit atoms" and correct chemical types of the cage

Start Refinement options and add a restriction nitrogen atoms to have the same ADP:



Run refinement

*Rietveld refinement converges with Robs~3.2%, Rp~2.4%, and GOF~5.2.*

*At this point ADP of nitrogens should be positive while ADP of carbons may still be close to zero*

Start "Edit atoms"

Add hydrogen atoms to carbons of the cage (automatic mode)

Run refinement

*Rietveld refinement converges with Robs~3.2%, Rp~2.5%, and GOF~5.4.These value are slightly worse than in the previous step but ADP of carbon atoms become positive*

Start File → Structure → Save As and make a **backup copy**

Start Parameters → Powder

Activate refinement of all powder parameters which were fixed before starting with the Rietveld refinement

Run refinement

*Rietveld refinement converges with almost the same Robs, Rp and GOF.*
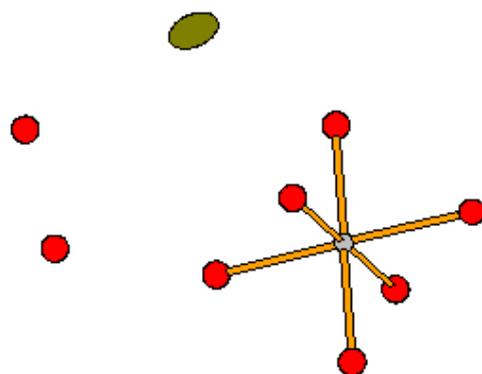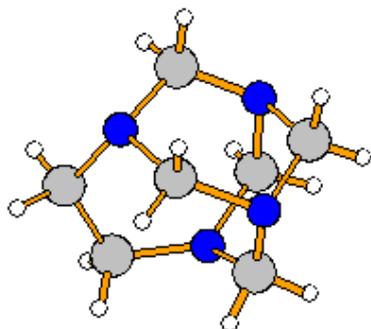
*All oxygen atoms belong to water. In order to include scattering power of hydrogen atoms without adding them explicitly, their occupancy must be refined.*
Activate refinement of occupancy of O1
Start refinement options, page "Various"
Start "Equations" and define the following equations:

equation : ai[o2]=ai[o1]

equation : ai[o3]=ai[o1]

equation : ai[o4]=ai[o1]

equation : ai[o5]=ai[o1]

Run refinement
*Rietveld refinement converges with Robs~2.5%, Rp~2.0%, and GOF~4.0.These value are significantly better.*

*Oxygen atoms of water, which is not coordinated to Mg, may have different ADP*
Start refinement options, page Various
Start  "Restrictions"
Delete the restriction for O*
Define separately the same ADP for O1, O2, O3 and for O4, O5:

restric O1 12 O2 O3

restric O4 12 O5

Run refinement
*The results are almost the same. Visual inspection of the powder profile shows good fit between the calculated and observed lines.*

# Example 2.3.2: MagCag

**Preparation of the rigid body template in M45**

**Revised: 4 March 2015**

The purpose of this example is to prepare a template of the cage $C_7N_4H_{14}$, which will be used for the solution of the example 2.3.3 as a rigid body. The template will be defined in the file M45 and used in solution of the example 2.3.3.

The preparation of M45 has no special support in the current version of Jana2006. Part of the job must be done with a text editor.

In the following steps we shall use the CSD structure HICTOD and we shall prepare two versions of the cage: with C1 symmetry and Cs symmetry.

Input files: HICTOD.cif from the CSD database

Expected chemical scheme:
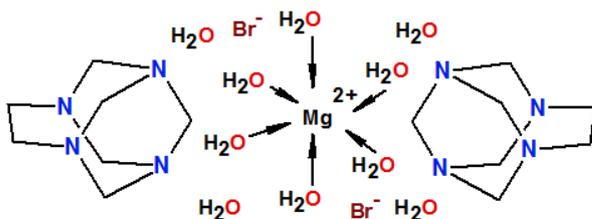


1. ***Reading structure from CIF***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory the input file
   Right pane: double-click HICTOD
   *[On the screen: Specify type of the file to be imported]*
   Select : Structure → From CIF; NEXT
   Select: HICTOD.CIF
   NO to import data

2. ***Deleting symmetry equivalent atoms***
   *It happens with some CSD CIF files that symmetry equivalent atoms are also present, which leads to their multiple occurrences when symmetry is applied. In the next step, we shall delete these atoms*
   Start "Edit Atoms"
   Select atoms ending with "g" and "d"
   Start "Action → Delete selected atoms"
   OK; YES to save changes

### 3. Getting the cage from HICTOD

Start "Plot structure"; "Draw + continue"

Use ⚏ , ⊞ and ✛ to plot atoms from M40

Use Picture → Viewing direction → c

Use ⬜ to display the unit cell

Use ⬡ to complete the fragments

Now the cage is clearly visible

The atoms of the cage are symmetry related by a mirror plane at y=0.25

Press Undo, to see again only the symmetry independent atoms

Select atoms (symmetry independent) not belonging the cage

Using the right mouse button activate ploting of their labels; note the labels

Quit Diamond and return to Jana

Start "Edit Atoms"

Delete the atoms not belonging to the cage; OK; YES to rewrite changes

Start "Plot structure" and verify that only atoms of the cage are present

Return to Jana

### 4. Transformations

*M45 templates contain information about the point group symmetry. The axis c is used as the unique axis of the point group. For this reason the unit cell taken from CSD must be transformed in order to get the mirror plane of the cage perpendicular to c and located at z=0. Moreover, all atoms of the cage (not only symmetry independent atoms) must be present in the template.*

Start "Tools → Transformations → Origin shift"

Move the origin to point 0, 0.25, 0

*Now the mirror plane of the cage is located at y=0 (can be verified in M40)*

Start "Edit Atoms"

Press "Select all"

Start "Action → Expand selected atoms"

Press "Next matrix" ; "Fill by a symmetry operation"

Select "x, -y, z"; OK;

OK; OK; YES to rewrite changes

Start "EditM50"

Change symmetry to P1; OK; YES to rewrite M50

Start "Edit Atoms"

Press "Select all"

Start "Action → Merge selected atoms"; use default merging distance;

*The program merges 7 atoms, resulting in 25 atoms of the cage*

Start "Tools → Transformations → Cell transformation"

Press "by a matrix"

Define transformation matrix -1 0 0 / 0 0 1 / 0 1 0

OK; OK; select "rewrite the old structure"; OK

Start "Edit Atoms"

Press "Select all"

Start "Action → Transform selected atoms"

Use unit transformation matrix and translation vector 1, 0, 0

*This transforms the x coordinates back to the unit cell*

Start "Plot structure"; "Draw + continue"

Use ⬡ , ⬡ and ✛ to plot atoms from M40

Use Picture → Viewing direction → b

Use ⬜ and ✛ to display the unit cell

*This shows the resulting cage of 25 atoms with mirror plane located at z=0*
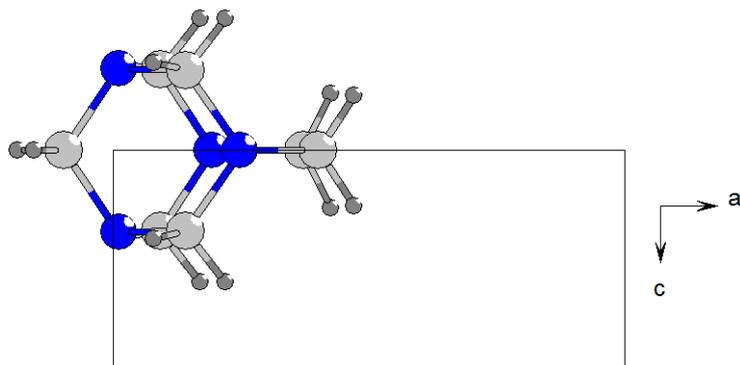


5.  **Labels**

Quit Diamond

Start "Edit Atoms"

Double-click the first atom

Using "Define" and "Edit" page change the suffix to "m" if z=0, "1" if z<0 and "2" if z>0

Arrows close to the "List" button can be used to move between atoms in the editing mode

*Renaming can also be done in a text editor (Edit/View → Edit of M40 file).*

*The resulting labels will have "m" for atoms at the mirror plane, "1" for atoms below the mirror plane and "2" for atoms above the mirror plane. The suffixes "1" and "2" resulted from the previous expansion by the mirror plane.*
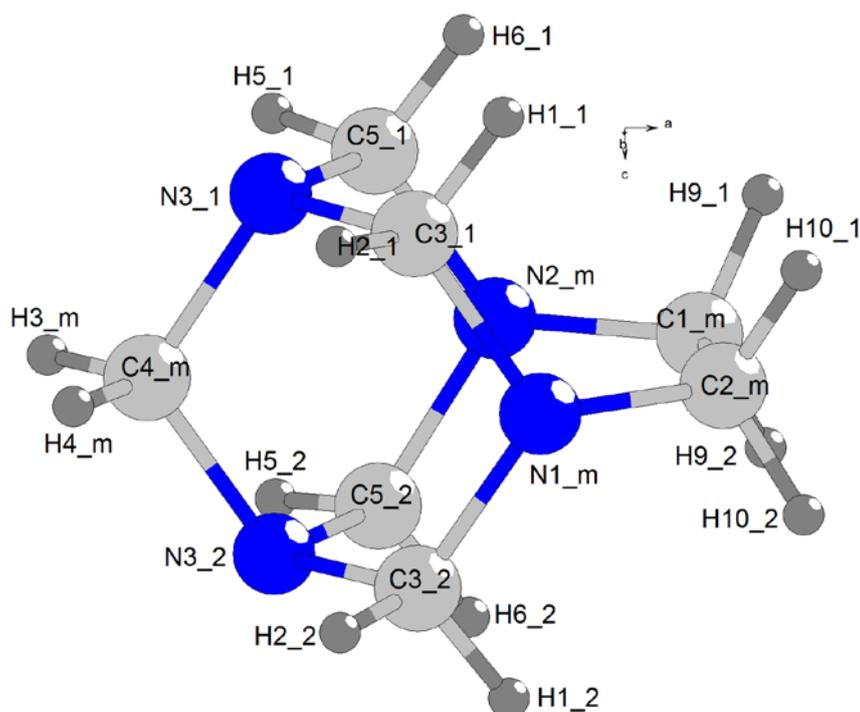
**6. Text editor**

Quit Diamond and Jana
Copy M40 to Magcag-symmC1.m45
Open Magcag-symmC1.m45 in a text editor
Delete five header lines
Delete the s.u. block
Delete every second line (i.e. the lines without atom label)
Add two spaces and "0" at the end of each line
Add the following header lines:
"cell 7.585 10.837 16.065 90 90 90" (this can be copied from M50)
"pgroup C1"
"scdist C-C 1.52"
Save the file and quit the editor.

*This is the resulting file Magcag-symmC1.m45:*

```
cell 7.585 10.837 16.065 90 90 90
pgroup C1
scdist C-C 1.52
N1_m       3  1     1.000000 0.250500 0.132420 0.000000  0
N2_m       3  1     1.000000 0.194100-0.129200 0.000000  0
N3_1       3  1     1.000000 0.011590 0.024260-0.075730  0
N3_2       3  1     1.000000 0.011590 0.024260 0.075730  0
C1_m       1  1     1.000000 0.373700-0.084900 0.000000  0
C2_m       1  1     1.000000 0.403100 0.054200 0.000000  0
C3_1       1  1     1.000000 0.142500 0.125210-0.074590  0
C3_2       1  1     1.000000 0.142500 0.125210 0.074590  0
H1_1       2  1     1.000000 0.219800 0.115500-0.122300  0
H1_2       2  1     1.000000 0.219800 0.115500 0.122300  0
H2_1       2  1     1.000000 0.080600 0.202900-0.081200  0
H2_2       2  1     1.000000 0.080600 0.202900 0.081200  0
C4_m       1  1     1.000000-0.095500 0.035800 0.000000  0
H3_m       2  1     1.000000-0.185600-0.027800 0.000000  0
H4_m       2  1     1.000000-0.154200 0.115300 0.000000  0
C5_1       1  1     1.000000 0.093300-0.099710-0.074750  0
C5_2       1  1     1.000000 0.093300-0.099710 0.074750  0
H5_1       2  1     1.000000 0.000900-0.160900-0.081200  0
H5_2       2  1     1.000000 0.000900-0.160900 0.081200  0
H6_1       2  1     1.000000 0.170800-0.106700-0.122500  0
H6_2       2  1     1.000000 0.170800-0.106700 0.122500  0
H9_2       2  1     1.000000 0.427000-0.121100 0.053300  0
H9_1       2  1     1.000000 0.427000-0.121100-0.053300  0
H10_2      2  1     1.000000 0.473000 0.074000 0.051500  0
H10_1      2  1     1.000000 0.473000 0.074000-0.051500  0
```

*The keyword scdist is used for scaling of the complete object using arbitrary number described with arbitrary identifier (without spaces). In our case the identifier is "C-C" and the number is a typical C-C distance in the cage. But the identifier could be also "scale" and the number could be 100.*
*Each line except header lines contains the following items: label, number of chemical type (indicates that chemical types are different - they will be specified during application of the rigid body in Jana2006), unused, site occupancy, x, y, z, symmetry identifier (0 means symmetry independent with respect to the used point group).*

Copy Magcag-symmC1.m45 to Magcag-symmCs.m45
Open Magcag-symmCs.m45 in a text editor
Replace the point group C1 with Cs
For atoms with the suffix "1", i.e. those with z<0, replace "0" at the end of each line with "1". This indicates the atoms are symmetry dependent
For atoms with the suffix "m" change the site occupancy to 0.5, because they are located at mirror plane

*This is the resulting file Magcag-symmCs.m45:*

```
cell 7.585 10.837 16.065 90 90 90
pgroup Cs
scdist C-C 1.52
N1_m     3 1     0.500000 0.250500 0.132420 0.000000  0
N2_m     3 1     0.500000 0.194100-0.129200 0.000000  0
N3_1     3 1     1.000000 0.011590 0.024260-0.075730  1
N3_2     3 1     1.000000 0.011590 0.024260 0.075730  0
C1_m     1 1     0.500000 0.373700-0.084900 0.000000  0
C2_m     1 1     0.500000 0.403100 0.054200 0.000000  0
C3_1     1 1     1.000000 0.142500 0.125210-0.074590  1
C3_2     1 1     1.000000 0.142500 0.125210 0.074590  0
H1_1     2 1     1.000000 0.219800 0.115500-0.122300  1
H1_2     2 1     1.000000 0.219800 0.115500 0.122300  0
H2_1     2 1     1.000000 0.080600 0.202900-0.081200  1
H2_2     2 1     1.000000 0.080600 0.202900 0.081200  0
C4_m     1 1     0.500000-0.095500 0.035800 0.000000  0
H3_m     2 1     0.500000-0.185600-0.027800 0.000000  0
H4_m     2 1     0.500000-0.154200 0.115300 0.000000  0
C5_1     1 1     1.000000 0.093300-0.099710-0.074750  1
C5_2     1 1     1.000000 0.093300-0.099710 0.074750  0
H5_1     2 1     1.000000 0.000900-0.160900-0.081200  1
H5_2     2 1     1.000000 0.000900-0.160900 0.081200  0
H6_1     2 1     1.000000 0.170800-0.106700-0.122500  1
H6_2     2 1     1.000000 0.170800-0.106700 0.122500  0
H9_2     2 1     1.000000 0.427000-0.121100 0.053300  0
H9_1     2 1     1.000000 0.427000-0.121100-0.053300  1
H10_2    2 1     1.000000 0.473000 0.074000 0.051500  0
H10_1    2 1     1.000000 0.473000 0.074000-0.051500  1
```

*The created templates, Magcag-symmC1.m45 and Magcag-symmCs.m45, could be accompanied with plots in jpeg format, Magcag-symmC1.jpg and Magcag-symmCs.jpg. In our example we don't need them.*

# Example 2.3.3: MagCag

**Solution of simple organometallic structure from powder data, using the rigid body template from M45**

**Revised: 4 October 2015**

Powder data measured with diffractometer Empyrean (PANalytical) using CuKα radiation, focusing mirror and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

Input files: magcag.xrdml with powder profile
Magcag-symmC1.m45 and Magcag-symmCs.m45: rigid body templates prepared in Example 2.3.2
Additional information:
unit cell 9.19 21.38 8.12 90 113.78 90
Expected scheme:
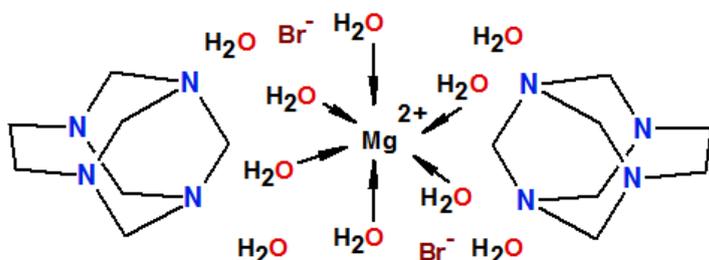


1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click magcag

2. ***Import procedure***
   Select "Powder data – various CW formats"; NEXT
   *[On the screen: Powder data form]*
   Select "PANalytical XRDML"
   For method select "Debye-Scherrer"
   *[On the screen: Complete/correct experimental parameters]*
   Fill cell parameters
   Check the radiation (should be interpreted from the xrdml file as Copper with doublet):

NEXT; FINISH; OK to close data repository; YES to accept the data set
*[On the screen: question how to continue]*
Select "Yes, I would like to continue with the wizard"; OK
*The typical steps for refinement of powder profile will be offered in the wizard. However, all steps can be also done separately from the basic window of Jana2006.*

3. ***Refinement of the powder profile***
   *[On the screen: refinement of the powder profile by the le Bail algorithm]*
   Press "Show powder profile"
   Press "Default" to see more details
   Press "Create new" to create a manual background
   *[On the screen: Options for generating background profile]*
   For "Number of manual background points" set 60
   OK; Quit powder viewer
   *[On the screen: A manual background has been created]*
   Select "Accept the new background" and "Reset polynomial coefficients to zero"
   *The manual background was created because with this data background calculated with Legendre polynomials would not be correct for high angle reflections.(For detail see example 2.4 – PFPhenyl)*
   Press "Edit profile parameters"
   In page "Profile" activate refinement of GW
   *Unlike for structure parameters, refinement keys of profile parameters are not set automatically*
   In page Corrections:
   Set 30 for "Number of terms" of Legendre polynomials
   *Polynomial background will be refined in addition to the manual one*
   Activate refinement of "shift";
   OK; Yes to rewrite
   Press "Edit refinement commands"
   Set 100 refinement cycles
   OK
   Press "Run Refine"
   *Refinement of profile slowly converges to the profile R value Rp~2.9% and GOF ~ 7.3. Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile  viewer.*
   "Show Powder profile"; "Default"

Move the slider towards low angles; "Fit Y"

*The calculated profile fits quite well with the experimental one but some profiles are too narrow, especially for low angles*

Quit profile viewer

"Edit profile parameters"

In page "Cell" activate refinement of a,b,c,beta

In page "Profile" activate refinement of GV

OK, YES to save changes

Run several cycles of Refine

*Refinement of profile slowly converges to the profile R value Rp~2.8% and GOF ~ 7*

*For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*

In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt" , activate refinement of LX and LY

OK, YES to save changes

"Run Refine"

*In case of oscillations press "Parameters" (during the refinement) and change "Damping factor" to 0.5*

*Refinement of profile slowly converges to the profile R value Rp~1.7% and GOF ~4.3.*

"Show Powder profile"

Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

*We are especially interesting whether asymmetry of peaks has been correctly described. Not correctly described asymmetry can be found for  low angle reflections:*
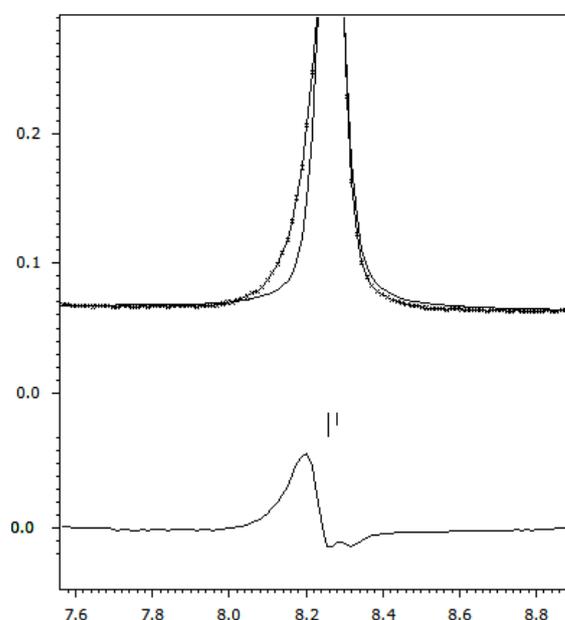


"Edit profile parameters"

In page "Asymmetry/Diffractometer" select "correction by divergence"

Activate refinement of "HpS/L" (do not refine HmS/L)

"Run Refine"

*Refinement of profile slowly converges to the profile R value Rp=1.4% and GOF ~3.1.* "Show Powder profile"

*The description of asymmetry for the low angle peak is considerably improved:*



Quit the profile viewer
Press "Save As" and **make a backup copy** of the structure
FINISH to close the Powder wizard

4. **Space group determination**
[On the screen: Tolerances for crystal system recognition]
Use default; NEXT
[On the screen: Select Laue symmetry]
Select the highest one – monoclinic; NEXT
[On the screen: Select cell centering]
Select P centering as it gives the best profile fit; NEXT
[On the screen: Select space group]
Select space group *P21/a*; NEXT
[On the screen: Final step of the space group test];
Accept the space group transformed into the original cell; FINISH
YES to refine profile parameters once more.
*This new profile refinement uses only independent Bragg reflections compatible with P21/a. The results are almost the same like for P-1 but calculation taking into the account the symmetry is faster.*

5. **Structure solution**
[On the screen: information that the solution wizard will start]
OK
Type formula Mg O10 H40 Br2 N8 C14; Formula units 2
Select "Use Superflip"
Check "Repeat Superflip: Number of runs" and choose 10 runs
*With this setting Superflip will run ten times and a solution with best R value will be used*
"Run Solution"
*In case that Superflip does not converge interrupt the calculation, discard the results and repeat it. It will start from a new set of random phases and the result may be different. The agreement factors of the symmetry printed at the bottom of the Superflip listing will be between 10-20, indicating rather worse fit for the screw axis.*

Press the button "Draw structure"

*The initial structure model contains octahedrally coordinated Mg located in one of inversion centers, isolated Br, two oxygens of the water molecules, a fragment of the $N_4C_7$ cage and probably some false maxima. For instance:*
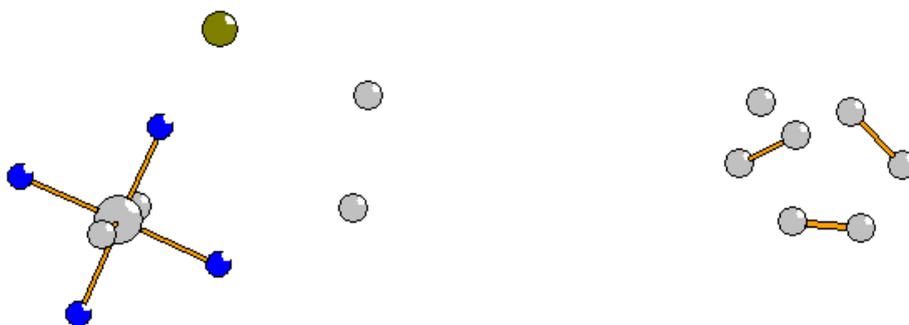
Press button "Accept last solution"

## 6. Preparation of the starting Rietveld refinement

Start "Edit atoms" and change chemical types of atoms coordinated to Mg to oxygen
Change to oxygen also the two carbon atoms, which are in fact lattice water molecules
Rename the changed atoms according to their chemical types
OK; YES to save changes
Start "Refine commads"; go to page "Basic"
Set 100 refinement cycles with Damping factor 0.1
Uncheck "Make only profile matching"
OK; YES to save changes without starting refinement
Start "Edit profile"
Fix all profile parameters: a, b, c, beta, GW, GP, LX, LY, HpS/L, shift
*This means that only Legendre background will be refined*
OK, YES to save changes
Start File → Structure → Save as and **make a backup copy** named "start"

## 7. Completing the cage

Start "Refine commands"; go to page "Various"
Press "Fixed commands"
Fix all parameters for O* Mg* Br*; OK
Press "Restrictions"
Restrict ADP of C* to be the same; OK
*Be careful not to restrict coordinates!*
OK; YES+Start
*During refinement you may change damping from 0.1 to 0.5*
*Refinement converges with R~11%, Rp~10%, GOF~23*
Run difference Fourier, YES to start procedure for inserting atoms
Insert new maxima in reasonable distances to the atoms of the cage
Repeat refinement
Repeat difference Fourier and inserting of maxima until 11 carbon atoms is present

*"Reasonable distance" should not be taken too strictly for Fourier maxima from powder data*
*Refinement converges with R~5%, Rp~4%, GOF~8*
Start File → Structure → Save as and make a backup copy named "cage_atomic"

8. ***Placing the cage template with point group symmetry C1***
Start "Plot structure"

Using the button ⊞ plot the atoms of the cage and ensure they make a symmetry contiguous motif. If not, return to Jana, start Edit atoms and put C* to symmetry contiguous motif. Otherwise placing of the molecule will not work.
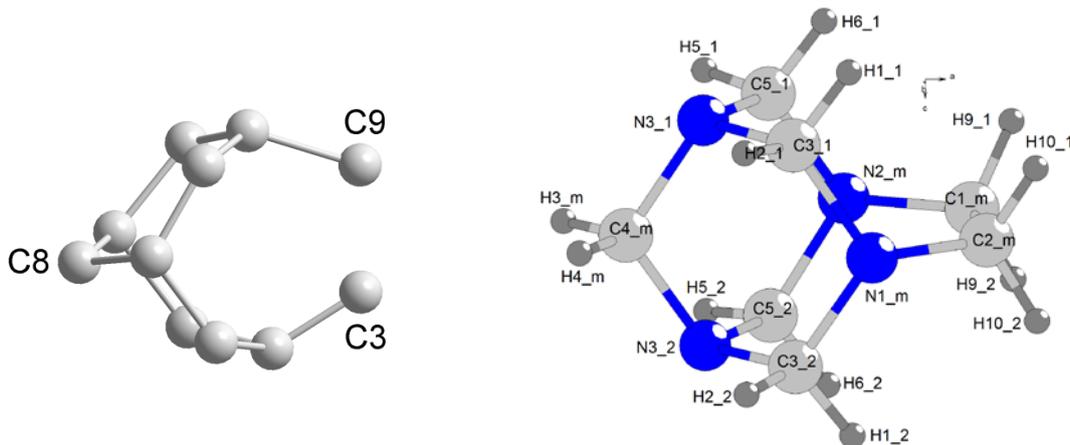


Plot the cage and compare with the template prepared in the previous example. Probably C9 corresponds to C1_m; C3 corresponds to C2_m; C8 corresponds to C4_m (**your labels can be different!**)
Return to Jana2006
Start "Parameters → Molecules → New molecule"
*[On the screen: Atoms of the new molecule from:"]*
Select "Model file"
For name of the molecule type "kage"
*We need a name not starting with C, N, O, B, H and M*
For "Model name" browse for "Magcag-symmC1.m45" created in the previous example
Keep the scaling distance unchanged
*"Show the model molecule" is disabled because we don't have Magcag-symmC1.jpg*
NEXT
*[On the screen: Specify atomic types in the model molecule]*
Do not change the suggested atomic types; NEXT
*[On the screen: Define the molecular reference point]*
Select "Explicit"
In "Reference point" textbox type N1_m
*The reference point should be some atom from the mirror plane in order to reflect the symmetry of the molecule. Such atoms in the model molecule have suffix _m (see Example 2.3.2)*
NEXT
*[On the screen: Define and complete molecular position #1]*
For the pairs "model atoms" – "actual positions" choose c1_m and C9; C2_m and C3; C4_m and C8 (**with actual names** taken previously from Diamond)

For "Maximal coincidence distance" type 0.5

*The coincidence ration should be 11/25 but it depends on the previous refinement*

Try to adjust the coincidence distance to reach 11 coinciding carbons.

*If carbons of the model molecule coincide e.g. with oxygens this means that the cage has been positioned incorrectly, probably because the carbon atoms in the atomic part do not form a symmetry contiguous motif.*

Press "Apply+End"

Start "Edit atoms"

Ensure that the atomic part does not contain carbon atoms.

OK, YES to save changes

Start "Plot structure"

*The structure with the cage should look like this (depending which carbon positions were used for placing the cage):*
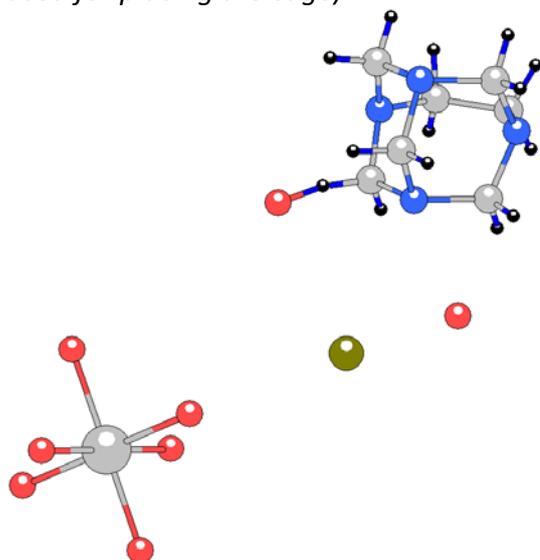


*In this example one water oxygen is too close to the cage but it may change during the refinement*

Return to Jana2006

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Fix "all parameters" for C*, H*, N* (i.e. for atoms of the cage)

*Because the molecule is called "kage", the wild character C* does not include the molecule and therefore molecular parameters (rotations and translation of the cage), will not be fixed.*

OK; OK; YES+START to save changes and start refinement

*During refinement you may change damping from 0.1 to 0.5*

*After many cycles refinement converges with R~4.5%, Rp~4%, GOF~9*

Start "Plot structure"

*The cage should be now in better position, i.e. without short distances to lattice water*

9. **Refinement of Mg, O and Br**

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Disable or delete the "fixed all" commands for Mg* O* Br*

OK

Go to page "Equations" and define the following equations:

equation : ai[o2]=ai[o1]

equation : ai[o3]=ai[o1]

equation : ai[o4]=ai[o1]

equation : ai[o5]=ai[o1]

*All oxygens belong to water; refinement of their occupancy mimics the missing hydrogens*
OK
Go to page "Various", press "restrictions"
Define the same ADP for all oxygen atoms (O*); OK
*Be careful not to make identical coordinates!*
OK; YES to save commands without starting Refine
Start "Edit atoms"
Set harmonic ADP for Br1
*This works because Br is slightly disordered*
Activate refinement of occupancy (ai) of O1
OK, YES to save changes
Start "Refine"
*The refinement converges with R~3%, Rp~2.3%, GOF~5*


**10. *Refinement of atoms of the cage***
Start "Edit atoms"
Select all carbon atoms of the cage (blue carbons)
Press "Action → Adding of hydrogen atoms"
*This procedure will not add hydrogens, because they are already present, but it will introduce Keep commands necessary for fixing of their geometry*
OK; YES to save changes
Start "Refine commads"; go to page "Various"
Press "Restrictions"
Define the same ADP for all nitrogen atoms (N*)
*Be careful not to make identical coordinates!*
OK
Press "Fixed commands"
Disable or delete the "fixed all" command for C* N* H*
OK; go to page Basic
Set "Damping factor" 0.1
OK; YES+START
*The refinement converges with R~2.8%, Rp~2.1%, GOF~4.3*
Start "Plot structure" verify the structure

*Final plot:*
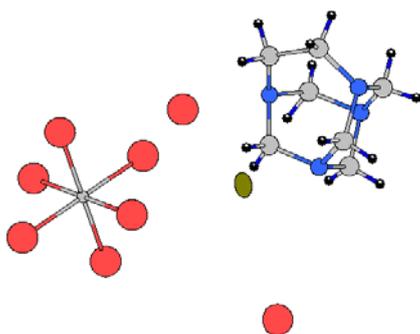
**Make backup copy**

## 11. *Placing the cage template with point group symmetry Cs*

*Now we shall test how the cage with Cs point symmetry would fit*

Start "Edit atoms"

Select the model molecule (blue atoms)

Start "Action → Atoms from molecule to atomic part"

OK; YES to rewrite changes

*The molecule had only one actual position and therefore this atomic structure model is equivalent with the previous one*

Start "Refine"

*R values must be the same like with the molecule*

*Now we shall place the template Cs in such a way that it coincides with the cage present in the atomic part*

*This is the template how it was created in the example 2.3.2:*
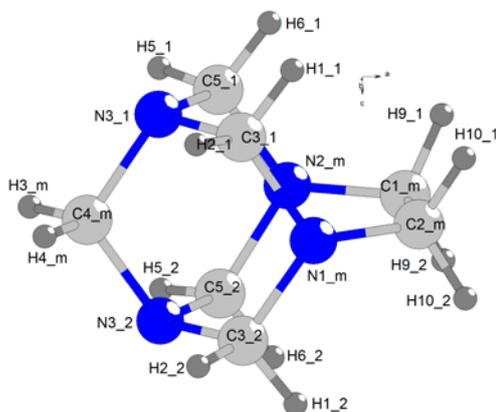


Start "Plot structure" and try to orient your cage similarly. Make use of the fact that there is only one C-C bond in the cage.
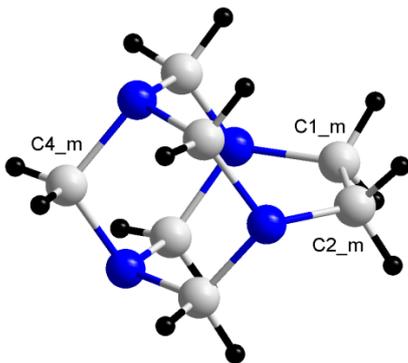
*From the comparison we can see which pairs of atoms should be used for placing the molecule*

Return to Jana2006

Start "Parameters → Molecule → New molecule"

*[On the screen: Atoms of the new molecule from:"]*

Select "Model file"

For name of the molecule type "kage"

For "Model name" browse for "Magcag-symmCs.m45" created in the previous example

Keep the scaling distance unchanged

*"Show the model molecule" is disabled because we don't have Magcag-symmC1.jpg*

NEXT

*[On the screen: Specify atomic types in the model molecule]*

Do not change the defaults atomic types; NEXT

*[On the screen: Define the molecular reference point]*

Select "Explicit"

In "Reference point" textbox type N1_m

*This should be some atom from the mirror plane*

NEXT

*[On the screen: Define and complete molecular position #1]*

For the pairs "model atoms" – "actual positions" type the three previously noted pairs

For "Maximal coincidence distance" type 0.6

Press "Show coinciding atoms"

*We should see the complete coincidence 25/25 and the coinciding atoms should have the same chemical types.*

| | Individual atomic positions | | | distance | to |
|---|---|---|---|---|---|
| N1_m | 0.773704 | 0.617148 | 0.286488 | 0.068 | N2_m |
| N2_m | 0.915984 | 0.683329 | 0.081966 | 0.058 | N3_2 |
| N3_1 | 0.819658 | 0.573639 | 0.028719 | 0.000 | N3_1 |
| N3_2 | 1.046434 | 0.599749 | 0.305107 | 0.020 | N1_m |
| C1_m | 0.812606 | 0.717724 | 0.144220 | 0.116 | C5_2 |
| C2_m | 0.737231 | 0.682379 | 0.252867 | 0.125 | C1_m |
| C3_1 | 0.715574 | 0.577568 | 0.127447 | 0.047 | C5_1 |
| C3_2 | 0.938936 | 0.603285 | 0.399674 | 0.044 | C2_m |
| H1_1 | 0.612403 | 0.593090 | 0.045690 | 0.509 | H6_1 |
| H1_2 | 0.978634 | 0.635256 | 0.492042 | 0.139 | H10_1 |
| H2_1 | 0.700096 | 0.535685 | 0.163343 | 0.595 | H5_1 |
| H2_2 | 0.943252 | 0.563681 | 0.459695 | 0.031 | H10_2 |
| C4_m | 0.977860 | 0.554390 | 0.158135 | 0.137 | C3_1 |
| H3_m | 1.048065 | 0.549993 | 0.096007 | 0.233 | H1_1 |

Ok

| | Individual atomic positions | | | distance | to |
|---|---|---|---|---|---|
| H4_m | 0.969985 | 0.513941 | 0.207965 | 0.215 | H2_1 |
| C5_1 | 0.837987 | 0.634247 | -0.048792 | 0.083 | C4_m |
| C5_2 | 1.061828 | 0.660019 | 0.224019 | 0.040 | C3_2 |
| H5_1 | 0.898539 | 0.627373 | -0.121264 | 0.076 | H4_m |
| H5_2 | 1.141694 | 0.655369 | 0.175087 | 0.047 | H2_2 |
| H6_1 | 0.733458 | 0.648971 | -0.128558 | 0.118 | H3_m |
| H6_2 | 1.100287 | 0.691206 | 0.318524 | 0.054 | H1_2 |
| H9_2 | 0.883607 | 0.752456 | 0.223110 | 0.371 | H6_2 |
| H9_1 | 0.723999 | 0.734079 | 0.028583 | 0.155 | H5_2 |
| H10_2 | 0.772972 | 0.703848 | 0.372985 | 0.114 | H1c1_m |
| H10_1 | 0.618753 | 0.686092 | 0.185028 | 0.391 | H2c1_m |

Ok

Press "Apply+End"

Start "Edit atoms"

The atomic part should contain only Br1, Mg1 and five oxygens

Start "Plot structure"

The cage should be correctly placed – verify by plotting

*In a plot slash "/" means the atoms is transformed by the point group symmetry of the molecule, while "a" indicates the first actual position of the molecule.*

## 12. Refinement of the cage with Cs point symmetry

Make backup copy

Start "Refine commands"; go to page "Various"

Press "Keep commands" and delete all of them

OK; OK; YES to save commands without starting Refine

Start "Edit Atoms"

Select all carbons

Start "Action → Adding of hydrogen atoms"

Select "Try automatic run"

*The procedure should not add any new hydrogen atoms*

OK; YES to quit "Edit atoms"and save changes

Start "Refine Commands"

Set zero refinement cycles; OK; YES+START

This applies the previously created keep commands

Start "Plot structure" and verify hydrogen positions

Start "Refine commands", set 100 refinement cycles with Damping factor 0.5

OK; YES+START to save commands and run refinement

*The refinement has difficulties to reach convergence*

*The fit is R~3.2%, Rp~2.3%, GOF~5, 53 structure parameters; i.e. only slightly worse fit comparing with the asymmetric cage*

# Example 2.4: PFPhenyl

**Refinement of moderately-sized organometallic structure from powder data with help of geometry constrains.**

**Revised: 11 October 2015**

Powder data measured with diffractometer Empyrean (PANalytical) using CuKα1 radiation and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

**Input files**:
pfphenyl.xrdml with powder profile
pfphenyl.cif with solution obtained by the program FOX
**Additional information**:
unit cell 10.77024 9.957075 26.70771 90 91.683 90
expected symmetry $P2_1/n$
composition $C_{30} N_3 H_{29} P O_2 F_3$ (Z=4)
Chemical scheme:
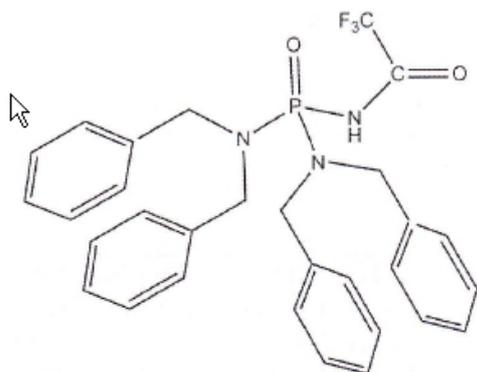


### 13. Creating new jobname
Start Jana2006
"File → Structure → New" opens a file manager
Left pane: locate directory with input files
Right textbox: type "pfphenyl"; OK

### 14. Import procedure
[On the screen: Specify type of the file to be imported]
Select "Structure – from CIF"; NEXT
[On the screen: select input CIF file]
Select pfphenyl.cif; OK
[On the screen: CIF does not contain any reflection block]
YES to import data from file
[On the screen: Specify type of the file to be imported]
Select "various CW formats"; NEXT
[On the screen: Powder data from:]
Select "PANalytical XRDML"
For method select "Debye-Scherrer"; NEXT
[On the screen: Complete/correct experimental parameters]

*Cell parameters were taken from CIF*
*Radiation was interpreted from the xrdml file as CuKα₁*

## 15. Refinement of the powder profile

*For refinement of the powder profile we shall use the le Bail wizard.*
Start "Wizards → le Bail wizard"
*[On the screen: Refinement of the powder profile by the le Bail algorithm]*
Press "Show powder profile" – just to see how it looks like
Press "Default" to see more details
Quit powder viewer
Press "Edit profile parameters"
In page "Profile" activate refinement of GW
*Unlike for structure parameters, refinement keys of profile parameters are not set*
*automatically*
In page Corrections:
Activate refinement of "shift";
Change number of Legendre terms for background to 30;
OK; Yes to rewrite
Press "Edit refinement commands"
Make sure that "Make only profile matching" is activated
*This means that the structure imported from CIF is not used in the refinement*
Set 100 refinement cycles
OK;
Press "Run Refine"
*Refinement of profile slowly converges to the profile R value Rp~2.9% and GOF ~ 3.5.*
*Waiting for the full convergence is not necessary. Refinement can be interrupted by End or*
*Cancel - in this case End should be used in order to see the latest difference curve in the*
*powder profile viewer.*
"Show Powder profile"
Press "Default"
Move the theta slider towards high angles

Press "Details ON"; YES to plot many component functions
Press "Fit Y"

*The calculated profiles show problem with background. The background is too low and the Bragg peaks are too high, giving together very nice fit between calculated and observed line, which is unfortunately false. We shall therefore use the manual background.*
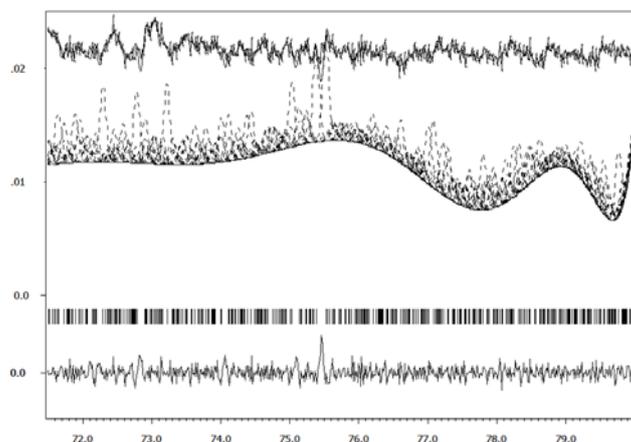


Press "Details OFF"
Press "Create new" button (lower right corner of the Powder profile viewer)
*[On the screen: Options for generating background profile]*
Use 60 background points and significance intensity level 1; OK
Using the slider check the manual background. It can be edited by dragging the points by mouse.
Press "Quit"
*[On the screen: A manual background has been created]*
Select "Accept the new manual background" and "Suppress using of polynomial terms"
OK
*Now we are back in the le Bail wizard*
Press "Run Refine"
*The refinement swiftly converges with Rp~2.8%, GOF~3.6.*
"Edit profile parameters"
In page "Cell" activate refinement of a,b,c,beta
In page "Profile" activate refinement of GV
OK, YES to save changes
Run Refine
*Refinement of profile converges to the profile R value Rp~2.5% and GOF ~ 3.1*
*For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*
"Edit profile parameters"
In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt" , activate refinement of LY
OK, YES to save changes
"Run Refine"
*Refinement of profile slowly converges to the profile R value Rp~2.5% and GOF ~3.0.*
"Show Powder profile"
Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

*Some low angle peaks exhibit strong asymmetry:*
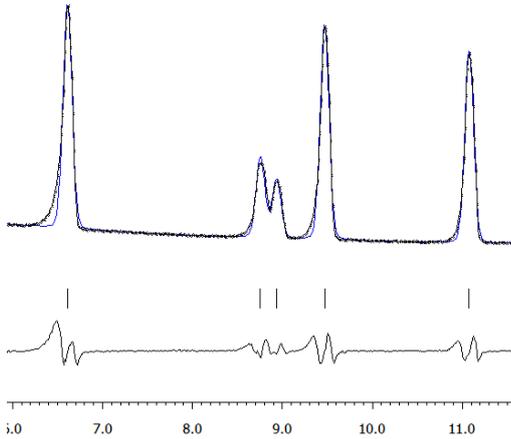


"Edit profile parameters"
In page "Asymmetry/Diffractometer" select "correction by divergence"
Activate refinement of "HpS/L" and fix to zero "HmS/L"
OK; YES to save changes
"Edit refinement commands"
In page "Basic" set "Damping factor" to 0.5
OK; YES to save changes
"Run Refine"
*Refinement of profile slowly converges to the profile R value Rp=1.9% and GOF ~1.8.*
*Waiting for full convergence is not necessary.*
 "Show Powder profile"
*Asymmetry seems to be well described*
Quit the profile viewer
Press "Save As" and **make a backup copy** of the structure
FINISH to close the Powder wizard

## 16. *Verification of symmetry*

Start File → Reflection file → Make space group test
YES to continue
*[On the screen: Tolerances for crystal system recognition]*
Use default; NEXT
*[On the screen: Select Laue symmetry]*
*Select the highest one – monoclinic; NEXT*
*[On the screen: Select cell centering]*
*(calculation takes time! It is finished when the program prints warning about cell centering at the end of the list of centering symbols).*
*The table shows $R_p$ values calculated for various centering vectors. For instance, for A centering the program discards corresponding extinct Bragg reflections and calculates $R_p$. If A centering would really exist, the new $R_p$ would be similar like the one for primitive unit cell because the discarded forbidden reflections would not be vital for the profile fit. In our case, A centering is not possible because the corresponding $R_p$ is much worse than for the primitive unit cell.*
*Select P centering as it gives the best profile fit; NEXT*
*[On the screen: Information about progress of space group tests. It takes some time…]*

*[On the screen: Select space group]*
*Among the space groups with good profile fit we are looking – in analogy with a single-crystal experiment – for a space group with maximum number of extinct reflections which are not needed for profile fit. The arguments are the same like for selecting the centering.*

*The space group P21/n, which is the space group used for the FOX solution has good FOM (figure of merit). This space group has been already entered with the CIF structure so we can cancel the process at this point. We could also consider P2/n but we will rely on the FOX symmetry.*
CANCEL

## 17. Refinement of the free atomic model
Make sure that the backup copy really exists
Start "Plot structure"
In Diamond use "Build → Connectivity" and suppress F-H and F-O bonds
Use ⬡ to plot the structure
*The structure from FOX solution is looking like this:*
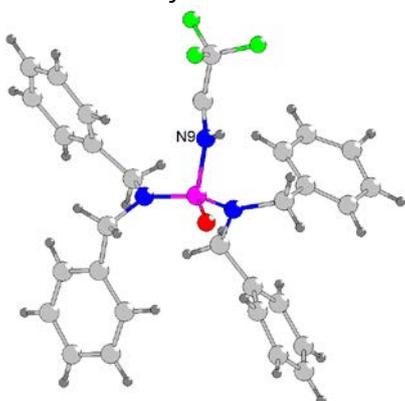


*Before refinement we have to fix geometry for hydrogen atoms. Hydrogen positions cannot be determined from this powder data set.*

Return to Jana
Start "Edit atoms"
Select all carbon atoms and N9
Start "Action → Adding of hydrogen atoms"
*[On the screen: Adding of "hydrogen" atoms"]*
Use default settings; OK
*Hydrogen atoms of carbon have been fixed automatically while for N9 the program offers a dialogue*
*[On the screen: Adding "hydrogen" atoms for "N9"]*
Select "Trigonal"; C28 and P1 for neighbors; H54 for hydrogen
Press "Apply → Go to next"
OK; YES to save changes
Start Refinement options (Right-click on the Refine icon)
Select the page "Basic"
Set 0 refinement cycles
Uncheck "Make only profile matching"
*This changes le Bail fitting into Rietveld refinement, where intensities of the profile points*

*are calculated from the structure model*

OK; YES+START

*R values are bad because no scales were refined. However, positions of hydrogen atoms were updated according to the previously introduced restrains and now we can check in the plotting program correctness of hydrogen positions.*

Start "Plot structure"

Verify hydrogen positions

Quit Diamond

Start "Edit Profile" and fix all profile parameters: a,b,c,beta,GV,GW,LY,HpS/L and shift.

OK, YES to save changes

Using "File → Structure → Save as" **make a backup copy named "pfphenyl_free"**

Start Refinement options; set 100 refinement cycles; set Damping factor 0.2

In page "Various" start "Restrictions"

Set the same ADP for all carbon atoms (C*)

Set the same ADP for all nitrogen atoms (N*)

Set the same ADP for all oxygen atoms (O*)

Set the same ADP for all fluorine atoms (F*)

```
restric C* 12
restric N* 12
restric O* 12
restric F* 12
```
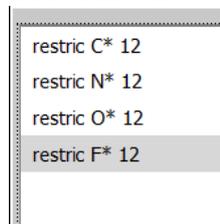
OK; YES (i.e. DO NOT start refinement)

Using "File → Structure → Save as" make a backup copy

Start "Refine"

*Now the structure is refined but the originally obtained profile parameters are fixed*

*The refinement converges slowly to Rp~2.2%, $R_{obs}$~6.5% and GOF~2.*

Start "Plot structure" and plot the refined structure
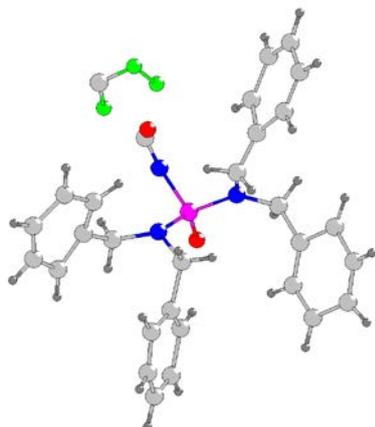


*We can see that the PN3O group has been refined correctly but phenyl groups are not planar and the CF3 group has been destroyed*

## 18. *Fixing geometry with keep commands*

Start "Tools → Recover files"

*This makes one step back. Otherwise "File → Structure → Copy in" would be used for importing the previously created backup file.*

Start "Plot structure" in order to see atom labels.

*With "Draw+continue" Jana2006 and Diamond can be used together and atom labels seen in Diamond can be immediately applied in Jana dialogues, provided that the computer screen is large enough. Otherwise please note the labels for later use or use the figure from the Cookbook*
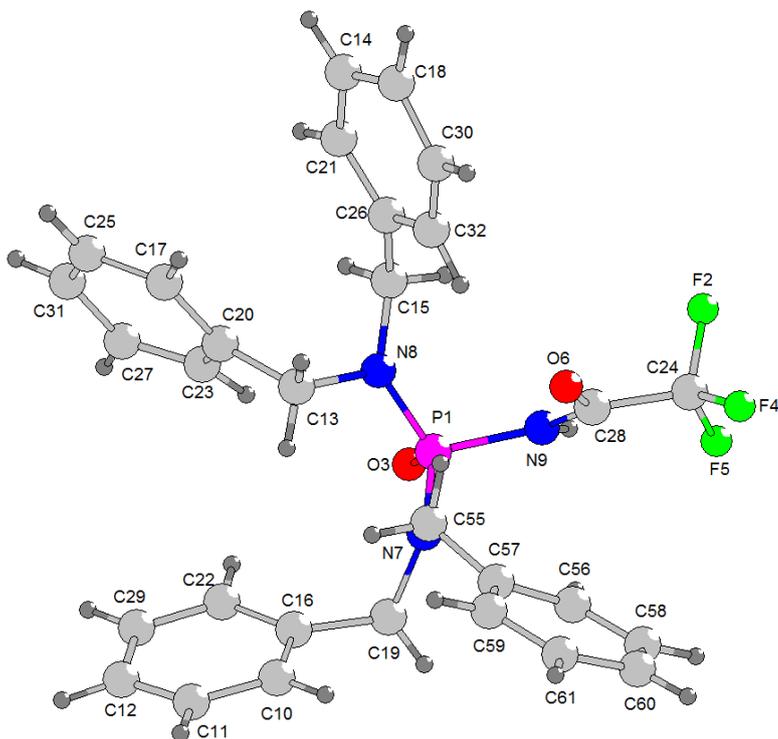


Start Refine Commands
In page Various start "Keep commands"
The already existing 50 commands keep the geometry of hydrogen atoms
Select "Geometry" and "Plane"
For "List of atoms" type labels of carbons in one of the Phenyl rings (without hydrogens)
Press "Add"
Repeat the process for the remaining Phenyl rings
Switch from "Plane" to "Rigid"
For "List of atoms" type C28 O6 C24 F2 F4 F5
Press "Add"
*The introduced keep commands:*

```
keep geom plane C17 C20 C23 C27 C31 C25
keep geom plane C14 C18 C30 C32 C26 C21
keep geom plane C57 C56 C58 C60 C61 C59
keep geom plane C10 C11 C12 C29 C22 C16
keep geom rigid C28 O6 C24 F2 F4 F5
```

OK; OK; YES+START
*The refinement converges slowly to Rp~2.6%, R~7.6% and GOF~2.4, i.e. slightly worse results comparing with unrestricted geometry*
*Damping factor may be changed to 1*
Start "Plot structure" and verify the result

The geometry is now much more reasonable, but some angles in the phenyl rings are too different of 120º.

**Make backup copy** of this refinement named (for instance) phphenyl_keepgeom
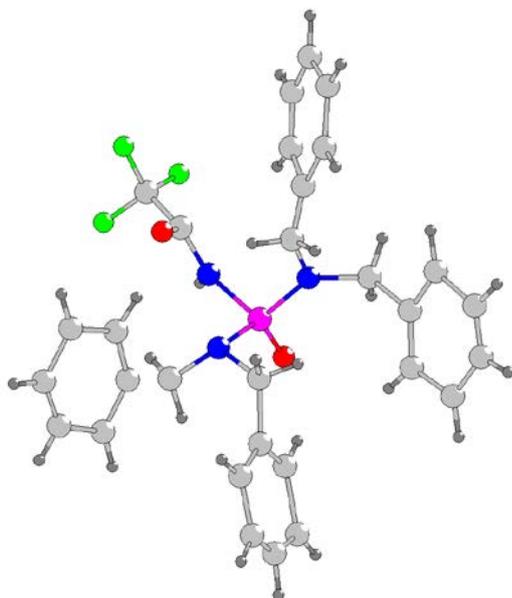


19. *Application of rigid body to phenyl rings*

*Start "Refinement options", go to the page "Various"*

*Start "Keep commands" and delete or disable the four "keep geom plane" commands ("keep geom rigid" should be retained)*

*OK; OK; YES to save commands without starting Refine*

*Start "Parameters → Molecules → New molecule"*

*[On the screen: Atoms of the new molecule from:]*

*Select "Atomic part"*

*Write "Phenyl" for the name of the molecule*

*NEXT*

*[On the screen: Select atoms for the molecule]*

*Select C10, C11, C12, C29, C22, C16, H46, H50, H33, H34, H35 (i.e. one of the phenyl rings)*

*OK*

*[On the screen: Define the molecular reference point:]*

*Select Geom. center*

*For molecules not located in a special position the position of the reference point is not important. For symmetrical molecules the reference point is used for derivation of symmetry restrictions*

*NEXT*

*[On the screen: Complete molecular position #1:]*

*Use Occupancy 1*

*The Coincidence ratio 11/11 means that all atoms of the actual position #1 coincide with atoms in the atomic part. This is obviously fulfilled, because the model molecule has been taken from the atomic part*

*Press "Apply+Next position"*

*[On the screen: Define and complete the molecular position #2:]*

*For model atoms select three carbons from the model molecule:  C16, C11 and C29*

*For the actual position choose three corresponding carbons from another existing phenyl*

*For "Maximal coincidence distance" type 0.6 (in Angstroms)*
*Press "Show coinciding atoms"*

It shows that the actual molecular position #2 coincides with another 11 atoms from the atomic part. These atoms will be automatically deleted in the atomic part.

| | | Define and complete molecular position # 2: | |
|---|---|---|---|

**Define and complete molecular position # 2:**

☐ Apply inversion

| | Model atom | Actual position/atom |
|---|---|---|
| 1st point | c16 | c57 |
| 2nd point | c11 | c58 |
| 3rd point | c29 | c61 |

Select the actual atom

Fill by a saved point

**Options for removing of atoms from atomic block coinciding with those generated from molecular position # 2:**

Maximal coincidence distance  0.6   Show coinciding atoms

Calculate molecular parameters

**Molecular parameters:**
Phi = 97.67 Chi = -0.31 Psi = -73.54 determinant = 1
Translation vector : -0.554602 0.048572 -0.029251

Occupancy  1        Coincidence ratio: 11/11

Apply+Next position    Apply+End    Quit

| | Individual atomic positions | | | distance | to |
|---|---|---|---|---|---|
| C10 | -0.202061 | 0.389799 | 0.552940 | 0.437 | C56 |
| C11 | -0.298377 | 0.496468 | 0.544273 | 0.226 | C58 |
| C12 | -0.316706 | 0.596045 | 0.568925 | 0.420 | C60 |
| C16 | -0.140155 | 0.429460 | 0.594416 | 0.000 | C57 |
| C22 | -0.145972 | 0.533765 | 0.626369 | 0.406 | C59 |
| C29 | -0.248215 | 0.632091 | 0.612199 | 0.317 | C61 |
| H33 | -0.188034 | 0.310964 | 0.533202 | 0.462 | H62 |
| H34 | -0.352530 | 0.484228 | 0.515442 | 0.193 | H63 |
| H35 | -0.382990 | 0.654549 | 0.558022 | 0.432 | H65 |
| H46 | -0.091110 | 0.544578 | 0.655067 | 0.518 | H64 |
| H50 | -0.264578 | 0.711780 | 0.631133 | 0.316 | H66 |

Ok

*Press "Apply+Next position"*
*For model atoms re-use C16, C11 and C29*
*For actual position use C26, C30 and C14*
Number of coinciding atoms should be again 11
*Press "Apply+Next position"*
*For model atoms re-use C16, C11 and C29*
*For the last actual position use C20, C25 and C27*
Number of coinciding atoms should be again 11
*Press "Apply+End"*
*Start "Edit atoms"*
The free atoms are black, the atoms of the model molecule are blue
*OK*
*Start "Plot structure"*
The structure should look more or less like before (with the difference that now we have four identical phenyl groups)

The old keep commands acting for atoms replaced by the actual molecular positions, except of those selected as a model molecule, were automatically deleted. The atoms will be still kept in ideal position as before but now through the keep commands applied to the model molecule.

However we have also used keep commands involving atoms from the phenyl groups and N-$CH_2$- group. The command defining positions of two hydrogen atoms bonded to C19 has not been deleted, and it still contains the atom C16, which belongs to the model molecule and not to some actual position. Therefore, C16 must be changed to C16a:

*Start Refine Commands*
*In page Various start "Keep commands" and load the relevant keep command:*
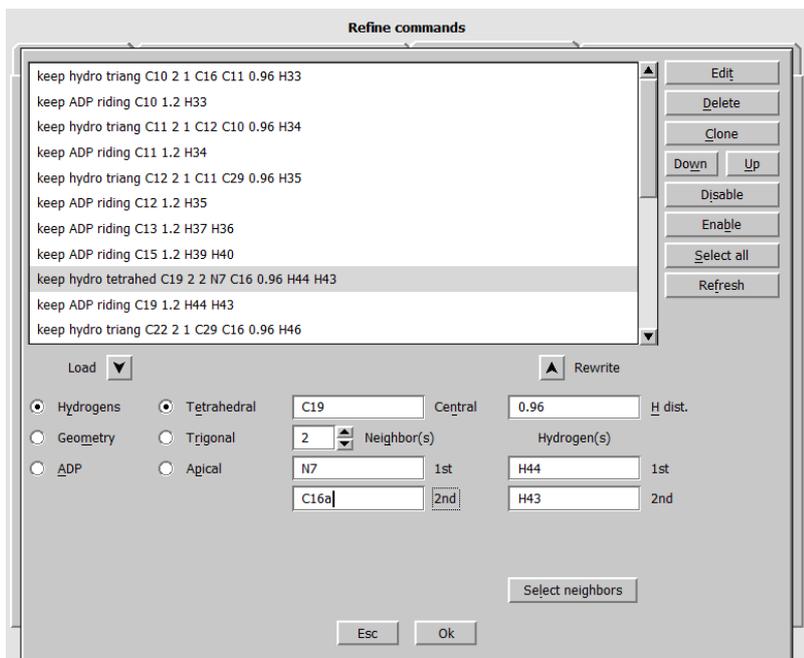
*Change C16 to C16a; Add*
*OK; OK; YES to save commands without starting Refine*

*The commands for keeping the geometry of hydrogen atoms in N-CH₂- groups for remaining three atoms (C55, C15 and C13) have to be re-defined:*

*Start "Edit atoms"*
*Select C55, C15 and C13*
*Start "Action → Adding of hydrogen atoms"*
*Use default settings; OK*
*(number of atoms should not change)*

*Here are the final keep commands:*

```
keep hydro triang C10 2 1 C16 C11 0.96 H33
keep ADP riding C10 1.2 H33
keep hydro triang C11 2 1 C12 C10 0.96 H34
keep ADP riding C11 1.2 H34
keep hydro triang C12 2 1 C11 C29 0.96 H35
keep ADP riding C12 1.2 H35
keep ADP riding C13 1.2 H36 H37
keep ADP riding C15 1.2 H40 H39
keep hydro tetrahed C19 2 2 N7 C16a 0.96 H44 H43
keep ADP riding C19 1.2 H44 H4
keep hydro triang C22 2 1 C29 C16 0.96 H46
keep ADP riding C22 1.2 H46
keep hydro triang C29 2 1 C22 C12 0.96 H50
keep ADP riding C29 1.2 H50
keep ADP riding C55 1.2 H68 H67
keep hydro triang N9 2 1 C28 P1 0.87 H54
keep ADP riding N9 1.2 H54
keep geom rigid C28 O6 C24 F2 F4 F5
keep hydro tetrahed C13 2 2 C16d N8 0.96 H36 H3
```

OK

Open the page "Basic"

Set number of cycles to 0; OK; YES+START to save commands and start refinement

This will apply keep commands without any further changes

Start "Plot structure"

Verify the structure after application of the new keep commands

There should be only small changes

Start "Refine Commands"

Change number of refinement cycles back to 100

OK; YES+START to save commands and start refinement

The refinement converges with Rp~2.6%, R~7.8% and GOF~2.4.

Start "Plot structure"

The resulting structure has much better geometry of phenyl groups

However, the distance C13-N8 is too large
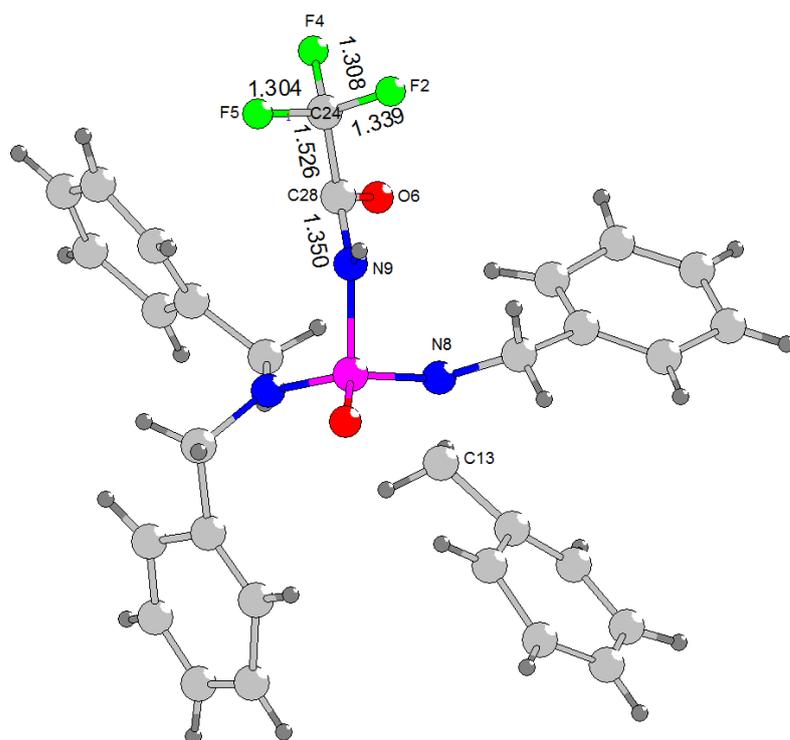


Make backup copy pfphenyl_rigid

## 20. Releasing the geometry of COCF$_3$

Start "Refine commands"

In page "Various" start "Keep commands"

Delete or disable the "keep geom rigid" command; OK

Start "Distance restrains"

Define the following restrains (with default s.u.):

"Keep a value equal for all items": C24 F5; C24 F2; C24 F4

"Fix to the specified value": C24 C28 to 1.526

"Fix to the specified value": C28 N9 to 1.35

```
distfix = 0.001 C24 F5; C24 F2; C24 F4;
distfix 1.526 0.001 C24 C28;
distfix 1.35 0.001 C28 N9;
```

OK; OK. YES+START to save commands and start refinement
*The refinement converges with Rp~2.5%, R~7.7% and GOF~2.3.*
Start "Plot structure"
*The geometry is correct and (as a side effect) the distance N8-C13 is now correct*
Make backup copy as phenyl_rigid_final

## 21. Refinement of structure and profile parameters together

*Up to now the profile parameters were fixed on values obtained in Le Bail refinement*
Start "Edit profile"
Activate refinement of a, b, c, beta, GW, GV, LY, HpS/L and shift
OK; YES to save changes
Start "Refine"
*The refinement converges with Rp~2.5%, R~7.5% and GOF~2.3.*
Start "Edit profile"
Go to page Corrections
Change number of Legendre polynomial terms to 20
OK; YES to save changes
Start "Refine"
*Now the manual background is combined with the polynomial background*
*The problem with the background refinement, which we have seen at the beginning of this example, cannot occur with Rietveld refinement because the intensities of the profile points are calculated from the structure factors*
*The refinement converges with Rp~2.4%, R~6.2% and GOF~2.2.*

## 22. Fixing planarity of phenyl

Start "Plot structure"
*The structure is correct except that the phenyl rings are not perfectly planar*
Start "Profile viewer"
*The profile is correctly described*
Start "Refine commands"
In page "Various" start "Keep commands"
Define "keep - geometry - plane" for C10, C11, C12, C16, C22 and C29, i.e. for the carbon atoms of the model molecule
OK; OK; YES+START
*The refinement converges with Rp~2.4%, R~6.4% and GOF~2.4*
Start "Plot structure"
*The phenyl rings are now perfectly planar, with reasonable distances and angles, although only the planarity has been kept.*
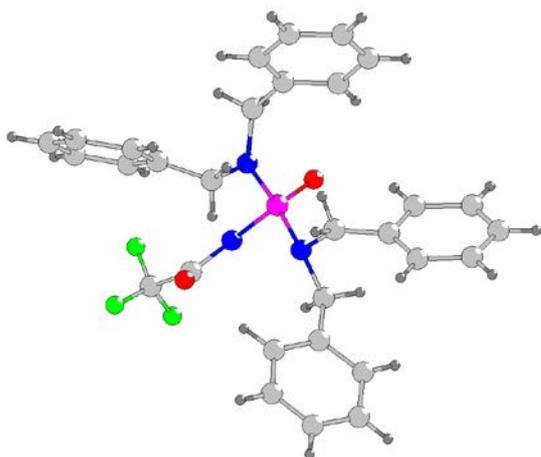
*Plot with default radii*          *Plot with radii scaled by isotropic ADP*
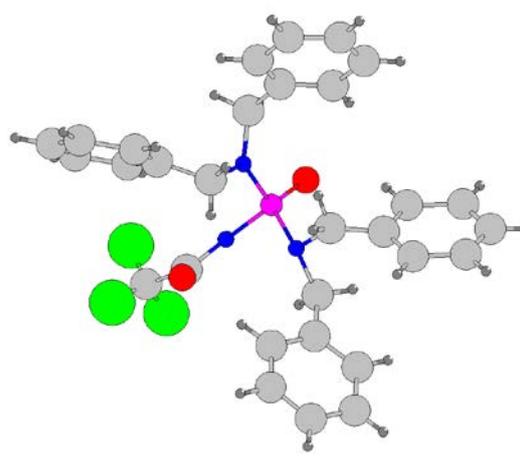
# Example 2.5: Twoph

**Multiphase powder refinement**
**Revised: 5 October 2015**

Room temperature (RT) phase of this sample is known from single crystal data. At cooling, a phase transition occured which repeatedly destroyed the single crystals. Therefore, the low temperature (LT) phase was measured at 150K as a powder. The powder sample at 150K still contained an admixture of the room temperature phase.

Unit cell of the LT phase was determined with CRYSFIRE 2004. Its structure was solved by direct methods implemented in the program FOX, using the RT structure as a starting template.

**Input files**:
**twoph.xrdml** with powder profile
**RT.cif** crystal structure of the RT phase solved and refined from single-crystal
**LT.cif** crystal structure of the LT phase solved from powder data by FOX. Not refined yet.

**Additional information**:
Powder measurement was done with Empyrean (PANalytical) using CuK$\alpha$ radiation, focusing mirror and Debye-Scherrer geometry (sample in a capillary)
RT phase unit cell: 6.81 8.56 17.78 90 96.8 90
RT phase symmetry: P2$_1$/n
LT phase unit cell: 8.54 17.68 7.15 90 111.25 90
LT phase symmetry: P2$_1$/a

**Chemical scheme of RT and LT:**
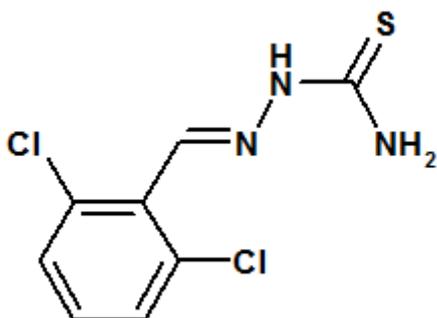


1. *Creating new job name*
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens the file manager
   Left pane: locate directory with input files
   Right pane: double-click twoph

2. *Import procedure*
   [On the screen: Specify type of the file to be imported]
   Select "Powder data – various CW formats"; NEXT

*[On the screen: Powder data from:]*
Select "PANalytical XRDML"
Select "Debye-Scherrer method"; NEXT
*[On the screen: Complete/correct experimental parameters]*
For "Cell parameters" type "6.81 8.56 17.78 90 96.8 90" (cell parameters of the RT phase)
Check the radiation (should be interpreted from the xrdml file as Copper with doublet):
NEXT; FINISH; OK to close data repository; YES to accept the data set
*[On the screen: question how to continue]*
Select "No, I shall go by my own way"; OK

3. ***Powder profile indicates a multiphase***
Start "Tools → Powder → Make Le Bail"
YES to start profile viewer
Press "Default" and move the slider to beginning of the powder profile
Some peaks, for example at 12.22°, do not have corresponding Bragg position. This is the indication of a multiphase (we believe our unit cell)
Quit

4. ***Importing of the second phase***
Start "Tools → Phases → New phase"
*[On the screen: New phase]*
Select "Manually"; OK
*[On the screen: Define/ modify basic structural parameters for phase: Phase#2]*
For "Cell parameters" type "8.54 17.68 7.15 90 111.25 90" (unit cell of the LT phase);
OK; YES to rewrite M50
*In the lower left corner of the Jana2006 basic window two new thumbnails appear:
"**Phase#1**" and "**Phase#2**". They are used for switching between the two phases. Many tools of Jana2006 work only with the active phase, for instance "Fourier", "Dist", "Contour", "Graphics viewer". Before starting these tools, the required phase must be activated. Some other tools like "EditM50" and "Edit profile" can switch the phase internally. "Refine" and "Profile viewer" work independently on the active phase, and the tool "Structure solution" places results to the first phase and deletes atoms of the other phases.*

5. ***Set Phase's labels and symmetry***
Start "EditM50"
*[On the screen: Define/ modify basic structural parameters for phase: Phase#1]*
Ensure that Phase#1 is selected in the bottom of the EditM50 window.
For "Phase label" type "RT"
Still in the EditM50 window, switch to the Phase#2
For "Phase label" type "LT"
Go to the page "Symmetry"
Select the phase RT and for "Space group" type "P21/n"; TAB
Select the phase LT and for "Space group" type "P21/a"; TAB
OK; YES to rewrite M50

6. ***Le Bail refinement***
Start "Edit profile"
*[On the screen: Powder options for phase: RT]*

*Ensure that the RT phase is selected at the bottom of the form.*
In page "Cell" activate refinement of a, b, c and beta (RT phase)
Select LT phase
In page "Cell" activate refinement keys of a, b, c and beta (LT phase)
Go to the page "Profile"
Select RT phase
Select "Pseudo-Voigt" and activate refinement keys for GW and LY
Select LT phase
Select "Pseudo-Voigt" and activate refinement keys for GW and LY
Go to the page "Corrections"
*Corrections are independent on a phase selection*
For "Background" select "Legendre polynomials" and for "Number of terms" type 25
OK; YES to rewrite changes

Right-Click on "Refine"
*[On the screen: Refine commands]*
Set "Number of cycles" to 30
OK; Yes+start
*Refinement converges with GOF~3.3%, Rp~1.27%, 37 profile parameters*

7. ***Correction for asymmetry***
   Start "Profile viewer" and investigate the powder profile
   *The peaks at low angles are slightly asymmetric, otherwise the profile fits very well*
   *Note two rows of Bragg positions*
   Quit the profile viewer
   Start "Edit profile"
   *[On the screen: Powder options for phase: RT]*
   Go to "Asymmetry/Diffractometer"
   Select "correction by divergence"
   Enable refining of HpS/L , set HmS/L to 0 and do not refine it.
   Go to "Corrections"
   Check "shift"
   OK; YES; Start Refine
   *R factors will fluctuate during the refinement.*
   In the refinement progress window, press "Parameters" and change the Damping factor to 0.5. OK to continue refinement.
   *Refinement converges to final $R_p$~1.2%*
   *Waiting for complete convergence is not necessary*

   Start "Profile viewer"
   Select by mouse the range between 9°2Theta to 19°2Theta
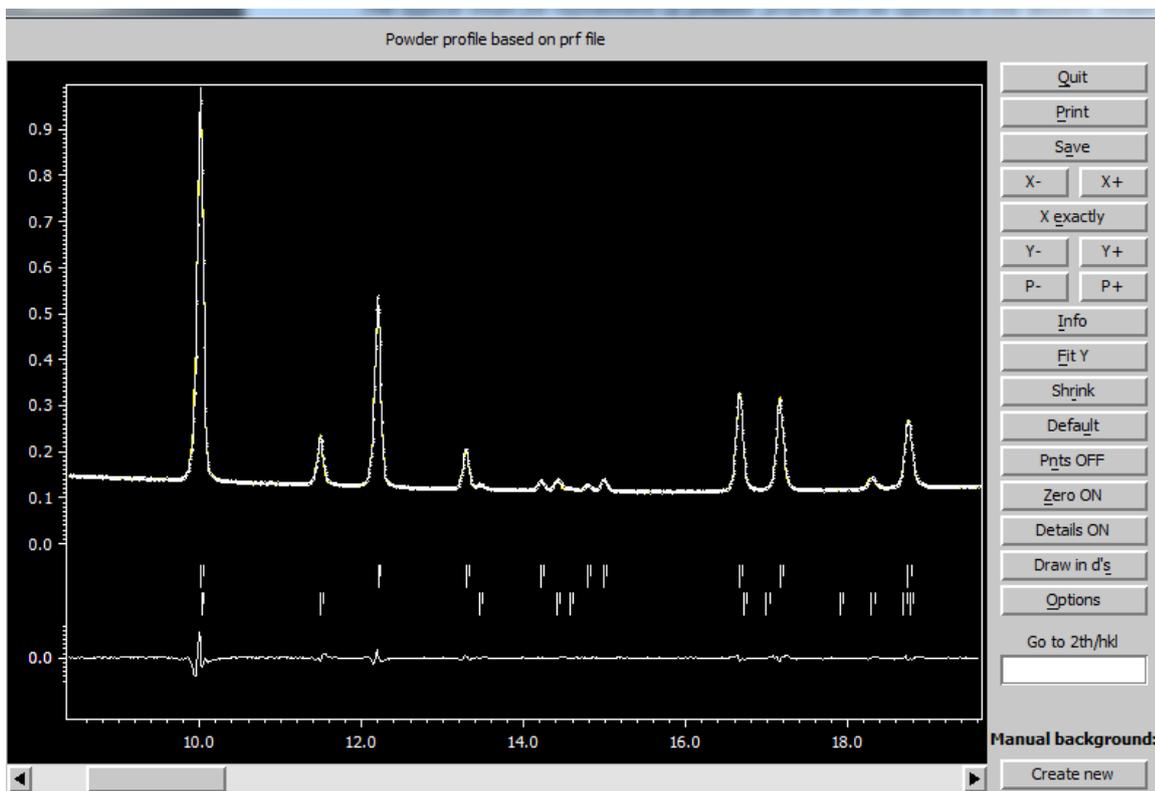
There are two rows of vertical bars. Clicking on some of them gives information about h k l, 2Theta position and about the corresponding phase. In this case, the top row corresponds to the LT phase while the bottom row corresponds to the RT phase.
Quit the profile viewer

8. **Backup copy**
   The Le Bail fitting is now complete, create a backup copy!
   Start "File → Structure → Save as"
   Make a backup copy "twoph_lebail"
   OK; NO (Do not continue with the new structure)

9. **Importing structure models for RT and LT**
   Note: in this example we could import structures of both phases already at the beginning and make Le Bail fit with "Make only profile matching" refinement option. By this way we demonstrate that structures can also be inported later on, e.g., in case when we need to test more structure models
   Structure models cannot be imported through "File → Import model from" because this would destroy the phases.
   In next steps, we rely that the backup copy created in the previous step exists!
   Start "Tools → Phases → Delete Phase" and delete the phase LT
   Start "File → Structure → Import model from → CIF" and import the file "RT.cif"
   The program retains the original unit cell, i.e. the one refined by the previous Le Bail fitting. This is important the unit cell in RT.cif corresponds to the room temperature measurement while this data set has been acquired at 150K
   Start "Tools → Phases → New Phase"
   [On the screen: New phase"]
   Select "Import from CIF format" and import the file "LT.cif"

Start "EditM50" and rename "Phase#1" to "RT", "Phase#2" to "LT"
Start "File → Structure → Copy In" and copy **only** M41 from the backup copy "twoph_lebail"
Start refinement option, page "Basic", and check "Make only profile matching"
Start refinement.
*There should be only small changes and quick convergence to $R_p$~1.2%*
Start "File → Structure → Save as"
Make a backup copy "twoph_rietveld_start"
OK; NO (Do not continue with the new structure)

10. ***Rietveld refinement of both phases with fixed parameters***
*In this example, we will use combination of rigid body with bond and bond-angle restraints. The rigid body approach will be applied on the RT phase because (i) this phase was known from single-crystal measurement and (ii) this is the minor phase. In fact, we are refining the RT phase only to get better results for the LT phase.*

Start "Edit profile"
*[On the screen: Powder options for phase: RT]*
Uncheck a, b, c and beta for both phases
Uncheck GW and LY for both phases
Uncheck asymmetry correction
Go to "Corrections"
uncheck shift
OK; YES

Right-Click on Refine
*[On the screen: Refine commands]*
Set "Number of cycles" to 100
Uncheck "Make only profile matching"
Go to "Various" and open "Fixed commands"
Fix all structure parameters ("*" for Atoms/parameters; "Add")
OK; OK; Yes+start
Refinement converges with $R_p$ ~ 6%

11. ***Keep commands for hydrogen atoms of the LT phase***
*[On the screen: Basic window of Jana2006]*
Select LT phase
Go to "Edit Atoms"
*Note: Be sure you are editing the LT phase!*
Select all hydrogen atoms and delete them.
Select all carbon atoms, N2_2 and N3_2
*N1_2, Cl1_2 and Cl2_2 should not be selected*
Click "Action" - > "Adding of hydrogen atoms"; OK
*[On the screen: Adding "hydrogen" atoms for "N2_2"]*
Ensure that geometry is "Trigonal" and neighbors are (C7_2, N1_2); "Apply->Go to ext"
*[On the screen: Adding "hydrogen" atoms for "N3_2"]*
Ensure that geometry is "Trigonal" and there is only one neighbor C7_2; "Apply "

OK; YES
*By this we have generated fixed commands for hydrogen atoms. Total number of atoms should be 21*

**12. Rigid body for the RT phase**

Right-Click on Refine
*[On the screen: Refine commands]*
Go to the page "Basic"
*Set Damping factor to 0.1*
*Go to the page "Various"; start "Keep commands"*
*Select "Geometry" and "Rigid" and click "Select atoms" button.*
*[On the screen: "Select atoms to define rigid body unit"]*
*Select all atoms of the RT phase (atoms **without** "_2"); OK; Add*
*The new keep command has the following form: "keep geom rigid Cl1 Cl2 S1 N1 N2 N3 C2 C3 C4 C5 C6 7 C8 C9 H1c2 H1c4 H1c6 H1c9 H1n3 H1n2 H2n3"*
OK;

**13. Set bond and bond-angle restraints**

*In the next we will use pre-prepared "distfix" and "anglefix" commands based on the geometry of the RT phase.  RT phase was solved from single crystal; hence, we suppose that its geometry is correct. The format of the commands is: key word, value of the restraint, sigma (connected to the weight of the restraint in the refinement), list of atoms*

*[On the screen: Refine commands]*
Go to "Distance restraints"
Click "Edit" to open the text file editor.
Copy (from distfix.txt) and Paste these lines:
*distfix 1.736 0.001 C5_2 Cl1_2*
*distfix 1.401 0.001 C3_2 C5_2*
*distfix 1.376 0.001 C4_2 C5_2*
*distfix 1.460 0.001 C2_2 C3_2*
*distfix 1.400 0.001 C8_2 C3_2*
*distfix 1.369 0.001 C6_2 C4_2*
*distfix 1.265 0.001 N1_2 C2_2*
*distfix 1.741 0.001 Cl2_2 C8_2*
*distfix 1.375 0.001 C9_2 C8_2*
*distfix 1.371 0.001 C9_2 C6_2*
*distfix 1.371 0.001 N2_2 N1_2*
*distfix 1.345 0.001 C7_2 N2_2*
*distfix 1.685 0.001 S1_2 C7_2*
*distfix 1.313 0.001 N3_2 C7_2*
Close text file editor and save changes
OK
*[On the screen: Refine commands]*
Go to "Angles restraints"
Click "Edit" to open the text file editor.
Copy (from anglefix.txt) Paste these lines:
*anglefix 121.977 0.01 C3_2 C5_2 Cl1_2*

*anglefix 115.676 0.01 C4_2 C5_2 Cl1_2*
*anglefix 122.347 0.01 C4_2 C5_2 C3_2*
*anglefix 126.236 0.01 C2_2 C3_2 C5_2*
*anglefix 114.761 0.01 C8_2 C3_2 C5_2*
*anglefix 120.262 0.01 C6_2 C4_2 C5_2*
*anglefix 118.989 0.01 C8_2 C3_2 C2_2*
*anglefix 124.469 0.01 N1_2 C2_2 C3_2*
*anglefix 120.003 0.01 Cl2_2 C8_2 C3_2*
*anglefix 123.439 0.01 C9_2 C8_2 C3_2*
*anglefix 119.969 0.01 C9_2 C6_2 C4_2*
*anglefix 116.048 0.01 N2_2 N1_2 C2_2*
*anglefix 116.553 0.01 C9_2 C8_2 Cl2_2*
*anglefix 119.211 0.01 C6_2 C9_2 C8_2*
*anglefix 119.412 0.01 C7_2 N2_2 N1_2*
*anglefix 119.203 0.01 S1_2 C7_2 N2_2*
*anglefix 116.961 0.01 N3_2 C7_2 N2_2*
*anglefix 123.835 0.01 N3_2 C7_2 S1_2*
OK

## 14. ADP for the RT and LT phase

*[On the screen: Refine commands]*
Start "Fixed commands"
Delete the "fixed all *" command created previously
Select "ADP harmonic parameters"
For "Atoms/Parameters" type "Cl1 Cl2 S1 N1 N2 N3 C2 C3 C4 C5 C6 C7 C8 C9 H1c2 H1c4 H1c6 H1c9 H1n3 H1n2 H2n3"
Add; OK
*This fixes ADP of all atoms of the RT phase to the values refined from the single crystal data*

*[On the screen: Refine commands]*
Go to "Restrictions"
*Set one ADP parameter identical for all non-hydrogen atoms of LT phase*
Uncheck "Make identical coordinates"
Check "Make identical ADP parameters"
For occupancies use "not restricted"
For "Atoms/Parameters" type "C5_2 C4_2 C6_2 C9_2 C8_2 C3_2 C2_2 N1_2 N2_2 C7_2 S1_2 N3_2 Cl1_2 Cl2_2"
Add; OK
*Using this restriction, the program will refine one ADP common for all atoms of the LT phase*

OK; Yes;
Make a backup copy (File->Structure->Save as)
Start refinement
Press "Use all" as a reply to the message about significant dicsrepancy
*Refinement converges with R~4.7% (RT), 4.3% (LT), Rp ~ 3%*

*Plot both structures by "Plot structure" and check them.*

*Check also the profile fit in "Profile viewer"*

## 15. Fine tuning the profile parameters

Start "Edit Profile"
*[On the screen: Powder options for phase: RT]*
Select the LT phase
Activate refinement of a, b, c, and beta
Go to the page "Profile"
Activate refinement of GW and LY of LT phase
Go to the page "Corrections"
Activate refinement of shift
Go to the page "Sample"
For Preferred orientation select "March-Dollase"
Set "pref1" to 1, activate its refinement and for "Direction" type "0 1 0"
*This corresponds to the longest unit cell parameter of LT*
Still in the Sample page, switch to the RT phase
For Preferred orientation select "March-Dollase"
Set "pref1" to 1, activate its refinement and for "Direction" type "0 0 1"
*This corresponds to the longest unit cell parameter of RT*
OK; YES (to save profile parameters)
Start refinement
*Refinement converges with R~4.0% (RT), 3.6% (LT), Rp ~ 2.6%*

## 16. Final model

*Finally, we will remove ADP restrictions for heavy atoms of the LT phase*
Right-click on Refine
*[On the screen: Refine commands]*
Go to the page "Various" and start "Restrictions"
Load the restriction command, delete Cl1_2, Cl2_2 and S1_2, rewrite the command
OK; OK; Yes+start
*Refinement converges with R~3.7% (RT), 3.3% (LT), Rp ~ 2.5%*
*In case the convergence is too slow, Marquard rerefinement can be activated by pressing
"Parameters" during the refinement. In such case damping factor can be increased to 0.5.*

***Note about cell parameters of the RT phase***

*The CIF for the RT contains unit cell determined at room temperatire. However, our powder pattern was measured at 150 K. The unit cell parameters are changing with temperature and it may happen that the change it so large that refinement from the room temperature unit cell does not converge.*

*We can estimate the deviation of the RT unit cell from the powder profile before its refinement:*

Right-click on Refine
*[On the screen: Refine commands]*
Set Number of cycles to 0;
Check "Make only profile matching" to perform only Le Bail refinement.
OK; Yes+start; (This calculate theoretical pattern)
Go to the "Profile viewer"
Display the range from 9° to 19° 2Θ.

*We can see that while for LT Bragg positions fit well, RT Bragg positions (second line in the plot) are deviated, e.g., 0 1 1, -1 0 1, 0 1 3.*
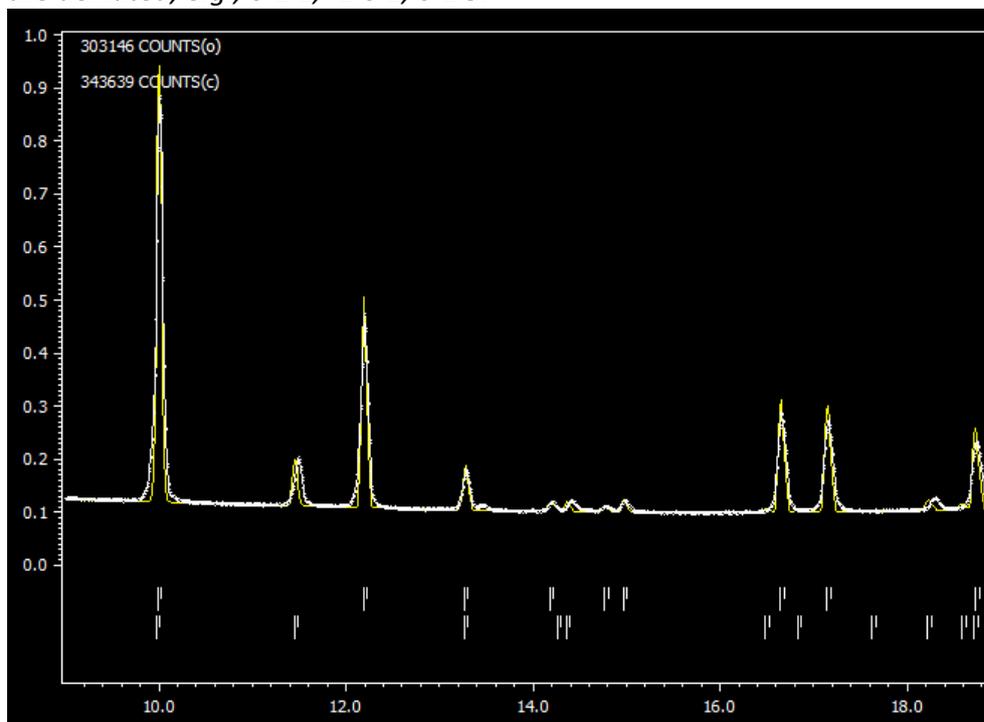


For rough estimation of the proper starting point for refinement of the RT unit cell, we can assume that beta does not change with temperature and we can calculate *a, b, c* from observed positions of $d_{011}$= 7.7 Å, $d_{013}$ = 4.85 Å and $d_{-101}$ = 6.58 Å: a = 6.84 Å, b = 8.55 Å, c = 17.77 Å.

For obtaining d, use "Draw in d's", find reflection hkl by "Go to" button and find its real position by "Info" line (it must stay a while at the peak position).

# Example 3.1: AD3

**Simple structure with pseudo-merohedric twinning and unequal twin volume fractions. Finding twinning matrix by Symmetry wizard. Creating publication CIF.**
**Revised: 15 October 2014**

**Bis[N-(2-benzylidenepropylidene)phenyl]ether**
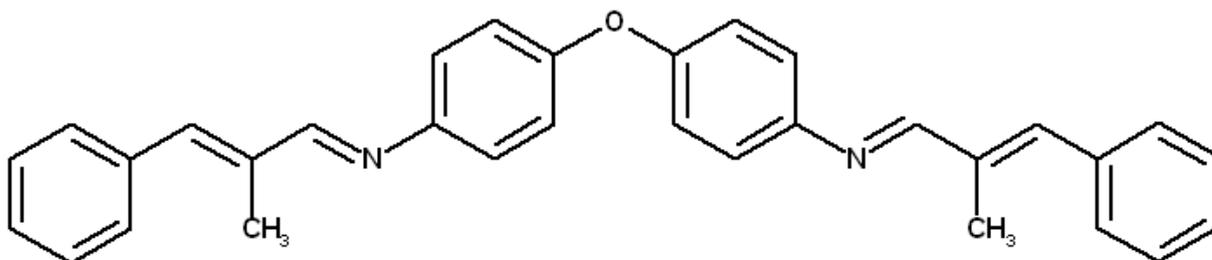


Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: AD3.hkl, AD3_red.sum
Frame scaling, absorption correction: done with software of diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click AD3

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction → CCD"; NEXT
   Select "Input from "sum" file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard, twinning*
   *[On the screen: "Tolerances for crystal system recognition".]*
   Select "Introduce twin laws in case of subgroups"
   Leave all other settings default; NEXT
   [On the screen: Select Laue symmetry]
   Select Monoclinic – setting "c"; NEXT
   The highest Laue symmetry consistent with cell parameters is orthorhombic. It has rather

high $R_{int}$ (~17%) which indicates that orthorhombic symmetry is slightly violated. Typical reason for such violation is presence of twinning where the structure of twins has lower symmetry and the twin domain fractions are different so the twins cannot simulate an exact orthorhombic Laue symmetry.

The selected Laue symmetry is monoclinic. In the previous step, we have activated an option "Introduce twin laws in case of subgroups". This means that the symmetry operation generating the orthorhombic symmetry from the selected monoclinic symmetry will be used as the twinning operation.

Select primitive unit cell; NEXT

*[On the screen: Select space group]*

Using the criteria described in the first example select P21/n, press "Details" to verify it is really acceptable; NEXT

The 46 reflections violating the extinction rules have mostly low I/ρ. Some additional spots in the diffraction pattern from e.g. small crystal attached at the surface of the measured sample might cause the violations. Without seeing the CCD frames we cannot be sure that the 46 reflections are really extinct but P21/n is the most probable symmetry.

Select "Accept twinning matrices induced by the space group test"

Select "Accept the space group in the standard setting"; FINISH

5. ***Creating refinement reflection file***

NEXT to confirm threshold 3sigm*a*

*[On the screen: settings for merging of reflections]*

Leave all settings default; NEXT

Accept the new DatBlock and calculate coverage; FINISH

6. ***Structure Solution Wizard***

*[On the screen: window of Structure solution]*

In "Formula" textbox type list of chemical elements for AD3: C N O H

Select "Superflip", "Peaks from Jana2006"; "Repeat Superflip: Number of runs" and 15 for number of runs; limit Maxcycles to 1000; leave other settings default



Press "Run Solution"

*[On the screen: listing of Superflip]*

*With this setting Superflip repeats calculation 15 times (from different randomly generated set of phases) and returns the result with the best fit between the electron density map and the user-defined symmetry. Because of twinning the fit of symmetry generators is worse and it may happen that Superflip suggests $P2_1$ instead of $P2_1/n$ - please ignore this fact, "n" is confirmed by systematic extictions. With this structure, the results of Superflip are significantly better when "Biso" is set to 3 in the charge flipping options; however, this would be an empirical step useless for another structures.*

Close listing of Superflip
Press "Draw structure" to see result of charge flipping
Quit Diamond without saving changes
In case of doubts repeat structure solution and plotting
Finally press "Quit" to close the structure solution wizard

7. ***Verification of the structure solution***
   Start "plot structure"
   Press "Draw+continue"
   *In this mode Jana will launch Diamond but it will not wait for its end*
   *[On the screen: window of Diamond]*

   Start "Build → Get molecules" or use ⬡ on the bottom toolbar

   Rotate the molecule (⊕ and ↻ on the bottom toolbar) to get an optimal view
   Draw rectangle to select all atoms of the molecule or press Ctrl-A
   Right-click on one of the selected atoms, choose "Add → Atom labels"
   *[On the screen: dialogue of Diamond for atom labeling]*
   For "Content" select: "Atom symbol"
   Define relative position of labels 0.3,0.3,10, OK
   *[On the screen: plot of the molecule with atom labels]*
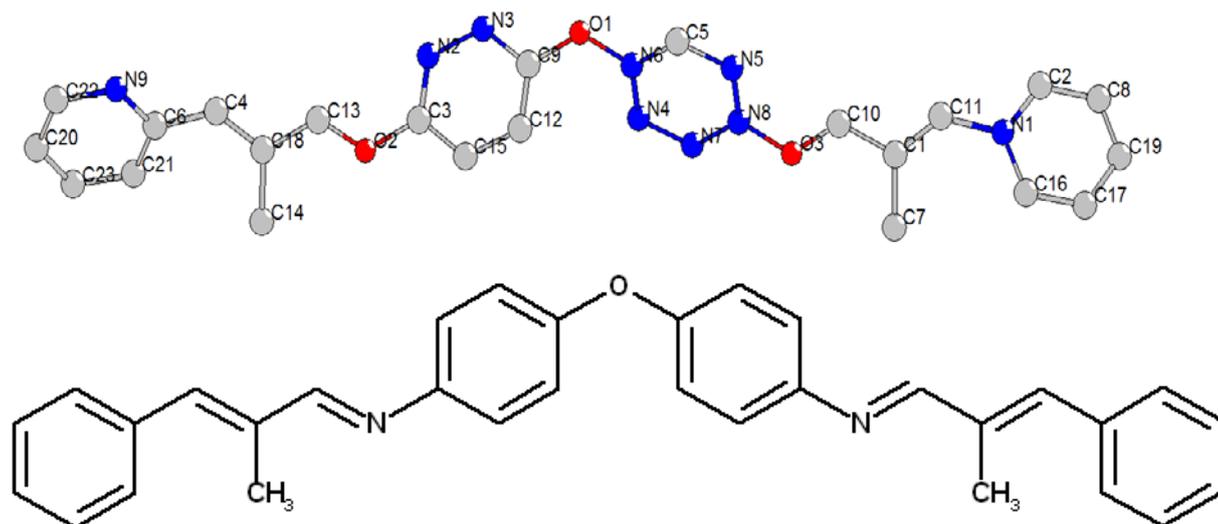


*The results may be slightly different for each run of Superflip. This is because Superflip starts from random phases and the resulting electron density map differs for each run. In our case the assignment of chemical types is wrong for many atoms of the structure.*

Compare the plot with the chemical scheme and note labels of atoms, which must be oxygen or nitrogen. *In our example, O2 and O3 will ne nitrogen and O1 will remain oxygen.*
Quit Diamond

8. ***Assignment of correct chemical types***
*[On the screen: basic Jana window]*
Start "Edit atoms"
*[On the screen: list of atoms]*
Press "Select all"
Start "Action → Edit/define"
Double-click "Type" textbox
*Double-click unlocks the "Type" textbox. This is locked for security reasons because the selected atoms have different chemical types.*
Select Carbon, OK
*[On the screen: list of atoms. The labels are still the original ones but the chemical type of all atoms is carbon]*
Press "Refresh"
Select the atom which should be oxygen (O1 in our example)
*Editing of one atom can be also started by right mouse button or by double-click*
Start "Action → Edit/define" and choose chemical type "O"; OK
Press "Refresh"
Hold Ctrl and select atoms which should be nitrogen (O2,O3 in our example)
Start "Action → Edit/define" and choose chemical type "N"; OK
*[On the screen: list of atoms, labels are still the original ones but chemical types are correct]*
Press "Select All"
Press "Action" or right-click on one of the selected atoms
Choose "Rename selected atoms to atom_type + number"
*[On the screen: list of atoms with labels corresponding to chemical types]*
*You should see one oxygen, two nitrogens and carbons. If not press ESC and start again* ☺
Press "Select All"
Press "Action" or right-click on one of the selected atoms
Choose "Make symmetrically contiguous motifs"
OK; YES to save the changes
Check chemical types with Diamond

9. ***Refinement***
*[On the screen: basic window of Jana]*
Right-click the icon of Refine.
*[On the screen: refinement options]*
Define 100 of cycles, Instability factor 0.02; OK
*This instability factor slightly lowers goodness of fit, which makes happy editors used for SHELX. Values below 0.01 or above 0.02 are usually in contradiction with the instrument characteristics.*
Choose "YES+START"
*Refinement converges with R value about 16%, GOF about 8, 141 refined parameters*

**10. _Twin volume fraction_**

Start "parameters → Twin fractions"

_The volume fraction of the twin domain introduced by the Symmetry wizard is 0.5 and twinning matrix relating the monoclinic and orthorhombic symmetry is (-1 0 0 | 0 1 0 | 0 0 1)._

Activate refinement of the twin fraction

Repeat refinement

_Refinement converges with R value about 11%, GOF about 7_

_Twin volume fraction drops to 0.29._

Start "Edit atoms"

[On the screen: list of atoms]

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters. _This defines anisotropic temperature parameters for all atoms._ OK, OK, YES _to save changes_

Double-click the icon Refine.

_Refinement converges with R value about 9%, GOF about 6, 317 refined parameters._

**11. _Adding of hydrogen atoms_**

_[On the screen: basic window of Jana]_

Start "Edit atoms"

In the textbox type "C*"; TAB.

_This will select atoms starting with C, i.e. carbons_

Start "Action → Adding of hydrogen atoms"

_[On the screen: Adding of hydrogen atoms dialogue]_

Leave all settings default; OK

_[On the screen: list of atoms with new hydrogens]_

_Total number of atoms should be 63 (can be verified using "Select All")_

_The hydrogens are kept in ideal geometry by commands which can be viewed or edited in "Refinement commands → Various → Keep commands"._

OK to close "Edit atoms"; Yes to save changes

"Plot structure" to check results of automatic hydrogen assignment

Make refinement of the final structure

_Oscillation may occur during the refinement. In such case do not break refinement, press Parameters, change Damping factor to 0.5 and close the dialogue. Refinement will continue with damping._

_Refinement converges with R value 3.7%, GOF 2.7, 317 refined parameters._

**12. _Creating CIF file_**

_The information for the CIF file is cumulated in the file M70 during the data processing as well as solution and refinement steps. For creating a publication CIF, repetition of the basic steps is recommended in order to refresh the information in M70._

Start "File → Reflection file → Create refinement reflection file"

_In our case this step is not necessary because it has been already done_

Repeat refinement

_In our case this step is not necessary because it has been already done_

Right-click Fourier; select "F(obs)-F(calc) - difference Fourier"; make sure that "Weighting of reflections" is checked and "Apply sin(th)/lambda limits" unchecked; in the page "Scope" press "Reset to default"; in the page "Peaks" choose "in a fixed sphere of radius

0.8"

OK; YES+START; NO to include new atoms; NO to see the listing

Right-click Dist icon

Select "d(max) derived from atomic radii and typical distances"; check "Calculate angles"; if needed adjust "expanded by" value; in needed, adjust limots for H-bonds;

In the page "Select atoms" check central atoms and neighbor atoms – usually we want to select all atoms;

OK; YES+START

Start "File → CIF utilities → Make CIF file"

# Example 3.2: PyNinit

**Simple structure with non-merohedric twinning. Handling twin overlaps in Jana2006.**

**Revised: 15 October 2014**
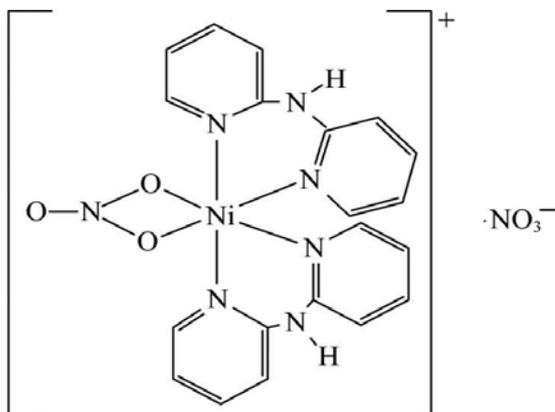


**Acta Cryst. (2009). C65, m260-m262**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files:
1st twin domain: pyNinit_twin1.hkl, pyNinit_twin1_red.sum
2nd twin domain: pyNinit_twin2.hkl, pyNinit_twin2_red.sum
hklf5: pyNinit_twin1_hklf5.hkl
Twinning matrix: (-1 0 -0.733| 0 -1 0| 0 0 1)
Frame scaling, absorption correction: done with software of diffractometer

1. *Creating new jobname*

   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click pyNinit_twin1

2. *Import Wizard (for the 1st twin domain)*

   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction-CCD"; NEXT
   Select "Input from "sum" file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged (leave Twinning checkbox clear); NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*

   *The line in data repository window corresponds to one data set.*
   OK; *YES* to accept the data set

### 4. Symmetry Wizard

*[On the screen: an information that symmetry wizard follows]*
NEXT
*[On the screen: "Tolerances for crystal system recognition".]*
Leave all settings default; NEXT
*[On the screen: Select Laue symmetry]*
Select Monoclicnic; NEXT
Select primitive unit cell; NEXT
*[On the screen: Select space group]*
Using the criteria described in the first example Select P2$_1$/c; NEXT
Accept the space group transformed into the original cell; FINISH
Follow the wizard for creation of the refinement reflection file

### 5. Structure solution

*[On the screen: window of Structure solution]*
In "Formula" textbox check list of chemical elements for PyNinit: Ni C N O H
Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run Solution"
*Superflip converges (after noise suppression) with R value 22%.*
Press CLOSE to leave the listing
Press "Draw structure" to see the result
Press "Quit" to close the Structure solution wizard

### 6. Completing the structure solution

In Refinement options set 100 refinement cycles, damping factor 0.5
Run Refine
*Refinement converges with R value about 19%.*
Use "Edit atoms" and "Select rejected" to delete atoms which may be automatically rejected during the refinement because of too large Uiso
*(The button is disabled when there are no such atoms)*
Using "Plot structure" identify the incorrectly assigned chemical types by comparison of the plot with the chemical scheme
Using "Edit atoms" correct the chemical types, delete wrong atoms, "rename atoms according to chemical type" and "create symmetrically contiguous motifs"
Repeat refinement
Run difference Fourier and complete the missing atoms
Repeat refinement
Using "Edit atoms" set harmonic ADP for all atoms
*Refinement converges with R value around 17%.*
Using "Edit atoms" add hydrogens to carbon and nitrogen atoms
*For nitrogen atoms skip cases when Ni is listed as a neighbor (this is the nitrogen coordinated to Ni) and skip also cases when nitrogen has three oxygen atoms as neighbors (this is NO$_3$ group).*
*Check the hydrogen atoms by plotting. The geometry is slightly distorted due to unresolved twinning which may confuse the automatic procedure for adding hydrogens.*
*Finally, the structure model should have 53 atoms*
Repeat refinement
*Refinement converges with R value around 16.6% and GOF 9*

*Several non positive definite ADPs are indicated in the List of serious warnings in the refinement listing*

**7. Twinning**

In "EditM50" check "Twinning" and define twinning matrix (-1 0 -0.733| 0 -1 0| 0 0 1)
*The twinning matrix is known from the diffractometer software and represents a rotation by 180º around c. The program offers re-creation of the refinement reflection file because twinning may change rules for merging of symmetrically equivalent reflections. In this case new merging is not necessary.*
In "Parameters → Twin fractions" enable refinement of "twvol2"
Repeat refinement
*Refinement converges with R value around 13% and GOF 7.5 for 317 parameters*
Open listing of Refine
*ADP tensors are still not positive definite for some atoms.*

*This twin has a diffraction pattern where some reflections are partially overlapped. In refinement options there are two limits available for treating partial overlaps. The reflections with difference in theta smaller than "Maximal angular difference for twin overlap" are treated as fully overlapped; the reflections with theta difference larger than "Minimal angular difference for full separation" are treated as fully separated; the reflections between the limits are discarded. The limits should be adjusted carefully not to discard too many reflections.*

In Refinement options change values of "Maximal angular difference for twin overlap" (L1 in the table) and "Minimal angular difference for full separation" (L2 in the table) and watch their impact on R factors, number of excluded reflections and ADP tensors. Find an optimal combination.

| L1 | L2 | $R_{obs}$ | GOF | discarded |
|------|-----|------|-----|-----------|
| 0    | 0   | 15.2 | 8.2 | 0         |
| 0.1  | 0   | 12.7 | 4.7 | 0         |
| 0.2  | 0   | 7.4  | 3.6 | 0         |
| 0.3  | 0   | 7.1  | 3.5 | 0         |
| 0.4  | 0   | 9.8  | 5.5 | 0         |
| 0.35 | 0   | 9.6  | 5.4 | 0         |
| 0.31 | 0   | 9.3  | 5.3 | 0         |
| 0.3  | 0.4 | 6.9  | 3.6 | 778       |
| 0.3  | 0.5 | 7.4  | 3.8 | 1264      |
| 0.3  | 0.6 | 7.9  | 4.1 | 1916      |
| 0.2  | 0.3 | 6.2  | 3.0 | 415       |
| 0.2  | 0.4 | 5.7  | 3.0 | 1193      |
| 0.15 | 0.3 | 5.3  | 2.4 | 709       |
| 0.1  | 0.3 | 4.8  | 1.9 | 1120      |
| 0.1  | 0.4 | 3.9  | 1.4 | 1848      |

*With maximal angular difference for twin overlap 0.1 and minimal angular difference for full separation 0.4, refinement converges with R value 3.9% and GOF 1.4, all ADP tensors are*

*positive, the fraction of the second twin domain refines as 0.468(2) (see "Parameters →
Twin fractions)".*
Using "Structure → Save as", create a backup copy, for instance pyNinit_1domain

8. **Import data of the second domain**
   *Usually (and also in this case) the first twin domain + twinning matrix is sufficient for the
   refinement. For equally strong domains we can add data processed for the second domain
   to get better refinement of the twin fraction.*
   "File → Reflection file → Import/modify the reflection file"; Import new
   Known diffractometer formats; Oxford Diffraction-CCD
   Browse for PyNinit_twin2.hkl
   Leave all settings unchanged; NEXT
   *[On the screen: Relationship to the reference cell/split by twinning]*
   *Here we have to define that reflections of the second domain were indexed according to
   orientation matrix of the second domain.*
   **Data related to domain #2**; NEXT; Accept cell parameters
   YES to suppress possibly duplicate reflections
   For absorption correction select "None or done before importing"; NEXT
   FINISH
   *[On the screen: Data repository]*
   *Each line in data repository window corresponds to one data set.*

| pyNinit_twin1.hkl | | Single crystal | | X-rays Mo K(alpha) | ▲ |
| pyNinit_twin2.hkl | | Single crystal | | X-rays Mo K(alpha) | |
| | | | | | ▼ |

   OK; YES to accept the data set;

**Modify grouping of data collection blocks into refinement blocks**

|  | Data refinement block | |
| --- | --- | --- |
| Data collection block | #1 | #2 |
| pyNinit_twin1.hkl->Single crystal/X-rays/Mo K(alpha) | ◉ | |
| pyNinit_twin2.hkl->Single crystal/X-rays/Mo K(alpha) | ◉ | ○ |

| Esc | Ok |
| --- | --- |
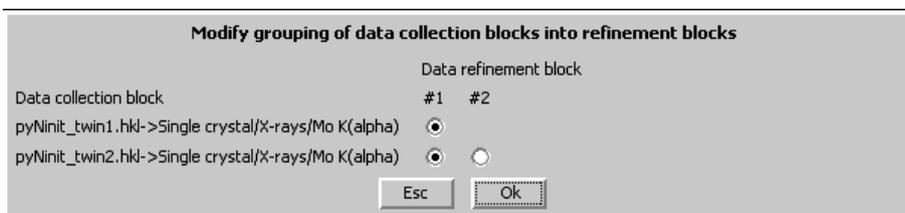
   *In this step the program offers sorting of the data sets to data blocks. Each data block has
   an independent scale factor. In our case both twin domains come from the same
   measurement and they should be used as one data block.*
   Set Data collection block #1 for both datasets
   Follow the wizard for creation of the refinement reflection file; select "on the same scale"
   for both data sets
   Refine
   *Refinement converges with R 4.1%, GOF 1.38, 3800 excluded reflections, fraction of the
   second domain is 0.4644(6) (the number with s.u. is printed in the refinement listing).*
   Create a backup copy, for instance pyNinit_2domains

9. **Are both domains really on the same scale?**
   *It may be unclear whether both data sets are on the same scale. Different scales would bias
   refinement of the volume fraction.*

"File → Reflection file → Import/modify the reflection file"
In Data repository highlight pyNinit_twin2.hkl  and use "Reimport"
Follow the import wizard as previously, but **do NOT suppress possibly duplicate reflections** in order to have enough data for finding the common scale
Follow the steps the wizard for creation of the refinement reflection file; select "**on DIFFERENT scales**" for both data sets; in the next step let Jana to determine the unique scale
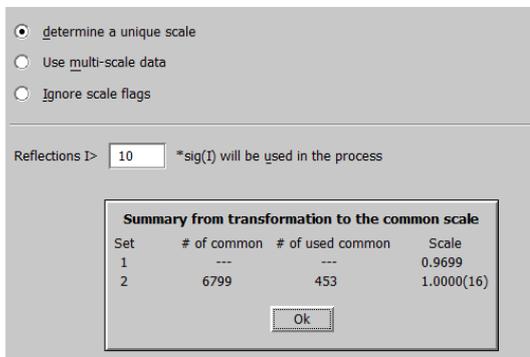


*The scale is calculated from 453 completely overlapped reflections which should have the same intensity in both data sets after the scaling.*

Refine

*Refinement converges with R about 4.1%, GOF 1.4, 3800 excluded reflections, fraction of the second twin domain is 0.4716(6).*

## 10. Use of HKLF5

*The diffractometer software should better detect overlaps of diffraction spots than the simple criterion in Jana2006. HKLF5 file produced by diffractometer software contains flags saying which reflections are overlapped. Jana2006 can work with HKLF5 if twinning is activated (twinning matrix can be arbitrary).*

"File → Reflection file → Import/modify the reflection file"; Delete both datasets;
Import new
*[On the screen: Specify type of the file to be imported]*
Choose "reflection file corrected for LP and absorption", NEXT
Browse for pyNinit_twin_hklf5.hkl; choose SHELX HKLF5; NEXT
Leave all settings unchanged; NEXT
Leave all settings unchanged; leave clear "HKLF5 file by Jana tools"; NEXT; FINISH; OK
Follow the wizard for averaging of reflections and creation of the refinement reflection file
*Jana2006 merges only fully separated reflections from both domains*
Refine

*Refinement converges with R 5.41%, GOF 1.6, fraction of the second domain is 0.4728(5). The R value is slightly worse than previously but we are using all reflections.*

*The following table summarizes refinement of the twin volume fraction*

|  | twvol2 |
|---|---|
| First twin domain, L1 = 0.1, L2 = 0.4 | 0.468(2) |
| Both domains, L1 = 0.1, L2 = 0.4 | 0.4644(6) |
| Both domains, L1 = 0.1, L2 = 0.4, scaling | 0.4716(6) |
| HKLF5 | 0.4728(5) |

# Example 3.3: CsLiSO₄

**Simple structure with pseudo-merohedric 3-fold twinning. Finding twinning matrix from group → subgroup transformation. Transformation to four times larger reciprocal cell.**

**Revised: 15 October 2014**

## CsLiSO₄

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: CsLiSO4.hkl, CsLiSO4_red.sum
Frame scaling, absorption correction: done with software of diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click CsLiSO4

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction-CCD"; NEXT
   Select "Input from "sum" file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged (leave Twinning checkbox clear); NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   *[On the screen: an information that symmetry wizard follows]*
   NEXT
   *[On the screen: "Tolerances for crystal system recognition".]*
   Leave all settings default; NEXT
   *[On the screen: Select Laue symmetry]*
   *It is evident that hexagonal symmetry is slightly violated, because its $R_{int}$ is about 14%. Because cell parameters are exactly hexagonal merohedric twinning is highly probable. One way how to continue would be to use monoclinic symmetry ($R_{int}$ ~ 6%) combined with merohedric twinning. However, this would generate six-fold twinning. Before trying the monoclinic symmetry we should test the orthorhombic case, which is not offered directly in the symmetry wizard because of the hexagonal unit cell. In order to test the orthorhombic symmetry, we shall select the highest hexagonal symmetry (6/mmm) and use group-subgroup transformation tool.*

Select Hexagonal – "6/mmm"; NEXT
Select primitive unit cell; NEXT
*[On the screen: Select space group]*
Using the criteria described in the first example Select P6₃/mmc; NEXT
Accept the space group transformed into the original cell; FINISH

CANCEL to skip creation of the refinement reflection file

5. ***Group-subgroup transformation***

*[On the screen: basic window of Jana]*
Start "Tools → Transformation → Go to subgroup structure"
*[On the screen: Define subgroup dialogue]*
Press "Select non-isomorfic subgroup"
Focus the first orthorhombic subgroup (all three possibilities would lead to an equivalent solution); OK
NEXT; NEXT to accept the long information
*[On the screen: Select one representative of the 2ⁿᵈ coset]*
*This window lists one of the symmetry elements (and its equivalents) which will be lost during transformation from P6₃/mmc to Cmcm.*
Select the first symmetry element in the list (all equivalents would lead to the same solution) as the twinning operation; NEXT
*The selected twinning operation defines the relationship between the 1ˢᵗ and 2ⁿᵈ twin domain.*
*[On the screen: Select one representative of the 3ʳᵈ coset]*
*This window lists another symmetry element (and its equivalents) which will be lost during transformation from P6₃/mmc to Cmcm.*
Select the first symmetry element in the list (all equivalents would lead to the same solution) as the twinning operation; NEXT
*The selected twinning operation defines the relationship between the 2ⁿᵈ and 3ʳᵈ twin domain. No other twinning operations are offered because the transformation from P6₃/mmc to Cmcm leads to a three-fold twin.*
[On the screen: Specify the output structure]
Choose a name for the new twinned structure, for example CsLiSO4_twin
Select "Make as twinned structure"; NEXT; FINISH
Follow the default steps for creating the refinement reflection file
*Rₐ₋ᵢₙₜ after merging of symmetry equivalent reflections should be 6.3%*
Accept suggested transformation to the standard setting
YES to continue with the new structure
*[On the screen: basic window of Jana]*
Check new cell parameters and symmetry with EditM50
*Cell parameters 10.8919 18.8653 8.8048 90 90 90 90 90 90*
*Space group Cmcm*
ESC
*[On the screen: basic window of Jana]*
Start "Parameters → Twin fractions"
Focus the textbox "twvol2" and press "Show twinning matrix"
*-0.5 0.5 0 / 1.5 0.5 0 / 0 0 -1*
Focus the textbox "twvol3" and press "Show twinning matrix"

*-0.5 -0.5 0 / -1.5 0.5 0 / 0 0 -1*

*The twinning matrices are now related to the new orthorhombic unit cell*

Return to the basic window

Start "Edit/view → Editing of M90 file"

```
eformat91 0
datblock Block1
nref 2021 obslim 3 norefitems 1 diffscales 1 dataave 1 scalelim 10 hklf5 0
indslowest 3 indfastest 1 addcentrsymm 0 sigimethod 1 multave 1
flimprint 5 flimcull -1
radtype 1 dattype 1
lambda 0.71073 lpfactor 1 monangle 6.082 perfmono 0.5
datcolltemp 293
end
Data Block1
    2   0   0     16.7      0.3   1   0   1   0.0000
    4   0   0  11515.1     35.7   1   0   1   0.0000
    6   0   0      1.4      0.9   1   0   1   0.0000
```

*The numbers indicated in bold are twin flags. All flags except several reflections at the end of the file have the twin flags equal to "1" because most reflections can be indexed in the first domain. Several reflections at the end of the file with the twim flag "2" are the ones, which cannot be transformed to the first domain because after such transformation they would break extinction rules for glide plane c. This is good example that twinning may change extinction rules.*

6. **The attempt to solve the twinned orthorhombic structure**

    *[On the screen: basic window of Jana]*

    "Run → Structure solution"

    *[On the screen: window of Structure solution]*

    In "Formula" textbox type list of chemical elements for CsLiSO4: Cs Li S O

    Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run Solution"

    *Superflip converges (after noise suppression) with R value 28%.*

    Press CLOSE to leave the listing

    Press "Draw structure"

    *[On the screen: window of Diamond]*

    Start "Build → Get molecules" or use  on the bottom toolbar

    *The solution looks unreasonably and other attempts to solve the structure (direct methods, use of different symmetries etc.) would fail as well.*

    Quit Diamond

    Quit the Structure solution wizard

7. **What is wrong?**

    *The figures of the structure produced by Superflip are looking like an overlap of several structures. In fact, with the three-fold twinning defined previously we could index all diffraction spots with four-time smaller (in the direct space) unit cell (see the figure).*
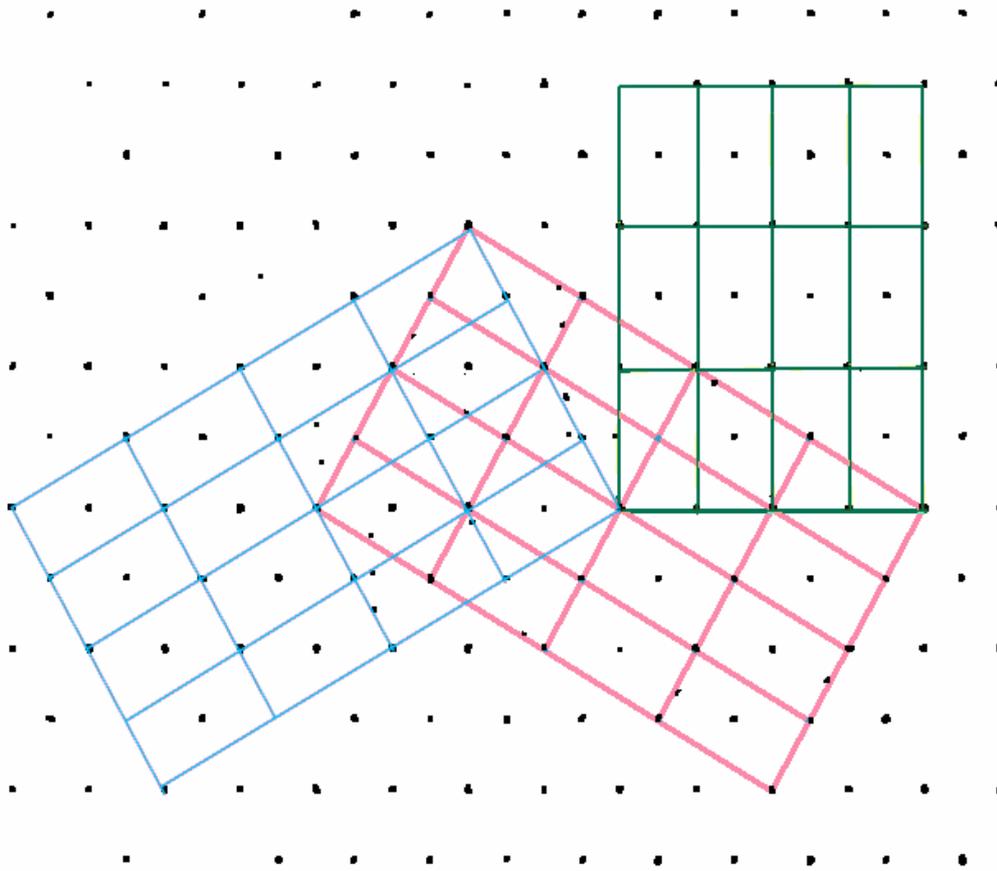
### 8. Transformation to four times larger reciprocal cell

Start "Tools → Transformations → Cell transformation".
Click "By matrix" and define the matrix:
"0.5 0 0 / 0 0.5 0 / 0 0 1"; OK; OK
OK to rewrite the old structure
Follow the wizard for creation of the refinement reflection file
Start "EditM50" to look what is the new symmetry after the transformation
Start "Edit/view → Editing of M90 file"
*The twin flags are now 1, 2 and 3 because some reflections cannot be indexed in the first domain. However, all three domains can index together the complete diffraction pattern.*
Start "Edit/view → Editing of M95 file"
*The file M95 still contains the original data indexed in the hexagonal unit cell. The transformation matrix in the header cumulates all transformations done up to now.*

### 9. Space group test and creating of refinement reflection file

*The used symmetry still follows from the originally selected $P6_3/mmc$. However, this symmetry was selected without any verification just to have some starting point*
Start "File → ReflCsection file → Make space group test".
YES to accept the warning
*[On the screen: "Tolerances for crystal system recognition"]*
Leave all settings default; NEXT
*[On the screen: Select supercell]*

Continue with the basic cell; NEXT
*[On the screen: Select Laue symmetry]*
Select Orthorhombic; NEXT
Select primitive unit cell; NEXT
*[On the screen: Select space group]*
Using the criteria described in the first example Select Pmcn; NEXT
Accept the space group transformed to the standard setting; FINISH
Follow the wizard for creation of the refinement reflection file
Accept the data block; FINISH

### 10. Structure solution

"Run → Structure solution"
*[On the screen: window of Structure solution]*
In "Formula" textbox check list of chemical elements for CsLiSO4: Cs Li S O
Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"
*Superflip converges (after noise suppression) with R value 22%. The suggested space group by Superflip is Imma but for twins the prediction may fail. On the other hand, Superflip confirms the symmetry elements of the current space group symmetry Pnma.*
Press CLOSE to leave the listing
Press "Draw structure"
*Because of twinning the electron density map produced by Superflip may be noisy and unreasonable maxima may appear. Li may be present in a wrong position or it may be missing. As usually, the results may be different for each run of Superflip because it starts from random phases.*
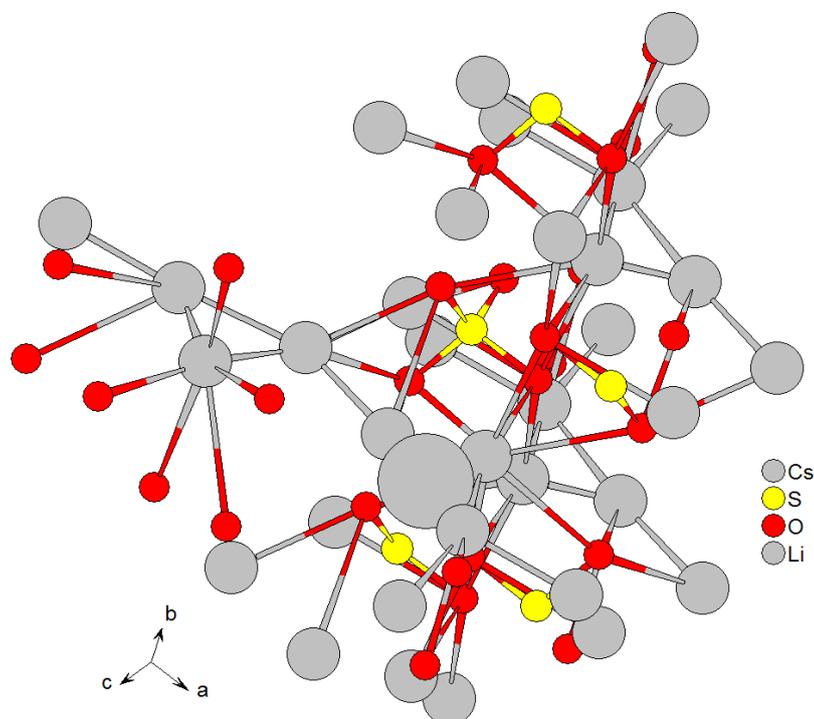


*Example of Superflip solution with wrong Li positions. The tetrahedra around the sulphur indicate that the solution is partially correct.*
Quit the Structure solution wizard

## 11. Completing the structure solution

In Refinement options set 100 refinement cycles and damping factor 0.5
Run Refine
*Refinement converges with R value about 9%.*
Using "Edit atoms" select and delete atoms which have been automatically rejected (if any) during the refinement because of too large Uiso
Start "Parameters → Twin fractions" and activate refinement of the twin volume fractions
Repeat refinement
*The R value should decrease significantly (to R ~ 5%) and the twin fractions will refine to values different of 1/3*
Using "Plot structure" identify the incorrectly assigned chemical types. Some oxygens of the SO4 tetrahedron may be wrongly assigned as Li, or there may be some additional spurious Li atoms
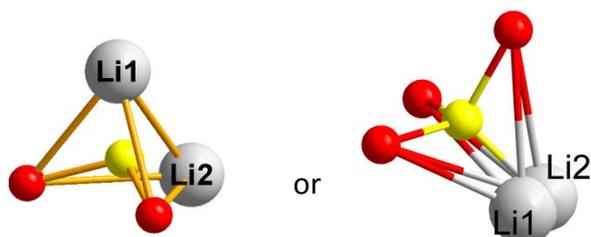


*Example of wrongly assigned chemical types (Li should be O)*

Using "Edit atoms" correct the chemical types and delete wrong atoms
Repeat refinement

## 12. Completeness of the structure

Start "EditM50"
Go to the page "Composition"; set 4 for "Formula units"; click "Formula from M40"
*The formula calculated from the structure model should be Cs Li S O4*
*If some atoms are missing (for instance Li), they must be found in difference Fourier map:*
OK to close EditM50
Start options for Fourier (the right mouse button on the icon "Fourier")
In page "Basic" select "Map type" = "Fobs-Fcalc - difference Fourier"
OK; YES+START
YES to start procedure for including new atoms
*In the next windows the left panel shows difference maxima, right panel shows the selected maximum in various symmetry equivalent positions with distances to already existing atoms. In the example below, for instance, Max1 (after proper transformation) can have a distance 1.9Å to O3, O2 and O1. This is probably the missing lithium*

| List of peaks | | | Equivalent coordinates | | | Distance | Atom |
|---|---|---|---|---|---|---|---|
| Max1 | | | 0.823328 | 0.250000 | 0.418222 - as read in | | |
| Max2 | | | 0.676672 | 0.750000 | -0.081778 | 1.92 | O3 |
| Max3 | | | 0.323328 | 0.250000 | 0.081778 | 1.94 | O2 |
| Max4 | | | 0.176672 | 0.750000 | -0.418222 | 1.96 | O1 |
| Max5 | | | | | | | |
| Max6 | | | | | | | |
| Max7 | | | | | | | |
| Max8 | | | | | | | |
| Max9 | | | | | | | |
| Max10 | | | | | | | |

Peak : Max1    Charge : 1.470                    Include selected peak

For adding a missing atom make the following steps:

Select the desired symmetry equivalent position of the maximum

*Here for instance 0.676672, 0.75, -0.081778 for Max1*

Click "Include selected peak"

Type name of the atom; TAB

*In our example type Li\**

OK

After adding all desired maxima:

Finish; YES to include new atoms

Repeat refinement

Using "Edit atoms" set harmonic ADP for all atoms

*Refinement converges with R value around 2.5% and GOF 2.9, for 42 parameters*
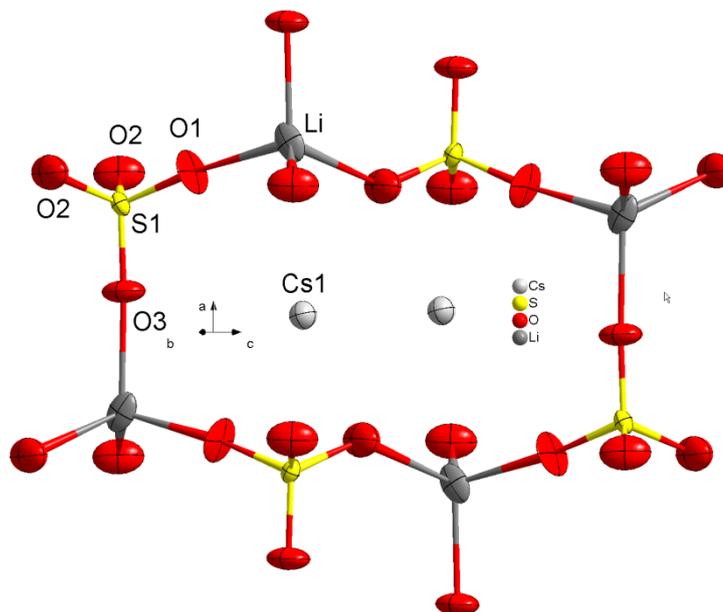


*The final structure*

# Example 3.4: Ca₂Fe₂O₅

**HT structural phase transition, coexistence of two phases in single crystal with strong overlaps.**

H. Kruger, V. Kahlenberg, V. Petříček, F. Phillipp & W. Wertl, *J. Solid State Chem.*, **182**, (2009), 1515-1523.

LT phase – orthorhombic, *Pnma*, cell parameters ~ 5.4707, 14.9897, 5.6302 Å
In one layer of Fe tetrahedrons there is only one type orientation (e.g. Left)
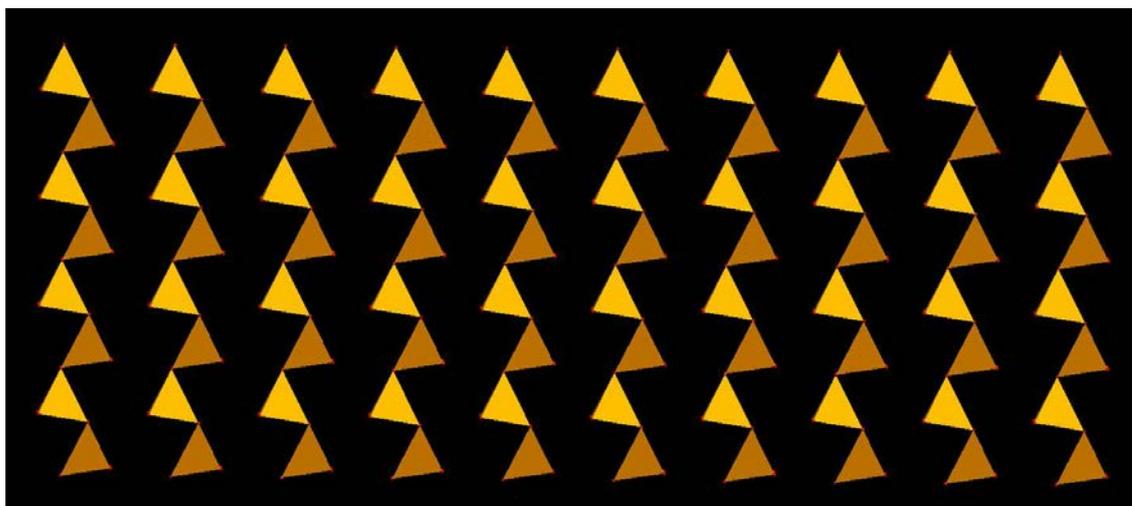


HT phase (>710°C) – orthorhombic, modulated, *Imma(00γ)s00*, cell parameters ~ 5.4707, 14.9897, 5.6302 Å, **q**=(0,0,0.58). In one layer of Fe tetrahedrons there are two different orientations (Left and Right) alternating with the period incommensurate to the basic cell.
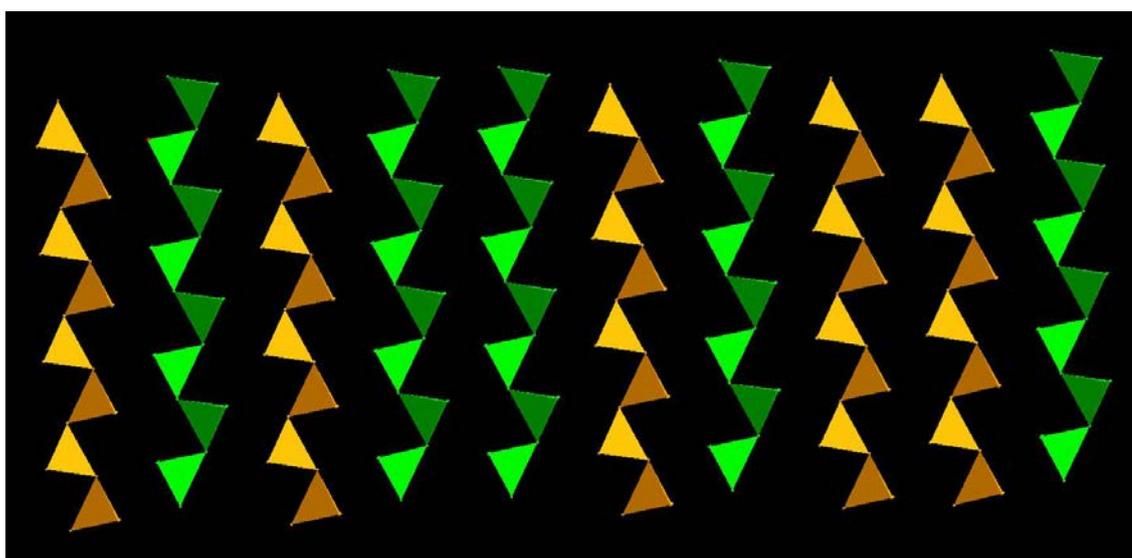
Diffraction pattern: Strong 1st order, no 2nd order and some weak 3rd order satellites → crenel like modulation with $\Delta \approx 1/2$.

Main features of the solution for the HT phase: The atoms Fe2 and O3 are occupying the positions close to the Wyckoff position 4(e), point group *mm2*. The mirror *m*, with normal along *a* axis, having half shift along the internal $x_4$ axis, transforms the "left" oriented ribbon of Fe tetrahedrons to the "right" ones and the occupational modulations of both atoms have a crenel like shape.

During the first order phase transition both phases (LT and HT) are coexisting in a wide region of temperatures and with x-ray diffraction they both contribute to the same diffraction pattern. In this example we shall start from the known structures of both phases and we shall demonstrate that the generalized twinning option in Jana2006 can also be applied to single crystals composed from two or more phases.

As a starting point you have at disposal the HT structure refined against the data set having the highest possible fraction of the HT phase from all measured data sets. In the first part of the example it is demonstrated main features of the solution. In the second part the LT phase will be read in from the supplied CIF file and then the final refinement will be performed.

Input files:     HT_phase.m40, HT_phase.m50, HT_phase.m90, HT_phase.m95 and LT_phase.cif.

1. ***Open the modulated phase***
   Start Jana2006
   "File → Structure → Open" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click HT_Phase

2. ***Check systematically extinct reflections***
   "File → Reflection file → Create refinement reflection file"
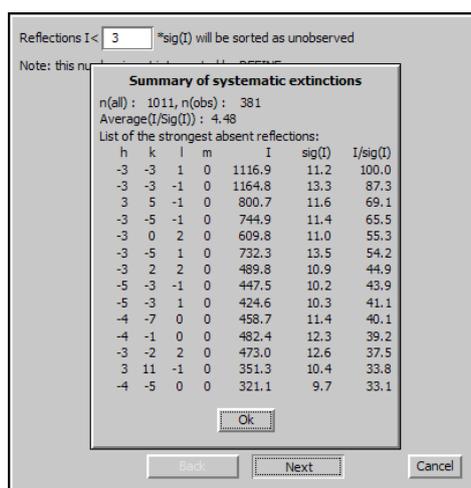


*There are 381 observed reflections, some of them relatively strong, which do not follow the extinction rules for Imma(00γ)s00. This means that the reflections of the second "P-centered" phase are really present.*

### 3. Run refinement

*[On the screen: basic window of Jana]*

Right-click the icon of Refine.

*[On the screen: refinement options]*

Define 100 of cycles, Damping factor 1; OK

Choose "YES+START"

*The refinement converges with R(obs) about 5.98%, 4.48% and 9.12%.*

### 4. Check the refinement model

*[On the screen: basic Jana window]*

Start "Edit atoms"

*[On the screen: list of atoms]*

Double-click on the first atom Fe1

*[On the screen: list of atoms]*

Go though all atoms (using arrows of the top-left text box) and check the modulation model.

*All atoms except Fe2 and O3 have just one harmonic positional wave. Atoms Fe2 and O3 have one crenel function.*

Write down coordinates of Fe2 and O3 and then go to "Edit" thumbnail, press the button "Occupancy" and write down also the values of delta and x40

*Fe2   (-0.052,0.25,0.568)   delta=0.5 (fixed)   x40~0.6404*

*O3   (-0.402,0.25,0.625)   delta=0.5 (fixed)   x40~0.6755*

Escape the form;

### 5. Run dist

*[On the screen: basic Jana window]*

Right-click the icon of Dist.

*[On the screen: distance commands]*

Use the default parameters except for the listing form which should be changed to "With symmetry code".

OK; Start the program;

Open the listing and look for Fe2 coordination;

*The atom Fe2 is coordinated by the atom O2, O2#s2, O3 and O3#s4c2t0,0,1.*

### 6. Draw modulation curves in Contour for Fe2 and O3

*[On the screen: basic Jana window]*

Double-click the icon Contour; Press the button "New plot" if active;

Select "Fourier map" and "Draw maps as calculated"; OK

In thumbnail "Basic" select "F(obs) – Fourier" and in thumbnail "Scope" select "by a central point";

Center "0 0.25 0.568"; Section $1^{st} \rightarrow$ x1, $2^{nd} \rightarrow$ x4, $3^{rd} \rightarrow$ x2, $4^{th} \rightarrow$ x3;

 x4 minimum $\rightarrow$ 0, maximum $\rightarrow$ 2, step 0.02

Scope $\rightarrow$ 3 0 0; Step $\rightarrow$ 0.02; OK

*[On the screen: the following map]*
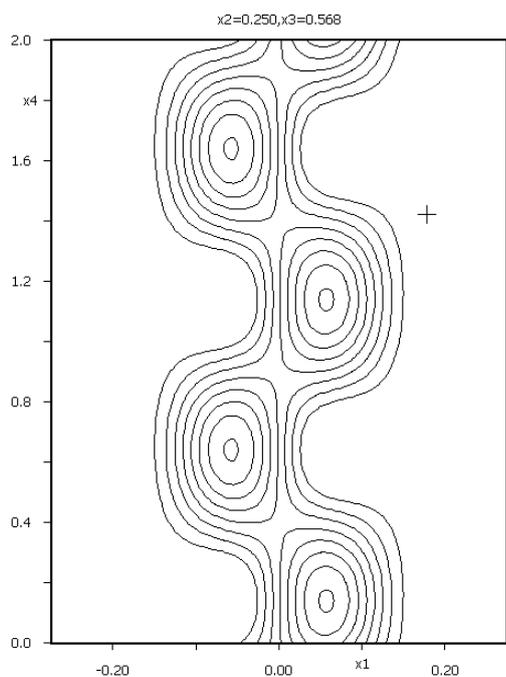
Press "Atom edit" and add two atoms Fe2 and Fe2#s8. The second one is the position generated by the eighth symmetry operation i.e. by $-x_1\ x_2\ x_3\ x_4+1/2$;

*[On the screen: the following map]*
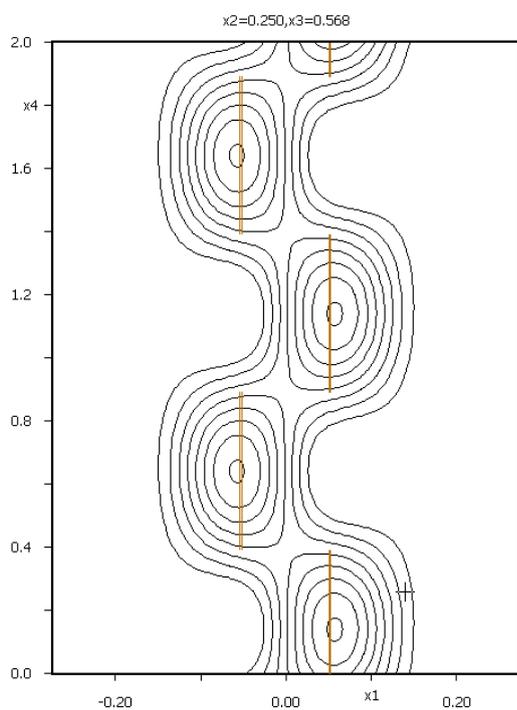


Repeat it for the center at -0.5 0.25 0.625 (a position close to O3);
Press the button "Atoms edit" to show the modulation curves for O3 and the symmetry related atom O3#s8t-1,0,0. The translation part -1,0,0 returns the symmetry related atom

*[On the screen: the following map]*

x2=0.250,x3=0.625
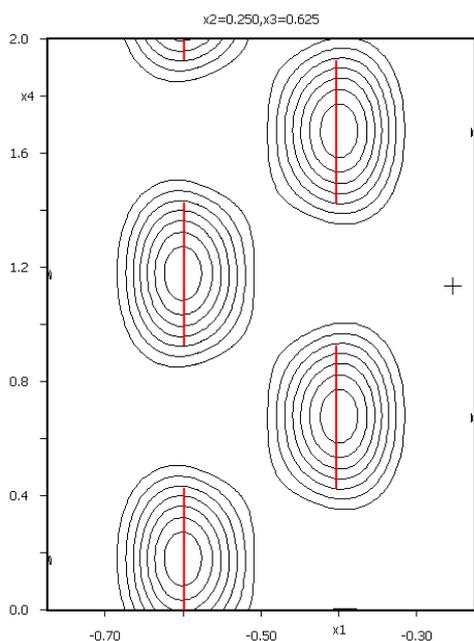


*The crenel function for atoms Fe2 and O3 assures the alternation between the "Left" and "Right" configurations of Fe tetrahedrons. During the refinement the "delta" values were fixed to 0.5 for both atoms. But there were no restrictions applied to x40. Now we have to check:*

*(a) if there is no overlap between two symmetry related positions of Fe2 and Fe2#s8 and O3 and O3#s8t-1,0,0.*

*The symmetry operation #8 has the following form: $-x_1, x_2, x_3, x_4+1/2$*
*for the atom Fe2 we have:* $t_{min} = x_{40} - \Delta/2 - \mathbf{q} \cdot \mathbf{r}$   $t_{max} = x_{40} + \Delta/2 - \mathbf{q} \cdot \mathbf{r}$ *and for the*
*symmetry related Fe2#s8:* $t_{min} = x_{40} + 1/2 - \Delta/2 - \mathbf{q} \cdot \mathbf{r}'$   $t_{max} = x_{40} + 1/2 + \Delta/2 - \mathbf{q} \cdot \mathbf{r}'$
*From the fact that the modulation vector is $(0,0,\gamma)$ and that the third component of the symmetry related atoms remains the same for both positions, it follows that the t intervals are fully separated with no overlaps.*
*The same conclusion is valid also for the atom O3.*

*(b) if the t intervals in which exist atom Fe2, O3 and O3#s4c2t0,0,1 are identical.*

*For Fe2 and O3 this means:*

$$t_{min}(\text{Fe}\,2) = x_{40}(\text{Fe}\,2) - \Delta(\text{Fe}\,2)/2 - \mathbf{q} \cdot \mathbf{r}(\text{Fe}\,2) = t_{min}(\text{O}\,3) = x_{40}(\text{O}\,3) - \Delta(\text{O}\,3)/2 - \mathbf{q} \cdot \mathbf{r}(\text{O}\,3) =$$

*taking into account the fact that* $\Delta(\text{Fe}\,2) = \Delta(\text{O}\,3) = 1/2$ *we have:*

$$x_{40}(\text{Fe}\,2) - \mathbf{q} \cdot \mathbf{r}(\text{Fe}\,2) = x_{40}(\text{O}\,3) - \mathbf{q} \cdot \mathbf{r}(\text{O}\,3) \quad \Rightarrow \quad x_{40}(\text{O}\,3) = x_{40}(\text{Fe}\,2) - \mathbf{q} \cdot [\mathbf{r}(\text{Fe}\,2) - \mathbf{r}(\text{O}\,3)]$$

*and finally* $x_{40}(\text{O}\,3) = x_{40}(\text{Fe}\,2) - \gamma \cdot [z(\text{Fe}\,2) - z(\text{O}\,3)]$ \qquad\qquad *(1)*

*Numerically:* $x_{40}(O3) = 0.6755 \approx 0.6404 - 0.6101 \cdot [0.568 - 0.625] = 0.6752$ *and*
$t_{min}(O3) = 0.6755 - 0.6101 \cdot 0.625 = 0.0442$

*This means that the refined value was really close to the ideal value*

*For O3#s4c2t0,0,1 the symmetry operation $s4c2t0,0,1$ is $x_1+1/2$ -$x_2+1/2$ -$x_3+3/2$ -$x_4+1/2$ modifies $t_{min}$ to:*

$$t_{min} = x_{40}(O3\#\, s4c2t0,0,1) - \Delta(O3\#\, s4c2t0,0,1)/2 - \mathbf{q} \cdot \mathbf{r}(O3\#\, s4c2t0,0,1)$$

*Numerically:* 
$$z(O3\#\, s4c2t0,0,1) = 3/2 - z(O3) = 0.825$$
$$x_{40}(O3\#\, s4c2t0,0,1) = 1/2 - x_{40}(O3) = -0.1755$$

*This means that:* $t_{min} = -0.1755 - 0.6101 \cdot 0.875 - 0.25 = -0.959$ *and therefore we have to modify the equation by adding one:*

$$t_{min}(Fe\,2) = x_{40}(Fe\,2) - \Delta(Fe\,2)/2 - \mathbf{q} \cdot \mathbf{r}(Fe\,2) =$$
$$x_{40}(O3\#\, s4c2t0,0,1) - \Delta(O3\#\, s4c2t0,0,1)/2 - \mathbf{q} \cdot \mathbf{r}(O3\#\, s4c2t0,0,1) + 1 \Rightarrow$$

$$x_{40}(O3\#\, s4c2t0,0,1) = x_{40}(Fe\,2) - \mathbf{q} \cdot [\mathbf{r}(Fe\,2) - \mathbf{r}(O3\#\, s4c2t0,0,1)] - 1$$

*and by applying the symmetry operation $s4c2t0,0,1 \sim x_1+1/2$ -$x_2+1/2$ -$x_3+3/2$ -$x_4+1/2$:*

$$1/2 - x_{40}(O3) = x_{40}(Fe\,2) - \gamma \cdot [z(Fe\,2) - 3/2 + z(O3)] - 1 \Rightarrow$$

$$x_{40}(O3) = -x_{40}(Fe\,2) + \gamma \cdot [z(Fe\,2) - 3/2 + z(O3)] + 3/2 \qquad\qquad (2)$$

*Combining (2) with the previous one we have for $x_{40}(Fe\,2)$:*

$$x_{40}(Fe\,2) = 3/4 \cdot (1 - \gamma) + \gamma \cdot z(Fe\,2) \quad \Rightarrow \quad t_{40}(Fe\,2) = 3/4 \cdot (1 - \gamma)$$

$$x_{40}(O3) = 3/4 \cdot (1 - \gamma) + \gamma \cdot z(O3) \quad \Rightarrow \quad t_{40}(O3) = 3/4 \cdot (1 - \gamma)$$

*Numerically:* $x_{40}(O3) = 0.6755 \approx 0.75 \cdot 0.3899 + 0.6101 \cdot 0.625 = 0.6737$
*This means that both t40 parameters can be fixed to the same constant value as Fe2.*

7. **Run restricted refinement**
   *[On the screen: basic window of Jana]*
   Right-click the icon of Refine.
   *[On the screen: refinement options]*

Select thumbnail "Various" and press the button "Equations":
Define equations:
t40[Fe2]=0.75-0.75*cq3
t40[O3]=0.75-0.75*cq3
OK; Start Refinement;
*The refinement converges with R(obs) about 5.99%, 4.49% and 9.14% which means that it had almost no effect.*
Open the listing to check the applied equation:

*Equations defined by user:*

*x40[Fe2]=0.2924+0.6101*z[Fe2]*
*x40[O3]=0.2924+0.6101*z[O3]*

8. **Continue with a new structure name**
   *[On the screen: basic window of Jana]*
   Start Jana2006
   "File → Structure → Save as" opens a file manager
   Right pane: Write a new structure name e.g. "Both_Phases"
   *[On the screen: "Continue with the new structure?"]*
   Yes;

9. **Adding of the LT phase**
   *[On the screen: basic window of Jana]*
   "Tools → Phases → New phase";
   Select "Import from CIF format"; Press "Browse" and select the file LT_Phase.cif;
   OK

10. **Define the twinning matrices**
    *[On the screen: the form for defining of twinning matrices]*
    *The "twinning" matrices define relationship between the phases and the reference cell parameters. Unlike real twinning they may change the unit cell. In our case both phases are defined in the same cell.*
    Both matrices are unit ones. The first is to be applied to the first phase and the second to the second phase.
    OK; follow the wizard for creating the refinement reflection file
    *Systematic extinctions are now much better fulfilled:*
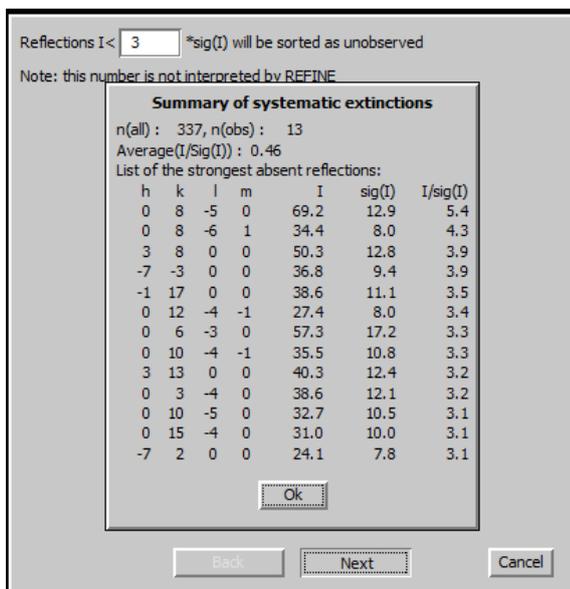
## 11. Run refinement

[On the screen: basic window of Jana]

Right-click the icon of Refine.

[On the screen: refinement options]

Change the damping factor to 0.5.

OK; Save and run the refinement;

The refinement converges with R(obs) about 4.99%, 4.09% and 7.37%.

## 12. Refine anisotropic ADP of atoms from the second phase

[On the screen: basic window of Jana]

Switch the phase to the Phase#2 (thumbnails in the lower-left corner)

Using "Edit atoms": select all atoms and change ADP to harmonic;

OK;

## 13. Run refinement

[On the screen: basic window of Jana]

Double-click the icon of Refine.

The refinement converges with R(obs) about 4.60%, 3.78% and 6.75%.

## 14. Check the phase fraction factor

[On the screen: basic window of Jana]

"Parameters → Twin fractions"

The fraction of the second domain was refined to 0.276

# Example 4.1: PtCu

**Disordered structure.**
**Revised 15 October 2014**

**[Cu(CH₃-NH-CH₂-CH₂-NH₂)₂] [Pt(CN)₄]**

**Polyhedron 2011, 30, 269-278.**

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: PtCu.hkl, PtCu_red.sum
Frame scaling, absorption correction: done with software of diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click PtCu

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction-CCD"; NEXT
   *[On the screen: "Define basic input file"]*
   Use "input from sum file"; OK
   *[On the screen: "Your sum file consists of 6 appended data reduction runs"]*
   OK;
   *[On the screen: "Complete/correct experimental parameters"]*
   Leave all settings unchanged; NEXT
   *[On the screen: "Define the reference cell/split by twinning"]*
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   *[On the screen: "Tolerances for crystal system recognition"]*
   Leave all settings default; NEXT
   [On the screen: Select Laue symmetry]
   Select Tetragonal Laue symmetry 4/m; NEXT
   *Although for 4/mmm Rint is relatively good and we are not using the maximal Laue symmetry, in this case twinning does not occurr*
   Select primitive unit cell; NEXT
   *[On the screen: Select space group]*
   Using the criteria described in the first example Select P42/m; NEXT

Select "Accept the space group transformed into the original cell"; FINISH

*Original cell is used because the suggested transformation does not change the unit cell and the space group symbol*

YES to create refinement reflection file M90

## 5. Creating refinement reflection file

NEXT to confirm threshold 3sigma

*[On the screen: settings for merging of reflections]*

Leave all settings default; NEXT

Accept the data block; FINISH

## 6. Structure Solution Wizard

*[On the screen: window of Structure solution]*

In "Formula" textbox type chemical composition C10 H20 Cu Pt N6, two formula units

Select "Use Superflip"

Leave other settings default; "Run Solution"

*[On the screen: listing of Superflip]*

*Superflip converges rapidly with R~18% and very good (i.e. low) agreement factors for the symmetry 42/m*

*The suggested centering vector (0,0,1/2) is in contradiction with found systematic extinctions, it cannot be used*

Close listing of Superflip

Press "Quit" to leave the Structure solution wizard

## 7. Completing the structure model

Plot the structure found by Superflip

*There should be a chain Pt – C – N – Cu visible in the plot. For this example, Superflip sometimes returns wrong positions of Pt, in such case the plot would show strange coordination of Pt (this should be planar) and R value of the following refinement would be large.*

Open Refinement options, change number if refinement cycles to 100

Run Refine

*Refinement converges with R value about 12%*

Start "Edit atoms" and define harmonic ADP for Pt1 and Cu1

Delete rejected atoms (if the button "Select rejected" is active)

Run Refine

*Refinement converges with R value about 9%*

Open Fourier options (right button on Fourier icon) and select Difference Fourier map, OK, YES+Start to execute Fourier calculation

YES to start the procedure for including of the new atoms

For "Show distances up to" type 4

*Alternatively we could use "Parameters → Atoms → New"*

*[On the screen: Inserting/replacing of atoms]*

OK

*[On the screen: list of peaks]*

*In the left panel Max1 is focused. Its integrated charge is displayed at the bottom. In the right panel we can see distances of symmetry equivalent positions of Max1 to already existing atoms of the structure model, up to the previously defined limit 4Å. We can expect*

*distances ~2 Å for Pt-C, ~1.5 Å for C-C, ~1 Å for C-N of cyano group and ~3 Å for Pt-N. By selecting proper symmetry equivalent position of the difference maximum we keep the atoms of the molecule together without need of transformation.*

In the left pane focus Max1 (or other if Max1 has no good distance)

In the right pane focus its reasonable position having good distance to some neighbor

Press "Include selected peak"

*[On the screen: Complete information for the new atom]*

For "Name of atom" type C* (even for nitrogen); TAB; OK

*The difference maximum has been added to the structure model in the symmetric position which is close to C2. The chemical type was assigned to carbon, the name will be C+sequence number.*

Using the name C* add the remaining difference maxima with proper distance. Skip distances below 1 Å as well as maxima with too small charge or strange distances. At this point all atoms shoudl be added as carbon, we shall distinguish between C and N later.

FINISH; YES to save the new atoms

*Finally the structure model should contain 9 atoms. It may happen that some improper maxima have been added – they will be discarded by the following refinement based on large ADP*

Run Refine

*Refinement converges with R value below 5%*

Start "Edit atoms" and check if the button "Select rejected" is enabled.

*If "Select rejected" is enabled some atoms have zero occupancy. It was set by Refine because their Uiso was refined above the limit defined in the Refinement options (default limit is 0.2).*

Delete rejected atoms.

Check with "Select all" that the structure contains 9 atoms

*If the structure model does not contain all 9 atoms, repeat calculation of difference Fourier*

Leave "Edit atoms"

Plot structure in Diamond
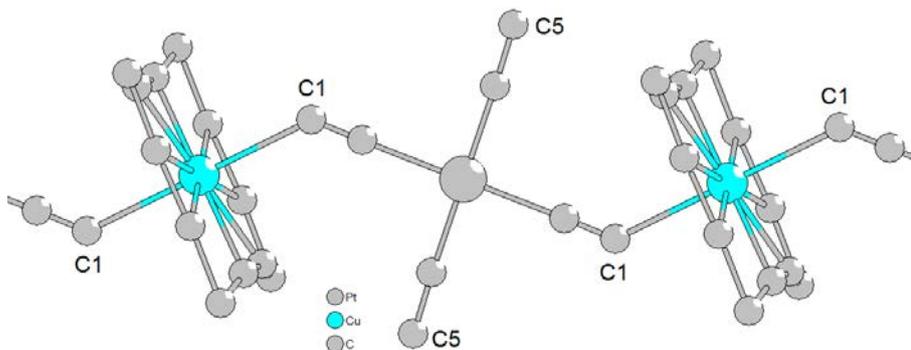


Note names of atoms (C1, C5 in our example) which should be nitrogen

Leave Diamond and change chemical type and names of C1, C5

Run Refine

Start "File → Structure → Save As" and create a backup copy, for instance PtCu_completed

## 8. Solution of disorder

Open "Edit atoms" and define harmonic ADP for all atoms

*Double-click is necessary in the locked option*

Run Refine

*Refinement converges with R value ~3% for 60 parameters*

Plot the disordered part of the structure
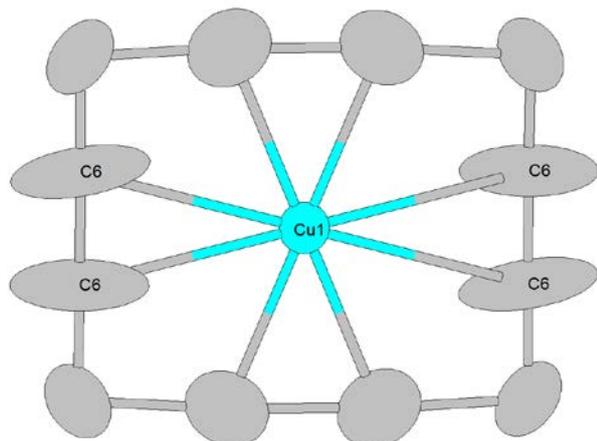


Open "Edit atoms", select C6 (in this calculation – it may differ!)
Choose "Split atomic position"
*[On the screen: split atomic position window]*
Leave all settings default; Apply
*[On the screen: list of atoms in "Edit atoms"]*
Select C6, go to "Edit/define atoms", switch to the page "Edit", activate refinement of occupancy ai
Close "Edit atoms", YES to save changes
*The next steps show automatically created restriction for C6, C6'*
Open Refinement options, go to the page "Various", press "Restrictions"
Focus the line "restric C6 2 C6'
Press Load
*In the lower part of the window there are listed properties of the restriction. The atom C6 was split to two positions, C6 and C6'. Both atoms will have the same ADP and their occupancy will be complementary.*
Leave Refinement options
Run Refine
*Refinement converges with R=~2%*
Plot the same part of the structure
*(to separate some atoms in Diamond select them by mouse, press Ctrl-I to invert selection and press Delete on the keyboard)*
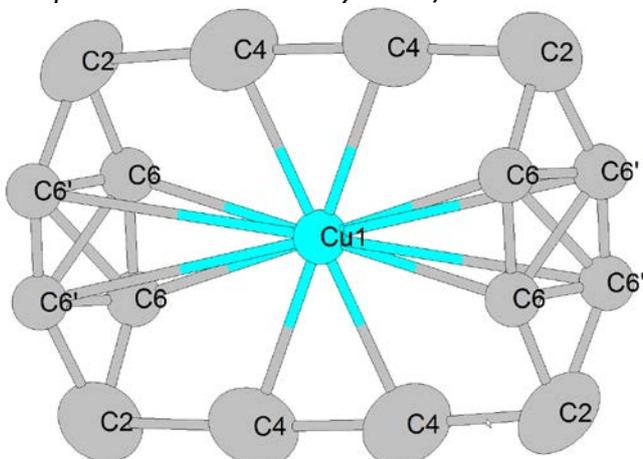


Open "Edit atoms"
Enable refinement of occupancy for C2 and C4 *(your labels may differ!)*

Run Refine
*Refinement converges with R=1.9%*
Note refined occupancies
Plot the same part of the structure and compare occupancies of carbons
*(Diamond only shows reduced occupancies and does not indicate cases when occupancy exceeds the full occupancy)*
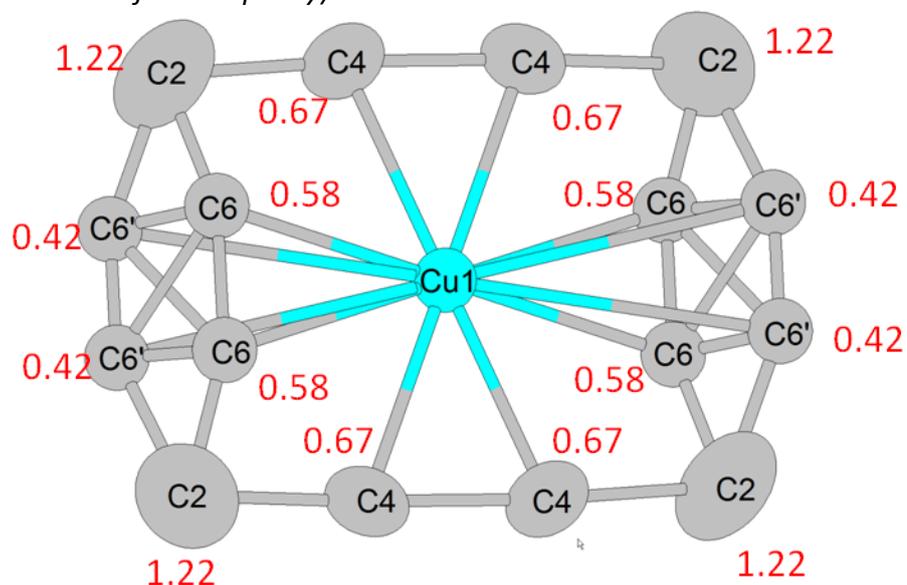


*From the occupancies we may speculate that the methyl-ethylenediamine chains will be oriented like in the next figure:*
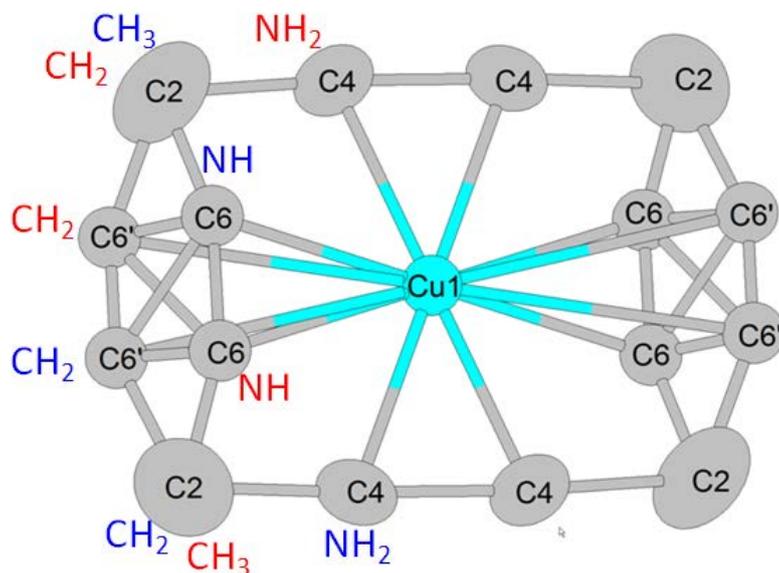


Open "Edit atoms" and change chemical type of C4 and C6 to nitrogen.
Rename C4 to N4 and C6 to N6 and C6' to C6.
*The names may differ in your solution*
*The atom names in the restrictions (page Various of the refinement commands) are renamed automatically*
Run Refine
Open "Edit atoms"

Change occupancy of C2 to 1
Split the position of C2 by the same tool and by the same way like C6 was split previously
Enable refinement of occupancy for C2
*The reason for changing the occupancy to 1 is that the restriction keeps the sum of occupancies.*
Run Refine
*A slight increase of R value is due to change of ADP to isotropic during splitting.*
Open "Edit atoms" and change ADP of C6 and N6 from isotropic to harmonic
Open Refinement options, go to the page "Various", press "Restrictions"
Load the restriction C6-N6 and uncheck "ADP parameters"; press "Rewrite"
*The atoms C6 and N6 are so far from each other that their ADP can be refined independently*
OK; OK; YES+Start to save changes and run refinement
*Refinement converges with R=1.7%*
Plot the structure
*Atom N4 represents in two symmetry equivalent positions the terminal nitrogen of both methyl-ethylenediamine groups. From this follows that both chains must have the same occupation 0.5*
Open "Edit atoms" and select all atoms of both methyl-ethylenediamine groups (N4,C2,C2',C6,N6 in our example)
Rewrite their occupations to 0.5 and disable their refinement
*Double-click will be necessary for the locked fields*
Run Refine
Create backup copy, for instance PtCu_beforeH
Plot the result

9. **Adding hydrogen atoms**

   *For adding hydrogen atoms the automatic procedure cannot be used because of disorder. In the following plot we can find how many hydrogen atoms we need for carbons and nitrogens. Warning: in your structure model the distances may differ significantly because hydrogen atoms are not yet present.*
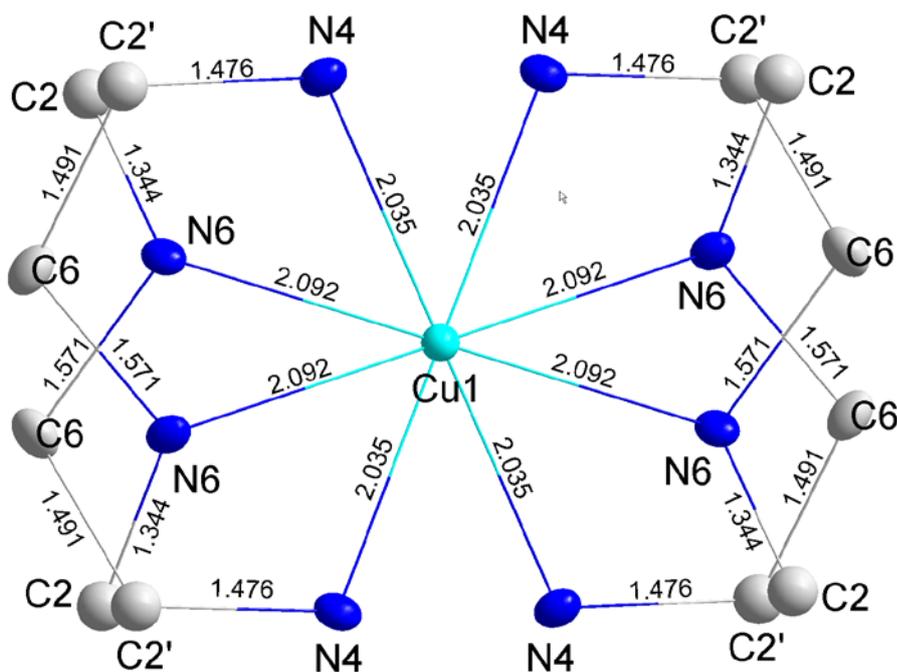
*C2 belongs to methyl*
*C2' and C6 belong to CH2*
*N4 belongs to NH2*
*N6 belongs to NH*

Open "Edit atoms"
Select C2, C2' and C6 *(labeling may differ)*
*N4 and N6 are skipped because position of their hydrogen atoms will be refined*
Start "Action → Adding of hydrogen atoms"
**Clear** "Try automatic run"; OK
*[On the screen: Adding hydrogen atoms for C2]*
*C2 belongs to methyl, therefore it has one neighbor and three hydrogen atoms*
Select "Tetrahedral"
Change number of neighbors to 1
Click in the textbox for the neighbor: this activates the button "Select neighbors" in the lower right corner
Press "Select neighbors"
Select N6; OK
In the textboxes for hydrogens type H1C2, H2C2 and H3C2
Press "Apply → Go to next"
*[On the screen: Adding hydrogen atoms for C2']*
*C2' belongs to CH2, therefore it has two neighbors and two hydrogen atoms*
Select "Tetrahedral"
Change number of neighbors to 2
Click in the first textbox for neighbors; button "Select neighbors" will be activated
Press "Select neighbors"
Select N4 and C6; OK
In the textboxes for hydrogens type H1C2' and H2C2'
Press "Apply → Go to next"
*Analogously continue for C6. For C6 two atoms N6 will be shown as neighbors but the one with too short distance belongs to the second chain*
Leave "Edit atoms"
Check in Diamond geometry of hydrogens
Run Refine
*Refinement converges with R value 1.6% for 67 parameters*
Open Fourier options
Select difference Fourier map
Check "Apply sin(th)/lambda limits"
Set maximal sin(th)/lambda to 0.5
*This setting enhances finding of hydrogens in the difference Fourier map*
Calculate difference Fourier map
Yes to start procedure for including of new atoms
*In this example, we assume that all hydrogen atoms of N4 and N6 are found in this difference map. It may also happen that only some of them are found. In such case the process must be repeated after the refinement and calculation new difference map.*
Set distances limit to 1.2 Å
Add two difference maxima which could be hydrogens of N4 like H1N4 and H2N4, with occupancy 0.5 (in the box "Complete information for the new atom" type 0.5 for

"Occupancy reduction")

Add one difference maximum which could be hydrogen of N6 like H1N6, with occupancy 0.5

Verify new hydrogens by plotting

Open Refinement options

Go to the page "Various" and press "Keep commands"

Select ADP, type "N4" to the textbox "Central"

Change number of hydrogens to 2

Click in the first textbox for hydrogens; press "Select hydrogens" and select H1N4, H2N4

Press Add

*By this procedure we have defined manually constrain for ADP of H1N4 and H2N4. They will be 1.2 multiple of the $U_{eq}$ of N4*

Create analogous constrain for H1N6

Leave "Keep commands"

*[On the screen: page "Various" of the refinement commands]*

Press "Distance restrains"

For "Atoms" type "N4 H1N4; N4 H2N4; N6 H1N6"

For Value type 0.87; press Add; OK

*By this procedure we have defined manually the restrain on the distances N4-H1N4, N4-H2N4 and N6-H1N6.*

Run Refine

*Refinement should converge with $R_{obs}$ slightly below 1.6% for 76 parameters*

Plot the final structure model
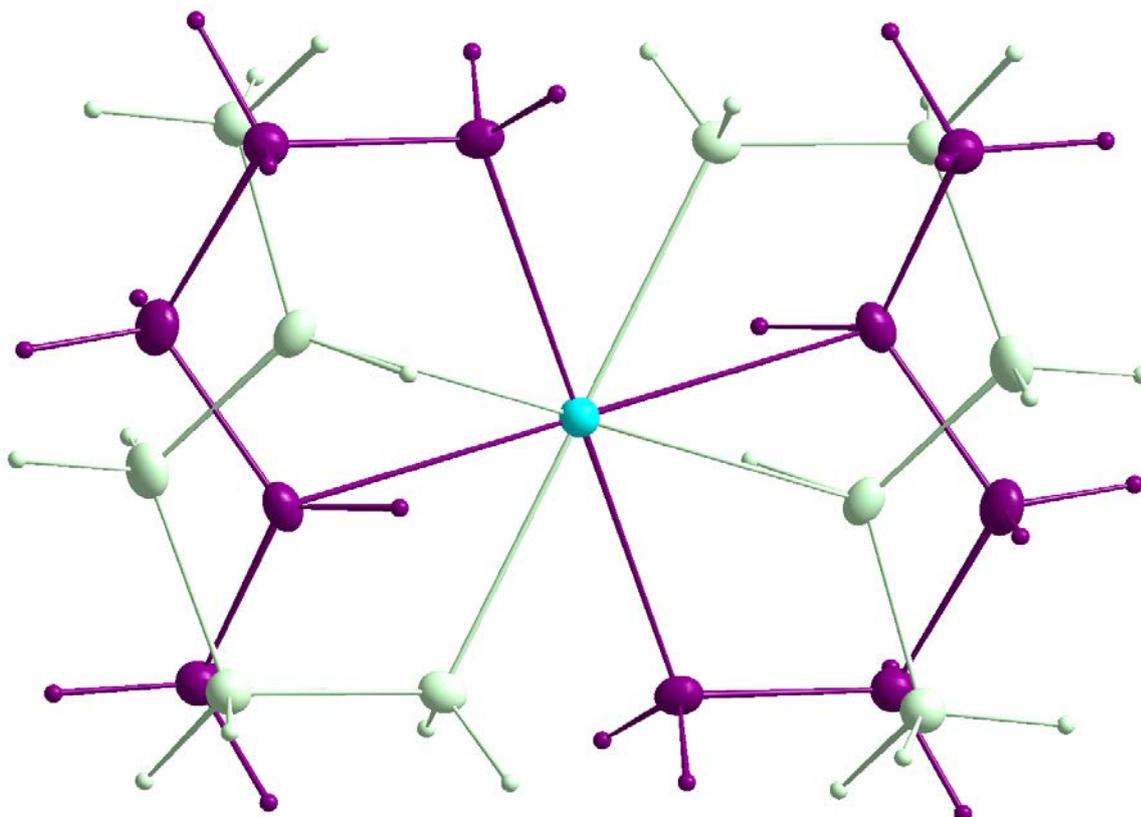
# Example 4.2: NaNiFe

**Structure with mixed sites.**

**Revised: 08 March 2012**

**Expected formula: $NaNiFe_2P_2O_{12}$**

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: NaNiFe.hkl, NaNiFe_red.sum
Frame scaling, absorption correction: done with software of diffractometer

1. ***Creating new jobname***
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click NaNiFe

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction $\rightarrow$ CCD"; NEXT
   Select "Input from cif_od file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   *7999 reflections has been imported*
   For absorption correction select "None or done before importing"; NEXT
   FINISH
   *[On the screen: Data repository]*
   OK; YES to accept the data set

3. ***Symmetry Wizard, merging of reflections***
   Go through the steps of the Symmetry wizard, select Laue symmetry 2/m, C centering and space group C2/c
   Accept the space group transformed into the original cell; FINISH
   Go through the steps of the Merging wizard leaving all settings default
   *Rint will be 2.57%*

4. ***Structure Solution Wizard***
   *[On the screen: window of Structure solution]*
   In "Formula" textbox type chemical composition Na Ni Fe P O, 4 formula units
   Select "Use Superflip"
   Select "Use a specific random seed" and for the random seed define 111
   *Fixing the random seed to 111 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. For normal work random seed should not be fixed*
   Leave other settings default; OK
   *[On the screen: listing of Superflip]*
   *Superflip converges rapidly with R~18% and very good (i.e. low) agreement factors for the*

*symmetry C2/m*
Close listing of Superflip and accept the results

5. **Checking the structure model**
Start EditM50, page Composition, press "Formula from M40"
*It shows the formula "Na Ni3 Fe0 P3 O13" (for Z=4). However, the expected disphosphate unit is $P_2O_{12}$ with negative charge -9. The positive charge NaNi3 is only 7. Why do we have 13 oxygens? Where is Iron?*
Leave to the basic window of Jana2006
Start refinement
*Refinement converges with R=5.7%.*
Using "Edit atoms" change all ADP to harmonic and repeat the refinement
*Refinement converges with R=4.4%*
Open Fourier options and select Difference Fourier
"Yes+Start" to save changes and start Fourier
YES to include new atoms
*The list of Fourier maxima does not display any useful maximum. The structure is complete.*
Return to the basic window of Jana2006 without adding new atoms
Open refinement listing
Go To → list of serious warnings
*The listing says that ADP of Na1 and O1 are not positive definite*
Return to the basic window of Jana2006

6. **Calculation of distances and bond valences**
Open Distances options (right-click the icon Dist)
Uncheck "d(max) derived from…"
For "d(max)" type 3.5
Press the button "Define coefficients for bond valences"
Select "1st atom type" Na; "2nd atom type" O
Press the button "From file" and select the first line for bond valences coefficients
*The list shows the coefficients like published in various sources. We are interested only in differences in coordinations and not in absolute values of bond valences sums. Therefore we shall use the first line for all cases.*
Press Add
Do the same for the pairs Ni-O, P-O and Fe-O
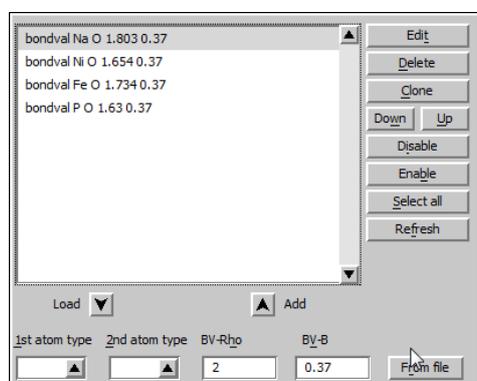


OK; OK; Yes+Start
Yes to open listing
Go To → List of distances

Go To → List of bond valences

*Summary ("BVS=bond valence sum"):*

*Ni1 is coordinated by six oxygens, Ni-O between 2.10 and 2.13 Å, BVS 1.75*

*Ni2 is coordinated by six oxygens, Ni-O between 1.95 and 2.12 Å, BVS 2.21*

*P1 and P2 are quite normal*

*Na1 is coordinated by eight oxygens, Na-O between 2.27 and 2.83 Å, BVS 1.43*

*O1 is coordinated by eight oxygens, O1-O between 2.38 and 2.87 Å*

*ADP of Na1 and O1 are negative*

*In plotting software we can get following picture with O1 in the void:*
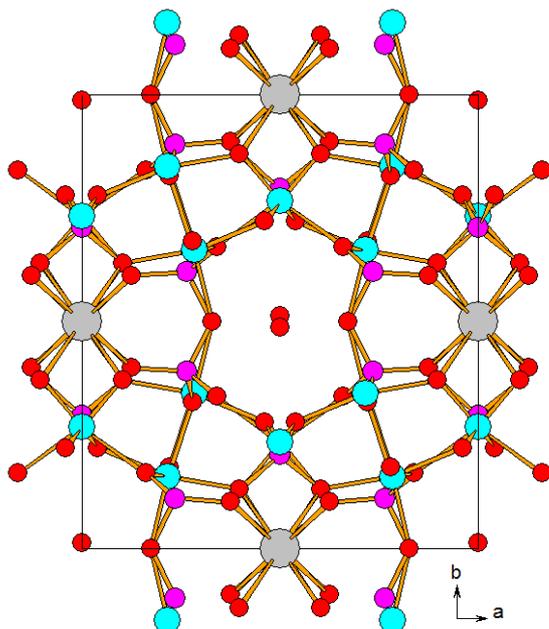


## 7. Refinement of occupancy Na1, O1

Using "Edit atoms" select that occupancy of Na1 and O1 will be refined



Start refinement

*Refinement converges with R=3.4%*

*Occupancy of Na1 refines to 0.62*

*Occupancy of O1 refines to 0.69*

*From refinement listing we can see there are no warnings about negative ADP*

*Na1 must be mixed with Ni or Fe because the refined occupancy exceeds the site occupancy. The BVS larger than 1 support this idea.*

*For oxygen 0.69\*2\*8=11; 2 is the site multiplicity, 8 is number of electrons. The result is not too far of 10 which is sum of electrons for water. Therefore, O1 could be water.*

Using "Edit atoms" change chemical type of O1 to Na without renaming

Run refinement

Calculate distances

*R value is the same. Occupancy of O1 (now chemical type Na) refines to 0.46. BVS of O1 is*

*1.0. Therefore O1 could be also sodium, but partially occupied because there is no lighter element available for mixing.*

***In the next part we shall consider O1 to be oxygen of a water molecule.***

8. ***Mixed site Na1-Ni3***

   Using "Edit Atoms" change chemical type of O1 back to oxygen
   Run refinement
   Using "File → Structure → Save As" create **a backup copy** of the structure but continue with the original one
   *Jana does not have a tool for creating mixed sites. It should be done in M40 by text editor.*
   Using "Edit/view → Edit M40 file" open M40
   Double the two lines belonging to Na1
   For the new atom change "Na1" to "Ni3"
   In the header change "12" to "13"
   Save and close M40
   *Jana checks the syntax of the changed M40. No warnings mean correct syntax.*

```
   13       0       0       0
 1.705377 0.000000 0.000000 0.000000 0.000000 0.000000        100000
 0.000000                                                           0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000         000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000         000000
Ni1        2  2     0.500000 0.000000 0.733296 0.250000
 0.008381 0.008306 0.007869 0.000000 0.003995 0.000000      0010111010
Ni2        2  2     1.000000 0.216297 0.841500 0.127834
 0.009660 0.008585 0.007484-0.000021 0.004403-0.000490      0111111111
P1         4  2     1.000000 0.235291 0.889897 0.622582
 0.006734 0.004603 0.004604-0.000255 0.002830-0.000091      0111111111
P2         4  2     0.500000 0.500000 0.793180 0.250000
 0.006112 0.006625 0.004608 0.000000 0.002692 0.000000      0010111010
Na1        1  2     0.618273 0.500000 1.000000 1.000000
 0.029444 0.008143 0.007628 0.000480-0.002180 0.002394      1000111111
Ni3        1  2     0.618273 0.500000 1.000000 1.000000
 0.029444 0.008143 0.007628 0.000480-0.002180 0.002394      1000111111
```

   Start "Atoms Edit"
   Change chemical type of Ni3 to nickel
   Change site occupancy of Na1 and Ni3 to 0.25 and activate their refinement keys
   *We need sum of occupancies equal to 0.5*
   Close "Edit Atoms" and open Refinement options
   Switch to page "Various" and press "Restrictions"
   For "Atoms/Molecules" type "Na1 Ni3"
   Select "Coordinates", "ADP parameters" and "keep overall sum"; press "Add"
   *It creates the restriction "restrict Na1 1 Ni3" with the following meaning: both atoms will have the same coordinates, the same ADP and constant sum of site occupancies*
   OK; OK, "Yes+Start" to run refinement
   *Refinement converges with R value still around 3.4%*
   *Site occupancies refine to 0.43 for Na1 and 0.07 for Ni3*
   *Similar results could be achieved with iron so at this point the chemical type of the metal is either nickel or iron*

### 9. Mixed sites Ni1-Fe1 and Ni2-Fe2

Using "Edit atoms" activate refinement of site occupancies for Ni1, Ni2
Run refinement
*Refinement converges with R=3.1% (improvement)*
*Occupancy of Ni1 refines to 0.47 (from 0.5)*
*Occupancy of Ni2 refines to 0.94 (from 1.0)*
*In refinement listing – "changes overview" – we can check that s.u. of occupancy parameters is small.*
*Maybe Ni1 and Ni2 are mixed with iron*
Using "Edit atoms" change occupancy of Ni1 to 0.25 and occupancy of Ni2 to 0.5
*With these numbers the doubled position will have the sum of occupancies equal to the site occupancy*
Using "Edit/view → Edit M40 file" double the two lines of Ni1 and also double the two lines of Ni2
Change the second "Ni1" to "Fe1" and the second "Ni2" to "Fe2"
Increase number of atoms in the header by 2; close the text editor
Using "Edit atoms" change chemical type of Fe1 and Fe2 to iron; make sure that site occupancy refinement keys are activated for Ni1,Fe1,Ni2,Fe2
Open Refinement options, page Various
Define restriction for the pair Ni1-Fe1 and for the pair Ni2-Fe2 (by the same way like previously for Na1-Ni3, keeping the overall sum)
Run refinement
*Refinement converges with R value 3.1%*
*Occupancy of the pair Ni1-Fe1 refines to 0.24, 0.26*
*Occupancy of the pair Ni2-Fe2 refines to 0.36, 0.64*

### 10. Calculation of the charge

Start "EditM50", page "Composition", and press "Formula from M40"
*It prints Na0.878 Ni1.309 Fe1.812 P3 O13.331*
*O13.331 is O12 when we subtract the "water"*
*Assuming that the valence of iron is three we can calculate: 1.81\*3+1.31\*2+0.88=8.93. This is very close to the required charge 9.*

*By this way we have created one possible model. Unfortunately there is a lot of another possibilities which should be checked, for instance:*

*The water could be partially occupied sodium (it slightly decreases R value to 3.07%) and the valence of the iron mixed with Ni could be 2+. The composition would be Na1.769 Ni1.27 Fe1.844 P3 O12.*
*1.844\*3+1.27\*2+1.769=9.84, i.e. exceed of positive charge*

*For the above case we could also consider mixed valence for Fe. To get easily the formula we can temporarily change chemical type of Fe1 to something else, for instance aluminium. But first it must be added to the end of the formula (to become available in "Edit atoms").*
*EditM50 then calculates the formula Na1.769 Ni1.269 Fe1.324 P3 O12 Al0.52.*
*For Al representing trivalent iron the charge would be 0.52\*3\*1.32\*2+1.27\*2+1.769=8.51, i.e. lack of positive charge*
*For Al representing divalent iron the charge would be 0.52\*2\*1.32\*3+1.27\*2+1.769=9.31,*

*i.e. exceed of positive charge*

*For the above case with lack of positive charge (sum 8.51) we can also consider mixing of Na1 not with nickel but with trivalent iron. It yields: Na1.748 Ni1.153 Fe1.325 P3 O12 Al0.656 with trivalent iron represented by aluminium. The charge is 0.66\*3+1.33\*2+1.15\*2+1.75=8.69, i.e. still lack of the positive charge*

*The Ni1 site is maybe not mixed (BVS is smaller than for Ni2 and mixing has small impact on R). But iron alone in this site increases R value. It can only be nickel alone yielding the formula: Na1.716 Ni1.713 Fe1.437 P3 O12. The charge would be 9.46 (trivalent iron), 8.02 (divalent iron), 8.2 or 9.3 (for mixed valence of iron).*

*It seems that another model with proper charge is not easy to find (maybe it will be discovered during the workshop). Good proof would be to find hydrogen atoms of water in the difference Fourier map but they are not there. Or we could find hydrogen in the P2O12 group which would allow the more logical solution with positive charge 8.02, but it is also not present in difference map.*

**Conclusions**:

The formula is either

**$Na_{0.878}$ $Ni_{1.309}$ $Fe_{1.812}$ $P_3$ $O_{12}$ . $H_2O$ with trivalent iron**

or

**$Na_{1.716}$ $Ni_{1.713}$ $Fe_{1.437}$ $HP_3$ $O_{11}$ OH with divalent iron**

*The latter yields slightly better R value and corresponds better to found bond valences sums. However, hydrogens cannot be determined from the data.*

*(Fast microprobe analysis yields Na1.56 Ni1.69 Fe0.78 P3 O6 which is insufficient precision for making a decision)*

# Example 5.1: YPO

**Simple modulated structure with crenel**

**Revised 15 October 2014**

## Y(PO$_3$)$_3$

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: YPO.hkl, YPO_red.sum
Frame scaling, absorption correction: done

1. *Creating new jobname*
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click YPO

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction $\rightarrow$ CCD"; NEXT
   *[On the screen: "Define basic input file:"]*
   Select "Input from sum file"; file name "ypo_red.sum"; OK
   *[On the screen: "Warning about appended data reduction runs"]*
   OK
   *[On the screen: "Complete/Correct experimental parameters"]*
   Leave all settings unchanged; NEXT
   *[On the screen: "Define the reference cell/split by twinning"]*
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set
   *[On the screen: "Information about starting symmetry wizard"]*
   NEXT

4. *Symmetry Wizard*
   *[On the screen: "Tolerances for crystal system recognition".]*
   *Symmetry wizard can be started separately by "File $\rightarrow$ Reflection file $\rightarrow$ Make space group test".*
   Leave all settings default; NEXT
   *[On the screen: Select supercell]*
   Select "Continue with the basic cell"; NEXT
   *[On the screen: Select Laue symmetry]*
   Select Monoclinic Laue symmetry; NEXT
   *[On the screen: Select cell centering]*

Select I centered unit cell; NEXT
*[On the screen: Select space group]*
Select C2/c; NEXT
*[On the screen: Select superspace group]*
C2/c(0b0)s0
*[On the screen: Final step of the superspace test]*
Accept the superspace group in the standard setting: C2/c(0b0)s0; FINISH


5. ***Creating refinement reflection file***
   *We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step we shall create the file M90 containing data set merged by symmetry, with extinct reflections omitted.*
   NEXT to confirm threshold 3sigma
   *[On the screen: settings for merging of reflections]*
   Leave all settings default; NEXT
   Accept the data block and calculate coverage; FINISH
   *[On the screen: Information that structure solution will start]*

6. ***Structure Solution Wizard***
   *[On the screen: window of Structure solution]*
   In "Formula" textbox type list of chemical elements for $Y(PO_3)_3$: Y P O
   Select "use Superflip"; "Peaks from Jana2006"
   **Select "Use a specific random seed" and type value 111**
   "Run solution"
   *Superflip converges (after noise suppression) with R value 21%. It confirms the symmetry C2/c(0b0)s0.*
   *Fixing the random seed to 111 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. Otherwise each run of Superflip would return slightly different electron density. For normal work random seed should be automatic because the convergence of charge flipping is not guaranteed for every value of random seed.*
   Close the listing and press "Quit" to leave the structure solution wizard

7. ***Verification of the structure solution***
   Start "Edit/View → editing of M40 file". *It shows the structure parameter file*
   Start "Edit atoms". *It shows the same in a graphical interface; parameters of atoms can be accessed by double clicking on atom or by "Action → Edit/Define atoms";*
   OK
   Start EditM50, go to page Composition, change "Formula units" to 4
   Press "Formula from M40"
   *[On the screen: Information about formula]*
   *With previously used "randomseed 111" the formula should be Y P3 O8 (for Z=4).*
   OK; YES for updating the formula
   Modify the formula to Y P3 O9; OK, YES to rewrite M50 file
   *Correct numbers of elements helps to find correct number of atoms in Fourier maps. It is also important for the final CIF generation.*
   Right-click the icon of Fourier and select thumbnail "Basic". Choose "Map type"

"F(obs) - Fourier" and in the thumbnail "Scope" select the following:
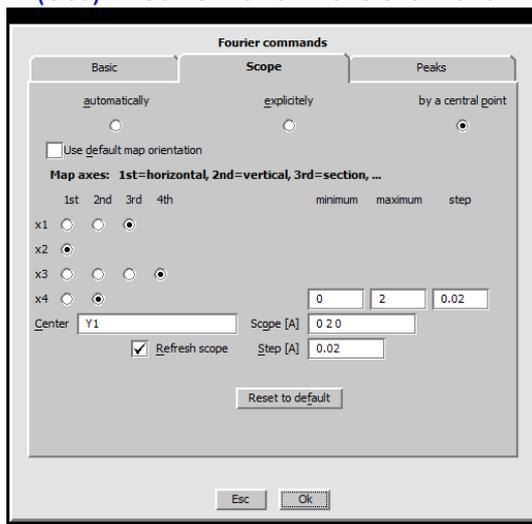


OK; YES+START to save Fourier options and execute Fourier

*Fourier reads as an input M80 with structure factors created previously by Superflip. M80 is re-created after regular end of structure refinement. In this case refinement did not run so M80 the original one from Superflip.*

Run Contour; start "New plot" – "Use old maps"+"Draw maps as calculated".

*Then the modulation density will appear. With "Atoms edit" define the Y1 atom to be visualized.*
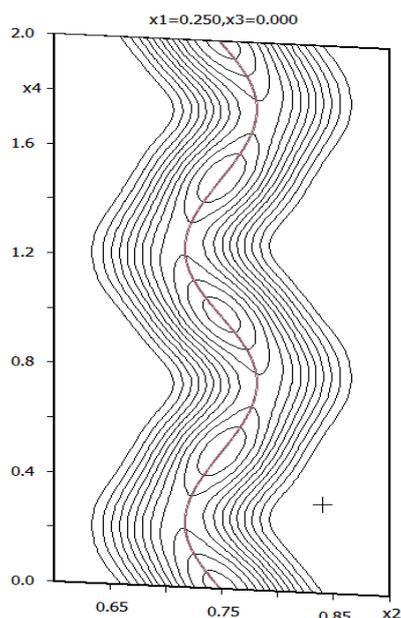


*The plot illustrates that the electron density from Superflip contains reliable information about position modulation. The modulation curve results by interpretation of the electron density map by Jana.*

Quit Contour

8. ***Origin shift to the position of Y***
   *The atom Y should be localized at the inversion center in one of the following Wyckoff*

*positions:*
*4d   (1/4,1/4,1/2);  (3/4,1/4,0)    + (1/2,1/2,0)*
*4c   (1/4,1/4,0);    (3/4,1/4,1/2)  + (1/2,1/2,0)*
*4b   (0,1/2,0);      (0,1/2,1/2)    + (1/2,1/2,0)*
*4a   (0,0,0);        (0,0,1/2)      + (1/2,1/2,0)*
*In the next step we shall shift the origin to the position of the Y atom. This step is not necessary for the structure solution and refinement but it assures that the coordinates and plots will look as described in this cookbook*
Start "Tools → Transformations → Origin shift"
*[On the screen: Move the origin to:]*
Select Atom Y1 and press OK.

9. ***Verification of modulated functions found by Superflip***
Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands", select "Modulation parameters" and type * to the Atoms/parameters textbox.
*This fixes modulation parameters for all atoms.*
Press the button "Add"; OK; OK
Start Refinement.
*The refinement should finish with R(obs) factors about 13%, 11%, 15% and 22% for all, main, $1^{st}$ order satellite and $2^{nd}$ order satellite reflections. This means that we have reasonably good starting point to continue the solution.*
*The screen output of Refine is closed after a delay. It is saved in refinement listing ("Edit/View → View of Refine → Go to → R-factors overview")*

10. ***Refinement of the modulated structure***
Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands" and disable or delete the previously used "Fixed command"
Run refinement.
*You should get R values about 12%, 10%, 14% and 21%.*
Start "Edit atoms"
Press "Select all" and "Action → Edit/define"
Choose "harmonic" for ADP parameters.
OK; OK; Yes to rewrite changes
Start Refinement.
*Refinement converges with R value about 11%, 8%, 12% and 20% for 94 parameters.*

11. ***Localization of the missing oxygen atom***
Right-click the icon of Fourier and select thumbnail "Basic" – select "Map type"
"F(obs)-F(calc) – difference Fourier"
In the thumbnail "Scope" select: "Automatically" and "Use default map orientation"
OK
Run Fourier
*The modulation curve of this additional atom is rather complicated and therefore we have to look to the density maps to see more details. First, we should check if the peak, representing possible position of the new oxygen atom, has been really localized in the difference Fourier map.*
*[On the screen: Do you want to start the procedure for including of new atoms?]*
Answer yes.

*[On the screen: Inserting/replacing of atoms – setting of distance limits]*

Use default 3 Å; OK

*(The dialogue for adding maxima is also available through "Parameters → Atoms → New")*

*The dominating maximum (with the largest charge) should be close to the special position at (-1/4,1/4,0) or to some of its equivalents, with reasonable distances to the atom P1 (about 1.5 Å).*

Note the coordinates of the dominating maximum in equivalent position close to P1

*For the current structure model (random seed 111) it should be 0.245, -0.254, 0.504*

Round the coordinates to the closest special position and note them

*For the current structure model (random seed 111) it should be: 0.25, -0.25, 0.5*

Leave the form **without** adding the new atom.

*Adding new atoms would add oxygen to a general position because its special position is not properly recognized.*

*Use Contour to see difference Fourier sections through the point (1/4, -1/4, 1/2).*

Start Contour, press "New plot"

Select "Calculate new ones" and "Draw maps as calculated"; OK

In Basic thumbnail select "F(obs)-F(calc) – difference Fourier" and in the thumbnail "Scope" define the vicinity of the point (1/4, -1/4, 1/2):
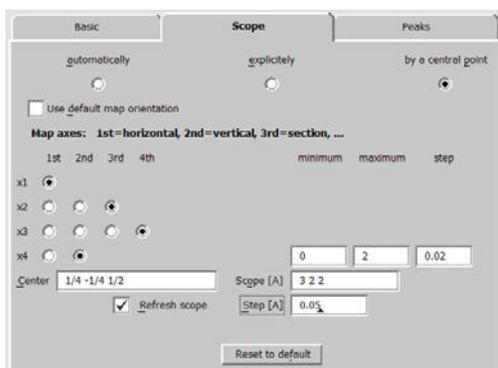


OK starts Fourier calculation

*The first section is immediately plotted:*
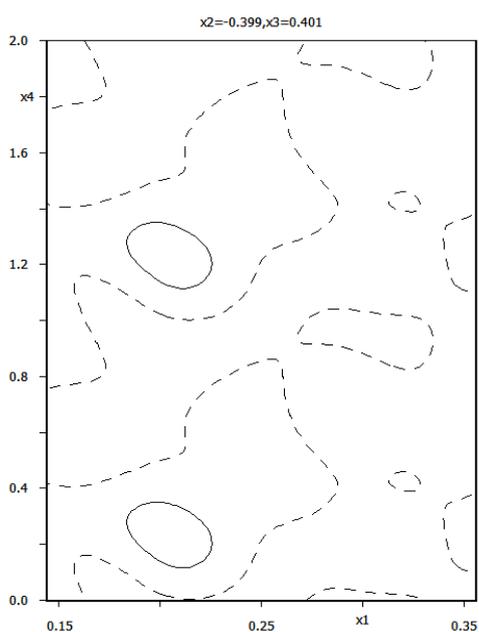
*The resulting map must be summed over x2, x3 direction to see the correct modulation curve*
Press "Sum ON"; select "x2" and "x3" leaving the intervals defaults; OK
*The resulting map shows the shape of modulation:*
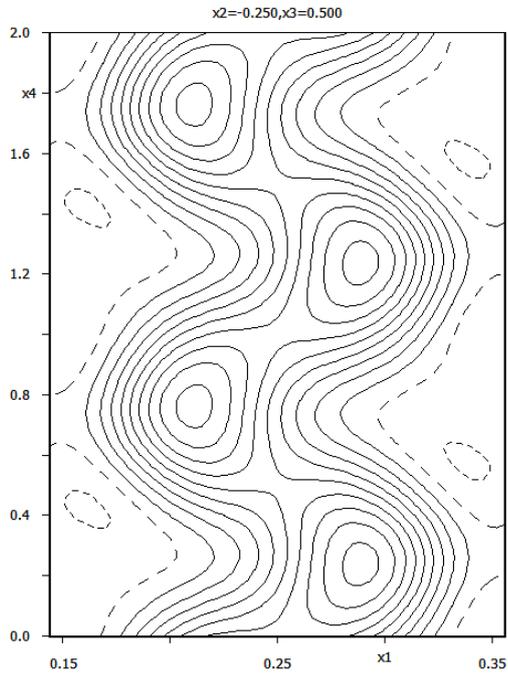


Analogously (starting with button "New plot" followed by "Calculate new ones"), calculate and plot the section x2-x4 and the section x3-x4:
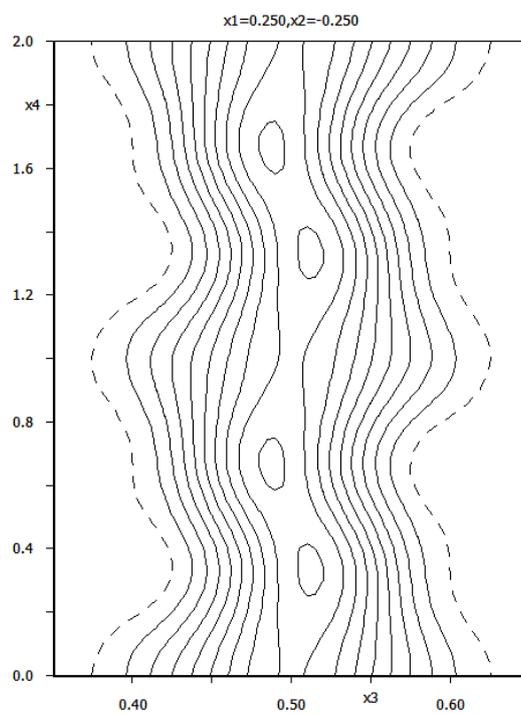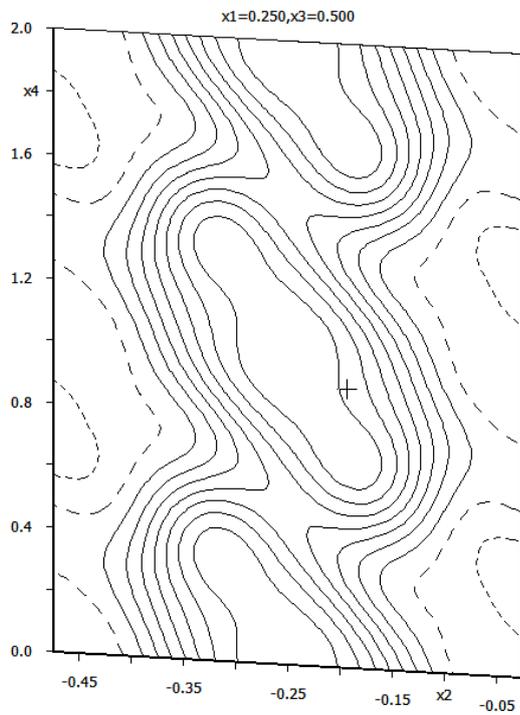
*The modulation has a discontinuity at the point with x4=0.5. This is clearly visible from the map showing evolution of the x2 atomic coordinate (the x2-x4 section).*

*As the difference Fourier is more sensitive to light oxygen atom we should save the temporary result for a final check of the refined modulation of that oxygen atom.*

Close "Contour"
"File → Structure → Save as" and use a new name for example "YPO-for-maps" but do not continue with the new structure.

### 12. Inserting the missing oxygen atom

*From the previous we know that the modulation function of the new atom at (1/4, -1/4, 1/2) has a discontinuity and therefore a crenel function will be used. In the x2-x4 difference section we found that the length (delta) of crenel is one and its center (x40) is located at 0.*

"Parameters → Atoms → New", select "Coordinates from keyboard"; OK
Type the coordinates *1/4 -1/4 1/2*, press "Use new coordinates"
Select the symmetrical position making the shortest distance to P1 and press "Include selected peaks".
*[On the screen: Complete information for the new atom]*
For "Name of atom" type "O*" followed by TAB
*This assures that the chemical type will be oxygen and the label will contain the closest free sequence number.*
OK; Finish; YES to include new atom

*Now we have to define the crenel function*

Run "Edit atoms" and select the new atom (probably O5).
"Action → Edit/define" check "crenel" and add also one position modulation wave in the textbox "Position"
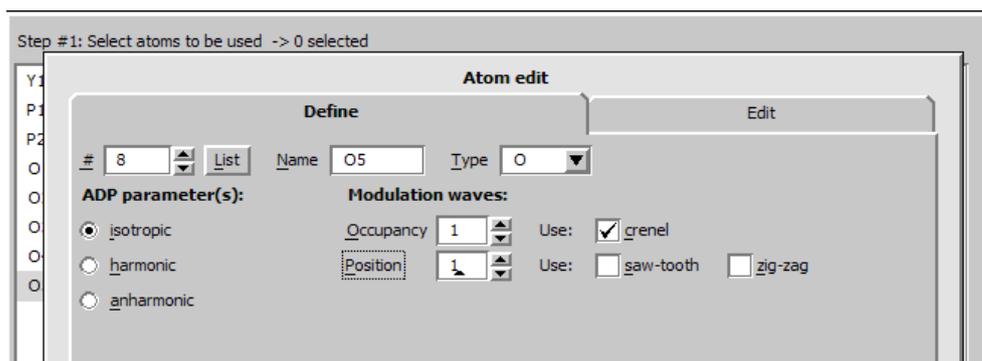


Switch to the page "Edit" and press the button "Occupancy", which is close to "Edit modulation parameters"
define "1" for "delta" and "0" for "x40"; OK
*This is width and centre of the crenel function*
Go to the page "Define"
Select "Legendre polynomials in crenel interval"

OK; OK; Yes to rewrite
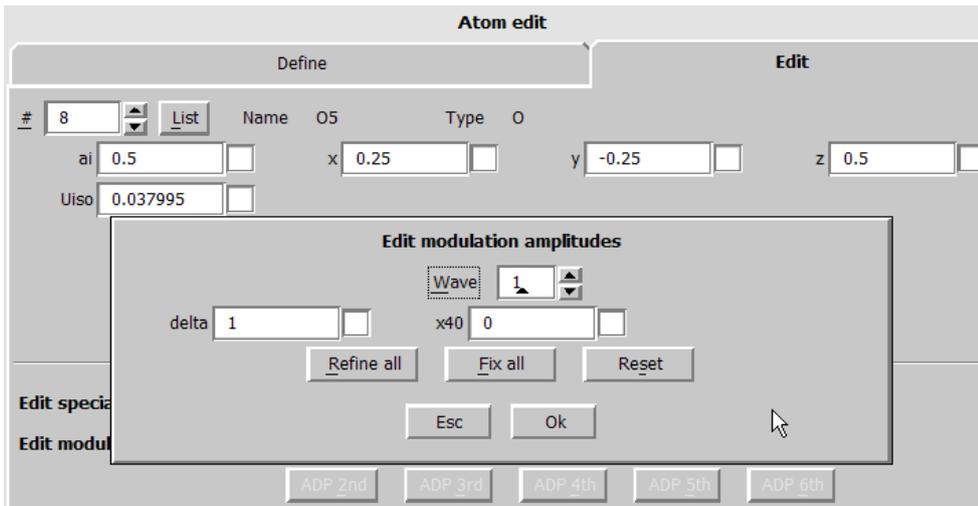


Draw Contour section x4-x2 for (1/4 -1/4 1/2) - like previously
Press "Atoms edit" and add O5; OK
*The Contour plot shows the initial modulation function for O5*
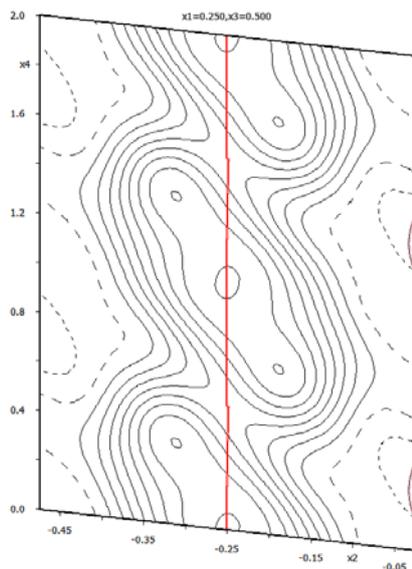


### 13. Refinement of the complete structure

Right click on the Refine icon, switch to "Basic"
Define there number of cycles 100 and damping factor 0.2.
*Damping factor multiplies the parameters changes*
Start refinement

→ *R about 9%, 6%, 10%, 20%*

Draw Contour section x4-x2 for (1/4 -1/4 1/2) - like previously
Press "Atoms edit" and add O5; OK
*The Contour plot shows the crenel modulation function for O5 combined with one modulation wave*
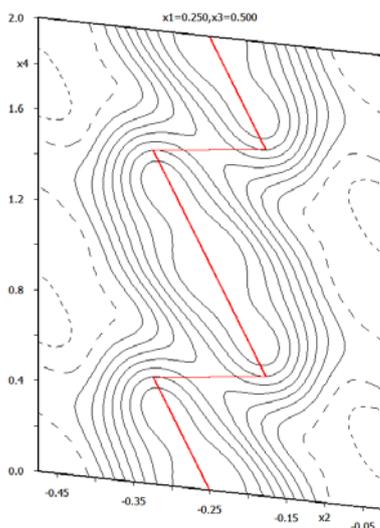
Run "Edit atoms", select all atoms, press "Action" and select "Edit/Define atoms"
Modify all ADP parameters to harmonic ones by double-clicking the corresponding radio button

*Yellow indicates locked objects. Locking occurs when the corresponding parameters are not the same (or of the same type) for the selected atoms. In our case ADP is harmonic for most of atoms but isotropic for the newly added O5, this is the reason for locking of radio buttons. The text box for site occupancy is also locked because some atoms are in special positions. A locked object can be unlocked by double-click.*

Add another one positional modulation wave for all atoms using the textbox "Position".
Save changes and start refinement

$\rightarrow$ *R about 5.6%, 3.4%, 6%, 18%*

Run "Edit atoms", select all atoms and (using the button "ADP $^{2nd}$") define two ADP modulation waves for all atoms.
Start refinement

$\rightarrow$ *R about 3.4%, 2.5%, 3.5%, 9.0% for 297 refined parameters*

### 14. Check modulation curves with maps for O5

*In this part we shall check whether the refined modulation function for oxygen O5 corresponds to the electron density map found previously by Superflip. We are making this check because refinement of sawtooth function for oxygen in the structure containing the heavy yttrium could be unreliable*

*Return to the result saved previously (YPO-for-maps):*
"File $\rightarrow$ Structure $\rightarrow$ Open": select the name of the previously saved structure ("YPO-for-maps")
"File $\rightarrow$ Structure $\rightarrow$ Save as": make a backup copy
Run Refine to re-generate phases
(*R factors 11%, 8%, 12% and 20%.*)
"File $\rightarrow$ Structure $\rightarrow$ Copy in" copy only (!!!) m40 from the final structure
**(From this point Refine must not be started)**
Run Contour as in the point 12 and draw atomic modulation curves for O5 (using "Atoms
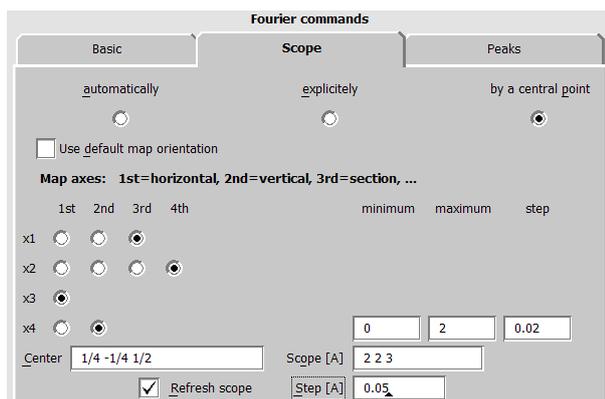
*The following maps should be obtained:*

x1=0.250,x2=-0.250
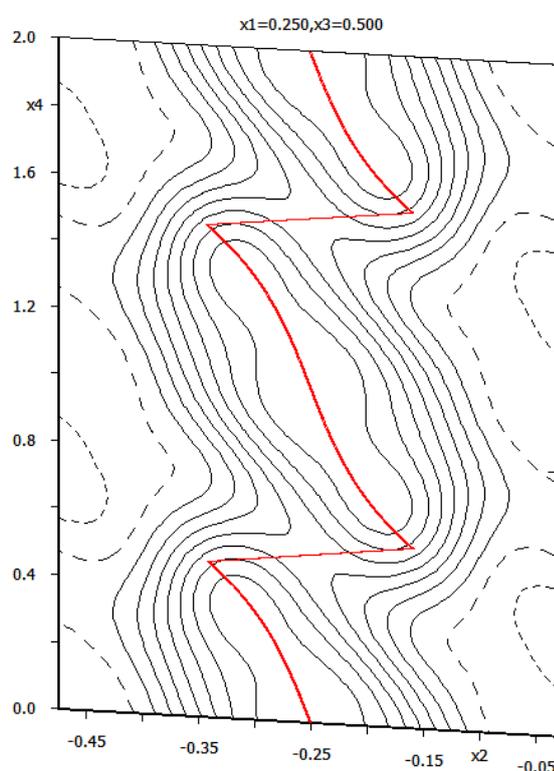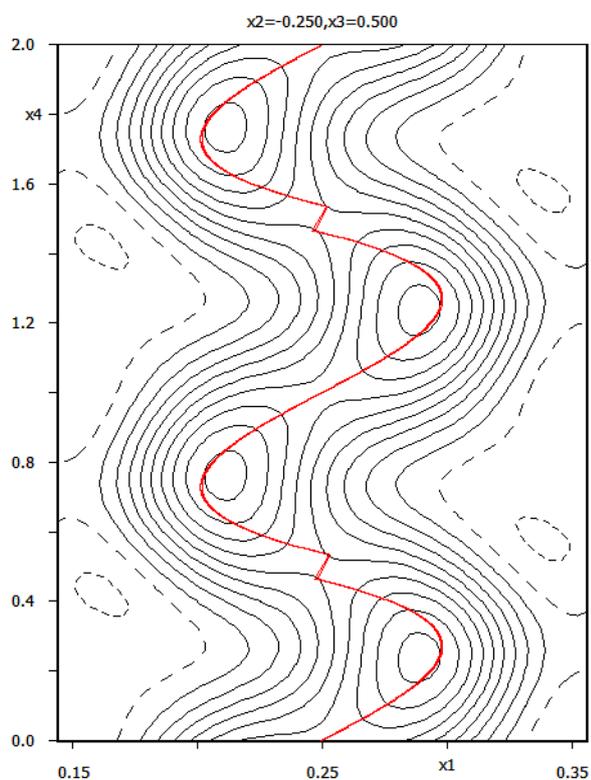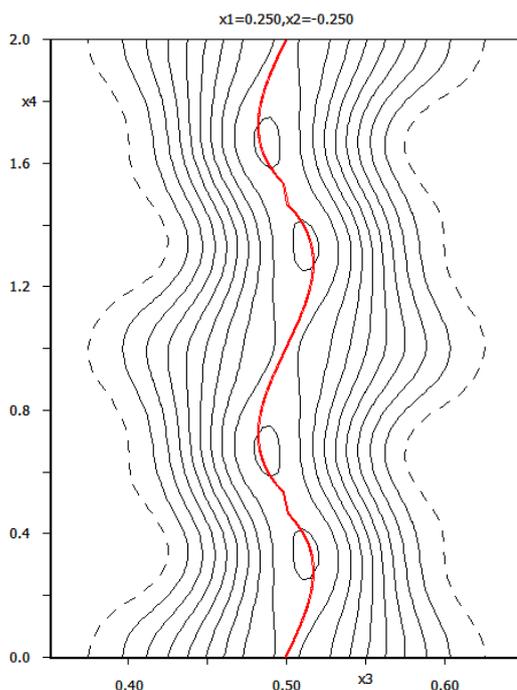


*By this procedure we plot the final refined modulation curve of O5 together with the previously calculated Fourier map. The technical trick consists in the fact that Fourier calculation does not use M40; it uses M80 created by Refine. Only the modulation curve displayd by Contour is based on parameters fromM40.*

### 15. Drawing of refined modulated structure

Return back to the refinement result using "File → Structure → History"

*Drawing programs such as Diamond cannot draw a modulated structure directly. Jana2006 creates an approximant based on the refined modulated functions. During this process the superspace symmetry is used to generate all atomic positions and the symmetry is reduced to P1. The size of approximant and the starting t value are to chosen to visualize different portions of the non-periodic matter. In our case the most convenient supercell is 1x8x1 as follows from the modulation vector being close to (0,3/8,0).*

"Plot structure"
*In Diamond symmetry operations must not be used for the approximant (on automatic structure, no supercell, no coordinations …. ). This is because Diamond does not know modulation displacements of newly created positions.*

### 16. Checking of refinement listing

Start "Edit/View → View of Refine"
Press "GoTo → List of serious warnings"
*The listing contains information that modulation of ADP leads to non-positive values for some values of t coordinate:*

```
******************************
*  List of serious warnings  *
******************************

Modulated harmonic ADP tensor of the atom "O2" is not positive in some regions
    For more details run "Grapht" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O4" is not positive in some regions
    For more details run "Grapht" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O5" is not positive in some regions
    For more details run "Grapht" and draw U(min) value
```

Start "Grapht"
Press New/Edit
For "Parameter to draw" select "ADP parameter"
For "Central atom" use "O2" (the label may differ)
For "Principal" select "U(min)"; OK

*The following plot shows that U(min) is negative for a small region of t*
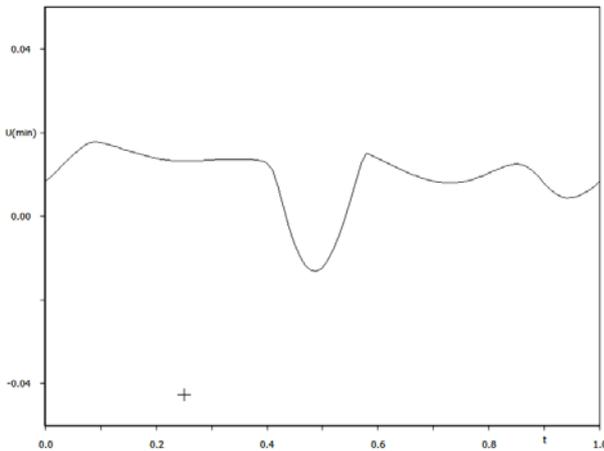


Create the same graphs for O4 and O5
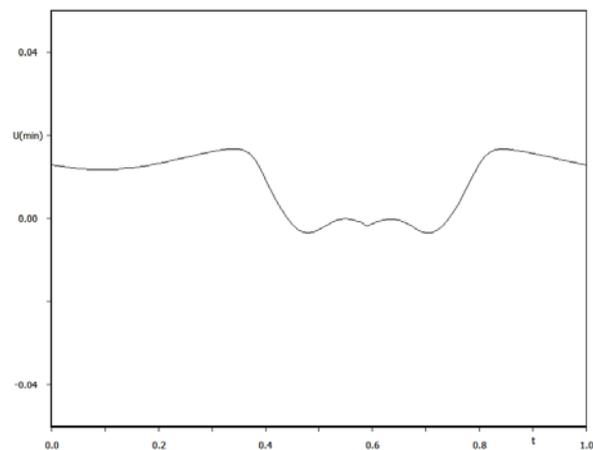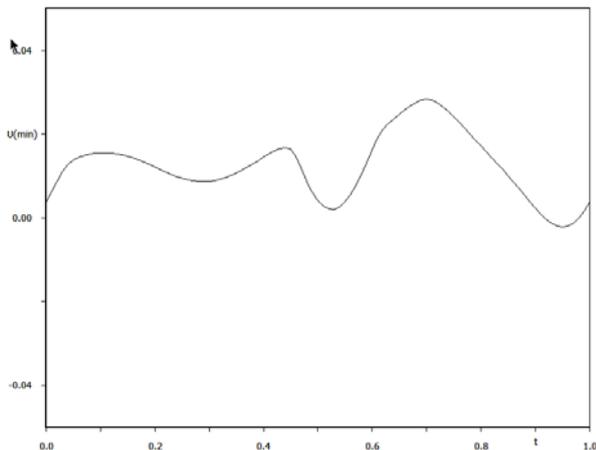


*Decreasing of number of ADP modulation waves often solves such situation:*
In Atoms/Edit select all oxygen atoms and decrease number of ADP modulation waves to 1
Check refinement listing and Grapht graphs
*In our case it only helps for O4. The reason for bad ADP modulation of some oxygen atoms is probably caused by the fact the sample is more complicated than presented here. High exposition reveals another set of weak satellites which need another q-vector for their indexing. The five-dimensional structure remains unsolved.*

# Example 5.2: Na₂CO₃

**Simple modulated structure from single crystal data**

**Revised 4 October 2015**

## Na₂CO₃

Single crystal data measured with KUMA four-circle diffractometer
(KUMA has changed to Oxford Diffraction, later on Varian, now Agilent)
Input files: naco.hkl, naco.cif_od
Frame scaling, absorption correction: done

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click  naco

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction → CCD"; NEXT
   *[On the screen: "Define basic input file:"]*
   Select "Input from cif_od file"; file name "naco.cif_od"; OK
   *[On the screen: "Complete/Correct experimental parameters"]*
   Leave all settings unchanged; NEXT
   *q-vector read from the cif_od file should be: 0.1776  0  0.3252*



*[On the screen: "Define the reference cell/split by twinning"]*
   Leave all settings unchanged; NEXT
   OK to confirm reading of 55555 reflections
   For absorption correction select "None or done before importing"; NEXT; FINISH

3. **Data Repository**

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

*[On the screen: "Information about starting symmetry wizard"]*

NEXT

4. **Symmetry Wizard**

*[On the screen: "Tolerances for crystal system recognition".]*

*Symmetry wizard can be started separately by "File → Reflection file → Make space group test".*

**Change "Maximal deviation for cell angles" to 0.3**

*Without this change unit cell angles will not be recognized as monoclinic*

Leave all other settings default; NEXT

*[On the screen: "Select supercell".]*

Leave all settings default; NEXT

*[On the screen: Select Laue symmetry]*

Select Monoclinic Laue symmetry; NEXT

*[On the screen: Select cell centering]*

Select C centered unit cell; NEXT

*[On the screen: Select space group]*

Select C2/m; NEXT

*[On the screen: Select superspace group]*

C2/m(a0g)0s

*[On the screen: Final step of the superspace test]*

Accept the superspace group transformed into the original cell: C2/m(a0g)0s; FINISH

5. **Creating refinement reflection file**

*We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step, we will create the file M90 containing data set merged by symmetry, with forbidden reflections omitted.*

NEXT to confirm threshold 3sigma

*[On the screen: settings for merging of reflections]*

Leave all settings default; NEXT

*The $R_{int}$ for observed reflections will be 4.18%*

Accept the data block and calculate coverage; FINISH

*[On the screen: Information that structure solution will start]*

6. **Structure Solution Wizard**

*[On the screen: window of Structure solution]*

In "Formula" textbox type list of chemical elements: Na C O

Select "use Superflip"; "Peaks from Jana2006"

**Select "Use a specific random seed" and type value 111**

"Run solution"

*Fixing random seed is necessary not for solution but for obtaining the same origin position as used in this cookbook. Otherwise, atomic positions and modulation functions may be shifted. For normal work, random seed should not be fixed because the convergence of charge flipping is not guaranteed for every value of random seed.*

*Superflip converges (after noise suppression) with R value 21%. It confirms the symmetry C2/m(a0g)0s.*

```
-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
    Tentative HM symbol: C12/m1(a0g)0s
    Fingerprint:         431222C0R96O028dXM1 (0,0,0,0)
    Centering vectors:
      0.000  0.000  0.000  0.000
      0.500  0.500  0.000  0.000
    Symmetry operations:
              1:        x1        x2        x3        x4
      m|s(0,1,0):       x1       -x2        x3    1/2+x4
      2|0(0,1,0):      -x1        x2       -x3    1/2-x4
             -1:       -x1       -x2       -x3       -x4



###############################################
# Search for the origin of the space group #
###############################################


Position of the origin in the CF map:
  0.9081  0.6298  0.6392  0.8946
Agreement factors of individual generators:
Number smb agreement
    4   m|s       0.28
    2   2|0       0.43

Overall agreement factor:   0.47
```

> This is symmetry found by Superflip in the electron density map

> This is fit of symmetry elements supplied by user (small numbers = good fit)

Close the listing and press "Accept last solution"

**7. Reflection report**

Start "Edit/View → View of Reflection report"

*Reflection report shows which symmetry operations were used for merging of reflections and which extinction rules were applied.*

**8. Verification of the structure solution**

Start "Edit/View → editing of M40 file".

*This is the file of structure parameters. Each atom has one modulation wave (number of waves and six parameters are indicated in red) found by Jana2006 in the electron density map from Superflip.*

```
Na1     1  1     0.500000 0.670666 0.000000 0.246168      000  0  1  0
 0.037995 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
 0.000000 0.066260 0.000000 0.000000-0.004772 0.000000      000000
 0.000000
```

*Note that there is no oxygen in M40 – later on some carbon atoms will be changed to oxygen.*

Close the editor

Start "Edit atoms". *It shows the same information in a graphical interface; parameters of atoms can be accessed by double clicking on atom or by "Action → Edit/Define atoms";*

OK

Start "Plot structure"

Select "Draw average structure"

Start "Draw+continue"

*With this option the basic 3d structure will be plotted*

In Diamond use Ctrl-A and Delete to remove an automatically created plot (if present)

In Diamond use ⬡⬡ to include all symmetry independent atoms from M40

Delete Na atoms

In Diamond use ◉ to add coordinated atoms

Using mouse cursor and rotations ✛ identify atoms which should be oxygens of $CO_3$ group: C1 and C2

Quit Diamond (without saving the plot)

Start "Edit atoms"

Change chemical type of C1, C2 to oxygen

Use "Action → Rename selected atoms to atom type + number" for oxygens and carbon

*The structure now contains: Na1, Na2, Na3, O1, O2, C1*

Return to the basic window

9. ***Refinement of modulated structure with modulations of positions***

In Refinement commands set 100 refinement cycles

Run refinement.

*Modulation waves are directly refined because the structure found by charge flipping has already modulation waves. Refinement converges with $R_{obs}$ factors 17%, 13%, 14%, 24%, 30% and 49% for all reflections, main reflections, $1^{st}$, $2^{nd}$, $3^{rd}$ and $4^{th}$ order satellites, respectively.*

Start "Edit atoms" and change ADP of all atoms to harmonic

Repeat refinement

*$R_{obs}$ factors: 13%, 8%, 11%, 21%, 26% and 49%*

Start "Edit atoms" and add another position modulation wave for all atoms
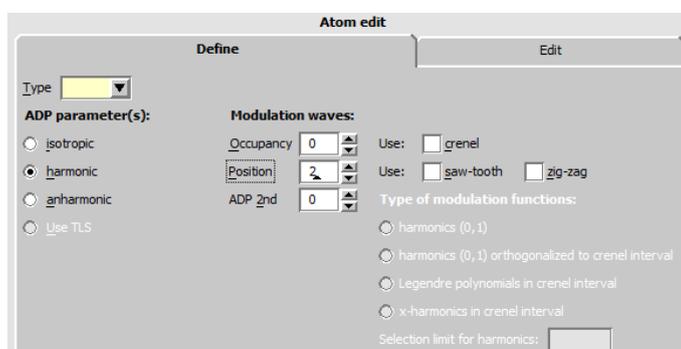


Repeat refinement

*$R_{obs}$ factors: 12%, 7%, 10%, 16%, 23%, 48%*

Start "Edit atoms" and add another position modulation wave for all atoms

Repeat refinement

*$R_{obs}$ factors: 8%, 8%, 7%, 9%, 15%, 25%*

Start "Edit atoms" and add another position modulation wave for all atoms

Repeat refinement

*$R_{obs}$ factors: 8%, 6%, 7%, 9%, 14%, 21%*

*Refinement with four position modulation waves is reasonable because there are satellites up to the $4^{th}$ order in data. However, it is not sure at this point that all atoms really need so many waves.*

Use "File → Structure → Save As" and create backup copy "naco_posmod"
*(Continue with the original structure)*

10. ***Fourier sections through atomic domains***

*In the next step modulation functions will be checked against observed and difference Fourier map.*

Start Fourier commands

For "Map type" select "F(obs) – Fourier"

Switch to the page "Scope"

Select "by a central point"; For "Map axes" select x1 for "1$^{st}$" column and x4 for "2$^{nd}$"

For "Center" type Na1

For "Scope [A]" type 2 1 1

Change "Step [A]" from 0.02 to 0.05 to speed-up the calculation
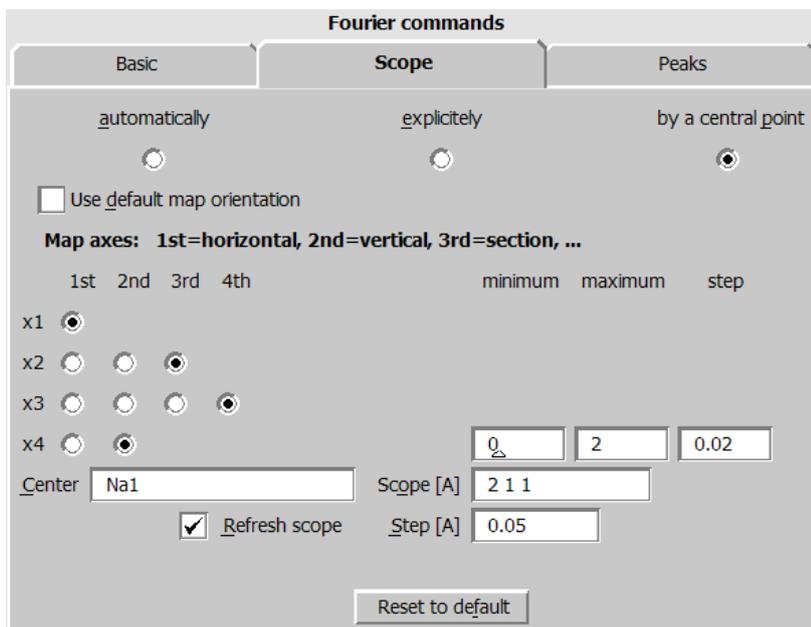


OK; Yes+start

*Fourier calculates a four-dimensional parallelepiped x1–x4–x2–x3 with dimensions 2-?-1-1 Å. In x4 the calculation will run over two periods: from 0 to 2 with step 0.02. The step in other directions will be 0.05 Å. The two-dimensional sections x1-x4 will be stacked along x2; the three-dimensional "sections" x1-x4-x2 will be stacked along x3.*

Start Contour; press "New plot"

Select "Use old maps" and "Draw maps as calculated"; OK

*[On the screen: the first x1-x4 section]*

Press "Sum on" and select summation over x2 and x3

*This merges all x1-x4 sections stacked along x2 and x3*

*[On the screen: merged section]*

Press "Atom edit"; for "Atom name" type Na1; Add; OK

*[On the screen: merged section with refined modulation function of Na1]*
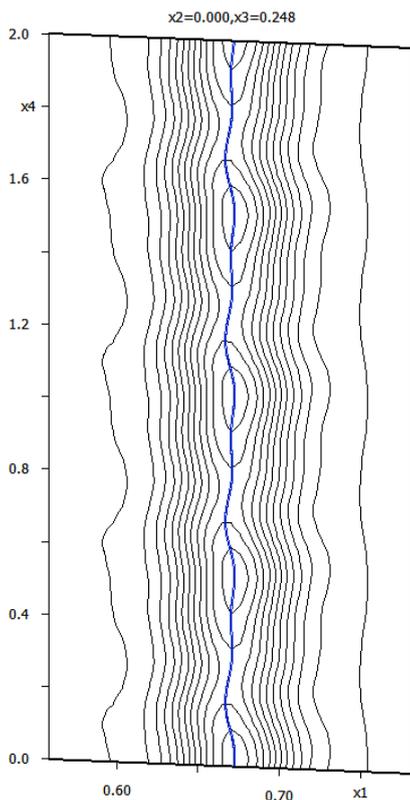
x2=0.000,x3=0.248

Press "New plot"

In the next dialogue select "Calculate new ones" and "Draw maps as calculated"

*[On the screen: Fourier commands, page Scope]*

Change "Map axes" to plot sections x2-x4 instead of x1-x4:



*"Scope" has been refreshed automatically.*

*Fourier will calculate a four-dimensional parallelepiped x2–x4–x1–x3 with dimensions 2-?-1-1 Å. In x4 the calculation will run over two periods: from 0 to 2 with step 0.02. The step in other directions will be 0.05 Å. The two-dimensional sections x2-x4 will be stacked along x1; the three-dimensional "sections" x2-x4-x1 will be stacked along x3.*

OK

*[On the screen: the first x2-x4 section]*

Press "Sum on" to merge the sections

*[On the screen: merged sections x2-x4 with modulation curve of Na1]*
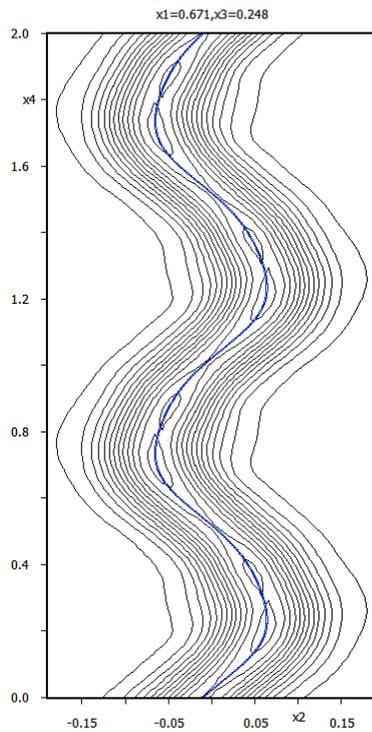
x1=0.671,x3=0.248

Press "New plot"

In the next dialogue select "Calculate new ones" and "Draw maps as calculated"

*[On the screen: Fourier commands, page Scope]*

Switch to page "Basic"

For "Map type" select "F(obs)-F(calc) – difference Fourier"

OK

Press "Sum on" and merge the sections

Press "Contours" and define step 0.1 for both positive and negative contours

*[On the screen: merged difference section x2-x4]*

*The difference peaks about 0.5 e$^-$/A$^3$ , indicating modulation of ADP*



x1=0.671,x3=0.248
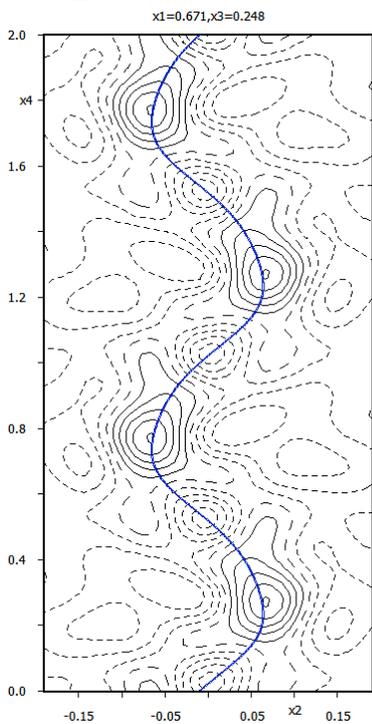
Repeat the process for other atoms of the structure. Identify the sections showing the strongest modulation and plot corresponding difference section. **Please note that in your calculation positions of atoms may be shifted (for instance y of Na2 from 0.5 to 0).**
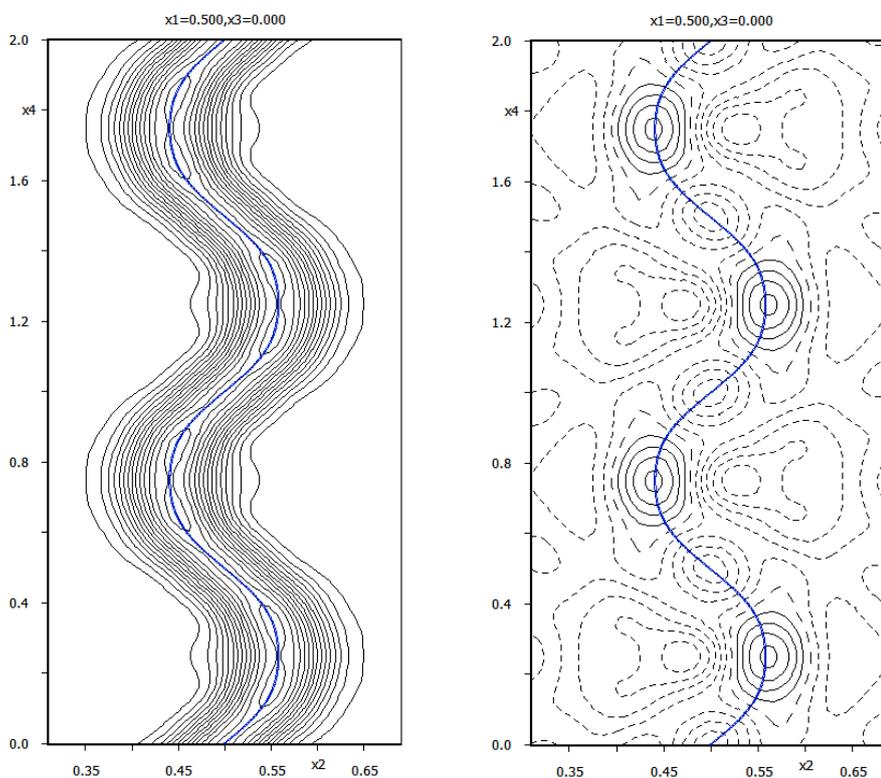


*x2-x4 for Na2: observed and difference Fourier map*
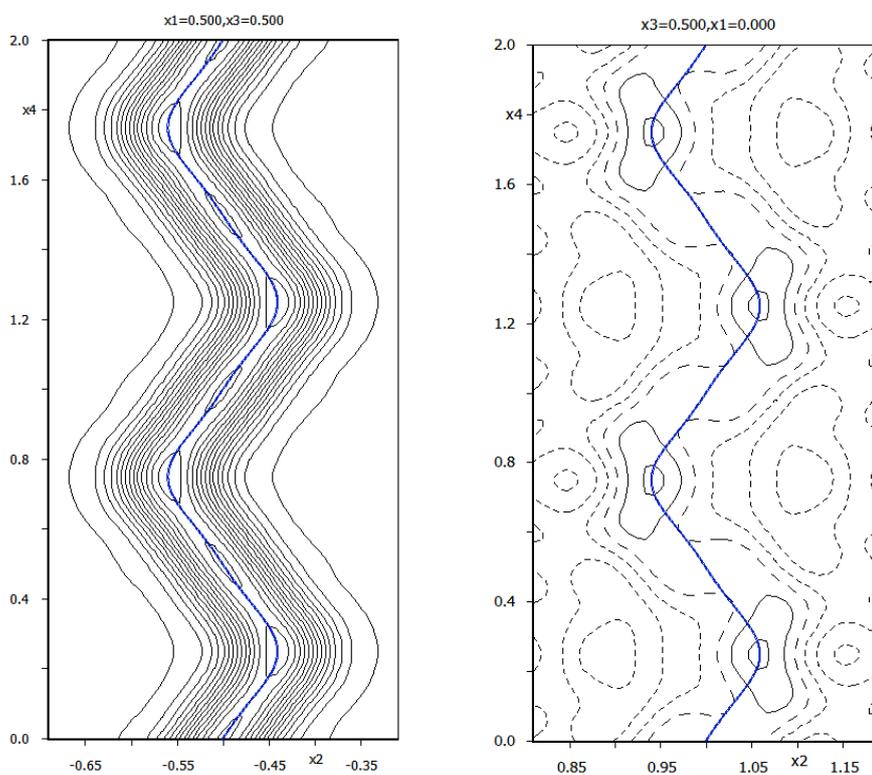


*x2-x4 for Na3: observed and difference Fourier map*
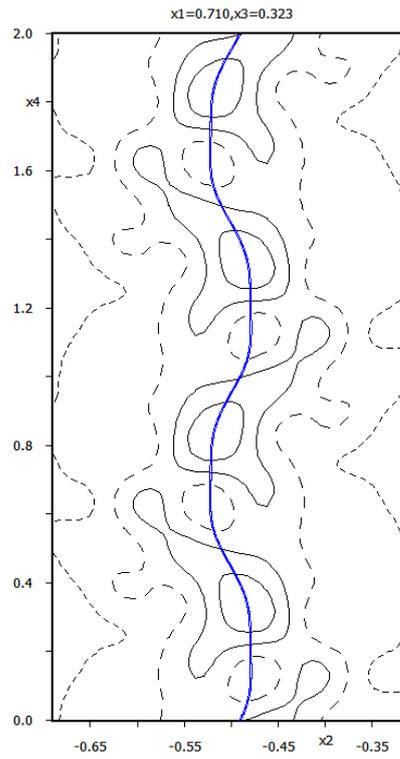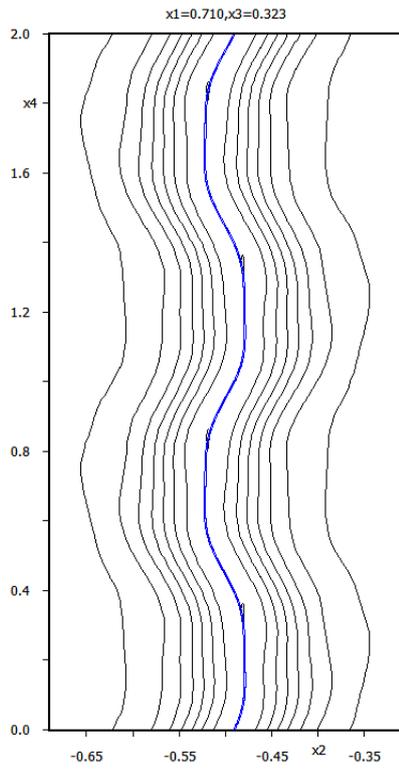
*x2-x4 for O1: observed and difference Fourier map*
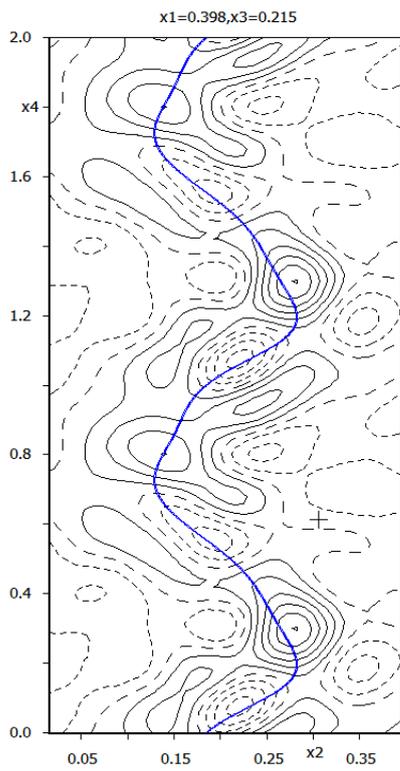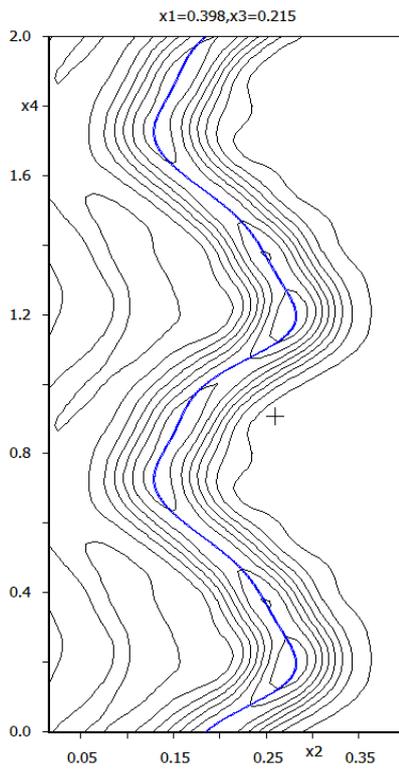


*x2-x4 for O2: observed and difference Fourier map*
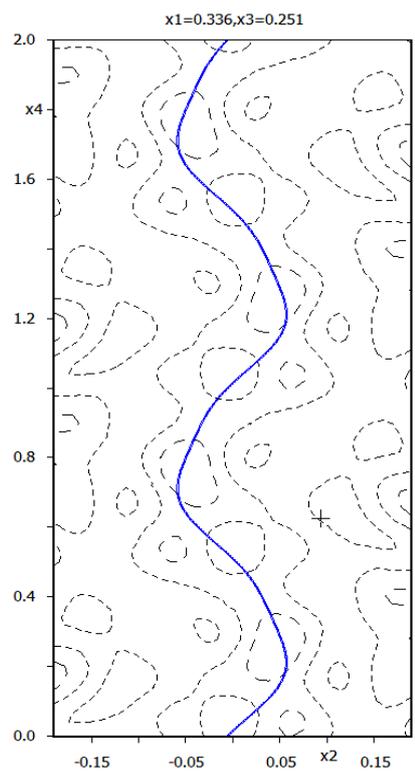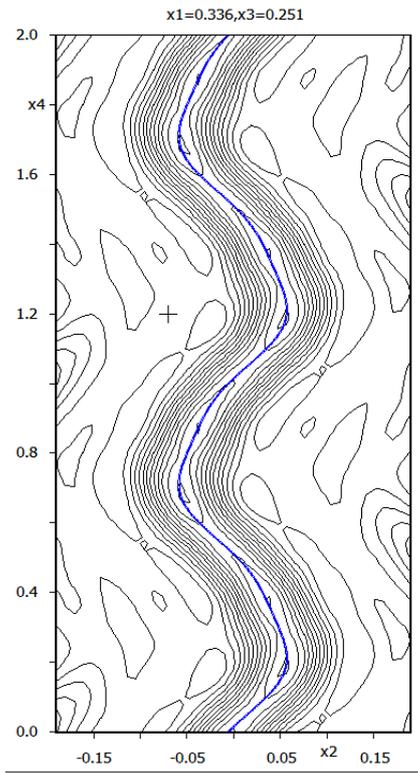
*x2-x4 for C1: observed and difference Fourier map*
*For C1 no ADP modulation is indicated in the difference Fourier sections*

## 11. Refinement of ADP modulations

Start "Edit Atoms"

Select all atoms except carbon and add one ADP modulation wave

The corresponding textbox has label "ADP 2$^{nd}$" which means ADP described by second order harmonic tensor
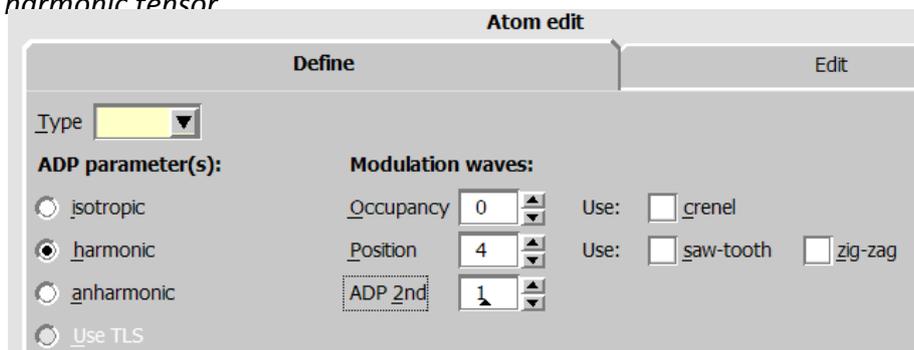


Run refinement

$R_{obs}$ factors: 6%, 5%, 5%, 7%, 12%, 20%

Start "Edit/View → editing of M40 file".

This is the structure parameter file. Each atom has four modulation waves (number of waves and 24 parameters indicated in red) and – except carbon – one ADP modulation wave (number of ADP modulation waves and 12 parameters indicated in blue)

```
Na1       1  2     0.500000 0.670641 0.000000 0.247961      000  0   4  1
 0.019755 0.023192 0.028421 0.000000 0.008258 0.000000      0101111010
 0.000000 0.065455 0.000000 0.000000-0.005129 0.000000      010010
-0.001028 0.000000-0.001123 0.001502 0.000000 0.004475      101101
 0.000000 0.001068 0.000000 0.000000-0.003381 0.000000      010010
 0.001307 0.000000 0.000797 0.000771 0.000000 0.000106      101101
 0.000000 0.000000 0.000000 0.000228 0.000000-0.001917      000101
 0.000000 0.000000 0.000000 0.004284 0.000000 0.001486      000101
 0.000000
```

Close the editor

Start "Edit Atoms"

Select all atoms except C1 and add another ADP modulation wave

Repeat refinement

$R_{obs}$ factors: 5%, 4%, 4%, 5%, 9%, 14%

The second smallest position modulations has O1. Because ADP modulation usually corresponds to changes in environment of an atom due to position modulation, we should check whether ADP modulation of O1 is reasonable.

Remove ADP modulation of O1

Run refinement

Add one ADP modulation wave for O1

Run refinement

Add another ADP modulation wave for O1

Run refinement

The first ADP modulation wave of O1 has improved fit significantly. For the second ADP wave the improvement was not so evident. Therefore, for O1 we shall use maximally two

*ADP waves.*

*For the remaining atoms we shall add ADP waves one-by-one to see where to stop.*
Add the 3$^{rd}$ ADP modulation wave for Na1
Run Refinement
*R$_{obs}$ factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%*
Add the 4$^{th}$ ADP modulation wave for Na1
Run Refinement
*R$_{obs}$ factors: 4.5%, 3.8%, 3.5%, 5.2%, 8.6%, 14.3%*
Remove the 4$^{th}$ ADP modulation wave for Na1
Run Refinement

Add the 3$^{rd}$ ADP modulation wave for Na2
Run Refinement
*R$_{obs}$ factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%*
Remove the 3$^{rd}$ ADP modulation wave for Na2
Run Refinement

Add the 3$^{rd}$ ADP modulation wave for Na3
Run Refinement
*R$_{obs}$ factors: 4.5%, 3.8%, 3.5%, 5.3%, 8.8%, 14.2%*
Remove the 3$^{rd}$ ADP modulation wave for Na3
Run Refinement

Add the 3$^{rd}$ ADP modulation wave for O2
Run Refinement
*R$_{obs}$ factors: 4.3%, 3.7%, 3.3%, 5.0%, 8.0%, 13.6%*
Add the 4$^{th}$ ADP modulation wave for O2
Run Refinement
*R$_{obs}$ factors: 4.2%, 3.8%, 3.2%, 4.6%, 8.0%, 12.0% (for 196 parameters)*

*Finally, we shall optimize position modulation of carbon:*
Remove the 4$^{th}$ position modulation wave for C1
Run Refinement
*R$_{obs}$ factors: 4.2%, 3.8%, 3.2%, 4.7%, 8.1%, 12.0%*
Remove the 3$^{rd}$ position modulation wave for C1
Run Refinement
*R$_{obs}$ factors: 4.9%, 3.8%, 4.0%, 6.0%, 9.9%, 16.0%*
Return the 3$^{rd}$ position modulation wave for C1
Run Refinement
*R$_{obs}$ factors: 4.2%, 3.8%, 3.2%, 4.7%, 8.1%, 12.0% (for 192 parameters)*

*This is the final parameters set:*

| Atom | Position waves | ADP waves |
|------|----------------|-----------|
| Na1  | 4              | 3         |
| Na2  | 4              | 2         |
| Na3  | 4              | 2         |
| O1   | 4              | 2         |
| O2   | 4              | 4         |
| C1   | 3              | 0         |

## 12. Extinction correction

Start "Edit/View → View of Refine"
Press "GoTo" and select "Statistics Fo, sin(th)/lamba after refinement"
*The shell of the strongest reflections has R factor 2.66% while the neighboring shell has 2.32%.*
Close the refinement listing
Start "Parameters → Extinction"
Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes
Run refinement
$R_{obs}$ *factors: 4.1%, 3.6%, 3.2%, 4.7%, 8.1%, 12.0% (for 193 parameters)*
Check refinement listing
*Partial R factor for the strongest reflections is better (2.48%) but still slightly worse than the neighboring shell.*

## 13. Final check of Fourier sections

Using the same options like before (merged sections with contour step 0.1) plot the relevant x2-x4 sections for all atoms of the final structure model

$x1=0.671,x3=0.248$  $x1=0.500,x3=0.000$  $x1=0.500,x3=0.500$

*Na1*  *Na2*  *Na3*

$x1=0.710,x3=0.322$  $x1=0.398,x3=0.215$  $x1=0.336,x3=0.251$

*O1*  *O2*  *C1*
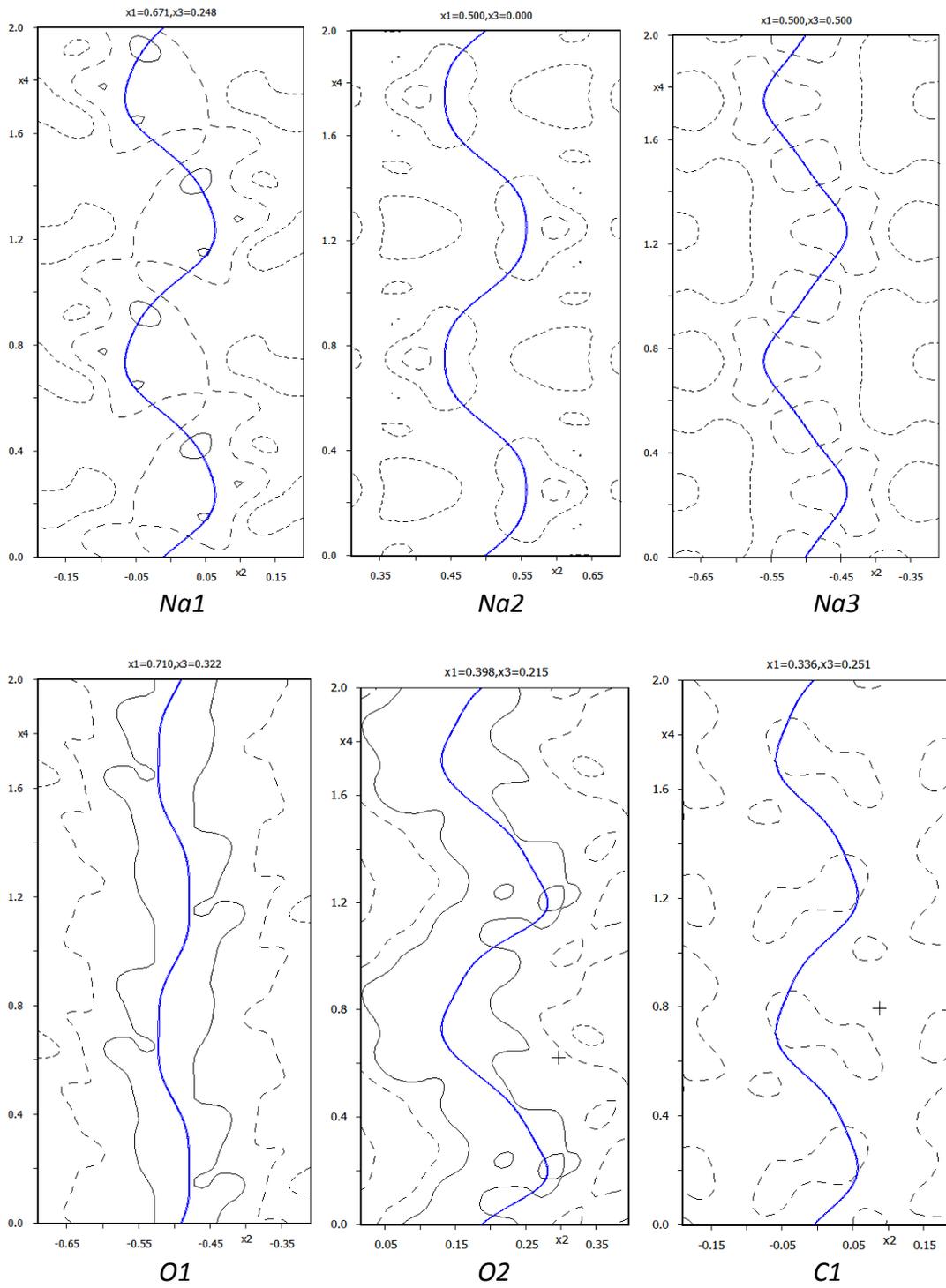
Use "File → Structure → Save As" and create backup copy "naco_final"

### 14. Plotting of sodium carbonate with Diamond

*In this part names of atoms and position of the origin may differ from your results*

Start "Plot structure"

*In the following dialogue we can either plot the average structure or the approximant structure. Average structure plot uses positions of the basic structure and 3d symmetry. For approximant structure, Jana2006 expands the modulated structure to a user-defined area. Then the expanded structure is exported to the plotting software with P1 symmetry. In the plotting software (here Diamond) no symmetry operations are allowed including translations! The reason is that the plotting software cannot transform modulation displacements.*

Select "Draw average structure"; start "Draw+continue"

Use Ctrl-A and Delete to remove an automatically created plot (if present)

Go to "Build → Fill → Super cell" and select "3x3x3" supercell

"Picture → Viewing direction → c"

 to plot unit cells

Go to "Build → Add cell edges" to define how many unit cells should be visible

"Objects → Coordinate system" to see axes

By selecting column of atoms and pressing  you can create the following figure:
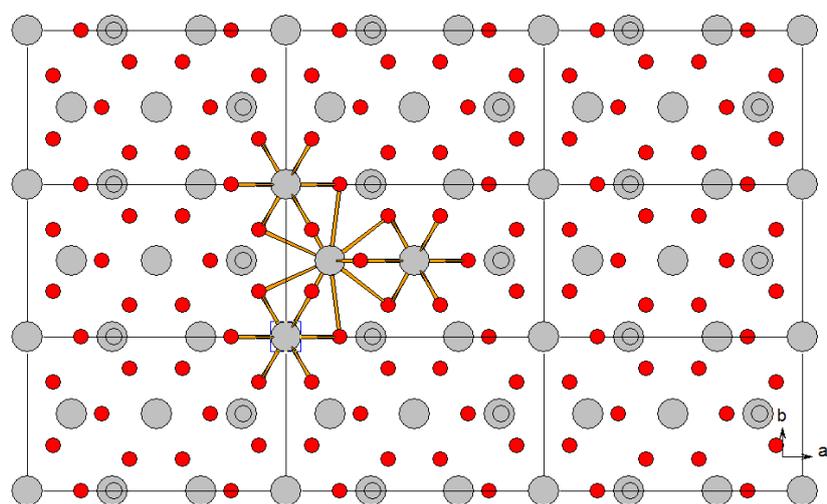


*This plot allows for estimation which supercell we shall need for plotting of approximant structure. We shall use supercell 2 x 3 x 10*

Close Diamond without saving

*[On the screen: basic window of Jana2006]*

Start "Plot structure"

Select "Draw approximant structure" and define supercell 2 x 3 x 10

*"Keep atom names" means that labels in Diamond will contain the original names from M40 followed by a sequence number"*

Start "Draw + continue"

*[On the screen: Diamond]*

Use  to add all atoms of the approximant to the plot. No operation creating new atomic positions is allowed

"Picture → Viewing direction → c"

 to connect atoms

On the right sidebar switch to "Table of atom groups"

Right-click Na, press "Select atoms by group"

In the plot hit the right mouse button on some of the selected sodium atoms

From the context menu Select "Edit → Atom design"

Switch to the page "Radius" and define radius 0.2 Å
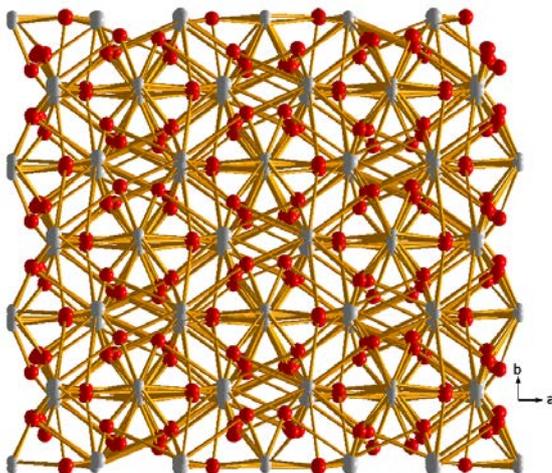
Using mouse and Delete (on the keyboard) and Ctrl-I (inverts selection) separate the following motif (three columns of sodium around the column of $CO_3$):
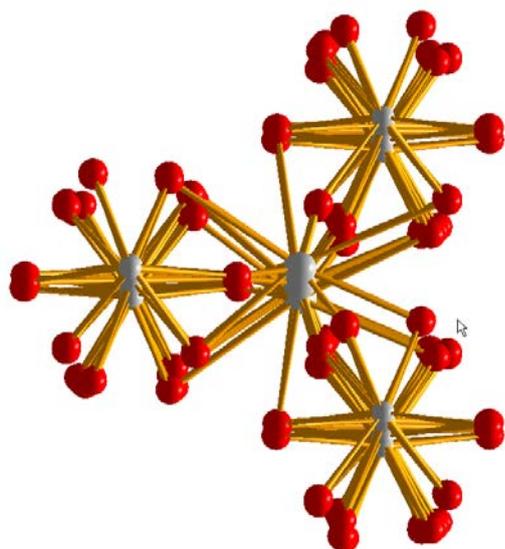


(In case bonds obscure atoms too much, use Ctrl-A + Right click on a selected object + Edit $\rightarrow$ Atom design and change bond style from "thick" to "thin")
Note starting letters (Na1, Na2 or Na3) of labels of sodium atoms which are not in the middle of the plot
On the right sidebar switch to the table "Table of created atoms"
Order atoms by name and select the noted sodium atoms
"Build $\rightarrow$ Polyhedra $\rightarrow$ Add coordination polyhedra"
Select oxygen for "Ligand atom groups"
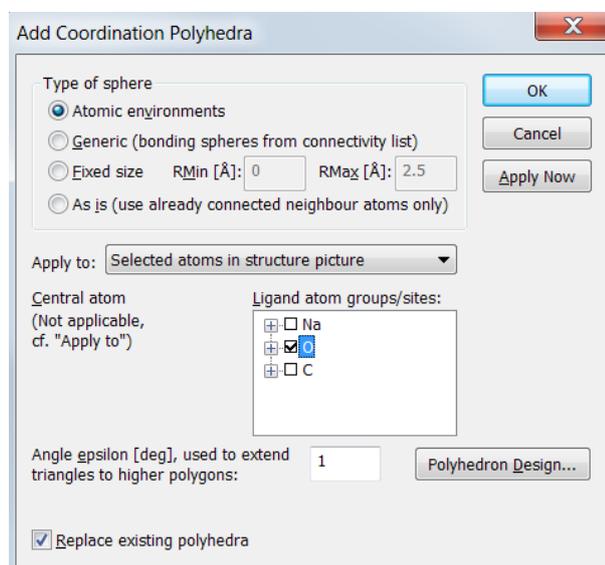


OK
With  make sure that Rendering and Lightning is activated
The resulting plot will be:
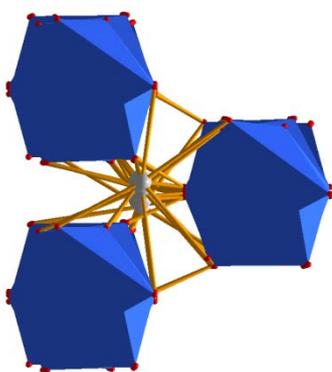
Press Ctrl-A to select all atoms
Hit some of the selected objects with the right mouse button
From the context menu select "Edit → Polyhedron design"
Define transparency 0.4; OK

Using rotations  and zooming tool  create the following figure:
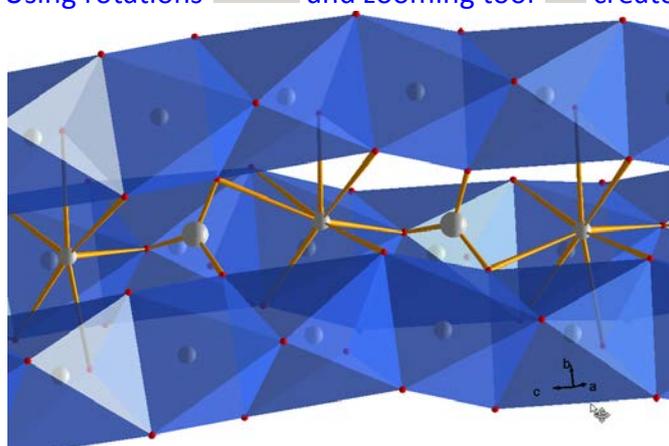


Select some sodium and carbon atoms
Hit one of them with the right mouse button
From the context menu select "Add → Atom labels"
For "Relative position" type "0 0 10". The last number will move the labels above the polyhedra
Correct positions of labels with mouse
*This is the final plot (labels may differ in your result):*
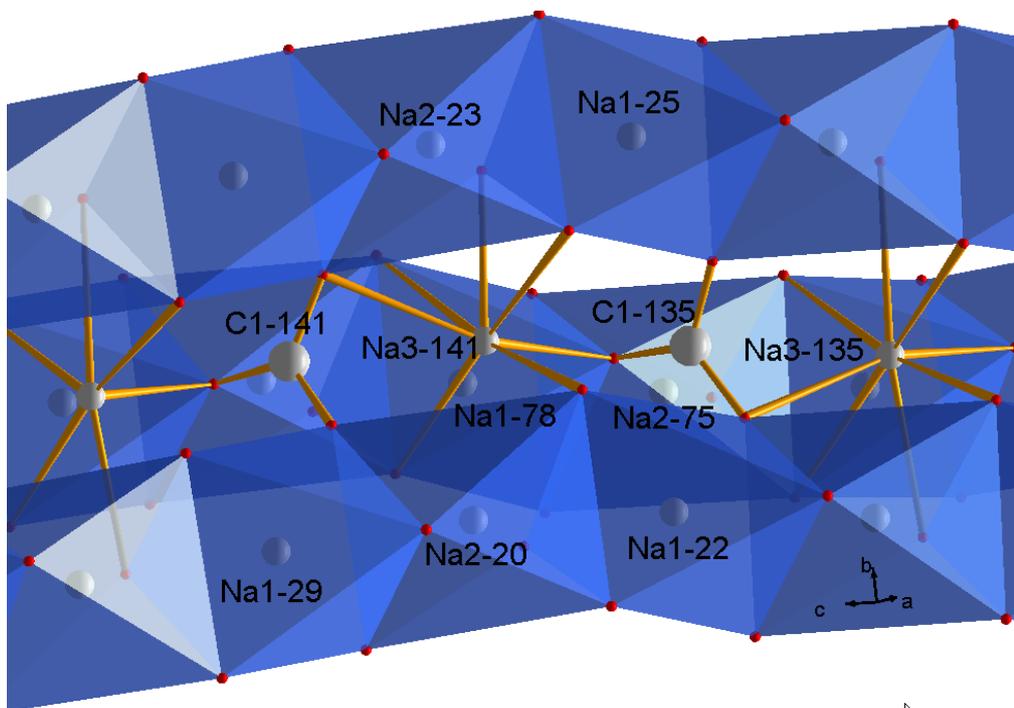
*In the middle column the CO₃ groups alternate with Na atoms.*

## 15. Properties of CO₃ anion

Start commands for Dist (click right mouse button on Dist icon)
In "Basic" page select "d(max) derived from atomic radii and typical distances"
*Jana uses typical distances from International Tables. When typical distance is not available, atomic radius is used instead. The d(max) value is expanded by user defined %. Both typical distances and atomic radii can be changed in EditM50-Page Composition*
For Listing form select "Without symmetry codes"
Press "Define coefficients for bond valences"
*[On the screen: dialogue for definition of bond valence constants]*
Select "1st atom type" carbon, "2nd atom type" oxygen
Press "From file" and select constants given in the second line
Add; OK
*[On the screen: Distance commands]*
Switch to the page "Select atoms"
Press "Refresh"; for central atom select (with ctrl-left mouse button) C1
For neighbor atoms select O1, O2
Switch to the page "Modulation"
Activate "Make coordination t- tables"
*The default parameters for t have the following meaning: distances will be calculated for t between 0 and 1 with step 0.01, i.e. for 100 values of t. The 100 calculated distances will be used for calculation of d(min), d(max) and d(ave) printed in the listing. These values will be followed by list of distances printed for each 10th value of t, i.e. for t between 0 and 1 with step 0.1*

**Distance commands**

| Basic | Select atoms | **Modulation** |

Calculate distances from t= 0   till t= 1   with step 0.01

Print each   10   th value

Make coordination t-tables ✓

Calculate if occupancies of all relevant atoms are larger then:   0

Indicate by "*" if occupancy of one of relevant atoms is smaller then:   0.01

OK; YES+Start; YES to open listing

*[On the screen: listing of Dist]*

Use "Goto → List of distances"

*Here the distances are shown as explained previously. The first distance (introduced with with dotted line) is the distance between reference positions of the basic structure, which does not occur in the real modulated structure*

Use "Goto → List of bond valences"

*Here minimum, maximum and average BVS for carbon is printed*

*At the bottom of the listing there is a Coordination table for carbon showing the three C-O distances for each step in t*

Close listing of Dist

*Similar information can be obtained from Grapht tool*

Start Grapht

Press "New/Edit"

For "Parameter to draw" select "Distances"

For "p" type lower limit 1 and upper limit 1.4

*"p" stands for "parameter" to be drawn*

For "Central atom" type C1

Press "Define neighbor atoms" and select O1, O2



**Item to be drawn**

|   | Minimum | Maximum | Step |
| t | 0 | 1 | 0.01 |   ☐ Use x4,x5,x6 instead of t,u,v
| p | 1 | 1.4 |   |   ☐ Draw non-modulated curves

Parameter to draw   Distances ▼

Name   C1   List

Define neighbour atoms

OK; OK

*[On the screen: Plot of three C-O distances as a function o t]*
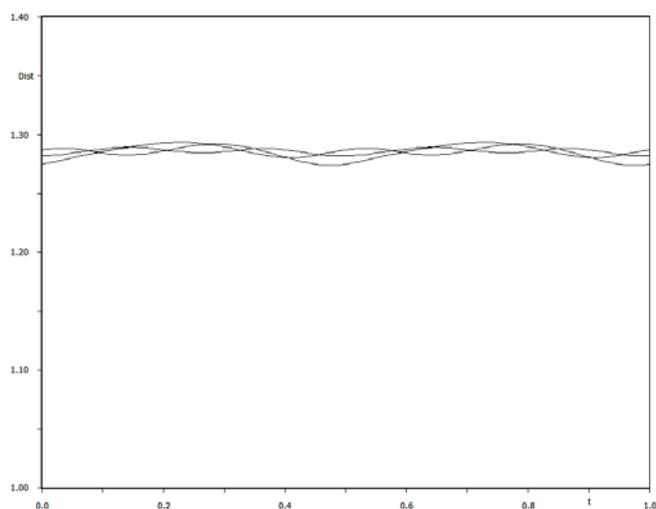
*As we have already seen in Dist listing, C-O distances are almost constant over the whole interval of t*

Press "New/Edit"

Change "Parameter to draw" to "Bond valence sum"

For "p" change lower limit to 3.5 and upper limit to 4.2

Press "Define bond valence coefficients"

*The dialogue shows the coefficients defined in Dist commands are still active*

OK; OK

*[On the screen: Plot of BVS of carbon as a function of t]*

*Using the mouse cursor we can find the fluctuation of BVS is between 3.94 and 4.04*

*Both Grapht and Dist confirm the C-O bonds are constant. Now we shall check planarity of the CO3 group:*

Start "Edit Atoms"

Select atoms O1, O2 and C1

Choose Action "Make symmetrically contiguous motif"

OK; YES to save changes

*With this procedure we transformed positions of C1, O1 and O2 to be connected without need of transformations*

Start commands for Dist

In page "Basic" for "Listing form" check "With symmetry code"

In Page "Select atoms" make sure the central atoms is carbon and the neighbor atoms are oxygens

OK; YES+Start; YES to open the listing

"Goto → List of distances"

```
Distances concerning atom C1
================================
C1-O1            1.2792(5)                    2nd: O1              x,y,z
  ave : 1.2859(13)  min : 1.2819(13)  max : 1.2892(13)
C1-O2            1.2621(3)                    2nd: O2              x,y,z
  ave : 1.2853(17)  min : 1.2741(17)  max : 1.2937(17)
C1-O2            1.2621(3)                    2nd: O2‡s4           x,-y,z
  ave : 1.2854(17)  min : 1.2741(17)  max : 1.2937(17)
--------------------------------------------------------------------------
```

*There are three distances: C1-O1, C1-O2 and C1-O2. For the third distance ,C1-O2, oxygen O2 must be transformed from the position given in M40 by the symmetry operation x,-y, z, which is encoded to the Jana symmetry code #s4 (i.e. the fourth symmetry operation). Other*

*distances do not need a transformation because "Symmetry contiguous motif" has been created in the previous step..*
Close the listing of Dist
Start commands for Dist
In page "Basic" press the button "Planes"
For "Atoms defining the best plane" type "O1   O2   O2#s4"
For "Additional atoms" type C1
Add; OK; OK; YES+Start; YES to open listing
"Goto → List of best planes"
*The listing shows that the distance of C1 from the plane of oxygens does not change with the t coordinate which means the planarity of $CO_3$ is not influenced by modulation.*

*At the next step we will test whether the atoms of $CO_3$ group move during modulation in the phase, i.e. like a rigid body. This can be visualized by animated plot in Contour.*
Run refinement (at least zero cycles) to get input M80 for Fourier calculation
Start Fourier commands, select "Map type" "F(obs) – Fourier"
In the page "Scope" select "automatically", "Use default map orientation"
OK; YES+Start; don't include new atoms; don't open listing
Start Contour; New Plot
Select "Use old map", "Draw a general section"; OK
*[On the screen: form for definition of the general section]*
For the first atom type O1
For the second atom type O2
For the third atom type O2#s4
*The three atoms define the plane of the section through the electron density map. The dimensions of the plot are defined in Scope*
For "Scope" type "4 4 0"
For "Interpolation step" type "0.02"
*This means the plot will be 4x4 Å. Number of parallel sections calculated by the program is 1+s3/is, where "s3" is the width of the section and "is" is the interpolation step. Here it means one section, because the third parameter is zero.*
For "First point put to" type "1 1 0"

| | Atom | Coordinates | | Difference to 1st |
|---|---|---|---|---|
| 1st | O1 | 0.789857 0 0.677631 | | |
| 2nd | O2 | 0.601607 0.2062 0.785329 | | -0.18825 0.2062 0.107698 |
| 3rd | O2#s4 | 0.601607 -0.2062 0.785329 | | -0.18825 -0.2062 0.107698 |

**Scope**

| Interpolation step | Scope of section | 1st point put to | |
|---|---|---|---|
| 0.02 | 4 4 0 | 1 1 0 | [Ang] |
| | | Adjust | |

*The first point of the plot is O1. The horizontal axis of the plot will be O1-O2. The last atom O2#s4 will be above the horizontal axis.*
OK
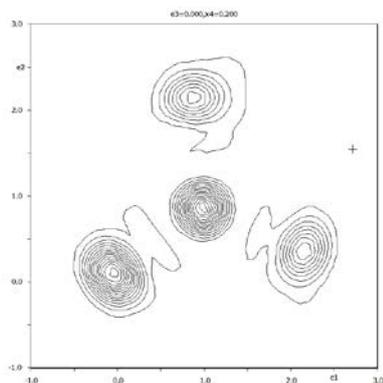
Click the middle maximum and select all close atoms; OK
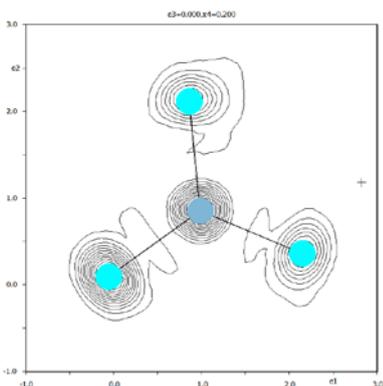


Press "Movie"; keep default parameters; OK

*The tool plots the successive sections calculated previously by Fourier for selected x4 values. Sampling in x4 na be changed in Fourier option - page Scope.*

ESC to break the movie

Press "t-map ON" and do the same animation for t-map.

*For this case geometry of A3-A3 map is similar to that in R3-R3 map. Atoms of $CO_3$ are moving in phase and probably they could be described by rigid body. The position of one of oxygens is very stable comparing to the other atoms. This is the oxygen described with less ADP waves.*

### 16. Sodium atoms

Using Grapht plot Na-O distances for Na1, Na2 and Na3. In the Grapht dialogue select "Draw non-modulated curves" – they will appear in the plots like dashed lines indicating distances in the basic structure.
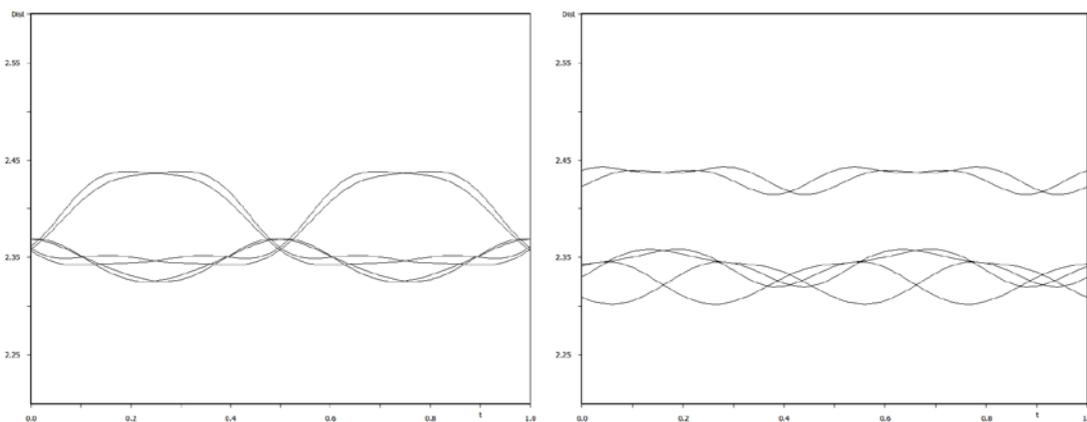
*Distances Na3-O*                                    *Distances Na2-O*
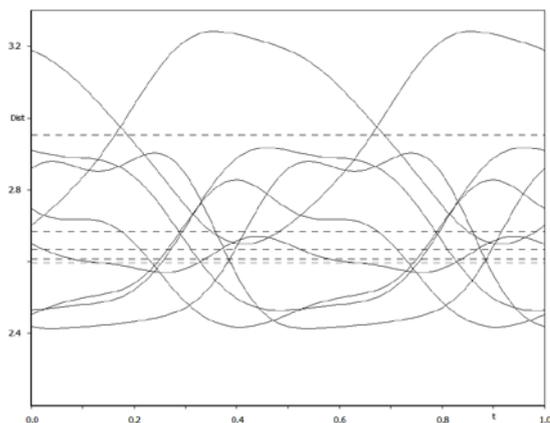


*Distances Na1-O*

*As it has been previously indicated by plot of the structure, Na1 which alternates with carbon in a column along c, has different coordination comparing with octahedrally coordinated Na2, Na3. Na1 has more neighbors with strongly varying distances which are all longer comparing with Na2 and Na3. Good test if this complicated model is reasonable provides plot of the bond valence sum.*

Using Grapht plot graphs of bond valence sums for Na1, Na2 and Na3 (do not forget to define coefficients for Na-O bond)
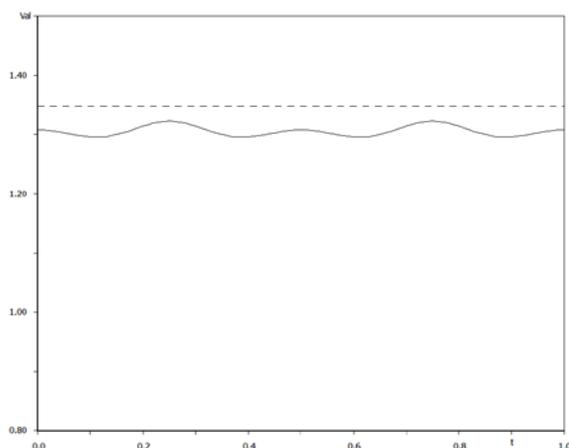


*BVS for Na3*                                        *BVS for Na2*
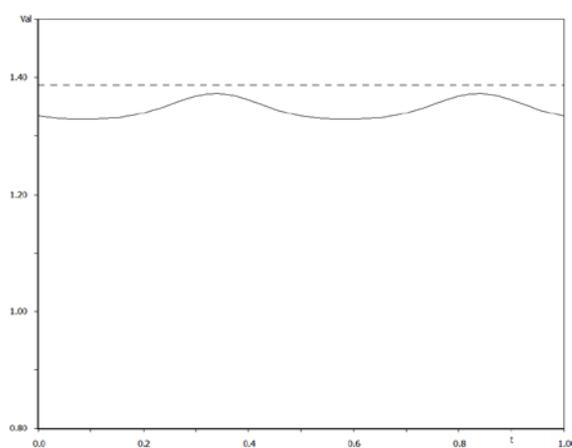
*BVS for Na1*
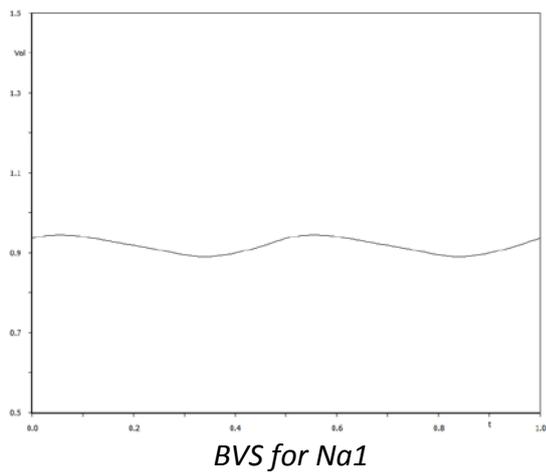
*Graphs of BVS show that Na1, Na2 are oversaturated while Na3 is slightly undersaturated. However, the fluctuation of BVS is in all cases small and similar. This means the modulation of Na3 and its coordination is properly described with approaching and departing oxygen atoms in balance.*

# Example 5.3.1: CrPO data

**Data processing for the room temperature incommensurate phase of $Cr_2P_2O_7$.**

**Revised: 3 March 2015**

### $Cr_2P_2O_7$

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: directory CrPO_RT available in [ftp://pc222.fzu.cz/cookbook](ftp://pc222.fzu.cz/cookbook), UID cookbook,
password jana2006

This example is based on the Crysalis 171.37.35. Crysalis is a program for controll and data
processing of Agilent diffractometers. It has very friendly licencing policy: everybody can install
Crysalis for processing data acquired with an Agilent instrument (which is the case of $Cr_2P_2O_7$).

1. ***Getting the file***
   Start your browser
   Connect to ftp://pc222.fzu.cz/cookbook
   Log in as cookbook with password jana2006
   Download the archive CrPO_RT.zip
   Unpack the archive
   *It will create directory CrPO_RT*

2. ***Starting Crysalis***
   Start Crysalis
   In a dialogue that follows locate the file CrPO_228_4.par
   *Crysalis opens the experiment.*

   Use ⊖ to decrease the image size
   *[On the screen: the basic window of Crysalis]*

### 3. Determination of the unit cell

Start Lattice wizard using the button

[On the screen: the window of Lattice Wizard]



In this wizard, each button has a default function started by pressing the centre of the button and various optional functionalities, which are offered after pressing ">" part of the button

Start "Peak hunting" with default options

*About 6500 peaks have been found*

Start "Unit cell finding" with default options

*The program finds a unit cell 7.03, 8.42, 4.64, 90, 108.60, 90 and indexes about 30% of peaks*
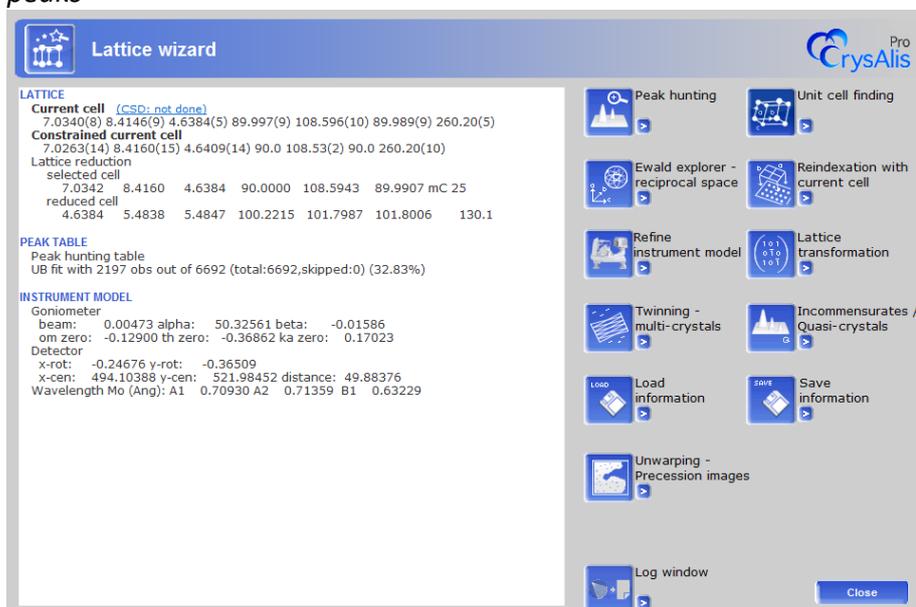


Start "Ewald Explorer" with default options

Use the buttons a* b* c* to see projections of the found peaks along the unit cell axes.

Set projection along b*

*[On the screen: Ewald – projection along b*]*
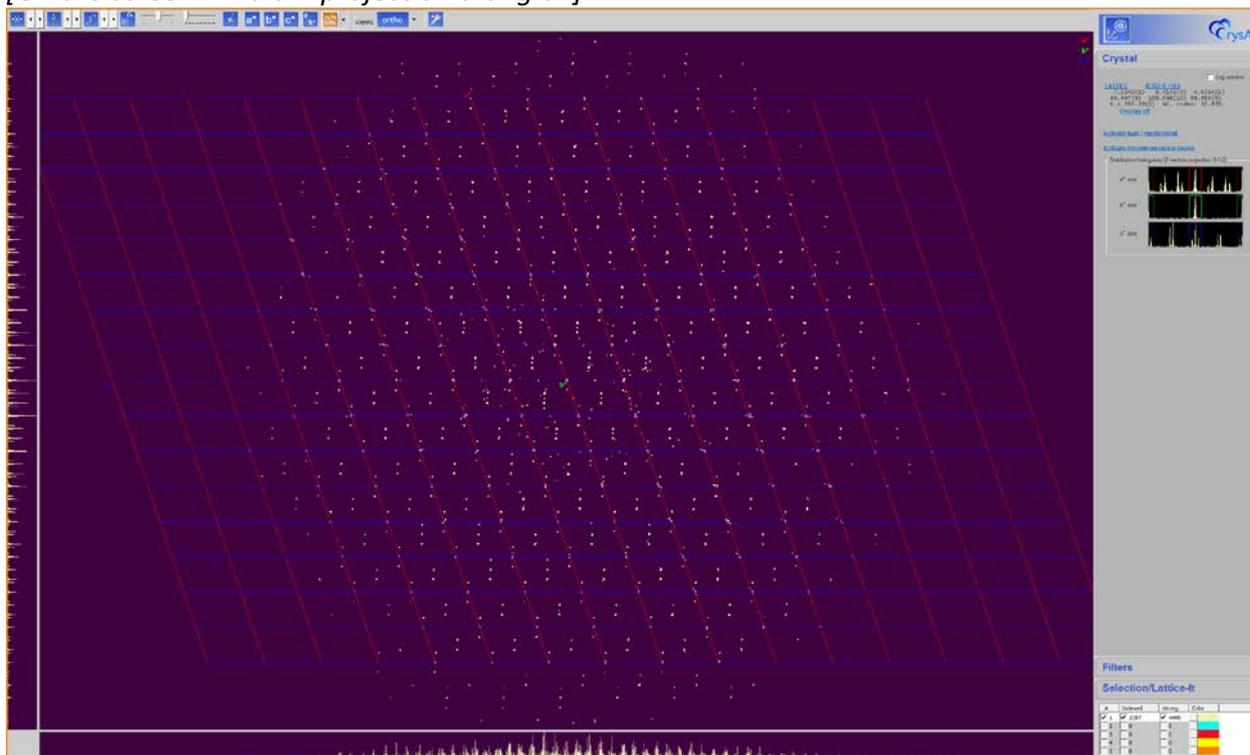


From this projectin, it is clear that the additional spots cannot be indexed by any reasonable supercell.

Set projection along a*

The peaks between the equidistant planes are evidently some spurious peaks arising e.g. from a small crystal attached on the main sample. We will now remove these peaks

In the right panel, switch to the page "Selection/Lattice-It"

Activate the radio button "Lattice-It"

*[On the screen: Ewald Explorer with activated function "Lattice-it"]*
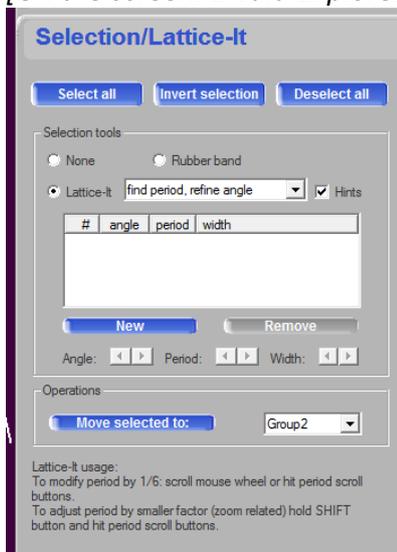


The cursor changes to a pair of white lines. Orient these lines parallel with the horizontal rows of the peaks. After some delay, the program automatically recognizes the periodicity.

*[On the screen: Ewald Explorer with activated function "Lattice-it" and recognized periodicity]*

In the right pane, press "Move selected to:" which will move the selected (green) peaks to the Group2



At the bottom of the right panel, clear the checkbox of the group 2. The spurious peaks now become invisible

At the right panel, switch to the page "Crystal"

Select vie along b*

Now we have a clear figure suitable for definition of the q-vector

4. **Determination of the q-vector**

   For selection of the q-vector we should consider the following:

   - All satellites must have the same direction with respect to their parent main reflection, and this direction is defined by the q-vector

   - First order satellites are usually stronger than the higher order ones

   - The projection of peaks onto a*, b* and c* in the right panel suggests that the q-vector has

the beta component zero

- in order to be consistent with the workshop example 5.3.2, we would like the alpha component positive (towards the label a*) and with the gamma component negative (opposite to the label c*). The labels a* (red) and b* (blue) are rather small, located at the end of the lattice vectors going through the origin.

From these considerations we can suggest a q-vector like this:
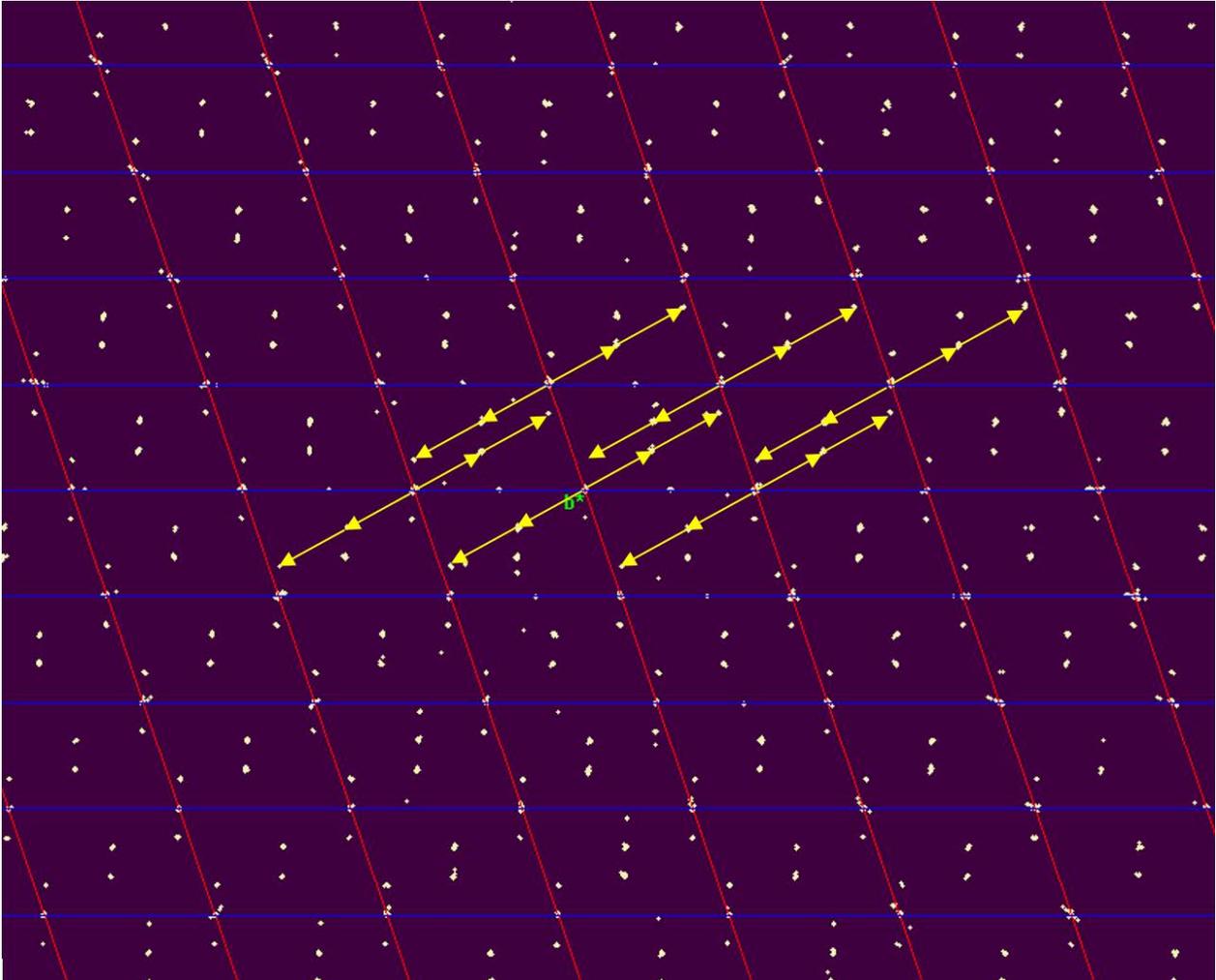


In the right panel, press "Activate incommensurate peaks" and select "Add 1d modulation vector (hklm)"
Activate the checkbox close to the q-vector and in the textbox that appears type estimated components of the q-vector and the satellite index:
0.33 0 -0.5 2
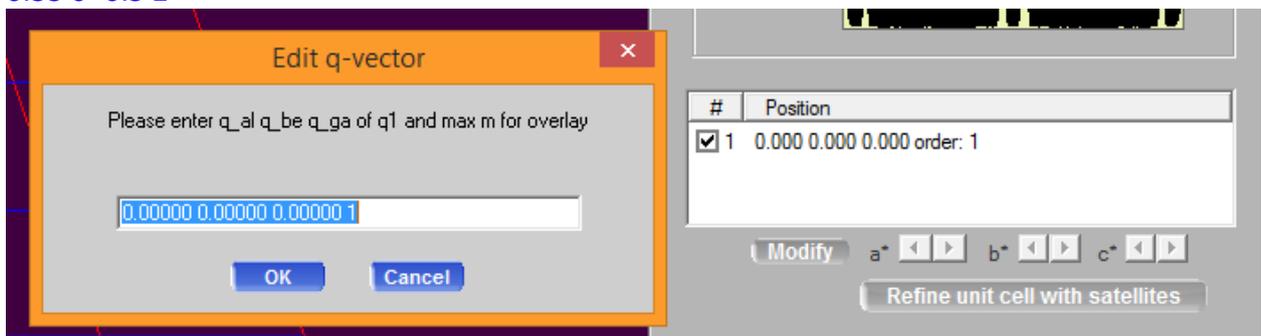
Play with the arrows close to "Modify" button until the satellite position fit with the projections



Toggle the checkbox close to the q-vector ☑ 1   0.362 -0.000 -0.465 order: 2   and check if the peak positions are properly described. In some areas we can see that there are also the 3$^{rd}$ order satellites:
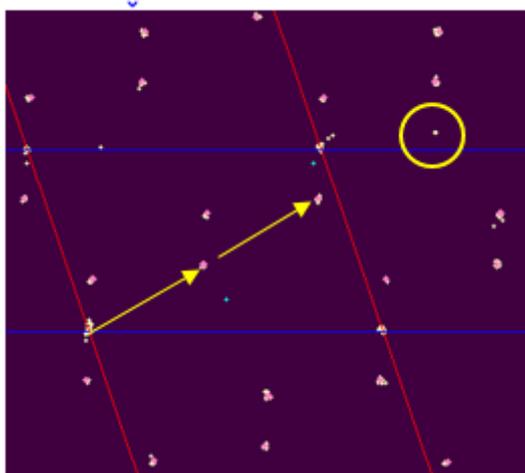


Using the button "Modify" at the right panel, increase the satellite intex to four. The reason for four is that when we can see the third order satellites by an eye there might be the forth order satellites not found by the default peak search



Check views along a* and c* to be sure that the  satellites are described
Close the window of the Ewakd explorer

**5. Refinement of the q-vector**

*[On the screen: Lattice wizard]*

Press the button "Incommensurates/Quasi-crystals"

In the appeared text box, define maximal satellite index (4) and the accuracy (0.05) defining the maximal tolerancy for an integer (for instance, 1.04 can be rounded to 1)

Please enter mmax crithkl q1 q2 q3 [q1 q2 q3 [q1 q2 q3]] (5,8,11 values)

```
4 0.05000 0.36216 -0.00006 -0.46547
```

OK    Cancel
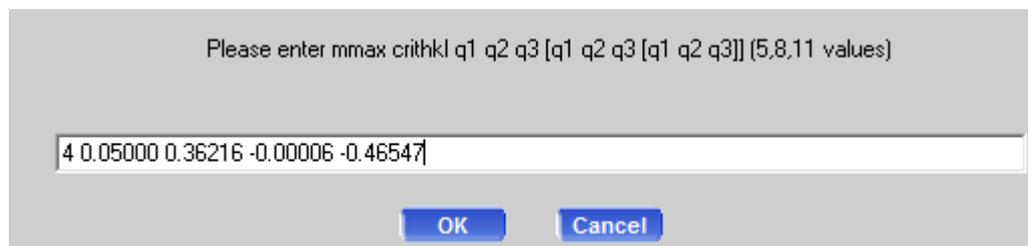
OK

The program refines the unit cell and q-vector an indexes 93% of the peaks. This is quite acceptable number because the refinement included also the previously suppressed

LATTICE
Current cell  (CSD: 0 +3L)
   7.0311(8) 8.4134(9) 4.6363(5) 90.009(9) 108.612(10) 90.000(9) 259.92(5)
Constrained current cell
   7.0256(14) 8.4174(15) 4.6407(14) 90.0 108.54(3) 90.0 260.20(10)
Lattice reduction
   selected cell
       7.0342   8.4160   4.6384   90.0000   108.5943   89.9907 mC 25
   reduced cell
       4.6384   5.4838   5.4847   100.2215   101.7987   101.8006   130.1
Incommensurate/quasi-crystal information
   q(1): 0.3622(3) 0(5e-004) -4.675e-001(3)

PEAK TABLE
   Peak hunting table
   UB fit with 6233 obs out of 6692 (total:6692,skipped:0) (93.14%)
   2041 main refl.; 4192 q1 satellites
   By order
   4192 q1: (2900,1243,46,3)

Press the ">" part of the button "Save information" and select "Save specific peak table only". Make backup copy of the peak table under some name which cannot be overwritten by Crysalis, e.g. "incommensurate"

SAVE  Save information
      > Save peak table only
        Save specific peak table only
        Save parameter file only
        Save specific parameter file only
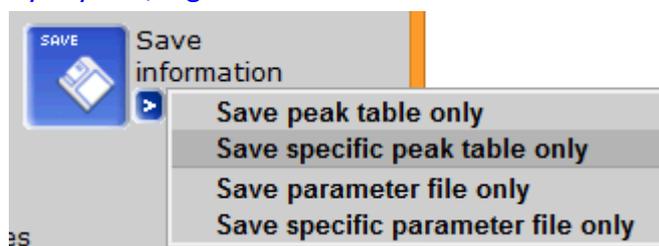
Close the window of the Lattice Wizard

**6. Data reduction**

*[On the screen: Basic window of Crysalis]*

In the right panel, press the button "Start-Stop"

In the next window, select "Data reduction with options"

*[On the screen: Step 1: Orientation matrix for data reduction]*
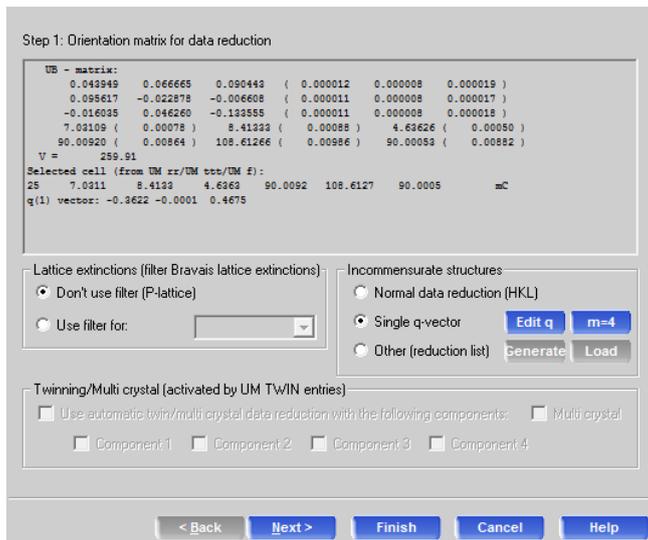
**Check the modulation vector (button "Edit q") and maximal satellite index (button "m=")**
The unit cell found previously is C-centered. Now we are having two options: "Use filter for C-lattice" or "Don't use filter (P-lattice)". Using the filter is good for cases with close diffraction spots because during the data processing, Crysalis finds optimal positions for diffraction spots and it could skip from a systematically absent satellite position to an existing position. On the other hand, with less dense diffraction pattern, not using the filter gives us the complete information and we can verify the C centering. For our example, the filter for C-centering is not necessary.

**NEXT; NEXT**
*[On the screen: Step 3: Basic algorithm parameters]*
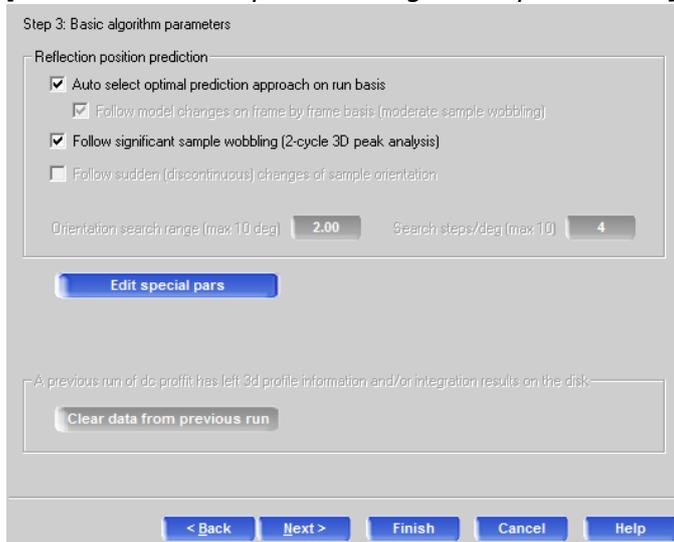


**Uncheck "Follow significant sample wobbling" (we know that the sample wa not wobbling)**
Note: In this case, no special parameters are necessary. For more complicated modulated structures, e.g. with short modulation vector, there are two typical parameters one should consider: (1) "Override integration mask size" available through the button "Edit special parameters"; (2) "Skip model refinement" available through the button "Edit special parameters" followed by Alt-E keyboard shortcut.

**NEXT;**
*[On the screen: Step4: Background evaluation]*

Keep all settings default; NEXT

The method "Average beckground" is faster and usually works well; the method "Smart background" is slower and only sometimes gives better results

*[On the screen: Step5: Outlier rejection]*

Keep all settings default; NEXT

Outlier rejection based on monoclinic Laue symmetry does not mean that the program would create a false monoclinic data for non-monoclinic case. Although the algorithm behind is undescribed, the process is quite conservative and rejects only few reflections. The resulting data are unmerged.

*[On the screen: Step6: Output]*

Keep all settings default; FINISH

Following is the data processing. In the first step, the program goes to the peaks positions predicted by the orientation matrix and make profile analysis to get accurate peak positions and some other hidden information. During profile analysis is accompanied by the background subtraction. In the second step the program makes data integration.

## 7. *Output*

1) The resulting data are placed to the directory struct\tmp. For Jana2006 we need the files CrPO_228_4.cif_od and CrPO_228_4.hkl

2) In the left toolbar of Crysalis, there is a button Jana. The button triggers the following actions: directory struct\ jana_CrPO_228_4 is created; files CrPO_228_4.cif_od and CrPO_228_4.hkl are copied to this directory; Jana2006 is launched

3) In the left toolbar of Crysalis, press the button 

*[On the screen: Inspect data reduction results]*

Go to the page "Data reduction output"

```
287-       49    3730   3700   883   4.2   125.04    3.45    0.146   0.174
 49-       21    3320   3270   883   3.7    30.37    1.52    0.433   0.514
 21-        9    3550   3513   883   4.0    13.21    0.89    0.657   0.919
  9-        4    4151   4125   883   4.7     5.85    0.47    0.869   1.782
  4-        0    4778   4772   883   5.4     1.87    0.20    0.979   4.448
  0-       -2    4872   4868   883   5.5    -0.87   -0.08    0.985   7.858
 -2-       -8    4071   4055   883   4.6    -4.52   -0.33    0.900   2.182
 -8-     -113    2476   2416   886   2.7   -15.09   -0.71    0.699   0.891
------------------------------------------------------------------------------
1081746-   -113  39154  38870  8833   4.4  4354.49    8.15    0.016   0.019


Statistics vs resolution - point group symmetry: P2/m (b-unique)
resolu-      #       #       #           average   mean    mean
tion(A)   measured  kept   unique       redundancy  F2    F2/sig(F2)  Rint   Rsigma   RsigmaA
------------------------------------------------------------------------------------------
 inf-1.73   6487    6432    892            7.2    5980.29   13.04    0.015   0.018   0.008
1.73-1.33   5921    5888    884            6.7    7164.86   11.19    0.015   0.016   0.009
1.33-1.12   5277    5249    886            5.9    4557.03    8.34    0.013   0.016   0.016
1.12-1.00   4699    4680    890            5.3    4206.26    7.35    0.015   0.016   0.018
1.00-0.92   4333    4300    892            4.8    3461.85    6.03    0.018   0.021   0.021
0.92-0.85   3504    3475    896            3.9    2539.49    5.84    0.021   0.024   0.032
0.85-0.80   3098    3065    890            3.4    2437.53    4.82    0.023   0.026   0.031
0.80-0.75   2539    2513    887            2.8    2454.15    4.94    0.023   0.024   0.034
0.75-0.70   1928    1907    887            2.1    2242.47    4.80    0.025   0.027   0.040
0.70-0.60   1368    1361    829            1.6    2481.02    4.50    0.026   0.025   0.039
------------------------------------------------------------------------------------------
 inf-0.60  39154   38870   8833            4.4    4354.49    8.15    0.016   0.019   0.016
 inf-0.80  33243   33015   6210            5.3    4696.12    8.73    0.016   0.018   0.015
Data reduction ended at Wed Mar 04 10:35:24 2015
```

This page shows the merging R values (Rint) sorted by intensity shell. When scrolled up, it also shows the same information separately for satellites:

```
1. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)
resolu-      #       #       #          average   mean      mean
tion(A)   measured  kept   unique      redundancy   F2    F2/sig(F2)   Rint   Rsigma  RsigmaA
-------------------------------------------------------------------------------------------
 inf-1.74    1471    1463    200          7.3     5012.48   21.08      0.017   0.021   0.016
1.74-1.34    1328    1322    198          6.7     4098.65   14.11      0.018   0.021   0.023
1.33-1.13    1163    1157    198          5.8     5962.89   13.96      0.016   0.019   0.021
1.13-1.02    1044    1039    199          5.2     3646.34   10.52      0.019   0.022   0.031
1.02-0.93     970     962    199          4.8     3101.18    9.66      0.022   0.026   0.038
0.93-0.86     769     759    198          3.8     3747.62    9.61      0.022   0.025   0.035
0.86-0.81     698     688    201          3.4     2927.31    8.13      0.022   0.023   0.041
0.81-0.76     545     540    199          2.7     2741.41    7.02      0.023   0.027   0.042
0.76-0.71     464     460    200          2.3     2136.91    6.29      0.031   0.031   0.053
0.71-0.61     313     312    193          1.6     1813.11    5.09      0.028   0.028   0.060
-------------------------------------------------------------------------------------------
 inf-0.61    8765    8702   1985          4.4     3942.78   12.30      0.019   0.023   0.027
 inf-0.80    7524    7470   1422          5.3     4240.08   13.32      0.018   0.022   0.025

2. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)
resolu-      #       #       #          average   mean      mean
tion(A)   measured  kept   unique      redundancy   F2    F2/sig(F2)   Rint   Rsigma  RsigmaA
-------------------------------------------------------------------------------------------
 inf-1.74    1460    1441    199          7.2      576.43    6.77      0.048   0.056   0.052
1.73-1.33    1335    1325    197          6.7      512.15    5.10      0.044   0.051   0.074
1.33-1.13    1180    1165    198          5.9      503.44    4.23      0.042   0.050   0.083
1.13-1.01    1046    1040    197          5.3      497.33    4.09      0.049   0.054   0.098
1.01-0.93     925     922    197          4.7      363.87    3.17      0.059   0.065   0.125
0.93-0.87     797     796    201          4.0      378.75    2.93      0.056   0.062   0.123
0.86-0.81     725     719    198          3.6      363.03    2.91      0.061   0.066   0.138
0.81-0.76     579     572    197          2.9      305.62    2.37      0.077   0.081   0.147
0.76-0.71     431     428    197          2.2      207.13    1.89      0.092   0.086   0.203
0.71-0.61     314     314    191          1.6      180.59    1.74      0.096   0.094   0.244
-------------------------------------------------------------------------------------------
 inf-0.61    8792    8722   1972          4.4      439.25    4.10      0.052   0.061   0.096
 inf-0.80    7506    7445   1401          5.3      474.04    4.46      0.049   0.057   0.088

3. order satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)
resolu-      #       #       #          average   mean      mean
tion(A)   measured  kept   unique      redundancy   F2    F2/sig(F2)   Rint   Rsigma  RsigmaA
-------------------------------------------------------------------------------------------
 inf-1.74    1406    1403    197          7.1       29.49    1.30      0.209   0.273   0.300
1.73-1.34    1348    1346    198          6.8       35.88    1.15      0.210   0.285   0.352
1.34-1.13    1163    1161    199          5.8       61.25    1.26      0.156   0.215   0.281
1.13-1.01    1039    1036    197          5.3       38.38    0.97      0.243   0.314   0.429
1.01-0.93     953     943    196          4.8       38.03    0.82      0.256   0.348   0.453
0.93-0.86     776     773    196          3.9       53.44    0.94      0.224   0.295   0.398
0.86-0.81     699     694    197          3.5       42.33    0.85      0.266   0.357   0.503
0.81-0.77     514     509    196          2.6       44.30    0.83      0.264   0.319   0.503
0.77-0.71     434     429    197          2.2       41.09    0.77      0.263   0.310   0.536
0.71-0.61     323     321    196          1.6       31.94    0.61      0.362   0.404   0.624
-------------------------------------------------------------------------------------------
 inf-0.61    8655    8615   1969          4.4       41.50    1.03      0.226   0.306   0.402
```

The Rint is calculated together for observed and unobserved reflections. In order to see Rint for observed reflections, Jana2006 must be used

Go to the page "Graphs"
The most important is the graph from the frame scaling. Too large fluctuation of this graph usually mean that an absorption correction by shape should be done.

Results of scaling correction done by scale3 abspack

Source data [ absscale ]          Plot [ Frame vs Scale,Run number ]
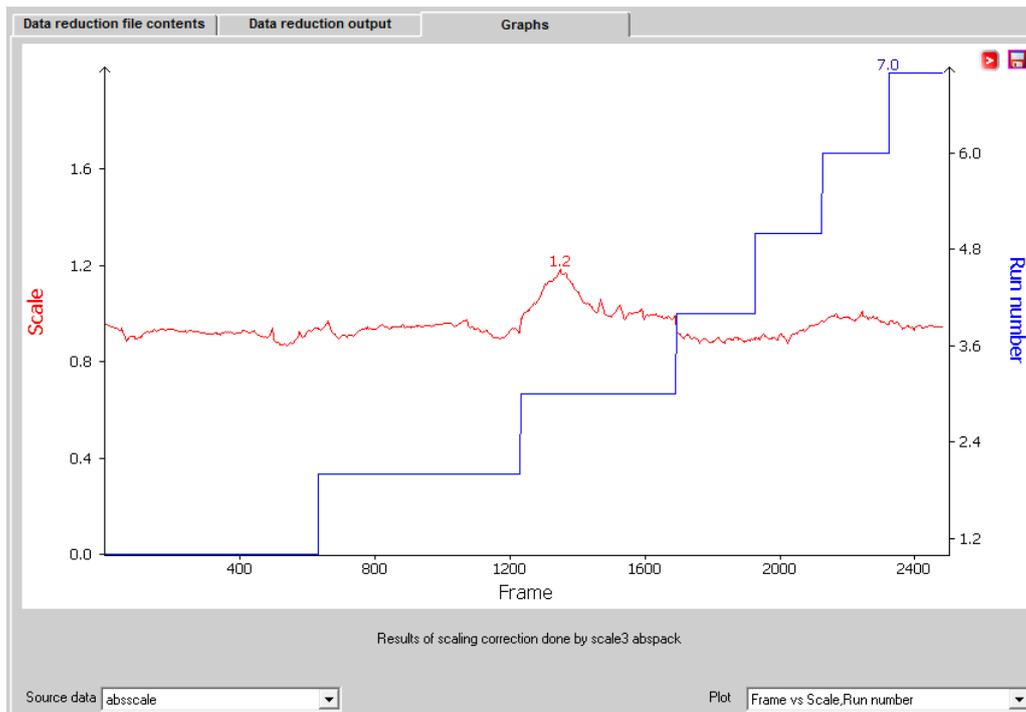
4) Note about the absorption correction

The data were automatically corrected using the empirical absorption correction, called ASSPACK in Crysalis. In order to improve the absorption correction the following steps should be done:

- At the bottom of the "Inspect data reduction results", press the button "Abs display". This opens a tool for indexing of the crystal shape
- At the bottom of the "Inspect data reduction results", press the button "Refinalize" and repeat the corrections.

Both tools offer rich possibilities and cannot be described within this basic example.

# Example 5.3.2: CrPO

**Solution of the room temperature incommensurate phase of $Cr_2P_2O_7$.**

**Revised: 5 March 2015**

**$Cr_2P_2O_7$**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: CrPOcom.hkl, CrPOcom_red.sum
Frame scaling, absorption correction: done with software of the diffractometer

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click crpo

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   In "Define basic input file" select "Input from cif_od file"; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH
   *[On the screen: Data repository]*
   OK; YES to accept the data set

3. ***Symmetry Wizard***
   Use default tolerances for crystal system recognition
   Select monoclinic Laue symmetry
   Select C centering
   Select space group C2/m
   Select superspace group C2/m(a0g)0s
   Accept the superspace group in the original cell

4. ***Creating refinement reflection file***
   Follow default steps of the wizard

5. ***Structure solution wizard***
   Type the formula Cr2 P2 O7, two formula units
   Select "Superflip" and "Peaks from Jana2006"
   Select "Use a specific random seed" and type "111" for random seed
   *With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work Random seed should not be fixed.*
   "Run solution"
   *Superflip converges with R around 19% and confirms the selected superspace group*

Close the listing of Superflip
Press "Accept last solution"
"Quit" to leave the Structure solution wizard

6. *Investigation of charge flipping results*

Start EditM50, page Composition; press "Formula from M40"

The formula based on structure model is $Cr_2P_2O_8$, i.e. one oxygen more

Start Options for Dist; for "Listing form" select "With symmetry codes"

Run Dist and open listing

In the listing make sure that the atoms P1, O1, O2 and O3 make symmetrically contiguous motif, i.e. that O1, O2 and O3 listed in coordination of P1 have one of their symmetry codes equal to "x,y,z". In this example, oxygens are NOT in correct symmetry positions and transformation is necessary.

Start "Edit atoms"

Select P1, O1, O2, O3

"Action $\rightarrow$ Make symmetrically contiguous motifs"

Repeat calculation of distances with symmetry codes. The listing of Dist should look as follows

```
Distances concerning atom P1
=================================
P1-O1            1.5561(4)                  2nd: O1             x,y,z
  ave : 1.5575(4)   min : 1.5561(4)   max : 1.5588(4)
P1-O2            1.5039(2)                  2nd: O2             x,y,z
  ave : 1.525542(10)  min : 1.49223(2)  max : 1.57991(2)
P1-O2            1.5039(2)                  2nd: O2#s4t0,1,0    x,-y+1,z
  ave : 1.526194(11)  min : 1.49223(2)  max : 1.57991(2)
P1-O3            1.6491(2)                  2nd: O3             x,y,z
  ave : 1.6607(4)   min : 1.5371(5)   max : 1.7813(5)
P1-O3            1.6491(2)                  2nd: O3#s3t0,1,3    -x,-y+1,-z+3
  ave : 1.6582(4)   min : 1.5079(5)   max : 1.7911(5)
---------------------------------------------------------------------------------
```

Start Contour and New plot

Select "Calculate new ones"; OK *(if the option is not active Contour has no old map and it will calculate new map by default)*

In Fourier option, page Basic, select "Map type" = "F(obs) – Fourier"

In page Scope set calculation of the x1-x4 section with the central point Cr1



OK;
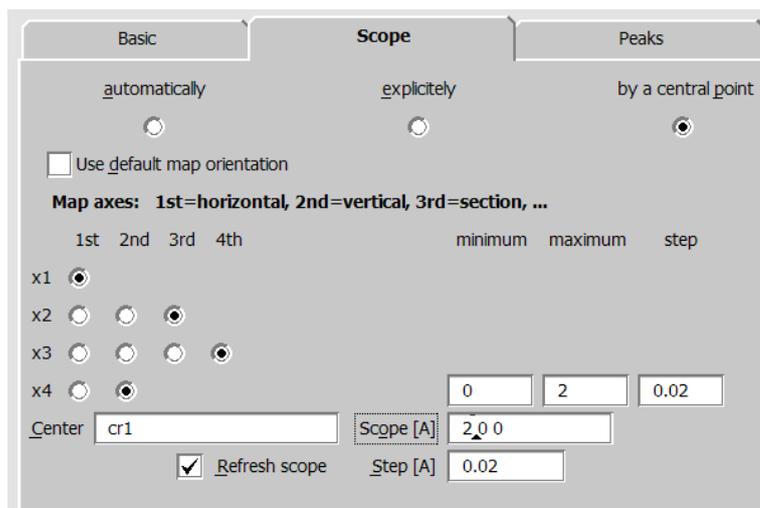
*[On the screen: Contour window with plot of x1-x4 section through position of Cr1]*

Press "Atoms edit" and add Cr1 to the list of atoms to be plotted

Repeat the steps to create sections shown in the following plots
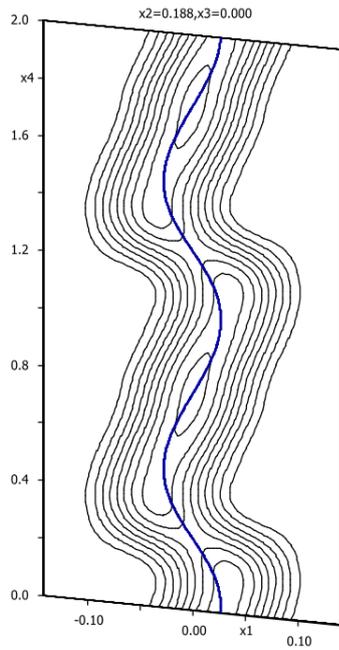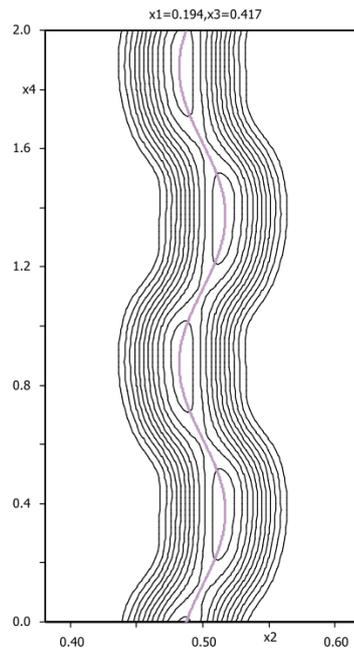


*Cr1: section x1-x4*          *P1: section x2-x4*          *O1: section x2-x4*
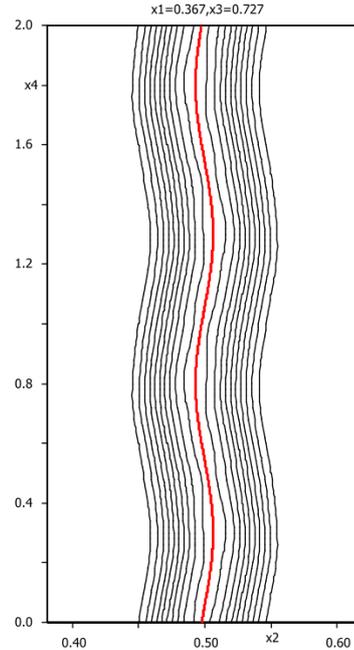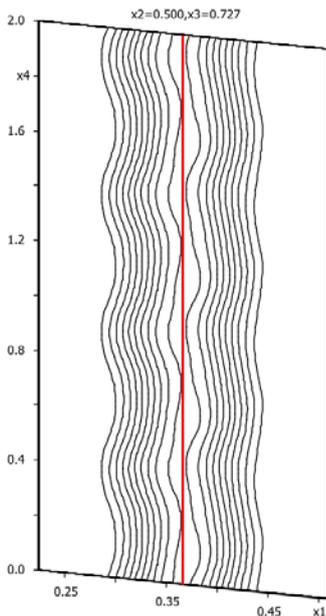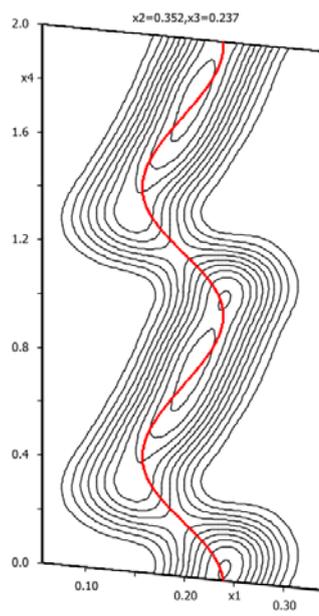


*O1: section x1-x4*          *O2: section x1-x4*          *O3: section x2-x4, scope along x2 is 4 Å*
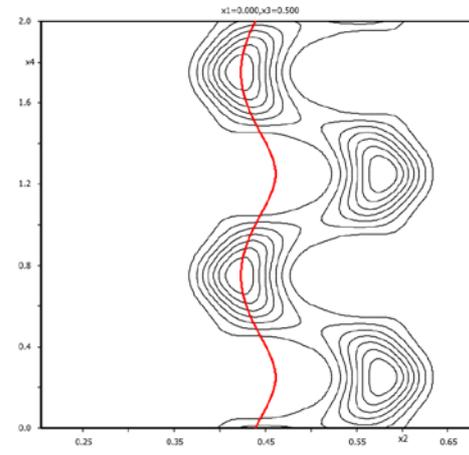
From the plots we can conclude:

Cr1 needs a sawtooth function with center at 0.75 and width 1

P1 needs more modulation waves

O1 seems to be properly described in x2-x4 section but not in x1-x4

O2 needs sawtooth function with center 0.75 and width 1

O3 needs a crenel function with centre 0.75 and width 0.5;. the remaining maxima could be described with modulation function related by symmetry operation -x, -y+1, -z+3, i.e. #s3t0,1,3 in Jana encoding (This can be found from the Dist listing)

7. ***Setting crenel and sawtooth functions***

   Use "File → Structure → Save As" and create backup copy "crpo_superflip"

Do not continue with the new structure
Start "Edit atoms"
Double-click Cr1
[On the screen: Atom Edit tool]
In page "Define" activate "crenel"
In page "Edit" press "Occupancy" and define delta=1 and x40=0.75; OK
Leave refinement boxes clear (we don't want refinement of x40 or delta)
Refinement keys of delta and x40 are not automatic
In page "Define" select "Legendre polynomials in crenel interval"
**The order of these three steps is important**! After selecting "Legendre polynomials in crenel *interval*" *the program fits the coefficients of the Legendre polynomials to be as close as possible to the previously used modulation function - in our case to the harmonic modulation function found from Superflip electron density. For this process, the information about delta and* x40 *is needed.*
OK

Repeat the process for O2 (here delta=1, x40=0.75)
Repeat the process for O3 (here delta=0.5 and x40=0.75)
Leave "Edit atoms", YES to save changes
After activation of Legendre polynomials, the keys "Legendre" will appear in M40 file.

Start EditM50, page Composition; press "Formula from M40"
The program now prints correct composition for Z=2: $Cr_2P_2O_7$. Number of oxygens has been reduced using crenel function with delta=0.5 for O3
Run Contour and plot the same sections like before for Cr1, O2 and O3:
The electron density will be still the one from Superflip because we did not run Refinement.



Cr1                               O2                               O3
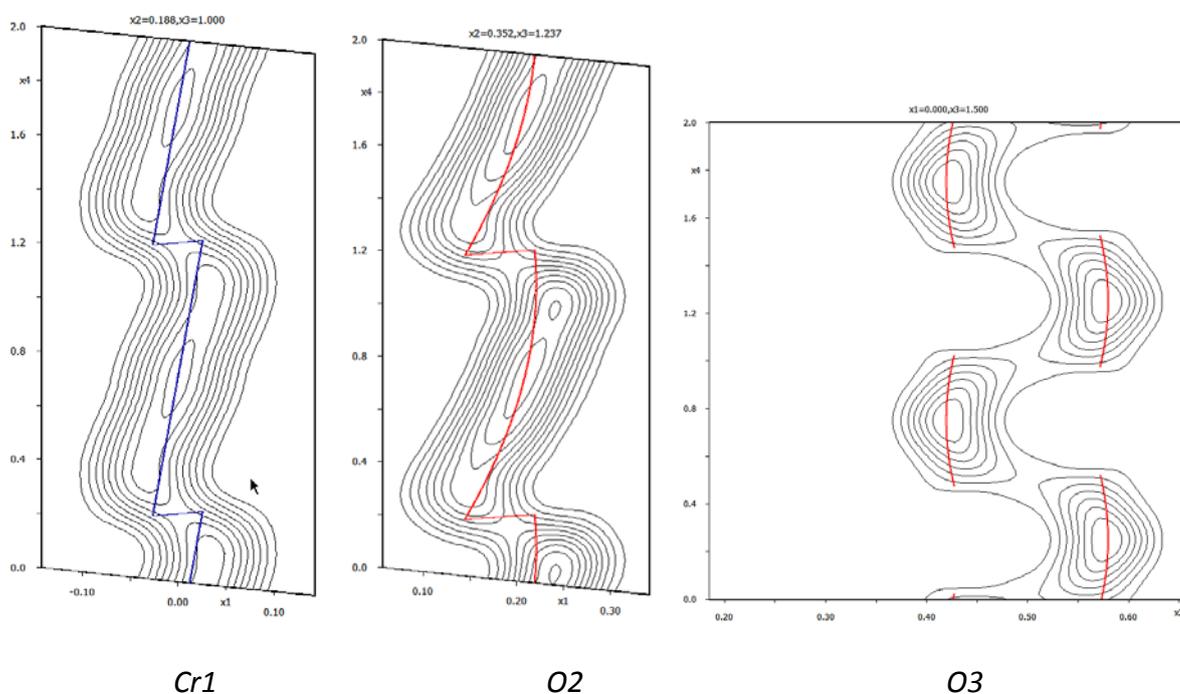
For O3 we plot also the modulation function related by symmetry operation O3#s3t0,1,3. The coefficients of Legendre polynomials are calculated such that the resulting modulation

function fits best with the original modulation function. However, the first modulation wave expressed by Legendre polynomials has only the linear (coefficients 1-3) and quadratic (coefficients 4-6) part so the shape cannot fit exactly.

Run refinement
Refinement converges with Robs factors 23%, 14%, 22%, 53%, 61% and 116%
Run Contour and plot again the three sections:
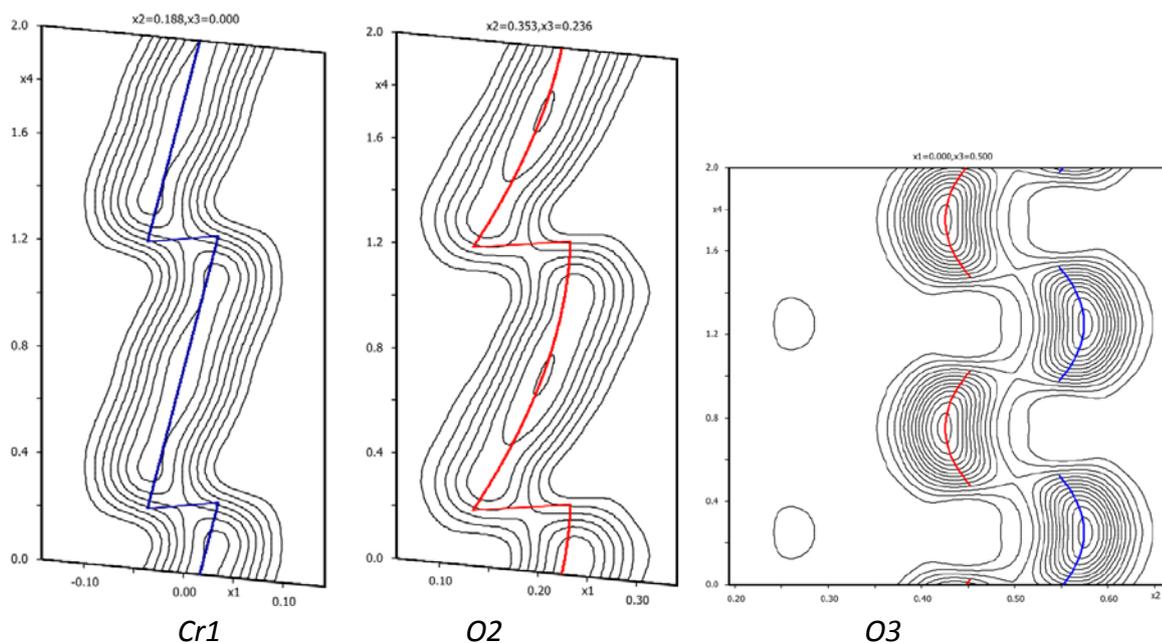


Cr1                                    O2                                    O3

Start Edit atoms and change ADP of all atoms to "harmonic"
Repeat refinement
Refinement converges with Robs factors 22%, 9%, 24%, 53%, 61% and 110%

Start Edit atoms and add another one position modulation wave for all atoms
Repeat refinement
Refinement converges with Robs factors 12%, 5%, 14%, 21%, 54% and 92% for 68 parameters
Make backup copy "crpo_initial_crenel"

8. *Binding discontinuity point of O2 and O3*
   The shape of the PO4 tetrahedron cannot be changed too much by modulation because it would contradict the chemistry. Thus the discontinuity points of crenel functions of oxygen atoms must have the same t coordinate.
   Start "Grapht"
   Press "New/Edit"
   For "Parameter to draw" select "Position"
   Select "x"
   For "Central atom" type O2
   For "p" type "-0.5" and "0.5"
   "p" determines the lower and upper limits of the visualized parameter

OK
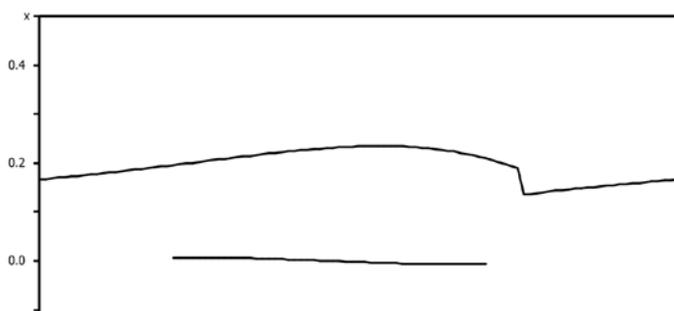
The resulting plot shows x coordinate of O2 (upper line) and O3 (lower line). The discontinuity points are slightly misaligned in t. This is however not possible because $PO_4$ cannot be too much distorted. Changes of oxygens must occur at the same t value.

The discontinuity points of O3 itself also look slightly misaligned but this is an artefact due to too large step used for t sampling. When we use step in t 0.0001 instead of 0.01 the plot will look like following:
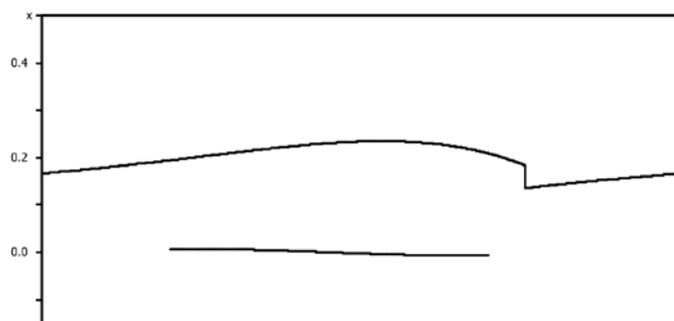
Similar information can be obtained when we plot the modulation displacement, for instance "dx", for O2 (the first graph – red), O3 (the second graph – blue) and O3#s3t0,1,3 (the third graph – blue).
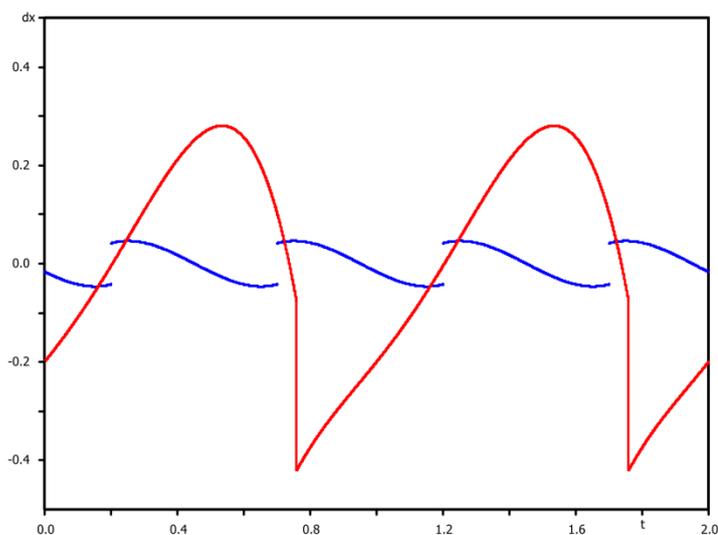
The centre x40 of the crenel function of O3 must be fixed in 0.75 because this atom is in a special position; otherwise there would be an overlap with symmetry related O3#s3t0,1,3

leading to a disordered structure. The t-coordinate of this centre is t40[O3].
For O3 delta=0.5, therefore one of the two discontinuity points is t40[O3]+0.25
For O2 delta=1.0 and one of the two discontinuity points is t40[O2]-0.50
The following equation will align the the two discontinuity points:
t40[O3]+0.25 = t40[O2]-0.50 => t40[O2]= t40[O3]+0.75
(The symbol t40 means x40 transformed to t coordinate.)

Start Refinement options, page "Various"
Press "Equations" and add equation t40[O2]=t40[O3]+0.75
Add; OK; OK; YES+Start
Refinement converges with Robs factors 11%, 5%, 13%, 20%, 54% and 99%; i.e. with very small changes
Start "Grapht" and repeat the same plot like before
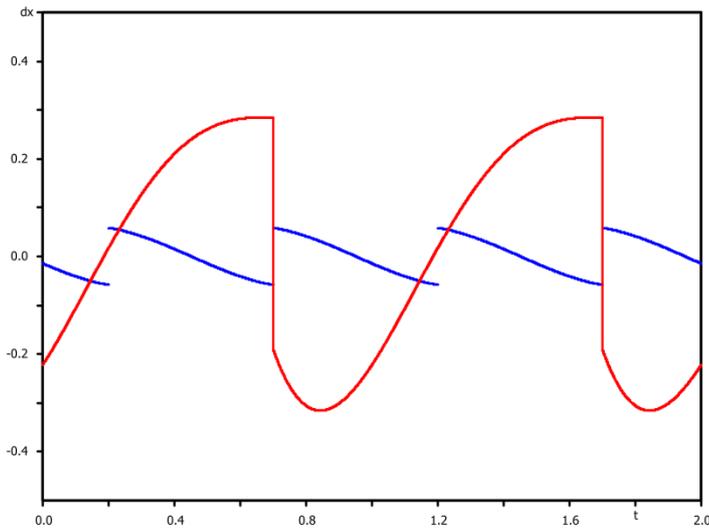


The discontinuity points for O2 and O3 now occur at exactly the same value of t
Make backup copy "crpo_aligned"

## 9. *Crenel function for phosphorus*
Start Contour and plot the section x2-x4 for P1
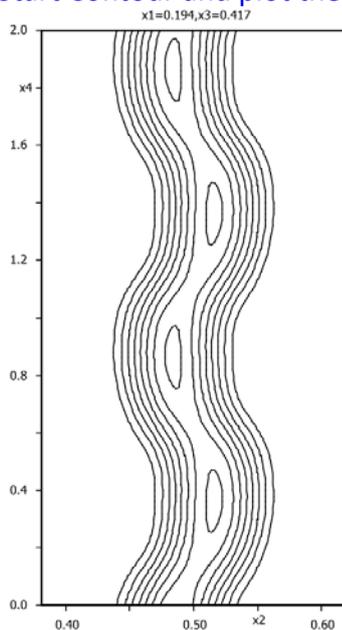
It seems that P1 has been sufficiently described with harmonic functions. However, careful analysis would reveal maxima in difference Fourier persisting even if ADP of P1 was modulated. For this reason we shall describe P1 similarly like in case of O3: with two symmetry equivalent crenel functions of the width 0.5

<span style="color:blue">Quit Contour</span>
<span style="color:blue">Start "Edit atoms"</span>
<span style="color:blue">For P1 activate crenel; define x40=0.86 and delta=0.5; activate Legendre polynomials; Return to Edit page</span>
<span style="color:blue">change y from 0.5 to 0.48</span> (this might be already done automatically by activation of Legendre); <span style="color:blue">change site occupancy from 0.5 to 1</span> (one half is now managed by crenel function)
<span style="color:blue">Close "Edit atoms"; check formula in EditM50 (should be Cr2 P2 O7 for Z=2)</span>
<span style="color:blue">Start Contour; use old maps</span>
<span style="color:blue">In "Atoms edit" of Contour add P1 and the symmetry equivalent P1#s4t0,1,0</span>



*or*
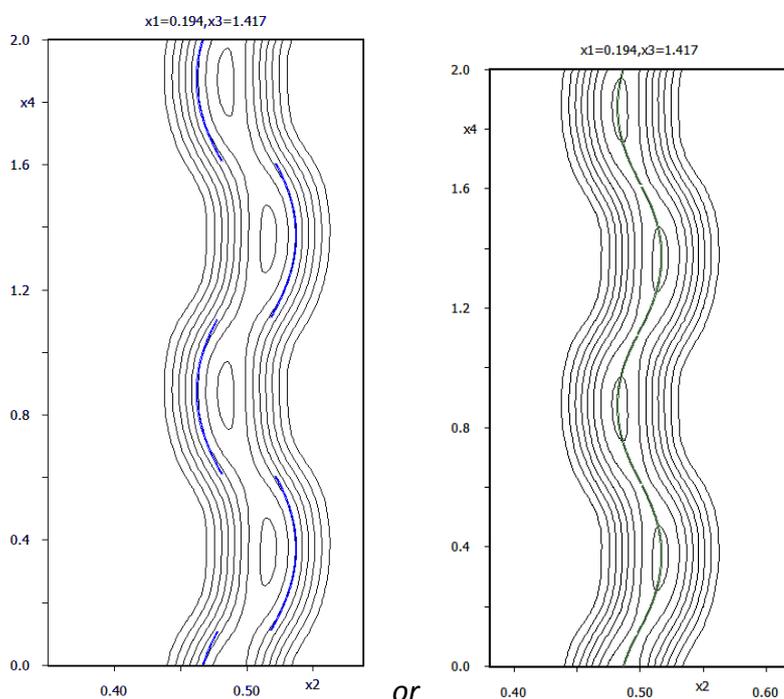
The left image is valid for the manual change of y[P1] to 0.48 while the right one arises when y[P1] is adjusted automatically during the conversion of the harmonic modulation function to Legendre polynomials.

<span style="color:blue">Quit Contour</span>
<span style="color:blue">Start Refinement option, page "Various", button "Equations"</span>
<span style="color:blue">Define equation t40[P1] = t40[O3]</span>
This bounds discontinuity points of P1 with O3
<span style="color:blue">Run refinement</span>
Refinement converges with Robs factors 10%, 5%, 11%, 15%, 54% and 106% (77 parameters), i.e. better fit for $1^{st}$ and $2^{nd}$ order satellites
<span style="color:blue">Make backup copy (rewrite crpo_aligned)</span>

## 10. *More modulation waves*

At this point all atoms have two position modulation waves and no modulation of ADP. We

will add position and ADP modulation waves until they improve R factors. Normally this would be result of trials and errors, here the process will be simplified.

Oxygen O1 is only slightly modulated and does not need more waves.

Add another one position modulation wave for Cr1, P1, O2 and O3
Refine
*Refinement converges with Robs factors 9%, 5%, 11%, 8%, 56% and 76%*
Start Refinement options, change number of refinement cycles to 100 and set damping factor 0.4
Add the first ADP modulation wave for Cr1, P1, O2 and O3
Refine
*Refinement converges with Robs factors 7%, 4%, 6%, 13%, 37% and 55%*
Add another ADP modulation wave for Cr1, P1, O2 and O3
Refine
*Refinement converges with Robs factors 5%, 3%, 5%, 10%, 24% and 39%*
Add another one position modulation wave only for Cr1
Refine
*Refinement converges with Robs factors 5%, 3%, 5%, 7%, 18% and 38%*
Add another one ADP modulation wave only for Cr1
Refine
*Refinement converges with Robs factors 4%, 3%, 4%, 6%, 18% and 34% with 176 refined parameters.*
Make backup copy: crpo_simple

```
R factors : [4235=2722+1513/176],   Damping factor:  0.5000
GOF(obs)= 3.44   GOF(all)= 2.90
R(obs)=  4.25     Rw(obs)=  6.48     R(all)=  6.05     Rw(all)=  6.91
R factors for main reflections : [491=488+3]
R(obs)=  2.75     Rw(obs)=  4.47     R(all)=  2.77     Rw(all)=  4.47
R factors for satellites of order 1 : [904=856+48]
R(obs)=  3.96     Rw(obs)=  5.32     R(all)=  4.14     Rw(all)=  5.36
R factors for satellites of order 2 : [989=780+209]
R(obs)=  6.40     Rw(obs)=  7.24     R(all)=  8.07     Rw(all)=  7.53
R factors for satellites of order 3 : [900=410+490]
R(obs)= 17.55     Rw(obs)= 22.78     R(all)= 31.65     Rw(all)= 24.92
R factors for satellites of order 4 : [951=188+763]
R(obs)= 34.14     Rw(obs)= 39.95     R(all)= 71.19     Rw(all)= 45.72
```

*The result obtained here is not bad but a question remains if the poor fit of the 3$^{rd}$ and 4$^{th}$ order satellites is caused by structure model or weak satellite intensity. For 3$^{rd}$ order satellites there is still 50 % of reflections above the observability limit. GOF 3.44 also suggests the model could be improved.*

Start "Edit/View → View of Reflection report"
Press "GoTo" and move to "Summary after averaging"
*Here we can see Rint for the 3$^{rd}$ order observed satellites (11%) and for the 4$^{th}$ order observed satellites (22%). This suggests the quality of high order satellites is not so bad.*

Start Contour and plot the following difference Fourier sections: x1-x4 for Cr1, x2-x4 for P1,

x1-x4 for O2 and x2-x4 for O3. For plotting use always the contour step 0.2.
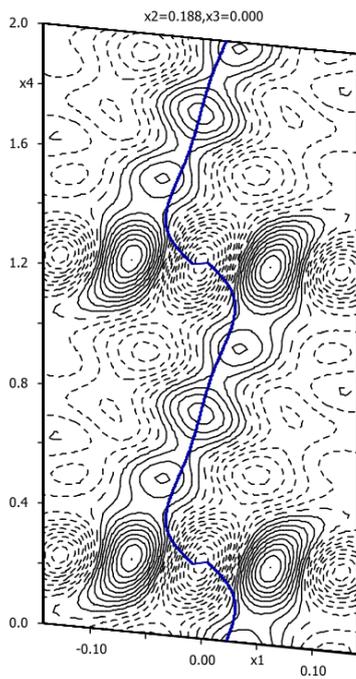


*Cr1: x1-x4*
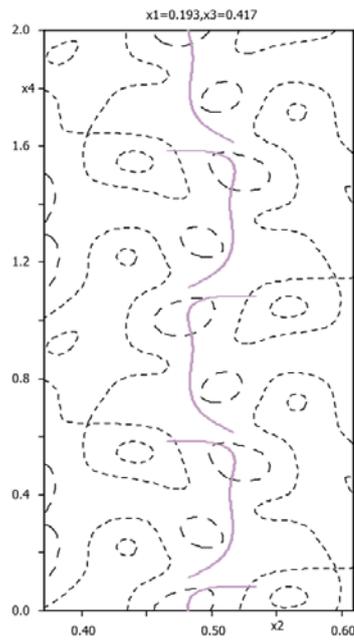
*P1: x2-x4*
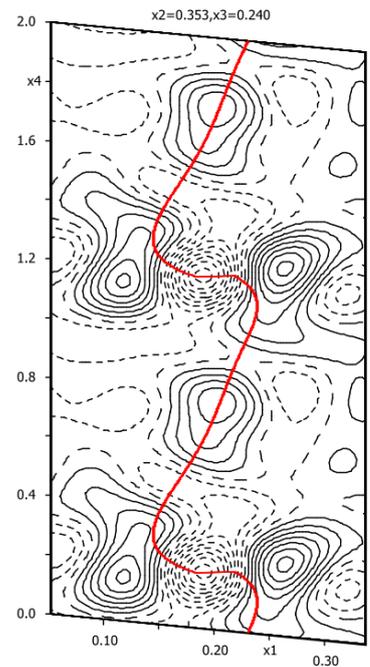
*O2: x1-x4*
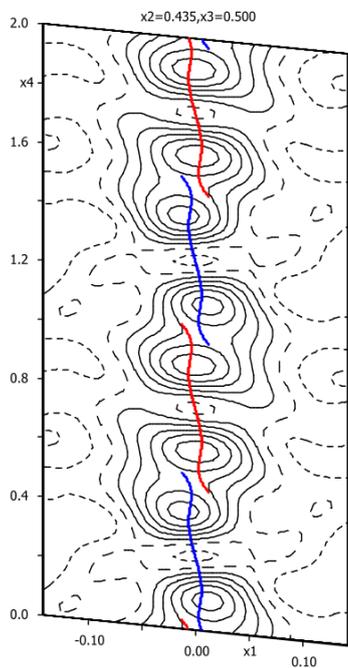
*O3: x1-x4*
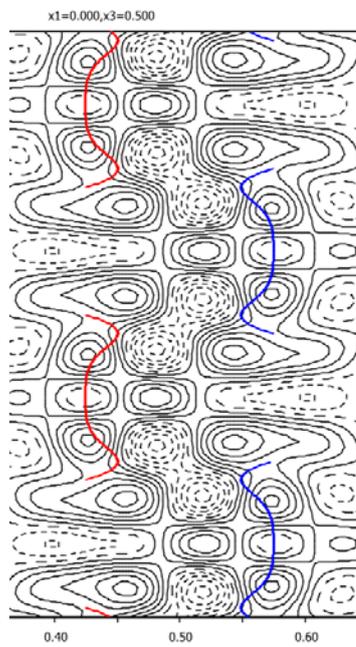
*O3: x2-x4*
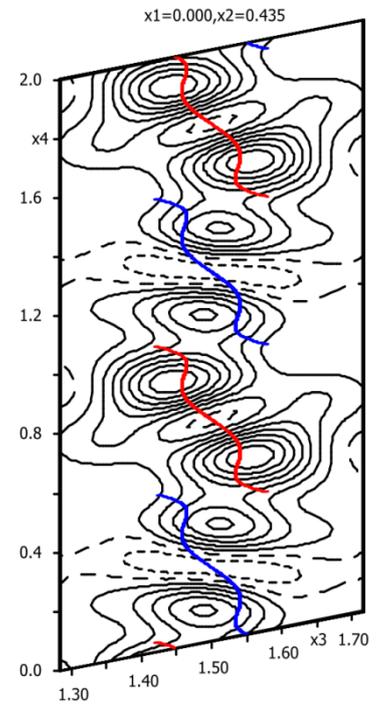
*O3: x3-x4*

## 11. Disordered structure

*The difference Fourier sections for Cr1, O2 and O3 indicate a disorder close to the discontinuity points of crenel function. At this part we shall create a structure model with initial modulation functions describing the disorder.*

*For each of the atoms delta will be shortened and additional atoms with small complementary delta will be placed to the difference maxima found in the Contour sections. The resulting structure model must keep formula unchanged. The delta of all disordered atoms will be kept the same.*

*Jana2006 does not have a tool for simple duplication of atomic position.*
Start "Edit/View → Editing of M40 file"
Using the text editor, duplicate Cr1 and name the duplicated atom Cr1'

```
Cr1       1  2      0.500000 0.000000 0.187879 1.000000      100  1  4  3
 0.013442 0.003782 0.008227 0.000000-0.003731 0.000000      0010111010
 1.000000          Legendre                                 0
 0.750000 0.000000                                          00
 0.032787 0.000000-0.024985 0.000000 0.002767 0.000000      101010
-0.020770 0.000000 0.018971 0.000000-0.001671 0.000000      101010
-0.010770 0.000000 0.003583 0.000000 0.000994 0.000000      101010
 0.003146 0.000000-0.003801 0.000000-0.001089 0.000000      101010
 0.000000 0.000000 0.000000-0.000491 0.000000 0.000395      000101
 0.019723-0.000428 0.002445 0.000000-0.008506 0.000000      111010
 0.000000 0.000000 0.000000-0.000288 0.000000 0.000435      000101
 0.020902-0.000752 0.003757 0.000000-0.009246 0.000000      111010
 0.000000 0.000000 0.000000 0.000525 0.000000-0.000152      000101
 0.015240-0.001211 0.001790 0.000000-0.006762 0.000000      111010
 0.000000                                                   0
Cr1'      1  2      0.500000 0.000000 0.187879 1.000000      100  1  4  3
 0.013442 0.003782 0.008227 0.000000-0.003731 0.000000      0010111010
 1.000000          Legendre                                 0
 0.750000 0.000000                                          00
 0.032787 0.000000-0.024985 0.000000 0.002767 0.000000      101010
-0.020770 0.000000 0.018971 0.000000-0.001671 0.000000      101010
-0.010770 0.000000 0.003583 0.000000 0.000994 0.000000      101010
 0.003146 0.000000-0.003801 0.000000-0.001089 0.000000      101010
 0.000000 0.000000 0.000000-0.000491 0.000000 0.000395      000101
 0.019723-0.000428 0.002445 0.000000-0.008506 0.000000      111010
 0.000000 0.000000 0.000000-0.000288 0.000000 0.000435      000101
 0.020902-0.000752 0.003757 0.000000-0.009246 0.000000      111010
 0.000000 0.000000 0.000000 0.000525 0.000000-0.000152      000101
 0.015240-0.001211 0.001790 0.000000-0.006762 0.000000      111010
 0.000000                                                   0
```

Triplicate O2, name new atoms O2' and O2''
Duplicate O3, name new atom O3'
In the header of M40 change number of atoms from 5 to 9
Save changes and close the editor
*The new positions will describe disorder at the discontinuity area. For Cr1' and O3' two positions are generated by symmetry; for O2 we have introduced both positions.*

Start "Edit atoms"
Select Cr1', O2', O2'', O3'
Change number of their position and ADP modulation waves to zero
Change ADP to isotropic
For Cr1' change x to 0.06
For O2' change x to 0.12 and occupancy to 0.5
For O2'' change x to 0.26 and site occupancy to 0.5
For O3' change z to 1.44
*New positions can be found on the above shown difference sections.*

Start Refinement option, page "Various"
Press "Equations" and define the following equations:

t40[Cr1']=t40[Cr1]+0.5

*This puts the additional atom Cr1' to proper position along x4 related to Cr1*

delta[Cr1']=1-delta[Cr1]

*This defines delta of the additional atom like complementary to the original atom*

t40[O2']=t40[O3]+0.25

*This puts the additional atom O2' to proper position along x4 related to O3.*
*t40[O2'] = t40[O2]-0.5 but we can substitute for t40[O2] from already defined equation*
*t40[O2] = t40[O3]+0.75*

delta[O2']=delta[Cr1']

*We want delta the same for all additional atoms*

t40[O2'']=t40[O3]+0.25

delta[O2'']=delta[Cr1']

delta[O2]=1-delta[Cr1']

t40[O3']=t40[O3]+0.25

delta[O3']=delta[Cr1']

delta[O3]=0.5-delta[Cr1']

*After applying these equations all delta intervals will depend on delta of Cr1 and the total occupation of atoms will be the same like in the simple model.*

In page Basic **set zero refinement cycles**

Run refinement

*The refinement applies the equations and calculates structure factors*
*Because delta[Cr1] is one all delta parameters of additional atoms are zero and R values are as before: 4%, 3%, 4%, 6%, 18% and 34%*

Start EditM50, page "Composition", and press "Formula from M40"

This shows correctly Cr2 P2 O7


*We want to assign some non-zero delta for additional atoms and view modulation functions but with the original electron density*

Start "Edit atoms" and change delta of Cr1 from 1 to 0.9

*In refinement we have still zero cycles*

Run refinement

*This recalculates delta based on equations and creates new (unwanted) input for Fourier*

Start "File → Structure → Save As" and create copy "tmp"

Do not continue with the new structure

Change delta of Cr1 back to 1

Run refinement (with zero cycles)

*This creates good input for Fourier*

Start "File → Structure → Copy in" and copy to the current structure only M40 from the previously created backup copy "tmp"

*Now we have old input for Fourier and new input for plotting modulation functions*

Start Contour

For Cr1 plot x1-x4 difference section and visualize Cr1, Cr1', Cr1'#s2t0,0,2

For O2 plot x1-x4 difference section and visualize O2, O2' and O2''

For O3 plot x3-x4 difference section and visualize O3, O3' and O3'#s2t0,1,3

| Cr1: x1-x4 | O2: x1-x4 | O3: x3-x4 |
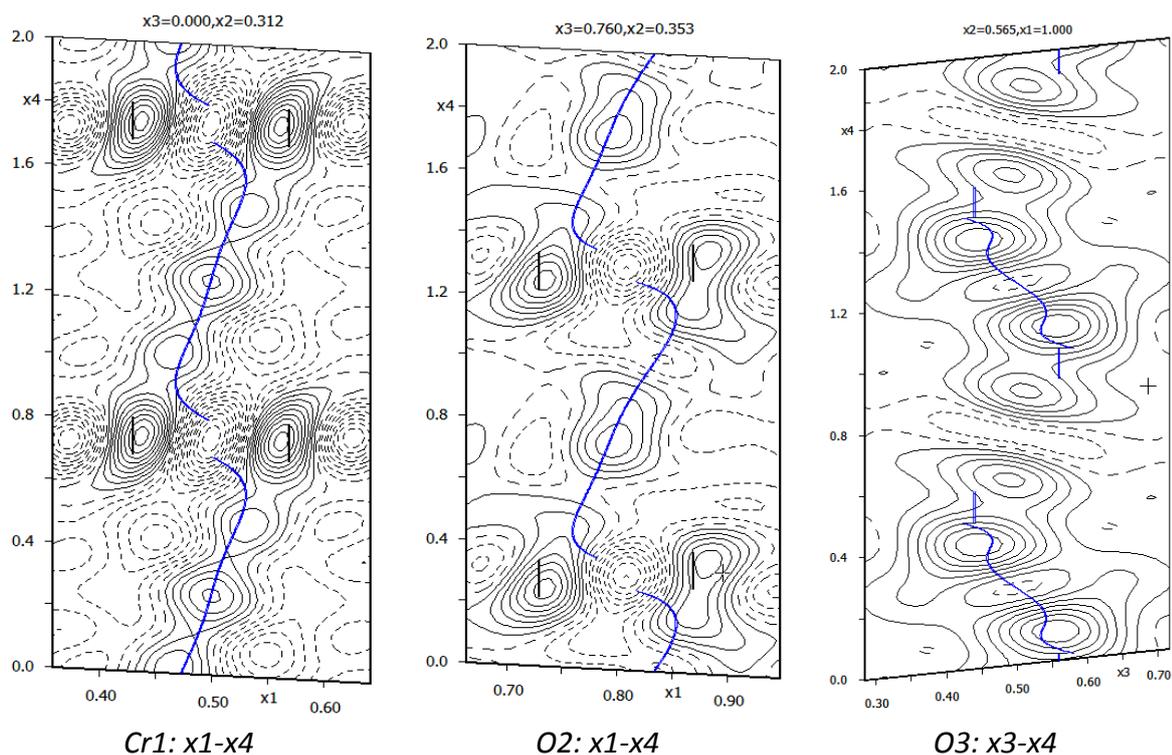
Make backup copy: crpo_disorder_initial

## 12. Refinement of disordered model

*Refinement of the disordered model is susceptible and must be started from very small delta of Cr1'. The purpose of this refinement is not to obtain proper geometry of the disordered atoms because the corresponding scattering power is very small: for O3 and delta=0.1 the disordered atom would have 0.1\*0.5\*8 electrons, which is less than 0.5 of hydrogen.*

Start "Edit Atoms"
Change delta of Cr1 to 0.98 and leave it fixed
Run zero refinement cycles
*This will create delta=0.02 for additional atoms*
Test Formula (EditM50 – must be Cr2 P2 O7)
Start Refinement options, set 100 refinement cycles with damping 0.4
Run refinement until convergence
*The simple model without disorder converged with Robs factors 4%, 3%, 4%, 6%, 18% and 34% for 176 refined parameters.*
*Now we have obtained Robs factors 3%, 2%, 3%, 4%, 10% and 25% for 192 refined parameters. This is convincing improvement.*
Start "Edit atoms" and activate refinement of delta for Cr1
Run refinement
*Refinement converges with Robs factors 2.7%, 2.3%, 2.2%, 3.7%, 9.2% and 18.3% for 193 refined parameters. Delta of additional atoms refines to 0.093.*
Start "Parameters → Extinction" and activate isotropic extinction correction
Run refinement
*Refinement converges with Robs factors 2.6%, 2.1%, 2.2%, 3.8%, 9.2% and 18.3% for 194*

*refined parameters.*

Start "Edit atoms" and add one position modulation wave to all additional atoms (Cr1', O2', O2'' and O3').
Run refinement
*Refinement converges with Robs factors 2.4%, 1.9%, 2.0%, 3.5%, 7.3% and 12.2% for 218 refined parameters. GOF = 1.97. Delta of additional atoms refines to 0.105.*

Make backup copy: crpo_disorder_final

## 13. Conclusions

*The disordered model does not provide proper geometry of disordered atoms. However, we can draw an approximant structure in large area and try to determine in which places of the real space the structure becomes disordered.*

Plot the structure expanded to 3x3x3 cells
Indicate the atoms with ' and '' in yellow
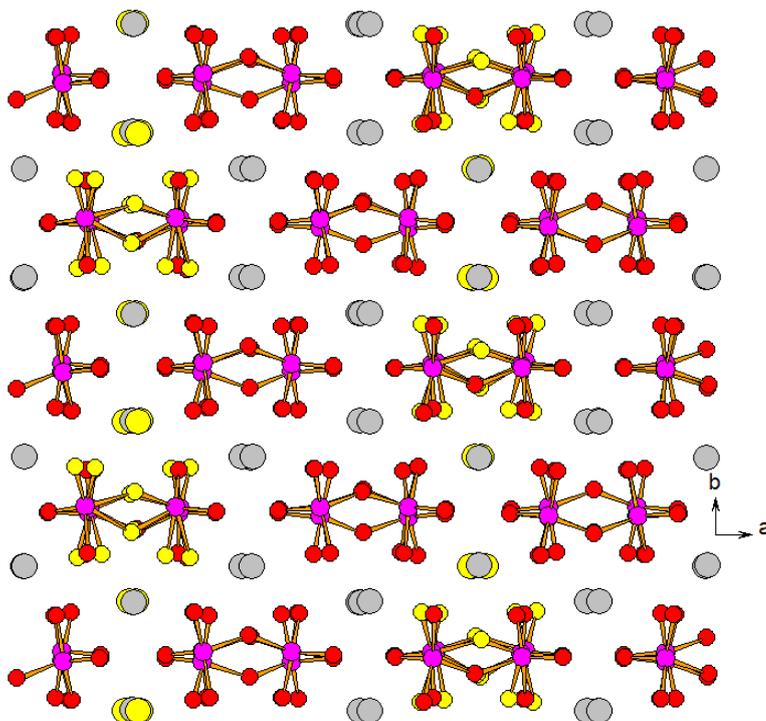


*In view along c we can distinguish columns without disorder and columns with disorder*

*Open the structure "crpo_simple"*
*Start Grapht, press "New/Edit"*
*Change step of t to 0.0001*
*Select "Parameters to draw" – "Distances"*
*Change limits of "p" to 1.2 (lower bonding limit) and 1.8 (upper bonding limit)*
*Select P1 for central atom*
*Select O1, O2, O3 for neighbors*
*OK*
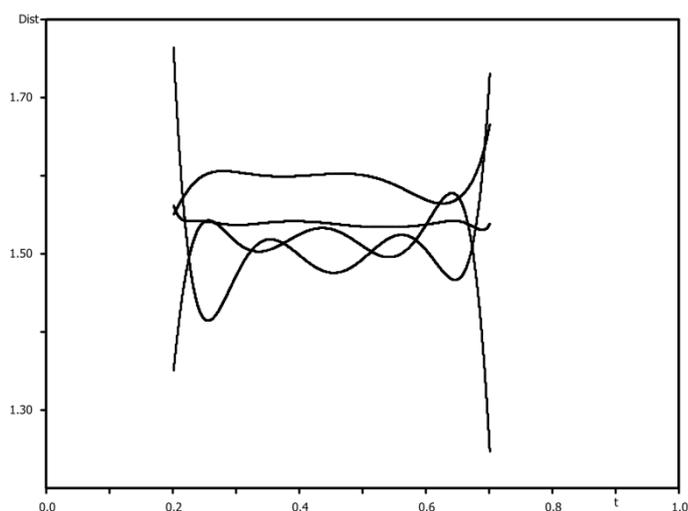
*The definition interval is limited to 0.5 because P1 has a crenel.*
*The distances at the end of the definition interval are unreasonable*
*We can read from the plot that the definition interval is approximately tmin=0.21, tmax=0.7*

*Press "New/Edit"*
*Change Minimum and Maximum for t: from 0.21 to 0.7*
*OK*
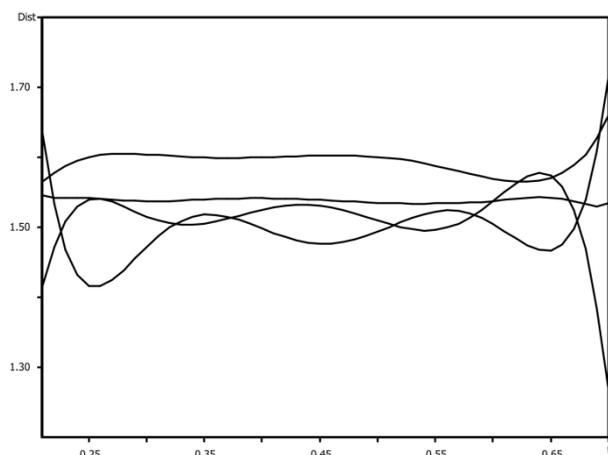


*From refinement of disordered structure we have found delta of the disordered area 0.105.*
*In order to get reliable distances from the simple model we limit the interval where distances are plotted to reliable interval.*

*Press New/Edit*
*Change Minimum and Maximum for t: from 0.21+0.05=0.26 to 0.7-0.05=0.65*
*OK*
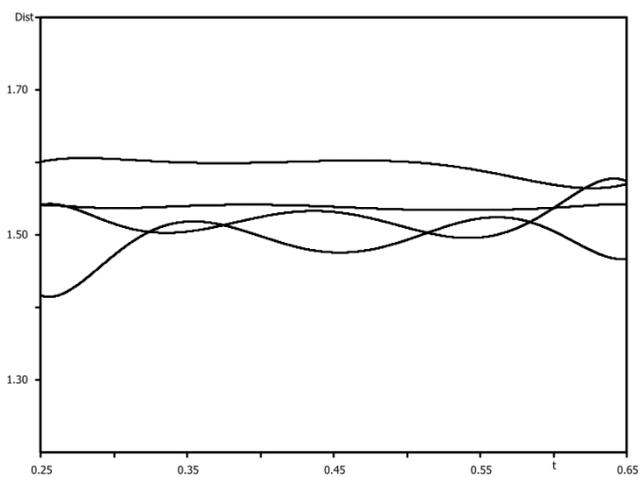
*In the interval found from refinement of disordered structure the distances are correct.*

# Example 5.4: Fresnoite

**Solution of (3+2)-dimensional incommensurately modulated structure.**

**$Ba_2TiSi_2O_8$**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: fresnoite.hkl, fresnoite.cif_od
Frame scaling, absorption correction: done with software of the diffractometer

1. ***Creating new jobname***
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click fresnoite

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   In "Define basic input file" select "Input from cif_od file"; OK
   Change all q-vector components to 0.302 keeping the original sign; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH
   *[On the screen: Data repository]*
   OK; YES to accept the data set

3. ***Symmetry Wizard***
   Use default tolerances for crystal system recognition
   Select tetragonal Laue symmetry 4/mmm
   Press Show/modify X centering
   *[On the screen: select individual centering vectors]*
   Select centering vectors: (0 0 0 0 0) and (0 0 1/2 1/2 1/2); OK; Next
   Select space group X4/mbm and note the non-centrosymmetric possibilities
   Accept the superspace group in the original cell
   *For five-dimensional structures the wizard does not offer selection of superspace group. It will be done later manually.*

4. ***Creating refinement reflection file***
   Follow default steps of the reflection wizard
   *The program discards 54372 reflections, 455 observed, Rint=3.28%*

5. ***Structure solution wizard***
   ESC

6. ***Solution of average structure – centrosymmetric solution***
   *Superflip for five-dimensional structure returns five-dimensional electron density map.*

*However, Jana2006 would not evaluate initial modulation functions from this map and we would get average structure. For this reason solution will be done separately for average structure*

Start "Tools → Transformation → Go to average 3d structure"

For name use "ave_centro"

Follow steps of the Reflection wizard

Continue with the new structure

Start "Run → Solution"

For Formula type "Ba Ti Si O"

Select "Superflip" and "Peaks from Jana2006"

Select "Use a specific random seed" and type "111" for random seed

*With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work Random seed should not be fixed.*

OK

*Superflip converges with R around 18% and confirms the selected space group*

Accept the result

Start EditM50 and check formula for Z=4: Ba2 Ti Si2 O4 (should be Ba2 Ti Si2 O8)

Run Refinement

*Refinement converges with Robs=14%*

Using "Edit Atoms": check Uiso of O1 is it rather high ~ 0.13 $Å^2$; Esc

Plot the average structure; Check that the O1 atom is in a close contact with Ba1 ~ 1.16 Å

Run "Edit atom" and delete the atom O1

Run refinement

*Refinement converges with Robs=13%*

Run difference Fourier

Add difference maxima Max1, Max2, Max3 as oxygens

Run refinement

*Refinement converges with Robs=12%*

In EditM50 check formula: Ba2 Ti Si2 O8

Run difference Fourier; Add difference maxima Max1 as a new oxygen atom

Run refinement

Check formula: Ba2 Ti Si2 O16

In EditM40 allow refinement of atomic occupancies – "ai" parameter – of all oxygen atoms;

*Refinement converges with Robs=9.1%*

Check formula: Ba2 Ti Si2 O9.2

Using "Edit atoms" change all ADP to harmonic

Run refinement

*Refinement converges with Robs=5.9%*

Check formula: Ba2 Ti Si2 O10.1

Plot average structure; make Si-O coordination; draw the projection along [0,0,1] and along [1,-1,0]

*Jana2006 sends to Diamond expanded structure in P1 symmetry. This is because of centering X which Diamond cannot use. In the plot the silicon atom is surrounded by eight partially occupied oxygen atoms. This can be either reality which would be described by*

*crenel functions or wrong symmetry for average structure.*
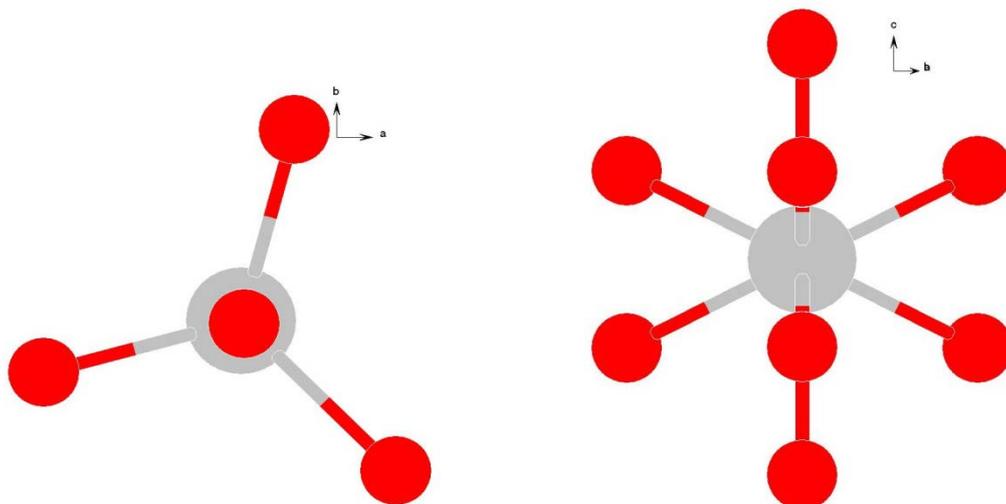


*The figures indicate a disorder of SiO$_4$ groups by the mirror perpendicular to the c axis. The disorder can be described alternatively by the two fold axis perpendicular to **c** and **a**+**c**. The disorder in the average structure can be produced either by the fact the structure is not centrosymmetric or by modulation. First we shall test non-centrosymmetric description.*

**7. Solution of average structure – non-centrosymmetric solution**
*In order to see all highest non-isomorphic subgroups we shall create a testing structure:*
Start "File → Structure → save as" and create a testing structure named "ave-test".
EditM50: change symmetry from X4/mbm to P4/mbm; Accept changes without re-creation of the diffraction file;
Start "Tools → Transformations → Go to subgroup structure"; Press the button "Select non-isomorphic subgroup:"
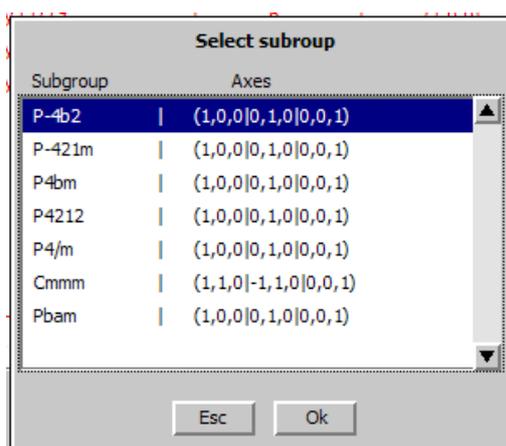


*The highest subgroups not giving a split model for SiO$_4$ group are P-42$_1$m and P4bm. Now we have to check if basic positions (x,y,z) of atoms Si1, O1, O2 and O4 belong to a unique tetrahedron.*
Return to the structure "ave-centro"; Set distance commands: in the "Basic" define calculation of angles and the listing form "with symmetry codes".

```
Si1-O1              1.670(14)                   2nd: O1            x,y,z
    O1-Si1-O1                  44.3(16)         3rd: O1#s4t1,0,0   -x+1,-y,-z
    O1-Si1-O2                  66.7(12)         3rd: O2            x,y,z
    O1-Si1-O2                 111.0(12)         3rd: O2#s10        x,y,-z
    O1-Si1-O4                 105.5(9)          3rd: O4            x,y,z
    O1-Si1-O4                 105.5(9)          3rd: O4#s6         -y+1/2,-x+1/2,z
    O1-Si1-O4                 124.9(7)          3rd: O4#s10        x,y,-z
    O1-Si1-O4                 124.9(7)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O1              1.670(14)                   2nd: O1#s4t1,0,0   -x+1,-y,-z
    O1-Si1-O2                 111.0(12)         3rd: O2            x,y,z
    O1-Si1-O2                  66.7(12)         3rd: O2#s10        x,y,-z
    O1-Si1-O4                 124.9(7)          3rd: O4            x,y,z
    O1-Si1-O4                 124.9(7)          3rd: O4#s6         -y+1/2,-x+1/2,z
    O1-Si1-O4                 105.5(9)          3rd: O4#s10        x,y,-z
    O1-Si1-O4                 105.5(9)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Calculating of distances, angles, torsion angles and best planes
structure :

Si1-O2              1.55(2)                     2nd: O2            x,y,z
    O2-Si1-O2                 177.6(7)          3rd: O2#s10        x,y,-z
    O2-Si1-O4                  66.7(8)          3rd: O4            x,y,z
    O2-Si1-O4                  66.7(8)          3rd: O4#s6         -y+1/2,-x+1/2,z
    O2-Si1-O4                 114.5(8)          3rd: O4#s10        x,y,-z
    O2-Si1-O4                 114.5(8)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O2              1.55(2)                     2nd: O2#s10        x,y,-z
    O2-Si1-O4                 114.5(8)          3rd: O4            x,y,z
    O2-Si1-O4                 114.5(8)          3rd: O4#s6         -y+1/2,-x+1/2,z
    O2-Si1-O4                  66.7(8)          3rd: O4#s10        x,y,-z
    O2-Si1-O4                  66.7(8)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O4              1.576(16)                   2nd: O4            x,y,z
    O4-Si1-O4                 105.1(8)          3rd: O4#s6         -y+1/2,-x+1/2,z
    O4-Si1-O4                  47.8(9)          3rd: O4#s10        x,y,-z
    O4-Si1-O4                 126.1(8)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O4              1.576(16)                   2nd: O4#s6         -y+1/2,-x+1/2,z
    O4-Si1-O4                 126.1(8)          3rd: O4#s10        x,y,-z
    O4-Si1-O4                  47.8(9)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O4              1.576(16)                   2nd: O4#s10        x,y,-z
    O4-Si1-O4                 105.1(8)          3rd: O4#s16        -y+1/2,-x+1/2,-z
Si1-O4              1.576(16)                   2nd: O4#s16        -y+1/2,-x+1/2,-z
```

*The blue lines indicate the bond distances and red lines bond angles of the basic SiO$_4$ group. From the symmetric codes we can see that only the atom O2 should be transformed by the symmetry operation #s10 i.e. by x,y,-z*

Start "Edit atoms": select the atom O2 and transform it by x,y,-z

*Before testing of non-centrosymmetric space groups we have to reset the occupancies to their the values corresponding the SiO$_4$ split. This means that their full values are to be reduced by 1/2. The atom O3 is coordinating Ti and it can also be shown that it has to represent a split position.*

Start "Edit atoms" set "ai" for O1, O2, O3 and O4 to 0.25, 0.5, 0.25 and 1, respectively.

*In the next step we shall test non-centrosymmetric space group X-42$_1$m*

Start "Tools → Transformation → Go to subgroup structure"

*[On the screen: Define subgroup]*

*The button for selecting non-isomorphic subgroup is missing because of non-standard*

*centering*

Select symmetry operator for the screw axis $2_1$ and rotation axis -4 of the space group *X-42₁m*

Press "Complete subgroup"

*The subgroup should be X-42₁m without changing axes*

Next; Next

*[On the screen: select one representative of the 2$^{nd}$ coset]*

Select inversion as operator for expansion to the subgroup; Next

Deselect "Make as twinned structure"

Type name of the structure (for instance "ave_-421m"); Next

Follow steps of the Reflection wizard

Continue with the new structure

Check formula – still Ba2 Ti Si2 O16 for Z=4

"Edit atoms": delete atoms O1_2, O2_2 and O4_2 and reduce the occupancy of O3 to 0.25.

Check formula – still Ba2 Ti Si2 O8 for Z=4

In "Refine commands" set damping factor to 0.5

Run Refinement

*Refinement converges with Robs=8.3%*

*In the next step we shall test non-centrosymmetric space group X4bm*

Start "File → Structure → Open" and return to the centrosymmetric average structure ("ave_centro")

Start "Tools → Transformation → Go to subgroup structure"

*[On the screen: Define subgroup]*

*The button for selecting subgroup is missing because of non-standard centering*

Select symmetry operator for glide plane b and rotation axis 4 of the space group X4bm

Press "Complete subgroup"

*The subgroup should be X4bm without changing axes*

Next; Next

*[On the screen: select one representative of the 2nd coset]*

Select inversion like operator for expansion to the subgroup; Next

Deselect "Make as twinned structure"

Type name of the structure (for instance "ave_4bm"); Next

Follow steps of the Reflection wizard

Continue with the new structure

Check formula – still Ba2 Ti Si2 O16 for Z=4

"Edit atoms": delete atoms O1_2, O2_2, O3_2 and O4_2.

Check formula – still Ba2 Ti Si2 O8 for Z=4

Run Refinement

*Refinement converges with Robs=2.27%*

"Edit atoms": rename oxygens to O1, O2, O3, O4 using "Rename selected atoms to atom

"File → Structure → Save As": ave_final

8. ***Back to the modulated structure***

"File → Structure → Open": open "fresnoite"

EditM50:

In "Composition page" type formula Ba Ti Si O and formula units 4

In "Symmetry" page change symmetry to X4bm
OK to confirm centering
OK for the first translation part
OK for the second translation part
Close Editm50
Re-create refinement reflection file
"File → Structure → Copy in": import **only** M40 from the average structure "ave_final"
Run refinement
Refinement confirms R value for the average structure:

```
R factors : [6599=4677+1922/37],  Damping factor:  1.0000
GOF(obs)= 22.66   GOF(all)= 19.14
R(obs)= 40.27    Rw(obs)= 61.44    R(all)= 43.31    Rw(all)= 61.61
R factors for main reflections : [796=789+7]
R(obs)=  2.27    Rw(obs)=  3.82    R(all)=  2.29    Rw(all)=  3.83
R factors for satellites of order 1 : [2858=2499+359]
R(obs)=100.00    Rw(obs)=100.00    R(all)=100.00    Rw(all)=100.00
R factors for satellites of order 2 : [2945=1389+1556]
R(obs)=100.00    Rw(obs)=100.00    R(all)=100.00    Rw(all)=100.00
Last Rw(all): 61.91 61.61 61.61 61.61
Maximum change/s.u. :   0.0058 for U11[O4]
```

9. *Superspace symmetry*
   In the previous paragraph the program asked for completion of the translation part of
   superspace symmetry operators. For the present case two symmetry operators should be
   completed:

| Complete translational part for the operator: | | Complete translational part for the operator: |
|---|---|---|
| -x2 x1 x3 -x5 x4 | | -x1+1/2 x2+1/2 x3 x5 x4 |

Left dialog:

Rotation / Translation
0 -1 0 0 0 → 0
1 0 0 0 0 → 0
0 0 1 0 0 → 0
0 0 0 0 -1 → 0
0 0 0 1 0 → 0
Ok

*and*

Right dialog:

Rotation / Translation
-1 0 0 0 0 → 1/2
0 1 0 0 0 → 1/2
0 0 1 0 0 → 0
0 0 0 0 1 → 0
0 0 0 1 0 → 0
Ok

*Each translation part has two elements which can be either 0 or 1/2. Thus we have sixteen combinations: 0 0 + 0 0, 0 0 + 1/2 0, 0 0 + 0 1/2, 0 0 + 1/2 1/2 … However, the translation part can be combined with the X centering (0 0 1/2 1/2 1/2) which makes equivalent for instance the pairs 0 0 + 1/2 1/2 and 1/2 1/2 + 0 0. Moreover, some combinations are forbidden because they lead to inconsistent translation (0 0 0 1/2 1/2).*
*Finally we have only two independent possibilities:*
*0 0 + 1/2 1/2*
*0 0 + 0 0*

Start EditM50
Go to page "Symmetry"
Focus the textbox "Space group" and press TAB. The program offers the first symmetry operator needing to complete.
At the first attempt try combination 0 0 for the first operator and 1/2 0 for the second one.
*The program will not allow it.*
Then try the combination 0 0 + 0 0. Close EditM50 and re-create refinement reflection file.
From the screen output of the symmetry wizard note number of rejected reflections: 54372 rejected reflections from which 455 is observed with the largest I/sigma(I) around 15
Return to EditM50
TAB in the textbox "Space group"
For translation parts use combination 0 0 + 1/2 1/2
Re-create refinement reflection file
*From the screen output of the symmetry wizard note number of rejected reflections: 55353 rejected reflections from which 463 is observed with the largest I/sigma(I) around 15*
*This means: the translation part 1/2 1/2 of the second operator leads to 1000 more forbiden reflections but the number and sigma level of the observed forbidden reflections remains almost the same like with the translation part 0 0. This confirms the presence of the translation part 1/2 1/2 for the second symmetry operator.*

### 10. Refinement of modulated structure – position modulation

Make backup copy: "fresnoite_backup"
Start "Parameters → Options"
Press "Define wave vectors"
For the third wave define 1 1
*This means modulation wave vector given by a sum of the q vectors*
For the fourth wave define -1 1
*This means modulation wave vector given by a difference of the q vectors*
"Edit atoms": set two position modulation waves for all atoms
*This means one harmonic wave along the first wave vector (q1) and one harmonic wave along the second wave vector (q2)*
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, $1^{st}$ and $2^{nd}$ order satellites: 10%, 3%, 13%, 51%*
*By second order satellites are considered reflections described by combination of q1 and q2: q1 + q2 or –q1 + g2.*
"Edit atoms": add another two position modulation waves for all atoms
*This mean one harmonic wave along the first wave vector combination (q1+q2) and one harmonic wave along the second wave vector combination (-q1+q2)*
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, $1^{st}$ and $2^{nd}$ order satellites: 4%, 2%, 7%, 6%*

### 11. Contour sections and ADP modulation

"Start Contour → New plot → Calculate new ones"
Select observed Fourier
For "Scope" define Ba1 as central atom
For map axes select x1, x4, x3, x2, x5 with limits as shown below
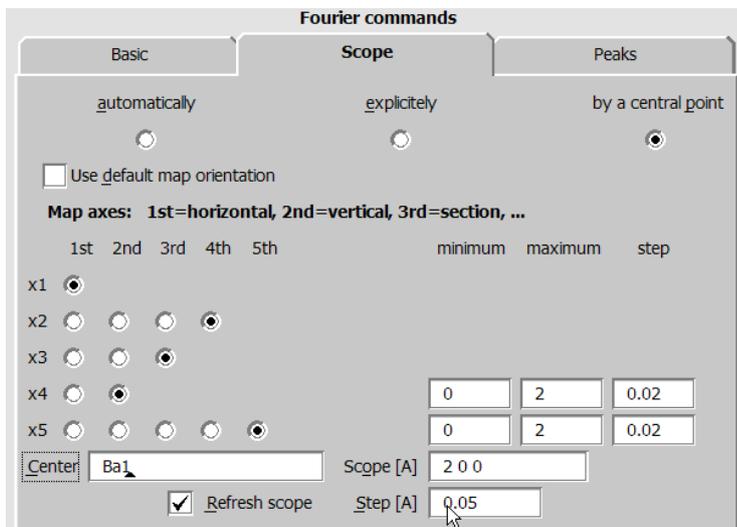


*This will plot section x1-x4 but the shape of atomic domain will be function of x5*
OK to calculate Fourier map
In Contour press "Atoms edit" and add Ba1
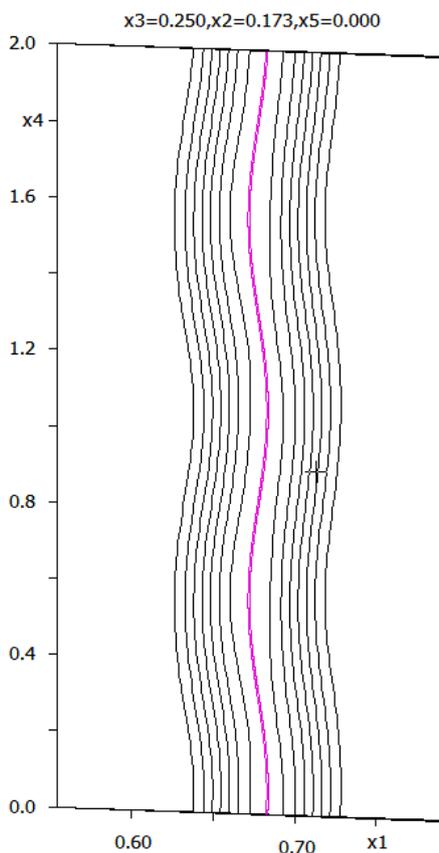


Press "Movie" to see the changes of this figure with x5

x3=0.250,x2=0.173,x5=0.660
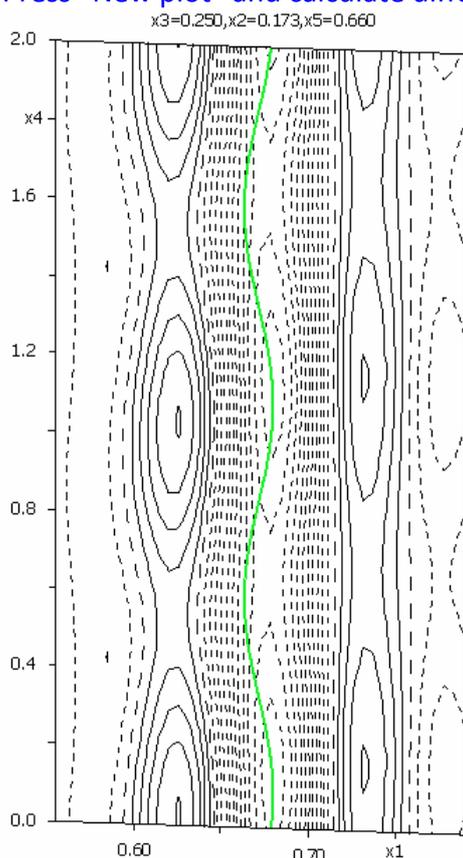


*The difference maxima around Ba1 are very strong indicating ADP modulation*

"Edit atoms": set two ADP modulation waves for Ba1
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, 1st and 2nd order satellites: 3%, 2%, 4%, 6% for 121 parameters*

## 12. Refinement of inversiontwin

*As the structure is non-centrosymmetric we cannot be sure that the proper absolute configuration has been reached. To prove the correct configuration we shall refine so called Flack's parameter which means the volume fraction of twins related by the inversion centre.*
"Start EditM50" to the page cell, define the twinning operation by inversion centre
Run "Parameters→ Twin fraction" and allow refinement of the twin ratio.
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, 1st and 2nd order satellites: 2.1%, 1.5%, 2.6%, 5.5% for 122 parameters.*
Run "Parameters→ Twin fraction" to see the refined volume fraction ~ 0.915. Which means the absolute configuration is opposite to that we got when going from the centrosymmetric to non-centrosymmetric description.
Make backup copy: "fresnoite_final"

## 13. Inverted barium position – false minimum

*Barium is located in a special position x, x-1/2, 1/4. Application of a two-fold axis creates a position -x, -x+1/2, 1/4, which becomes – after application of the three-dimensional part of*

*the X centering 0 0 1/2 1/2 1/2 – equivalent to the inverted position –x, -x+1/2, -1/4. Thus in average structure position of barium can be inverted. In modulated structure inversion of barium yields different modulation functions because of the 4$^{th}$ and 5$^{th}$ component of the centering vector.*

*Refinement of fresnoite tends to be trapped in a false minimum because of very good fit of main reflections and relatively weak satellites. Inversion of the position of barium helps to leave the false minimum.*

Start "Edit Atoms", select Ba1
"Action → Transform selected atoms" and apply inversion -x1,-x2,-x3,-x4,-x5
Save the result, leave "Edit atoms"
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, 1$^{st}$ and 2$^{nd}$ order satellites: 7.6%, 2.7%, 15.6%, 14.2%. This means that the structure can reach a false minimum but also stable minimum.*

# Example 5.5.1: Melilite data

**Data processing of a (3+2)-dimensional incommensurately modulated structure with overlaps of satellites, using Crysalis.**

**Revised: 4 March 2015**

**$Ca_2MgSi_2O_7$**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: directory Melilite available in [ftp://pc222.fzu.cz/cookbook](ftp://pc222.fzu.cz/cookbook), UID cookbook, password jana2006

This example is based on the Crysalis 171.37.35. Crysalis is a program for controll and data processing of Agilent diffractometers. It has very friendly licencing policy: everybody can install Crysalis for processing data acquired with an Agilent instrument (which is also the case of Melilite).

1. ***Getting the file***
   Start your browser
   Connect to ftp://pc222.fzu.cz/cookbook
   Log in as cookbook with password jana2006
   Download the archive Melilite.zip
   Unpack the archive
   *It will create directory Melilite*

2. ***Starting Crysalis***
   Start Crysalis
   In a dialogue that follows locate the file run.par
   *Crysalis opens the experiment.*
   Use  to decrease the image size

3. ***Determination of the unit cell***

   Start Lattice wizard using the button 
   *[On the screen: the window of Lattice Wizard]*
   Start "Peak hunting" with default options
   *About 30000 peaks have been found*
   Start "Unit cell finding" with default options
   *The program finds a unit cell 7.84 7.84 5.02 90 90 90 and indexes about 70% of peaks*

**LATTICE**
  **Current cell**   (CSD: not done)
    7.8437(3) 7.8451(2) 5.01487(15) 90.005(2) 90.005(3) 90.005(3) 308.587(17)
  **Constrained current cell**
    7.8448(2) 7.8448(2) 5.01429(18) 90.0 90.0 90.0 308.587(17)
  Lattice reduction
    selected cell
      7.8437   7.8451   5.0149   90.0053   90.0049   90.0054 tP 21
    reduced cell
      5.0149   7.8437   7.8451   90.0054   90.0053   90.0049     308.6

**PEAK TABLE**
  Peak hunting table
  UB fit with 21276 obs out of 30622 (total:30622,skipped:0) (69.48%)

Start "Ewald Explorer" with default options

Use the  buttons a* b* c* to see projections of the found peaks along the unit cell axes.
Set projection along c*
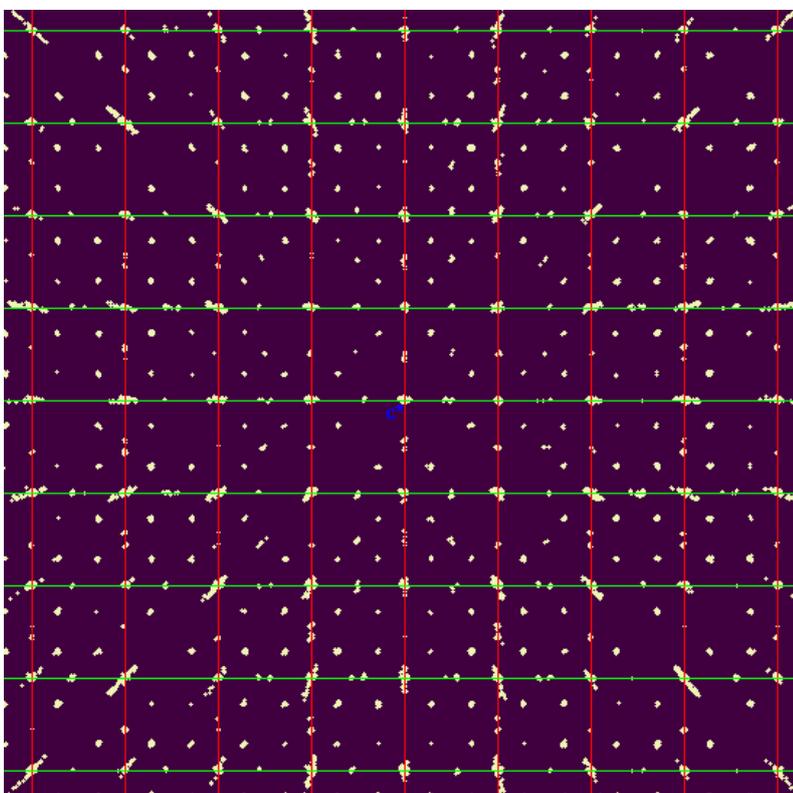


The projection shows main reflections with radial distribution of spurious peaks. These peaks are tails of very strong reflection and their radial distriction allows quick conclusion that these are not satellites.

Enlarge the peak projection using the right mouse button
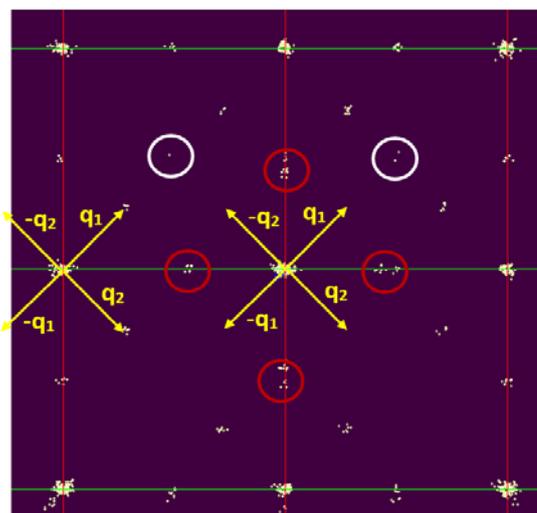
Majority of satellite peaks can be described by two q-vectors: $q_1 = (\alpha, \alpha, 0)$, $q_2 = (-\alpha, \alpha, 0)$. The positive direction of a* and b* is indicated in the shrinked Ewald view by very small labels.

The peaks indicated by white circles are λ/2 reflections. The experiment was done with classical Mo x-ray tube and graphite monochromator and with this equipment such reflections may exist between very strong regular reflections.

The most important are weak reflections indicated by red circles. These reflection are described by combination of $q_1$ and $q_2$, which proves that our structure is (3+2)-dimensional. Without the combinations there would also be possibility of a (4+1)-dimensional crystal twinned by 90° rotation around c*.

The combined satellites are also visible in the projections:
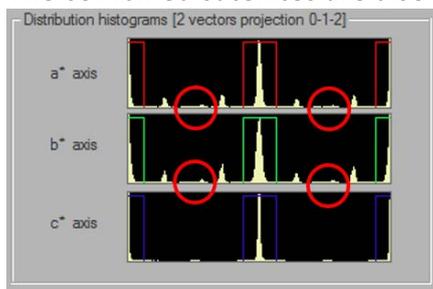


The projections also indicate that the combined satellites may be overlapped due to short distance between them

In the next step, we will visualize the reciprocal plane 0,k,l and 1,k,l to see better the combined satellites

4. ***Unwarping***
Close the Ewald explorer
In Lattice wizard, press "Unwarping – precession images"
NEXT; NEXT
*[On the screen: Step 3: Creation of a layer list"]*
Press "Generate layers"

Type 1 for "max order", 1.2 for "resolution"
Delete all layers except 1_k_l
NEXT
*[On the screen: Step 4: Use background subtraction"]*
Check "Use background subtraction"
NEXT
*[On the screen: Step 5: Data corrections"]*
Press "Edit user scale"
Define a user scale 40 (to see weak features)
Check "Don't apply final convolution filter" (to see better separation of spots)
OK; FINISH
Check the radio button "Layer" to see the progress of the unwarp procedure.
Open the menu in the lowr right cornes of Crysalis and select "Unwarp reciprocal lattice grid"
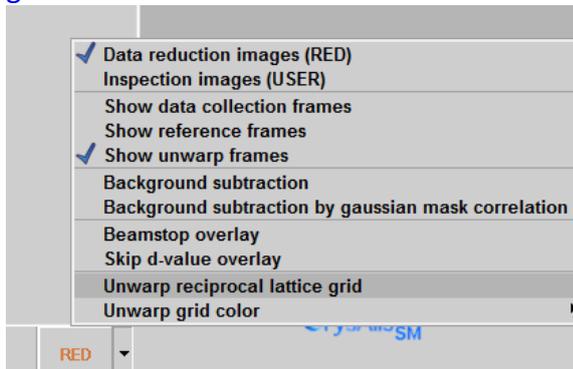


This is the resulting unwarped reciprocal plane (precession-like image):
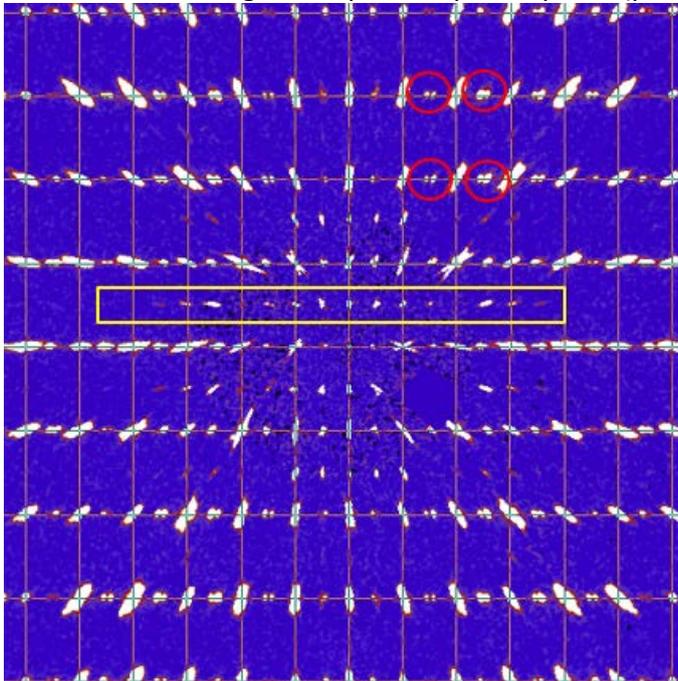


The weak spots indicated by yellow rectangle are the λ/2 reflections. The ones indicated by red circles are the combined satellites. Again, the possibility of overlaps between the combined satellites is evident.

## 5. Setting up the (3+2)d structure, refinement of q-vectors

Start Lattice wizard and Ewald explorer

Press "Activate incommensurate peaks" and select "Add 2d modulation vectors (hklmn)"

Define two q-vectors: (0.3, 0.3, 0) and (-0.3, 0.3, 0)
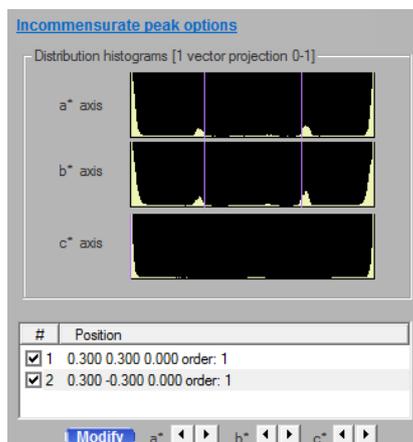


Using the sliders, modify the componets to fit with the projected peaks
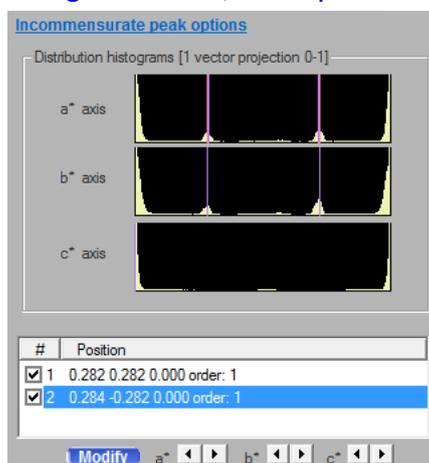


Close Ewald explorer

In Lattice wizard, press "Incommensurates/Quasi--crystals"

Use default settings (with mmax = 1); OK

The refined unit cell + q-vectors index 92% of peaks. The procedure could index about 1800

```
LATTICE
   Current cell   (CSD: 0 +8L)
      7.8437(3) 7.8451(2) 5.01487(15) 90.005(2) 90.005(3) 90.005(3) 308.587(17)
   Constrained current cell
      7.8448(2) 7.8448(2) 5.01429(18) 90.0 90.0 90.0 308.587(17)
   Lattice reduction
      selected cell
         7.8437    7.8451    5.0149    90.0053    90.0049    90.0054 tP 21
      reduced cell
         5.0149    7.8437    7.8451    90.0054    90.0053    90.0049    308.6
Incommensurate/quasi-crystal information
   q(1): 0.2815(3)  0.2822(4)  0(3e-004) q(2): 0.2819(3)  -2.819e-001(4)  0(2e-004)

PEAK TABLE
   Peak hunting table
   UB fit with 28137 obs out of 30622 (total:30622,skipped:0) (91.88%)
   19823 main refl.; 3285 q1 ; 3187 q2 satellites; 1842 cross q1/q2
```

## 6. Combined satellites in Jana2006 indexing tool

In the left toolbar, press the button "CMD"



This command saves peak table in old ascii format. Jana could also read the new binary format of the peak table but without orientation matrix.

Save the peak table as oldtab.tab

Start Jana2006 and open any structure

Start Tools → Graphic → Indexing

In the file manager of Jana2006, locate oldtab.tab; double click it; OK

Select Mo KAlpha radiation; OK

*[On the screen: Jana2006 indexing tool]*
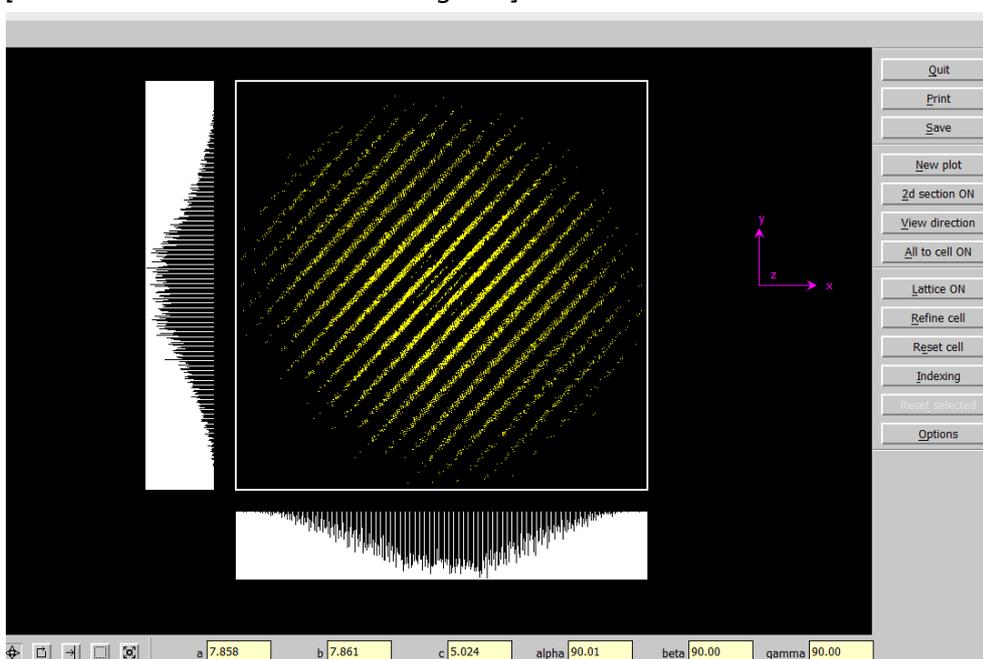


Press "View directions" and select c*
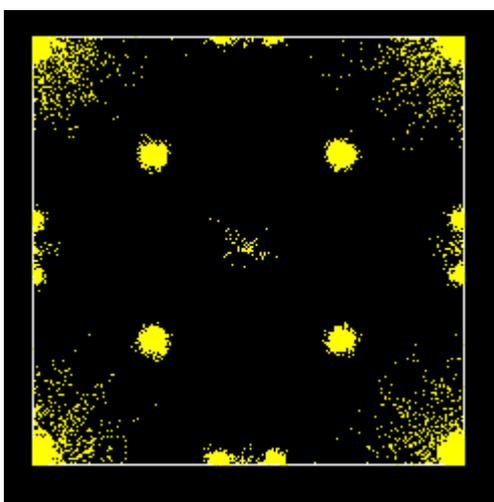
The resulting image projects all peaks positions into one unit cell. We can recognize q1 and q2 satellites, combined satellites (the double-points in the middle of the unit cell axes) and the λ/2 reflections in the middle of the plot.
Quit Jana2006

7. *Data reduction*

In the right panel of Crysalis, press "Start/Stop" and select "Data reduction with options"
*[On the screen: Step1: Orientation matrix for data reduction]*
Select "Other (reduction list)"
OK to confirm a message about non-existing reduction list
Press "Generate"
*[On the screen: Proffit reduction list generation]*
This tool generates list of reflections, which will be used for the data reduction.
Crysalis could also read an existing list of reflections (the "Load" button). This list can be produced by Jana2006 and it is very useful for cases when the list cannot be generated by Crysalis, e.g. for composite structures or for structures with X centering vectors. In this case, however, we can generate the list by Crysalis.
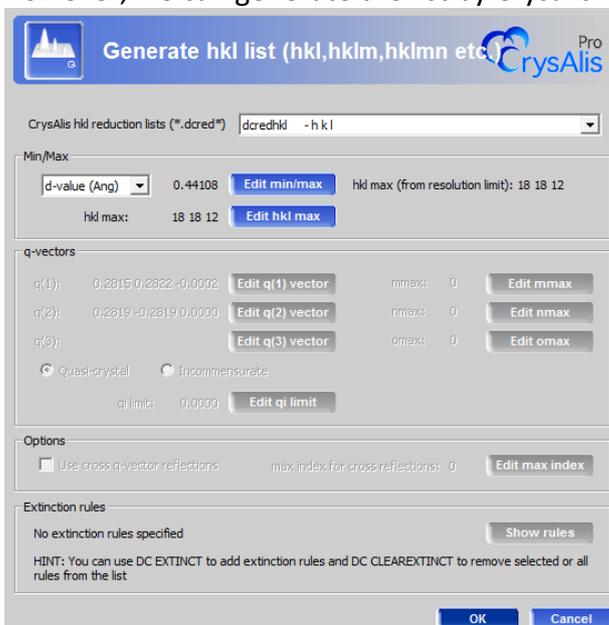


Activate (3+2)d type of the list
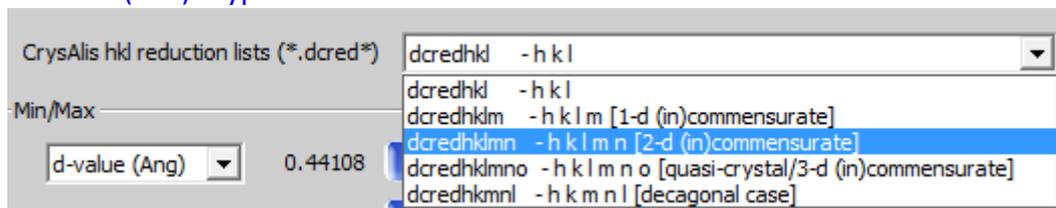


Check "use cross q-vector reflections"
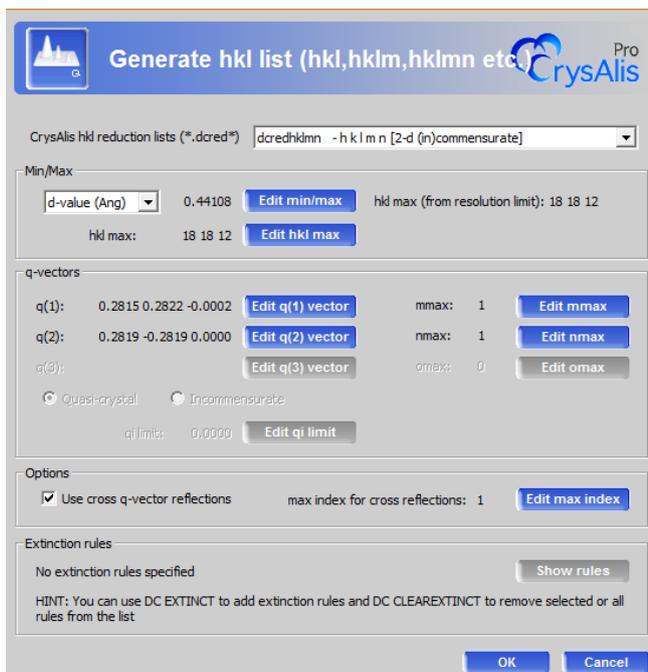
In the case of a structure with well separated spots, the generated list would cover all reflections needed for the data reduction.

In the case of Melilite, the combined satellites need a special treatment. The previous attempts showed that these satellites are partially overlapped and that the best way is to make the data reduction with a large integration mask. With such mask, the combined satellites are integrated as a one spot and this can be taken into the account in the Jana2006 refinement. However, this large mask is not suitable for main reflections and for the q1/q2 satellites. For this reason, the combined satellites must be processed separately.

**Clear** "use cross q-vector reflections"
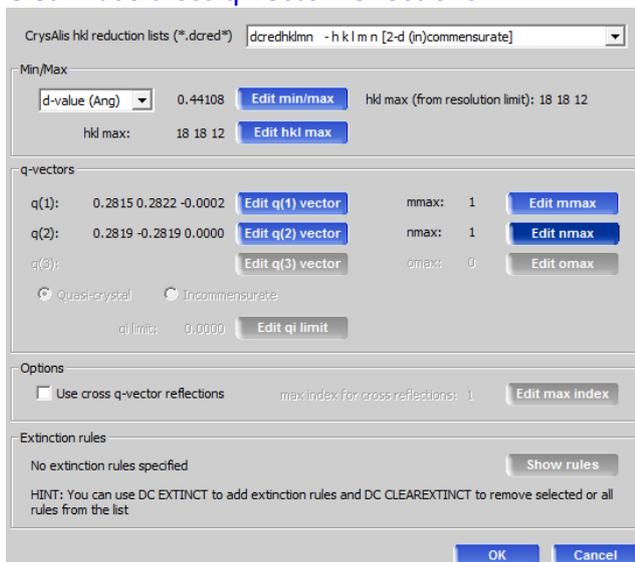


OK; NEXT; NEXT
In the Step 3, clear "Follow significant sample wobbling"; NEXT; NEXT
In the Step 5, use outlier rejection for 4/m; NEXT
In the Step 6, press "Change output name" and define "q1_xor_q2" as an output file name
FINISH

The program makes data reduction for main reflections, q1 satellites and q2 satellites, using the default integration mask

In the left toolbar of Crysalis, press

Select the page "Data reduction output" and look at Rint of main reflections and satellites

```
Main reflections

Statistics vs resolution - point group symmetry: P4/m
resolu-       #        #        #        average    mean       mean
tion(A)    measured   kept    unique   redundancy   F2      F2/sig(F2)   Rint    Rsigma    RsigmaA
-----------------------------------------------------------------------------------------------------
 inf-1.01    5291     5280      181        29.2    31566.87    105.58     0.018    0.022     0.007
1.01-0.80    5776     5773      181        31.9    11264.42     47.38     0.021    0.025     0.016
0.80-0.69    4924     4924      181        27.2     6738.68     31.62     0.024    0.027     0.025
0.69-0.63    4160     4158      181        23.0     3836.20     21.45     0.028    0.033     0.036
0.63-0.58    3254     3254      181        18.0     2863.33     17.59     0.028    0.033     0.045
0.58-0.54    2852     2851      181        15.8     1956.26     13.90     0.036    0.044     0.057
0.54-0.51    2355     2355      181        13.0     1638.44     12.03     0.038    0.049     0.063
0.51-0.49     858      856      182         4.7     1307.86     12.08     0.036    0.043     0.065
0.49-0.47     802      802      181         4.4      764.54      8.81     0.047    0.054     0.088
0.47-0.45     662      662      185         3.6      685.43      8.59     0.049    0.057     0.092
-----------------------------------------------------------------------------------------------------
 inf-0.45   30934    30915     1815        17.0     9761.42     39.60     0.021    0.027     0.016
 inf-0.80   10916    10902      357        30.5    21106.57     75.59     0.019    0.023     0.010

Satellite reflections

Statistics vs resolution - point group symmetry: P4/m
resolu-       #        #        #        average    mean       mean
tion(A)    measured   kept    unique   redundancy   F2      F2/sig(F2)   Rint    Rsigma    RsigmaA
-----------------------------------------------------------------------------------------------------
 inf-1.21   18677    18259     2099         8.7      391.24     10.24     0.283    0.141     0.074
1.21-0.93   20306    20183     2100         9.6      289.83      6.57     0.322    0.170     0.121
0.92-0.79   18154    18087     2088         8.7      251.25      4.97     0.328    0.192     0.156
0.79-0.71   15747    15720     2090         7.5      215.78      4.12     0.343    0.216     0.195
0.71-0.65   14015    13996     2090         6.7      153.35      2.97     0.401    0.261     0.269
0.65-0.60   12016    11988     2099         5.7      140.98      2.65     0.355    0.255     0.302
0.60-0.57    9505     9479     2083         4.6      117.99      2.33     0.399    0.314     0.355
0.57-0.54    7392     7354     2085         3.5       96.71      1.99     0.409    0.351     0.410
0.54-0.50    4420     4364     2083         2.1       77.42      1.77     0.476    0.440     0.471
0.50-0.45    3600     3545     2010         1.8       58.78      1.50     0.477    0.499     0.564
-----------------------------------------------------------------------------------------------------
 inf-0.45  123832   122975    20827         5.9      220.71      4.86     0.331    0.210     0.173
 inf-0.80   55943    55338     6148         9.0      311.47      7.30     0.307    0.163     0.110
```

The Rint of satellites is poor but we should consider that the program does not show separately the observed satellites. Rint of observed satellites will be shown in the Reflection report of Jana2006.

Select the page Graphs
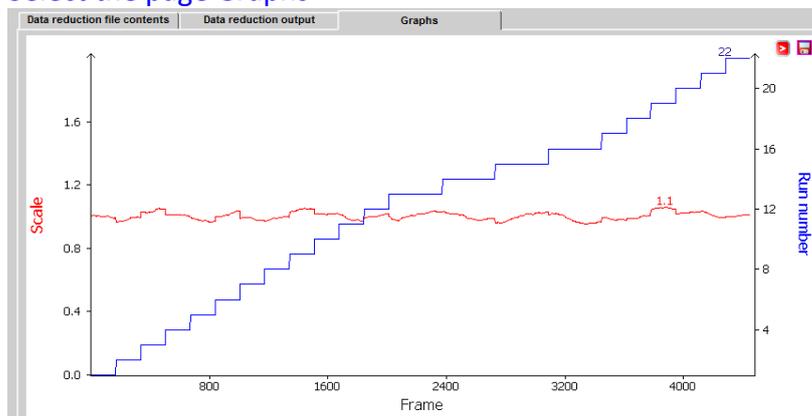


The graph of frame scaling is almost flat, indicating sufficient absorption correction

In the next step, we will process the combined satellites
Quit the tool "Inspect data reduction results"

In the right panel of Crysalis, press "Start/Stop" and select "Data reduction with options"
*[On the screen: Step1: Orientation matrix for data reduction]*
Select "Other (reduction list)"
Press "Generate"
In the line for q1, press "Edit mmax" and define mmax=0
In the line for q1, press "Edit mmax" and define mmax=0
Check "Use cross q-vector reflections"
Press "Edit max index" for the cross q-vector reflections and define mmax=1
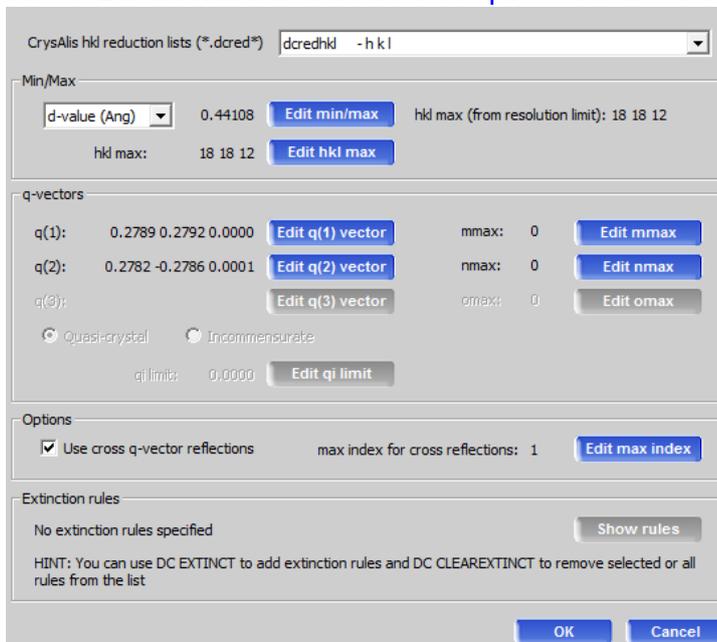


OK; YES to confirm that we really want such a list
Out of Crysalis, go to the experimental directory and open in a text editor the file run.dcredhklmn

```
 0    5   -8    0    0
 1    5   -8    0    0
 2    5   -8    0    0
 3    5   -8    0    0
 4    5   -8    0    0
 5    5   -8    0    0
 6    5   -8    0    0
 7    5   -8    0    0
 8    5   -8    0    0
 9    5   -8    0    0
10    5   -8    0    0
11    5   -8    0    0
-11   6   -8    0    0
-10   6   -8    0    0
 -9   6   -8    0    0
 -8   6   -8    0    0
 -7   6   -8    0    0
 -6   6   -8    0    0
 -5   6   -8    0    0
```

The file only contains main reflections. This means the current version of Crysalis cannot generate the list we need. However, we can use the full list + a custom extinction rule

CANCEL; CANCEL
In the main window of Crysalis - the left toolbar, press the button CMD
Type command "dc extinct hklmn 0 0 0 1 1 2 1"; ENTER
This defines that reflections with m+n odd will be skipped
In the right panel of Crysalis, press "Start/Stop" and select "Data reduction with options"
*[On the screen: Step1: Orientation matrix for data reduction]*
Select "Other (reduction list)"
Press "Generate"
In the line for q1, press "Edit mmax" and define mmax=1

In the line for q1, press "Edit mmax" and define mmax=1
Check "Use cross q-vector reflections"
Press "Edit max index" for the cross q-vector reflections and define mmax=1



At the bottom of the "Generate hkl list" window we can see that our custom extinction rule is active
OK;
Out of Crysalis, go to the experimental directory and open in a text editor the file run.dcredhklmn

| | | | | |
|---|---|---|---|---|
| -1 | -4 | -11 | -1 | -1 |
| 0 | -4 | -11 | -1 | -1 |
| 1 | -4 | -11 | -1 | -1 |
| 2 | -4 | -11 | -1 | -1 |
| -2 | -3 | -11 | -1 | -1 |
| -1 | -3 | -11 | -1 | -1 |
| 0 | -3 | -11 | -1 | -1 |
| 1 | -3 | -11 | -1 | -1 |
| 2 | -3 | -11 | -1 | -1 |
| 3 | -3 | -11 | -1 | -1 |
| -3 | -2 | -11 | -1 | -1 |
| -2 | -2 | -11 | -1 | -1 |
| -1 | -2 | -11 | -1 | -1 |
| 0 | -2 | -11 | -1 | -1 |
| 1 | -2 | -11 | -1 | -1 |
| 2 | -2 | -11 | -1 | -1 |
| 3 | -2 | -11 | -1 | -1 |

Now the file contains the combined satellites
(Back in Crysalis)
NEXT; NEXT
*[On the screen: Step3: Basic algorithm parameters]*
Press "Edit special pars"
Check "Override integration mask size"
Define size 1.50 (correct number can only be found by refinement trials)
OK; NEXT; NEXT; NEXT;

## 8. Results of data reduction

After finishing the data reduction, start "Inspect data reduction" by pressing
The results for combined satellites are poor but this might be caused by their weakness. We cannot make any conclusion without refinement of a structure model.

```
Main reflections

Statistics vs resolution - point group symmetry: P4/m
resolu-        #       #       #              average    mean      mean
tion(A)    measured  kept    unique          redundancy  F2      F2/sig(F2)  Rint   Rsigma   Rs
----------------------------------------------------------------------------------------------
 inf-1.01     5188    5182     180             28.8     33156.72   62.31    0.019   0.024
1.01-0.80     5685    5682     180             31.6     11746.62   28.15    0.021   0.026
0.80-0.69     4880    4880     180             27.1      7230.31   19.22    0.023   0.027
0.69-0.63     4029    4027     180             22.4      4122.85   13.23    0.028   0.034
0.63-0.58     3225    3225     180             17.9      2953.07   10.77    0.029   0.034
0.58-0.54     2843    2842     182             15.6      2080.72    8.75    0.036   0.044
0.54-0.52     2356    2355     180             13.1      1744.32    7.74    0.039   0.050
0.52-0.49      846     845     180              4.7      1411.25    7.96    0.036   0.042
0.49-0.47      793     793     181              4.4       818.72    6.09    0.049   0.058
0.47-0.45      666     662     185              3.6       745.48    5.96    0.052   0.062
----------------------------------------------------------------------------------------------
 inf-0.45    30511   30493    1808             16.9     10242.65   23.72    0.021   0.028
 inf-0.80    10746   10737     356             30.2     22135.16   44.71    0.019   0.024

Satellite reflections

Statistics vs resolution - point group symmetry: P4/m
resolu-        #       #       #              average    mean      mean
tion(A)    measured  kept    unique          redundancy  F2      F2/sig(F2)  Rint   Rsigma   Rs
----------------------------------------------------------------------------------------------
 inf-1.22    17468   17230    2057              8.4       235.75    4.47    0.374   0.246
1.22-0.93    20260   20169    2054              9.8       197.11    3.20    0.366   0.241
0.93-0.80    17679   17631    2055              8.6       187.39    2.72    0.361   0.240
0.80-0.71    16214   16181    2056              7.9       154.33    2.29    0.340   0.259
0.71-0.65    14607   14580    2062              7.1       124.60    1.97    0.364   0.284
0.65-0.60    12059   12038    2061              5.8       106.87    1.76    0.364   0.303
0.60-0.56     9511    9462    2069              4.6        90.02    1.60    0.378   0.346
0.56-0.53     7060    7002    2062              3.4        76.80    1.54    0.399   0.393
0.53-0.50     3873    3829    2065              1.9        60.05    1.41    0.461   0.502
0.50-0.45     3346    3312    1996              1.7        53.24    1.32    0.489   0.539
----------------------------------------------------------------------------------------------
 inf-0.45   122077  121434   20537              5.9       154.30    2.57    0.366   0.276
 inf-0.80    55026   54649    6132              8.9       206.74    3.46    0.367   0.243
```

The input files for Jana2006 are in the directory /struct/tmp:
q1_xor_q2.hkl; q1_xor_q2.cif_od
q1_and_q2.hkl; q1_and_q2.cif_od

The example 5.5.2. where structure of melilite is solved uses different input files: 4d data for q1, 4d data for q2 and 5d data for combined satellites. The data created in this example will be used in some future version of this cookbook.

# Example 5.5.2: Melilite

**Solution of a (3+2)-dimensional incommensurately modulated structure with overlaps of satellites.**

### $Ca_2MgSi_2O_7$

**Revised: 6 March 2015**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer

The structure has two q-vectors: $q1=(\alpha,\alpha,0)$ and $q2=(-\alpha,\alpha,0)$. Satellite reflections h,k,l,m,0 and h,k,l,0,n are always well separated in the CCD frames. Combined satellites hklmn, m≠0, n≠0, are sometimes separated and sometimes overlapped, depending on their geometry in particular CDD frame (i.e. angle ψ). The combined satellites needed different data processing strategy using large integration mask because we want to treat them like "always fully overlapped".
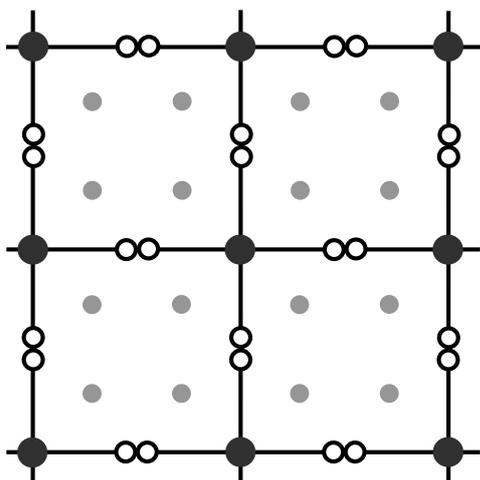


Schematic view of the diffraction pattern in melilite. Main reflections are indicated by large dark circles, small circles symbolize first-order satellites (grey for m x n = 0 and white for m x n = ±1 satellites, respectively).

Input files:
q1.hkl, q1.cif_od (main reflections + satellites described by q1)
q2.hkl, q2.cif_od (main reflections + satellites described by q2)
q1q2.hkl, q1q2.cif_od (main reflections + combined overlapped satellites)
Frame scaling, absorption correction: done with software of the diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane – textbox: type "melilite"
   OK

2. **Import Wizard**

Select "Known diffractometer formats"; NEXT
Select "Oxford Diffraction – CCD";
For "File name" select q1.hkl; NEXT
In "Define basic input file" select "Input from cif_od file"; OK
Change the modulation vector to 0.278 0.278 0; NEXT
*The used q-vector refinement software does not allow restriction that would keep all components of the two q-vectors the same*
*[On the screen: Define the reference cell / split by twinning]*
Change target dimension to 5
For 2nd modulation vector type -0.278 0.278 0; NEXT
*The program reads 92323 reflections*
For absorption correction select "None or done before importing"; NEXT
FINISH
*[On the screen: Data repository]*
Import new
Select "Known diffractometer formats"; NEXT
Select "Oxford Diffraction – CCD";
For File name choose q2.hkl; NEXT
In "Define basic input file" select "Input from cif_od file"; OK
Change the 1st modulation vector to -0.278 0.278 0; NEXT
Check "Import only satellites";
*New import of the same main reflections would bias their weighting scheme*
Define transformation matrix (1 0 0 0 0 | 0 1 0 0 0 | 0 0 1 0 0 | 0 0 0 0 1 | 0 0 0 1 0); OK
*This will convert hklm from the input file to hkl0n*
NEXT
*The program reads 92522 reflections, including discarded main reflections*
For absorption correction select "None or done before importing"; NEXT
FINISH
*[On the screen: Data repository]*
Import new;
Select "Known diffractometer formats"; NEXT
Select "Oxford Diffraction – CCD";
For File name choose q1q2.hkl; NEXT
In "Define basic input file" select "Input from cif_od file"; OK
Change the 1st modulation vector to 0.278 0.278 0
Change the 2nd modulation vector to -0.278 0.278 0; NEXT
Check "Import only satellites"; NEXT
YES to accept cell parameters;
*The program reads 147857 reflections, including discarded main reflections*
For absorption correction select "None or done before importing"; NEXT
FINISH
OK; YES to accept the data sets


3. **Symmetry Wizard**

Use all data blocks for the space group test
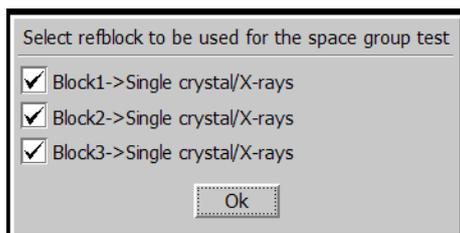


default tolerances for crystal system recognition

For "Maximal ave(I/sig(I)) for extinctions type "20"; NEXT

Select tetragonal Laue symmetry 4/mmm

Select P centering

Select space group P-421m

*At this point there is no difference between P-421m and P4212, the decision is expected from the symmetry test of Superflip*

Accept the superspace group in the original cell

*For five-dimensional structures the wizard does not offer selection of superspace group. It will be done later manually.*

4. **Creating refinement reflection file**

Follow steps of the reflection wizard, the data sets are **on the same scale**

*The program discards 206 reflections, 96 observed, Rint=3.31%*

*In case that the same scale of the data sets would not be sure, a temporary structure should be created with data sets imported together with main reflections. Then we could select "different scales" and Jana would use main reflections for finding scaling factors. Then the data set would be re-imported with the found scale factors and with main reflections only in the first data set.*

5. **Structure solution wizard**

Quit

6. **Solution of average structure**

*Superflip for five-dimensional structure returns five-dimensional electron density map. However, Jana2006 would not evaluate initial modulation functions from this map and we would get only average structure. For this reason solution will be done separately for average structure*

Start "Tools → Transformation → Go to average 3d structure"

For name use "aver"

Follow steps of the Reflection wizard

Continue with the new structure

Start "Run → Structure solution"

For Formula type "Ca Mg Si O"

Select "Superflip" and "Peaks from Jana2006"

Select "Use a specific random seed" and type "333" for random seed

*With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work Random seed should not be fixed.*

"Run solution"

*Superflip converges with R around 13% and confirms the selected space group*

"Accept last solution"; "Quit" to leave the Structure solution wizard

Start EditM50; Go to the page "Composition"; for "Formula units" type "2"; press "Formula from M40"age

*It returns Ca2 Mg0 Si3 O7. The expected formula is Ca2 Mg Si2 O7, therefore one of silicon atoms is probably magnesium.*

Run Refinement

*Refinement converges with Robs around 14%*

Open "Dist" commands; clear "d(max) derived from atomic radii and typical distances"; run "Dist"

Open listing of "Dist" and check Si-O distances.

*Si2-O3 distances are unusually large (around 1.921 Å), that means Si2 should be changed to magnesium*

Using "Edit Atoms", change atomic type of Si2 to Mg and its name to Mg1

Run refinement

*Refinement converges with Robs around 14%*

"Edit atoms": change ADP of all atoms to harmonic

Run refinement

*Refinement converges with Robs 3.7%*

"Plot structure"
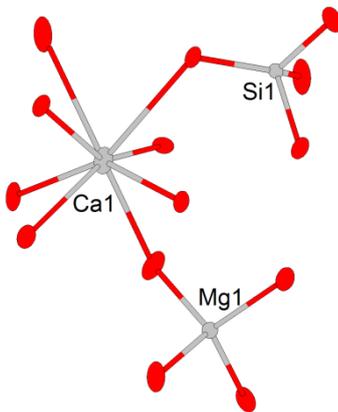


*The structure looks normally but ADPs are unusually large*

7. **Back to the modulated structure**

"File → Structure → Open": open "melilite"

"EditM50, Composition page": type formula Ca2 Mg Si2 O7, Z=2

Close Editm50, save changes

"File → Structure → Copy in": import **only** M40 from the average structure

Run refinement to confirm R value for the average structure:

```
R factors : [15407=11807+3600/34],   Damping factor: 0.5000
GOF(obs)= 33.66   GOF(all)= 29.50
R(obs)= 56.84     Rw(obs)= 77.49     R(all)= 59.37     Rw(all)= 77.53
R factors for main reflections : [1832=1784+48]
R(obs)=  3.73     Rw(obs)=  5.62     R(all)=  3.83     Rw(all)=  5.63
R factors for satellites of order 1 : [6745=4943+1802]
R(obs)=100.00     Rw(obs)=100.00     R(all)=100.00     Rw(all)=100.00
R factors for satellites of order 2 : [6830=5080+1750]
R(obs)=100.00     Rw(obs)=100.00     R(all)=100.00     Rw(all)=100.00
Last Rw(all):
Maximum change/s.u. :   0.0016 for x[Si1]
```

## 8. Superspace symmetry

*We will need to complete the translation part of superspace symmetry operators.*

"EditM50 → Symmetry": focus the textbox with the space group symbol and press TAB.

*The program shows two symmetry operators where the translation part in x4 and x5 needs to be completed:*



*and*

*Each translation part has two elements which can be either 0 or 1/2. Thus we have sixteen combinations: 0 0 + 0 0, 0 0 + 1/2 0, 0 0 + 0 1/2, 0 0 + 1/2 1/2 … However, some of them are forbidden because they lead to a non-consistent translation vector, which cannot ne used for generation of the superspace group. Finally we have only eight combinations. In the following table we show number of extinct reflections (observed/unobserved) which Jana2006 reports for each of these possibilities:*

| Translations in x4,x5 | 0 0 | 1/2 1/2 |
|---|---|---|
| 0 0 | 96/206 | 181/5369 |
| 1/2 1/2 | 181/5369 | 96/206 |
| 1/2 0 | 96/206 | 181/5369 |
| 0 1/2 | 181/5369 | 96/206 |

*Only four possibilities lead to additional extinctions. They are all equivalent as we can judge from the exactly same number of extinct reflections as well as from the fact that EditM50 does not offer creation of new refinement reflection file when we switch between them. Another four possibilities without additional extinctions are equivalent, too.*

*Thus we have two possibilities for the superspace group: with and without additional extinctions. The choice is simple because the additional extinctions mostly concern unobserved reflections and therefore the symmetry leading to additional extinctions is confirmed by the experiment.*

*In order to be consistent with the published structure we shall choose 0 0 for the first symmetry operator and 1/2 1/2 for the second one.*

Select 0 0 and 1/2 1/2 for the first and the second symmetry operator, respectively

Close EditM50, save the result
Create new refinement reflection file


**9. *Refinement of modulated structure – position modulation***

Start "File → Structure → Save As" and make backup copy: "melilite_backup"
Start "Parameters → Options"
Press "Define wave vectors"
For the third wave define 1 1
*This means modulation wave vector given by a sum of the q vectors*
For the fourth wave define 1 -1
*This means modulation wave vector given by a difference of the q vectors*
"Edit atoms": set two position modulation waves for all atoms
*This means one harmonic wave with wave vector q1 and one harmonic wave with wave vector q2*
In Refinement commands switch to window "Modulation"; for "Overlap option" select "Closest reflections"; "max. satellite index" 1; "max. difference in degs" 0.5
*With this settings pair of combined satellites will be treated as fully overlapped reflections.*
Run refinement
*Refinement converges after approx. 20 cycles with the following Robs values for all reflections, main reflections, 1$^{st}$ and 2$^{nd}$ order satellites: 23%, 12%, 28%, 37%*
*By second order satellites are considered reflections described by combination of q1 and q2: q1 + q2 or -q1 + q2.*
"Edit atoms": add another two position modulation waves for all atoms
*This means one harmonic wave with wave vector q1+q2 and one harmonic wave with wave vector -q1+q2*
Run refinement
*Refinement converges with the following Robs values for all reflections, main reflections, 1$^{st}$ and 2$^{nd}$ order satellites: 9%, 6%, 13%, 11%*


**10. *Contour sections and ADP modulation***

"Start Contour → New plot → Calculate new ones"
*(If no old map exists from previous calculations this option is not active but Contour will use it)*
Select observed Fourier
For "Scope" define Ca1 as a central atom
For map axes select x1, x4, x3, x2, x5 with limits as shown below

*This will calculate section x1-x4 through Ca1 as a function of x5*
OK to calculate Fourier map
In Contour press "Atoms edit" and add Ca1
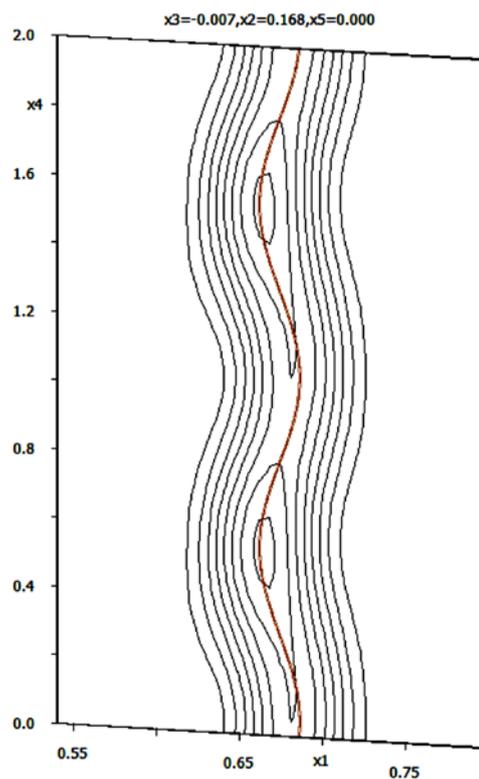


Press "Movie" to see the changes of this figure with x5. ESC to stop.

Press "New plot" and calculate difference Fourier map for the same section
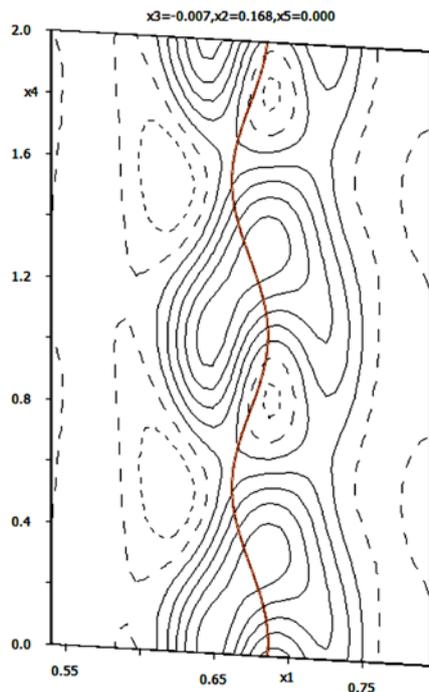


*The difference maxima around Ca1 indicate ADP modulation*

Calculate and plot corresponding difference Fourier sections for the other atoms

*All atoms have strong difference maxima and minima*

"Edit atoms": set two ADP modulation waves for all atoms

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1$^{st}$ and 2$^{nd}$ order satellites: 6.1%, 3.7%, 5.3%, 11.1% for 166 parameters*

Start Contour and repeat plotting of the difference section through Ca1

*The difference maxima are not so large but still not acceptable*

"Edit atoms": set additional two ADP modulation waves for all atoms

Run refinement

*Refinement converges with the following Robs values for all reflections, main reflections, 1$^{st}$ and 2$^{nd}$ order satellites: 4.8%, 3.1%, 4.5%, 8.1% for 238 parameters*

Run Grapht and investigate distances, bond valence sums etc. All obtained graphs will depend on "u" coordinate which can be changed by "Movie" button.

# Example 6.1: KSm

**Modulated structure solved from powder data. Basic steps with powder refinement, mixed sites in 4d.**

**Revised: 4 October 2015**

## K Sm Mo₂ O₈

Powder data measured with synchrotron radiation
Input files:    KSm.dat (powder profile data)
               KSm.txt (additional information)
               KSm.pdf (article about this compound)

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click KSm

2. ***Import Wizard***
   Select "Various CW format", NEXT
   *CW stands for constant wavelength*
   Type "File name" KSm.dat
   Select "Free format of 2th, I, [sig(I)]" and "Another/unknown method"; NEXT
   Fill cell parameters 5.5304 5.3019 11.7893 90 90 91.138
   *The string can be copied from KSm.txt by CtrlC + CtrlV*
   Change "Target dimension" to 4 and fill q vector 0.56883 -0.12885 0
   *The string can be copied from KSm.txt by CtrlC + CtrlV*
   For wavelength type 0.7114 and select "Linearly polarized beam"; NEXT; FINISH
   Accept the data in Data repository
   Select "Yes, I would like to continue with the wizard"; OK

3. ***Checking data***
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *Profile viewer shows experimental powder profile*
   *The powder profile is stored in KSm.m95 and in KSm.m90 in analogy to single crystal data*
   Leave profile viewer
   "Edit refinement commands"; 0 refinement cycles; OK
   "Run Refine"
   "Show powder profile"
   *Now the profile viewer shows experimental and calculated powder profile. The calculated profile is based on default profile parameters. Bragg positions of satellites are green. By default satellites up to the order 1 are used.*
   *The calculated profile is stored in KSm.prf*
   Leave profile viewer
   "Edit profile parameters"

*This opens "Powder options" where profile parameters will be edited*
*The profile parameters are stored in file KSm.m41*

4. ***Refinement of profile parameters***
*[On the screen: Powder options]*
*In the initial state refinement of cell parameters and q-vector is disabled; in page "Profile" only GW has non-zero value and it is also fixed; in "Corrections" page zero background is predefined.*
In "Profile" page activate refinement of "GW"
In "Corrections" page activate refinement of "shift"
*Refinement of background terms is enabled by default*
Leave Powder options, save changes
"Edit refinement commands"
Set 100 refinement cycles; OK; "Run Refine"
*Refinement converges with Rp~3.7%*
*The convergence may be slow. You can interrupt the refinement when Rp reaches 3.7% by button "End" pressed at the moment when LeBail decomposition is not running*
"Edit profile parameters": activate refinement of cell parameters (a, b, c, gamma) and components (q1,q2) of the modulation vector;
set number of Legendre terms for background to 16
"Run Refine"
*Refinement converges with Rp~3.1%*
In "Edit profile parameters" switch to the page "Profile" and activate refinement of GU, GV run Refine
*Refinement converges with Rp~2.5%. Waiting for the full convergence is not necessary. Although the profile viewer shows that profile description could be further improved, for structure solution this starting point is sufficient.*
FINISH; NEXT to open a wizard for the space group test

5. ***Space group determination***
*[On the screen: Tolerances for crystal system recognition]*
Use default; NEXT
*[On the screen: Select Laue symmetry]*
Select the highest one – monoclinic; NEXT
*[On the screen: Select cell centering]*
Select I centering; NEXT
*[On the screen: Information about progress of space group tests. It takes some time…]*
*[On the screen: Select space group];*
Select C2/c; NEXT
*[On the screen: Final step of the space group test];*
Accept the space group **transformed into the original cell**; Finish
*[On the screen: "Do you want to refine profile parameters one more"];*
Yes
*Now the used symmetry speeds up the profile refinement. $R_p$ is slightly higher because we don't use forbidden Bragg positions*

**6. Structure solution**
Select "Use Superflip"
Type formula K Sm Mo2 O8; Formula units 2
Select "Repeat Superflip: Until the convergence detected" and 2000 cycles
Peak from Jana2006
"Run solution"
In case the convergence was detected, press "Accept last solution "

*Because charge flipping for powders is difficult, it may happen that the convergence is not detected but the solution is anyway present in the density map. If the previous procedure has not returned any result, do the following:*

 Select "Repeat Superflip: Number of runs", type 10 runs and 3000 cycles
*Superflip runs from ten different random phase sets and returns the "best" density in terms of symmetry fit and other criteria*

*If the above procedure still does not yield any result, it can be repeated with "Starting model" = "Patterson superposition map"*

*In case no results are obtained please note that there are also different powder-specific procedures like histogram matching. These procedures are described in the Superflip manual.*

"Accept last solution " closes the structure solution wizard
"Quit" closes the structure solution wizard and ignores any solution

***At this point the powder wizard finishes***
*The components of the powder wizard can be started separately like*
*"Parameters → Powder"*
*"Tools → Powder → Profile viewer"*
*"Run → Solution"*

Start "Edit atoms" or "Edit/View → Editing of M40" and make sure the atomic positions returned by Superflip are as follows (or symmetry transformed):

```
Sm1 0.500000 0.250000 0.147357
Mo1 0.000000 0.750000 0.120140
```

*For different result or no convergence of Superflip:*
Start "File → Structure → Copy in"
Import M40 and M50 from the structure "KSm-solution".

**7. Completing average structure**
*Atoms in the initial structure model have already modulation functions, which were found in the electron density map from Superflip. However, for this example it is better to use the classical approach: calculating first the average structure and then refining modulation waves from small starting displacements.*
Start "Parameters → Powder", switch to page "Cell", and check "Use only satellites

corresponding to existing modulation waves" and disable refinement of q vector components.

Start "Edit atoms" and delete all light atoms (if present)

*In our case we will delete all oxygen atoms. Positions of light atoms found from Superflip electron density map may be unreliable.*

In "Edit atoms" dialogue select heavy atoms (Sm1 and Mo1), go to "Action → Edit/define" and delete position modulation wave (if present).

In Refinement options go to page "Basic" and set Damping factor to 0.25

**Uncheck "Make only profile matching"**

Run refinement

*Refinement converges with Rp=22%, R=11%*

Activate refinement of occupancy (parameter "ai") for Sm1 and run Refine

*Rp slightly improves, Occupancy of Sm1 changes from 0.5 to 0.4 and ADP of Mo1 becomes positive. The decrease in occupancy of Sm1 indicates that it could be mixed with potassium.*

Open options for Fourier and select difference Fourier map, automatic Scope and default map orientation. In the "Peaks" page – "Interpretation of displacement waves" change "No. of harmonics" to 0.

Run difference Fourier

NO (skip procedure for including new atoms)

*The fact that both heavy atoms are located at the special positions and with interatomic vector about (0,0,0.5) leads to a false symmetry in the map. However, the true maxima should form a tetrahedron around Mo1. In the next steps, we will plot Mo1 and neighboring Fourier maxima in Diamond.*

Run "Plot structure"; Select "Draw average structure";

Press "Add Fourier peaks"; select all maxima; OK; "Draw+continue" to start Diamond

*[On the screen: Diamond]*

*Diamond assigns to the Fourier maxima the lightest chemical element in the formula. For our formula, this is the oxygen. Sometimes it may be practical to append another light atom to the end of the formula, for instance hydrogen.*

Delete the automatically created structure

With button ⊹○ from the bottom toolbar select Mo1 as the only atom to be plotted

With "Build → Connectivity" focus Mo-O distance and set the limits above 1.5 Å and below 2 Å; OK

Focus Mo1 and plot its coordination with button ⊚

Rotate the plot until you recognize a tetrahedron formed by four maxima
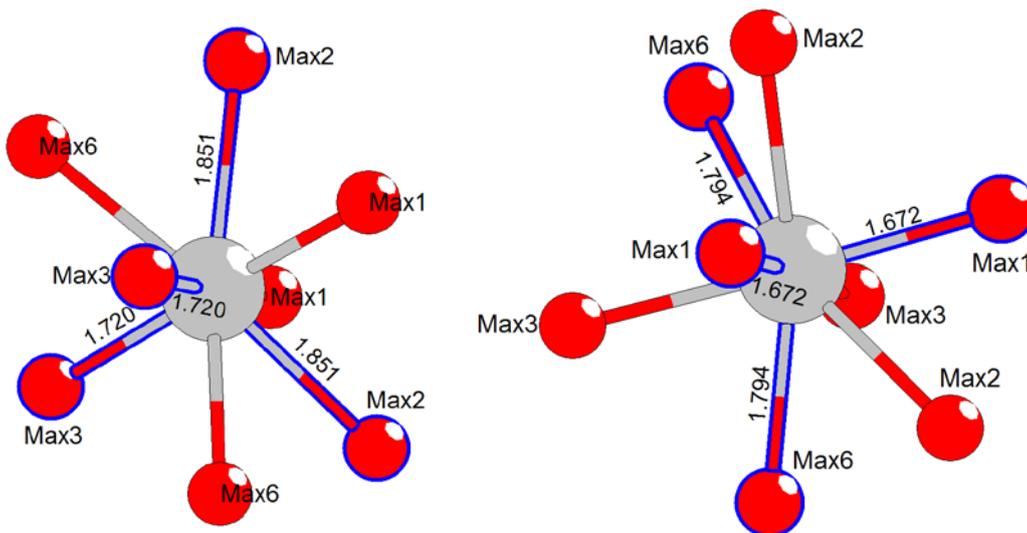
*In our example we can make a tetrahedron from Max2 and Max3 as well as from Max1 and Max6 and thay have different bond lengths. The second tetraqhedron is a product of the false symmetry induced by additional translation symmetry mentioned above In our case it is difficult to say which one is better so we will exclude the second one because Max6 may be too weak maximum (maxima are numbered sequentially by their intensity).*

Start "Parameters → Atoms → New" and include the maxima previously selected in Diamond (Max2 and Max3 in our case) as O1 and O2.

Run refinement

*Refinement converges with Rp=13%, R=6%*

Start "File → Structure → Save As" and make a backup copy of the average structure, for instance KSm_ave
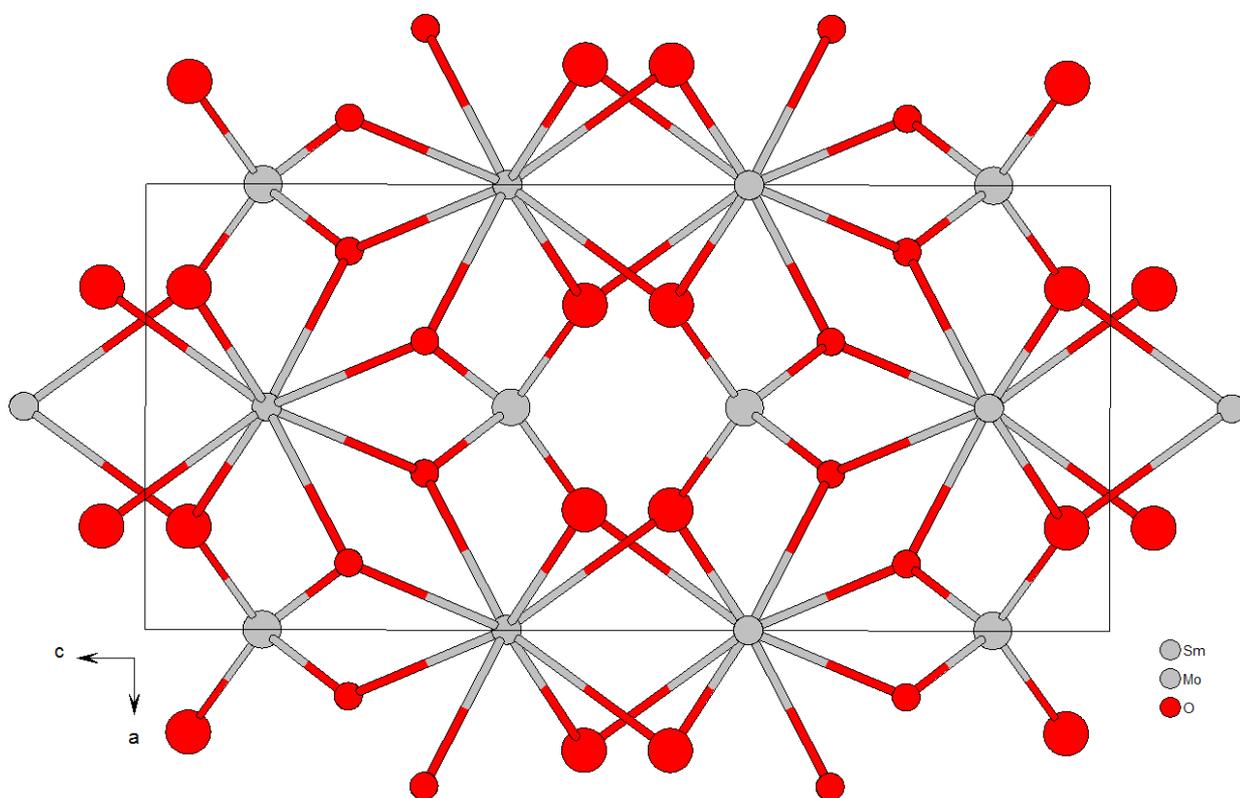
## 8. Refinement of modulated structure

Start "Edit atoms" and set one position modulation wave for Sm1

Run refinement

Add one position modulation wave for Mo1

Run refinement

Refinement converges with Rp=12%, R(main)=5% and R(sat)=15%.

Open options for Fourier, select observed Fourier map

In the page "Scope" choose "by a central point", clear the checkbox "Use default map orientation", select first axis x1 and second axis x4 (i.e. the x1-x4 section), type Sm1 for the Center and "2 1 1" for the section scope.
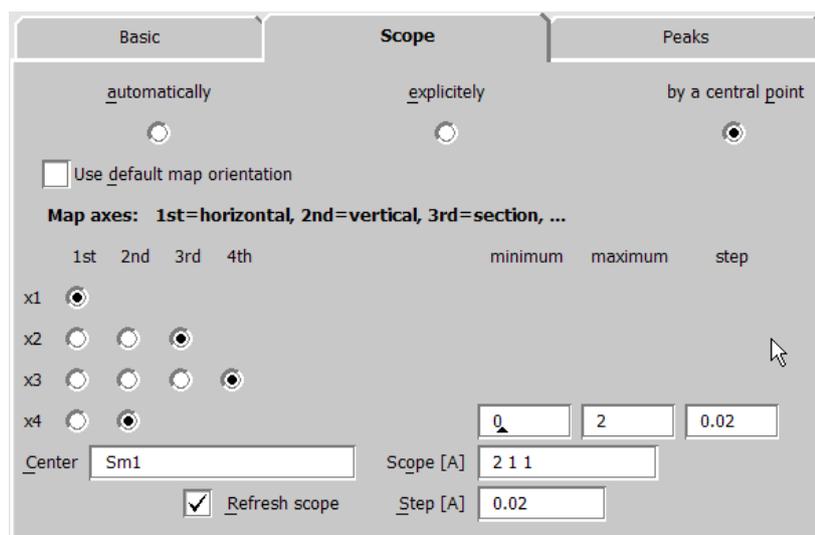


Run Fourier

Run Contour, press "New plot", OK

Press "Sum on" and check "x2" and "x3"

Press "Atom edit" and add Sm1 to the list of atoms which will be indicated in the map

The resulting modulation function of Sm1 looks continuously. However, when we follow the line by mouse cursor the Density window in the lower right corner displays fluctuation of density between 68 and 51 $e^-A^{-3}$. Because position of potassium does not appear in the average structure and the occupation of samarium is lower than 0.5 we assume that samarium mixes with potassium. In modulated structure, classical disorder is often replaced by distribution of elements along x4. We can speculate that the area with lower electron density corresponds to the interval (in x4) where potassium exists instead of samarium. However, better background for this consideration will be difference Fourier map.
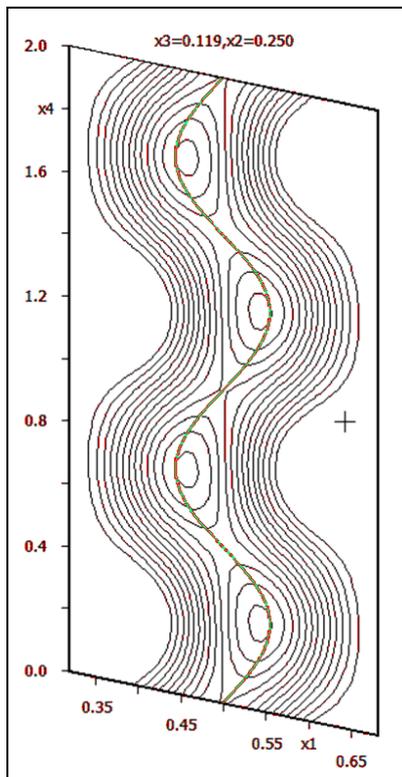
*[On the screen: Contour window]*
Press "New plot", select "Calculate new ones", OK
In Fourier commands select difference Fourier map, OK
In Contour window that has automatically appeared press "Sum ON" and make summation along "x3" and "x2"
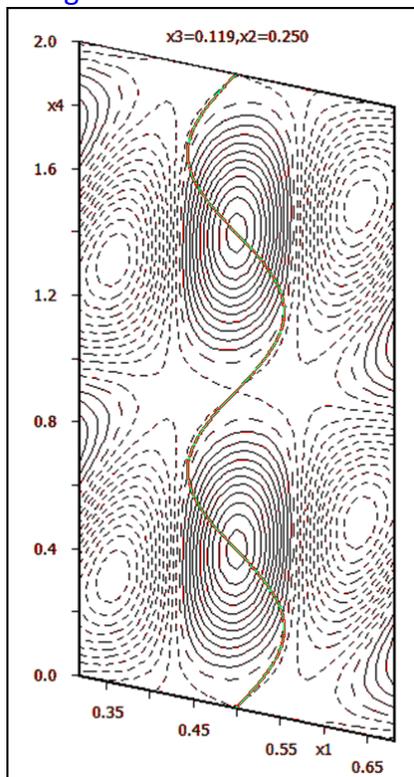


*The positive maximum in the difference map indicates region with lack of electron density. This is the area where fully occupied samarium should be present (instead of the partially*

*occupied one). From this map we can conclude that the definition interval of potassium has centre in x4=0 and width 0.5. Samarium would occupy a complementary interval with centre at x4=0.5 and width 0.5.*

Leave Contour and start "Edit atoms"
Right-click Sm1 and select "Split atomic position"
In the dialogue that follows:
Type "K1" for "Name of the split atom"
Select "K" for "Atomic type"
Type "0.5" for "Relative occupancy of the split atom"
Type "0 0 0" for "Shift of the split atom"
Clear "Generate restrict command for Refine"
Apply

**Split atomic position for : Sm1**

| | |
|---|---|
| Name of the split atom: | K1 |
| Atomic type | K |
| Relative occupancy of the split atom: | 0.5 |
| Shift of the split atom: | 0 0 0 |

☐ Generate restrict commands for REFINE
☐ Restrict the split atoms to have identical positions

Avoid    Quit    Apply
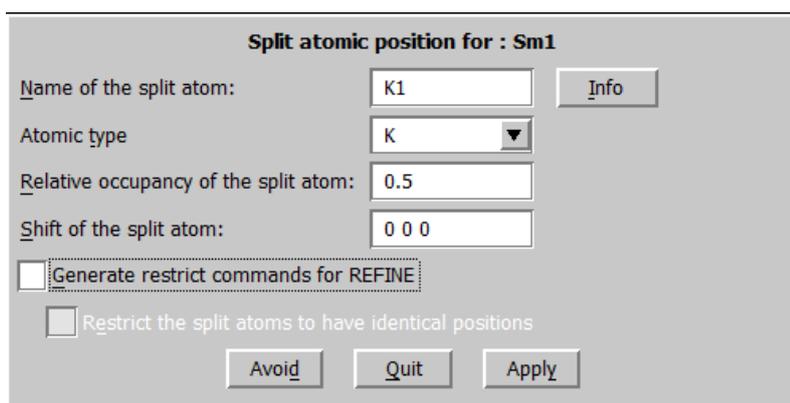
*By this way we have duplicated Sm1, assigned the name K1 and chemical type K to the duplicated atom and reduced occupancy of both atoms by 1/2.*

*[On the screen: list of atoms in "Edit atoms"]*

Select Sm1 and K1, go to "Action → Edit/define atoms" and check "crenel"

| Define | Edit |
|---|---|

Type [    ]

**ADP parameter(s):**          **Modulation waves:**

◉ isotropic          Occupancy  1    Use:  ☑ crenel

○ harmonic          Position  1    Use:  ☐ saw-tooth    ☐ zig-zag

○ anharmonic          **Type of modulation functions:**

○ Use TLS          ◉ harmonics (0,1)

          ○ harmonics (0,1) orthogonalized to crenel interval

          ○ Legendre polynomials in crenel interval

          ○ x-harmonics in crenel interval

          Selection limit for harmonics: [    ]
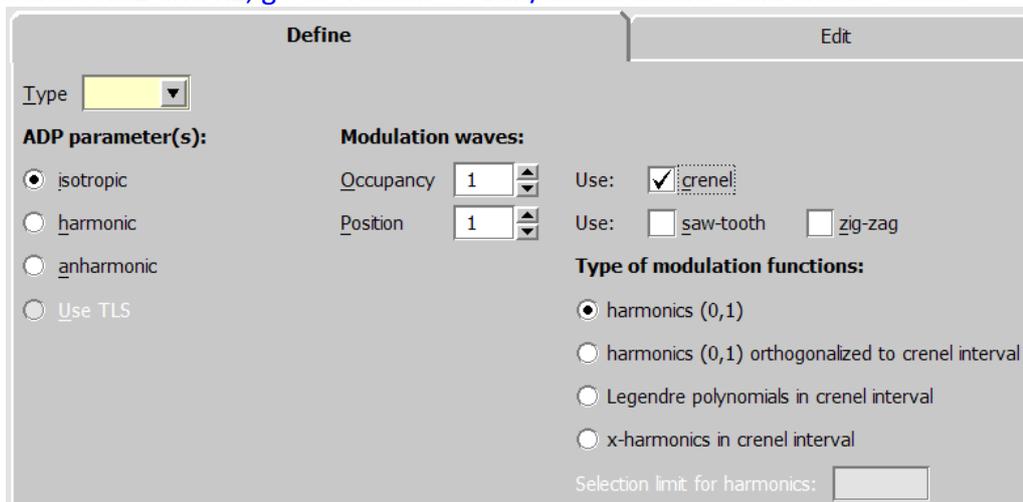
Switch to the page "Edit", ensure that "ai" = 0.5 and its refinement is disabled
Press "Occupancy"
Type 0.5 for "delta" and 0.5 for x40, OK, OK
*By this way we have defined two identical crenel functions for both atoms Sm1 and K1. Note that the occupancy "ai" was recalculated back from 0.25 to 0.5*
*[On the screen: list of atoms in "Edit atoms"]*

Unselect Sm1

Right-click K1, go to "Action → Edit/define atoms"

Switch to page "Edit"; press "Occupancy", change x40 from 0.5 to 0; OK; OK

Close "Edit atoms" and save changes

Start Contour and plot the previous difference Fourier map

Make summation

Press "Atoms edit and add K1 to the list"

Make the same for observed Fourier map

*The section shows complementary modulation functions of Sm1 and K1*
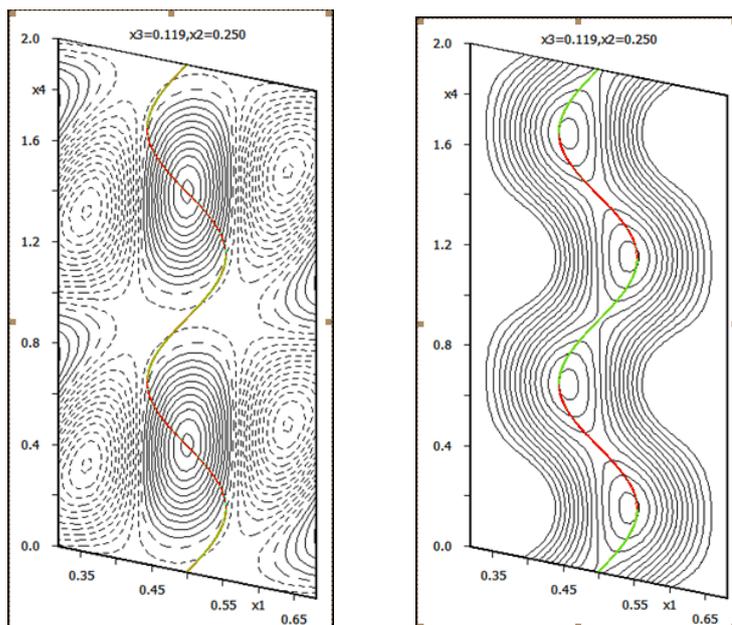


Open Refinement options, go to the page "Various", press Restrictions

In the textbox type "Sm1 K1"

Check "Coordinates", "Modulations" and "ADP parameters"

For "Occupancies" select "not restricted"; press "Add"

*This restriction makes the two atoms Sm1 and K1 identical except the definition interval in x4*

Leave Refinement options, save them without starting refinement (YES)

Create backup copy "KSm_crenel"

Run Refine

*The refinement converges with Rp=6%, R(main)=2% and R(sat)=6.5%*

Add one position modulation wave for O1 and O2

Start "Parameters → Powder", go to the page "Cell" and enable refinement of "q1" and "q2"

*The components of q vector were fixed because they can be refined only when modulation waves are present due to the option "Use only satellites corresponding to existing modulation waves"*

Run Refine

*The refinement converges with Rp=6%, R(main)=2% and R(sat)=5.5%*

Plot observed and difference Fourier map for Sm1

| x1-x4 difference | x1-x4 observed | x2-x4 observed |
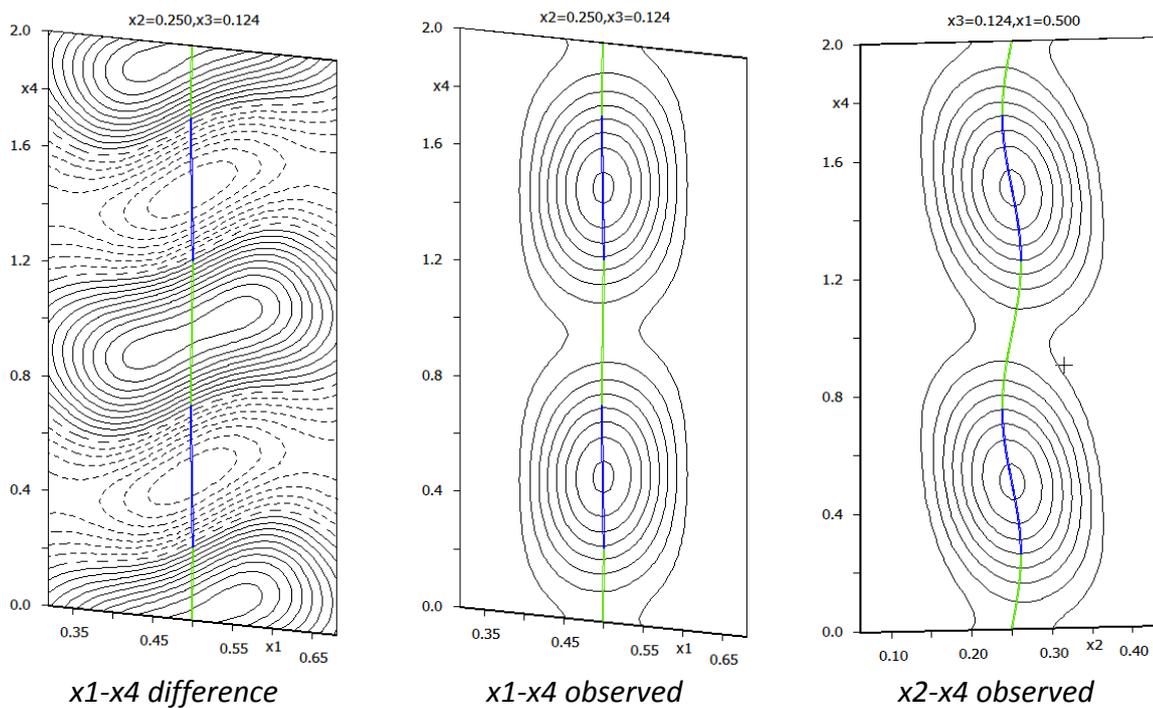
*Contour step in the difference map is 0.1. The residua in the difference Fourier map are smaller and in different places than before. The position modulation now occurs in x2-x4 section. The previously observed modulation in the x1-x4 section was caused by pseudosymmetry.*

## 9. Better profile description

Create backup copy KSm_mod
Start "Tools → Powder → Profile viewer" and examine the first two peaks of the profile
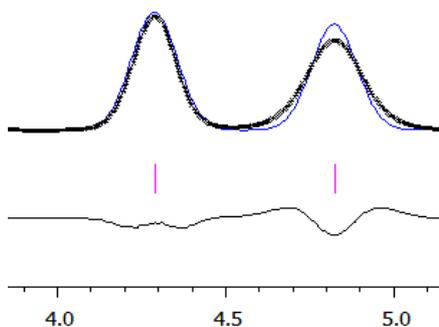


*The profile width can be probably better described with anisotropic strain broadening*
Start "Parameters → Powder", go to the page "Profile"
Select "Tensor method"
Press "Edit tensor parameters"
Press "Refine all"
Leave "Powder options"
Run Refine
In case that Singularity warning occurs select "Continue refine"
In case the refinement cannot converge note the St parameter responsible for oscillations and fix it to zero in "Edit tensor parameters".
*The refinement converges with Rp=3.8%, R(main)=1.8% and R(sat)=2.9%*

Check Powder profile
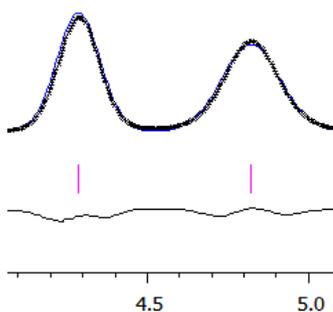


The width of reflections is now described correctly
Open "Powder options", go to the page "Profile"
Select "Pseudo-Voight" and activate refinement of "Lx" and "Ly"
Run Refine
*The refinement converges with Rp=3.0%, R(main)=1.4% and R(sat)=2.1%*
*Some St tensor component may cause oscillations. A careful analysis would be needed to select the St components really necessary for profile description. We can for instance fix the components with low parameter-to-sigma ratio (using the button "Show p/sig(p)" to see the ratio)*
Plot difference Fourier for Sm1, section x1-x4
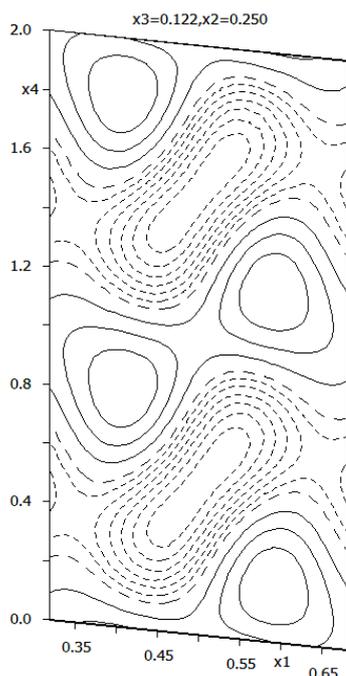


*The section now displays very small residual density. Depending on the fixed St components the resulting section may look differently.*


Start "Plot structure" and try to plot the structure in Diamond
*Sufficiently large area must be selected for the plot because in Diamond we can only plot the supplied atoms. No symmetry transformation (rotation as well as translation) is allowed in Diamond because it does not use modulation functions. The recommended way is to add atoms supplied by Jana2006 using button* *, connect them using button*  *and then make only selections and rotations.*
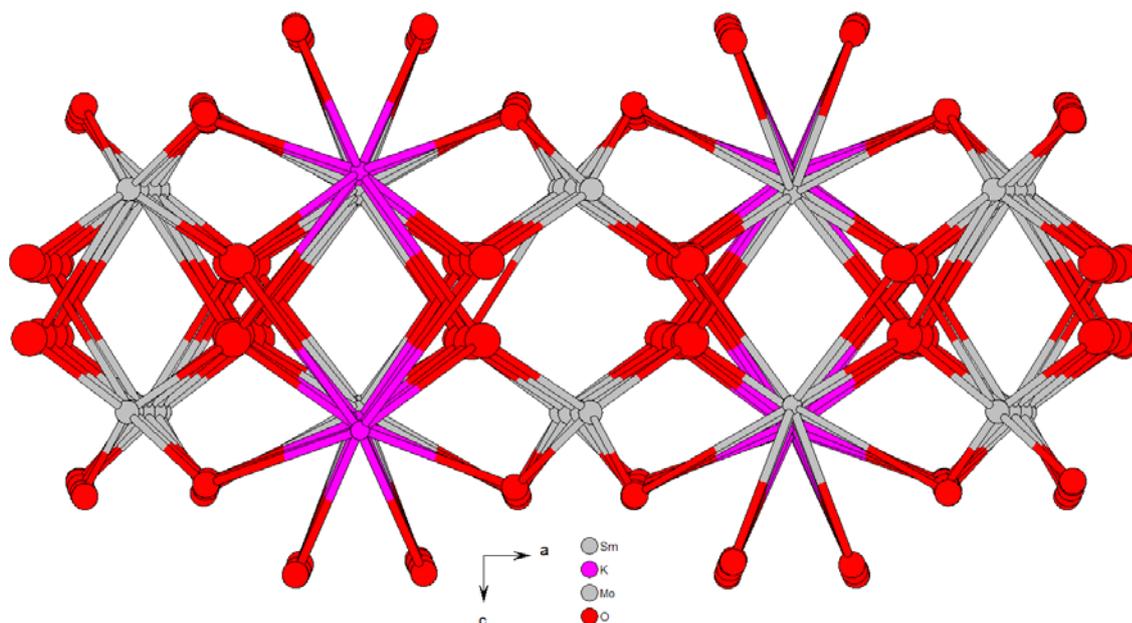
### Alternatives

*The fact that the Sm/K position is half occupied by samarium and potassium makes its scattering power almost identical with Mo atoms. This induces a pseudo-translation symmetry (0,0,1/2) which strongly affects the solution. The chosen approach is not the only possible one. Another way would be to start – after completing the average structure – with refinement of position modulation of both Mo1 and Sm1 together with harmonic occupation wave of samarium. With this way the "false" modulation in the x1-x4 section would not appear.*

# Example 7.1: Ephedrine

**Commensurately modulated structure**

**Revised: 26 May 2012**

**C$_{10}$H$_{16}$NOCl**
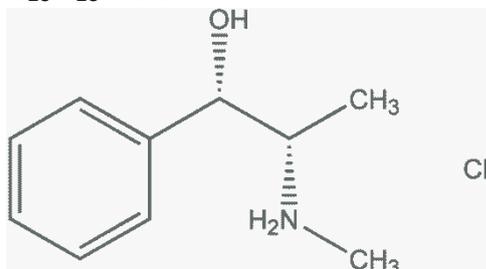


Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: Ehpedrine.hkl, Ehpedrine.ins
Frame scaling, absorption correction: done

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click Ephedrine

2. ***Import Wizard***
   Select "reflection file corrected for LP and absorption"; NEXT
   Select "SHELX on I"; File "Ephedrine.hkl" NEXT
   *The measurement was done in a supercell using three indices*
   *[On the screen: complete/correct experimental parameters]*
   Fill supercell parameters as used in data collection. They can be copied (Ctrl-C) from the file
   Ephedrine.ins and pasted (Ctrl-V) to the "Cell parameters" textbox; NEXT
   *[On the screen: Define the reference cell/split by twinning]*
   Change target dimension for 4
   Define modulation vector 0 0 1/4
   Press "Define transformation matrix" and fill the matrix array by

   1 0 0 0
   0 1 0 0
   0 0 1/4 0
   0 0 0 1

   NEXT; FINISH

3. ***Data Repository***
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. **Symmetry Wizard**
   *[On the screen: "Define space group" window]*
   Press "Make test"
   *[On the screen: "Tolerances for crystal system recognition".]*
   Leave all settings default; NEXT
   [On the screen: Select Laue symmetry]
   Select Orthorhombic Laue symmetry; NEXT
   *[On the screen: Select cell centering]*
   Select P centered unit cell; NEXT
   *[On the screen: Select space group]*
   Select P212121; NEXT
   *[On the screen: Select superspace group]*
   P212121(00g)000
   *[On the screen: Final step of the superspace test]*
   Accept the superspace group transformed into the original cell: P212121(00g)000; FINISH
   *[On the screen: Define superspace group]*
   OK

5. **Creating refinement reflection file**
   *In this step we have M95 (i.e. the data from diffractometer converted to Jana format) and symmetry. For refinement we need M90 containing data set merged by symmetry and with discarded extinct reflections.*
   NEXT to confirm threshold 3sigma
   *[On the screen: settings for merging of reflections]*
   Leave all settings default; NEXT
   Accept the data block; FINISH

6. **Structure Solution Wizard**
   *[On the screen: window of Structure solution]*
   In "Formula" textbox type list of chemical elements for $C_{10}H_{16}NOCl$: C H N O Cl
   Select "Superflip", "Peaks from Jana2006"; OK
   *[On the screen: window of Superflip replaced later on by listing of Superflip]*
   *Superflip converges (after noise suppression) with R value between 20 and 30%.*
   *Note that we don't fix random seed and the exact result of Superflip will differ between runs*
   Close the listing of Superflip
   Press "Accept the result"

7. **Verification of the structure solution**
   Start EditM50; go to page "Composition"; press "Formula from M40"
   *[On the screen: Information about formula]*
   *It should display formula C10 H0 N O Cl which means that all atoms except hydrogen atoms were localized. In the case that some atoms are missing they can be found from subsequent refinement and difference Fourier maps. In the case that the Superflip gives some additional false atoms they usually are detected in the refinement as atoms having non-realistic (too high) isotropic ADP and they will be automatically eliminated by putting their occupancy to zero. The atoms being eliminated can be later deleted in "Edit atoms" with help of button "Select rejected".*
   Start "Plot structure" to check assignment of chemical types (by comparing with the

structure formula given at the beginning of this chapter). Use the option "Draw average structure".
*If some atom in the plot looks like a false maximum it should be deleted by "Atoms edit"*

8. **Refinement of the modulated structure**
   Start Refine with default parameters.
   *You should get R values about 9.3%, 7.5%, 7.6% and 31.2%.*
   *If some atoms are missing they should be found in difference Fourier, added to the structure model and the refinement should be repeated*
   Start "Edit atoms", select all atoms, change ADP to harmonic ones and repeat the refinement.
   *You should get R values about 8.4%, 6.4%, 6.5% and 31.4%.*

9. **Adding hydrogen atoms**
   Start "Edit atoms", select all carbon and nitrogen atoms and add hydrogen atoms automatically.
   *For nitrogen atoms automatic procedure is not reliable, hydrogen atoms will be added manually*
   *[On the screen: Adding of hydrogen atoms for N1]*
   Select "Tetrahedric", change number of neighbors to 2
   *You can verify the neighbors by focusing the textbox with the first neighbor and clicking "Select neighbors"*
   Define names of hydrogens, for instance H1N1 and H2N1
   "Apply"

   *Run EditM50 and go to page Composition, press Formula from M40. The found formula should be C10 H15 N O Cl which means that one hydrogen atom bounded to O is missing. This atom will be localized later from the Fourier map.*
   Run refinement
   *Refinement converges with R value about 6.2%, 3.4%, 4.9% and 31.6%.*

10. **Localization of the remaining hydrogen atom**
    Right-click the icon of Fourier
    In page "Basic" select "Map type" as "F(obs)-F(calc) – difference Fourier"
    In page "Scope" select "Automatically" and use the default parameters for "Independent parallelepiped"
    Run Fourier.
    *[On the screen: Do you want to start the procedure for including of new atoms?]*
    Answer yes.
    *One of the dominating maxima should have a reasonable hydrogen distance to the oxygen atom O1. Add it as a new hydrogen atom (named e.g. H1O1).*
    Right-click the icon of Refine; select page "Various"; press the button "Keep commands"
    Restrict ADP parameter of the newly introduced hydrogen atom.
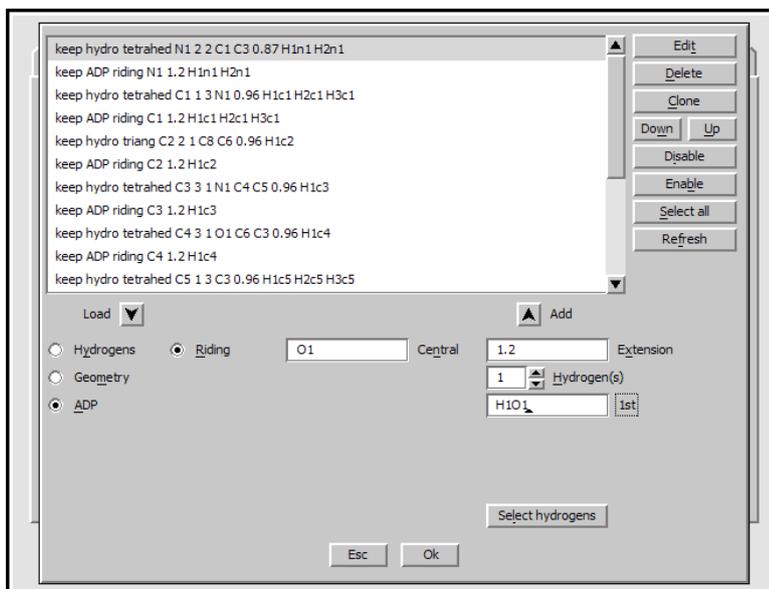
Add the new keep command and start the refinement procedure.

*Refinement converges with R value about 6.0%, 3.2%, 4.9% and 31.60%.*

Verify by plotting that the hydrogen in OH has a reasonable position

Save the structure with a new name e.g. "Ephedrine-incomm" but continue with the old

one. *This structure will be used for a final comparison with two commensurate cases.*

## 11. *Introduction of the commensurate option and twinning*

Start EditM50, go to page Cell.

Select "Commensurate case" and "Use simple supercell"

In text box "Supercell" type "1 1 4"

Press button: "Select supercell group" and select Tzero = 0 + n/4 which represent
monoclinic symmetry with two-fold screw axis along a.

*As the supercell symmetry is lower than orthorhombic we may have two twinning domains
related either by two fold axis along b or along c direction.*

Select twinning and define the twinning matrix as a 180 degrees rotation along c axis.

*The selection of the commensurate model leads to different Laue symmetry and different
extinctions and therefore we should generally redo the creation of the reflection file for the
refinement. But for better comparison of tested models we shall skip this point.*

NO in order to skip re-creation of the reflection file

Run Refine.

*Refinement converges with R value about 3.8%, 2.9%, 4.1 and 8.0%.*

Save the structure with a new name e.g. "Ephedrine-comm-1" but continue with the old
one.

*This structure will be used for a final comparison with two commensurate cases.*

## 12. *Commensurate case for $t_0=1/16$*

*Repeat the point 11 for $t_0=1/16$.*

NO in order to skip re-creation of the reflection file

Run Refine.

*Refinement converges with R value about 3.8%, 2.9%, 4.1 and 8.0%.*

*The result is similar like in the previous commensurate model*

Save the structure with a new name e.g. "Ephedrine-comm-2"

**13. Incommensurate model with overlap option**

Go to "File → Structure → open" and select files containing the incommensurate refinement.

*In the incommensurate refinement we are not taking into account the fact that main reflections are overlapped with satellites of fourth order and the satellites of the first order are overlapped with those of the third order. Even more serious are overlaps of the second order satellites as they have in average similar intensities.*

*For the commensurate structure the program calculates structure factors as a summation over really existing t sections, taking into account $t_0$ value and with symmetry elements being closed in the supercell. Thus we get the same result for reflections:*

*(h,k,l,m), (h,k,l+1,m-4), (h,k,l-1,m+4) e.t.c.*

*On the other hand, in incommensurate structure model overlaps must be determined based on the proximity of reflection angles*

Start Refinement options
Select page "Modulation" and activate overlap option "Closest reflections"; OK
Run Refinement

*Refinement converges with R value about 3.8%, 2.9%, 4.1 and 8.0%.*


*Conclusion: Modulations are not very strong and therefore all three models give very similar results*

*Another possible steps:*

*- for selected model second modulation wave can be added, but it has almost no influence on results*

*- we can deactivate twinning and verify by refinement if it was really needed (it was!)*

*- hydrogen of OH group probably should not have individual modulation waves. They can be made the same like modulations of the parent atom in "Refinement options → page Various → Restrictions"*

*- In the incommensurate refinement the overlaps detected by the program can be printed in the refinement listing if we activate the option in "Refinement options → page Select/Listing → Print twin/overlap details"*

# Example 7.2: CrPOcom

**Solution of the low temperature commensurate phase of $Cr_2P_2O_7$.**

**Revised: 5 March 2015**

**$Cr_2P_2O_7$**

Single crystal data measured with Oxford Diffraction four-cycle diffractometer
Input files: CrPOcom.hkl, CrPOcom_red.sum
Frame scaling, absorption correction: done with software of the diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click CrPOcom

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Define basic input file: select Input from "sum" file; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   Use default tolerances for crystal system recognition
   Select monoclinic Laue symmetry
   Select C centering
   Select space group C2/m
   Select superspace group C2/m(a0g)0s
   Accept the superspace group in the original cell

5. *Creating refinement reflection file*
   Follow default steps of the wizard

6. *Structure solution wizard*
   Type the formula Cr2 P2 O7, two formula units
   Select "Superflip" and "Peaks from Jana2006"; "Run solution"
   *Superflip converges with R around 25%, confirms the selected superspace group*

7. ***Workaround to get the same atomic positions like in this cookbook***
*Superflip returns arbitrary symmetry equivalent origin position. This would complicate reading of the cookbook because atomic positions and Fourier sections could be different (shifted, transformed) than it is described in the text. At this point, we shall use a saved Superflip solution compatible with the cookbook:*
With your file manager:
copy superflip.m40 to jobname.m40 ("jobname" is name of your current job)
copy superflip.m80 to jobname.m80
copy superflip.m81 to jobname.m81
*Jana2006 can be open during copying as it always unlocks the files when going to the basic window*
*M40 contains structure model from Superflip, M80 contains structure factors found by Superflip, M81 is the electron density map calculated from M80*

Plot the average structure with Diamond
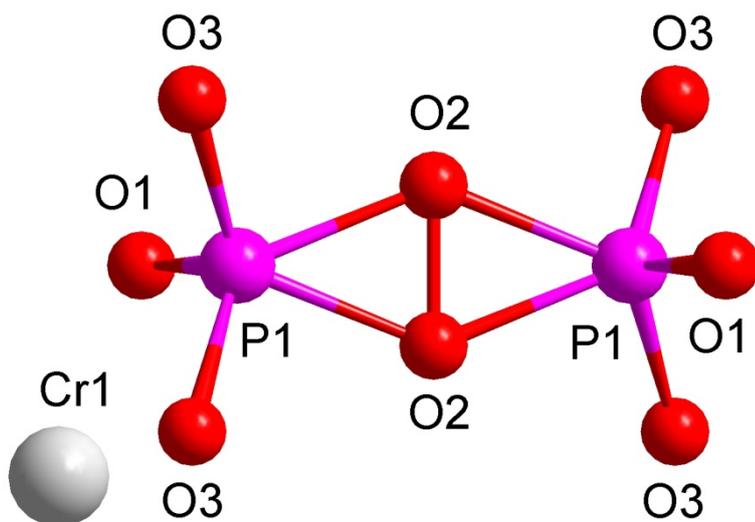


*From the plot it is clear that the two positions of the bridging oxygen O2 should be separated in the modulated structure with a crenel function*

8. ***Inspecting modulation functions returned by Superflip***
In "Fourier commands" set map type "F(obs)-Fourier"; scope by central point; center O2; map axes x2,x4,x1,x3; Scope 1 4 1; Step 0.05; OK; run Fourier
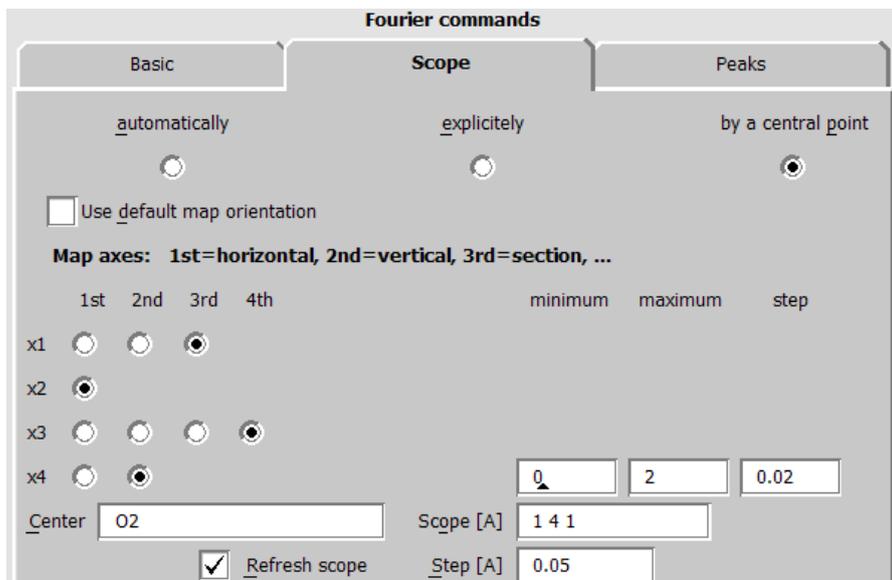
Plot the section in Contour
Use "Sum on" to project all the sections into one
Use "Atoms edit" (in Contour) and "Atoms ON" to see modulation function of O2
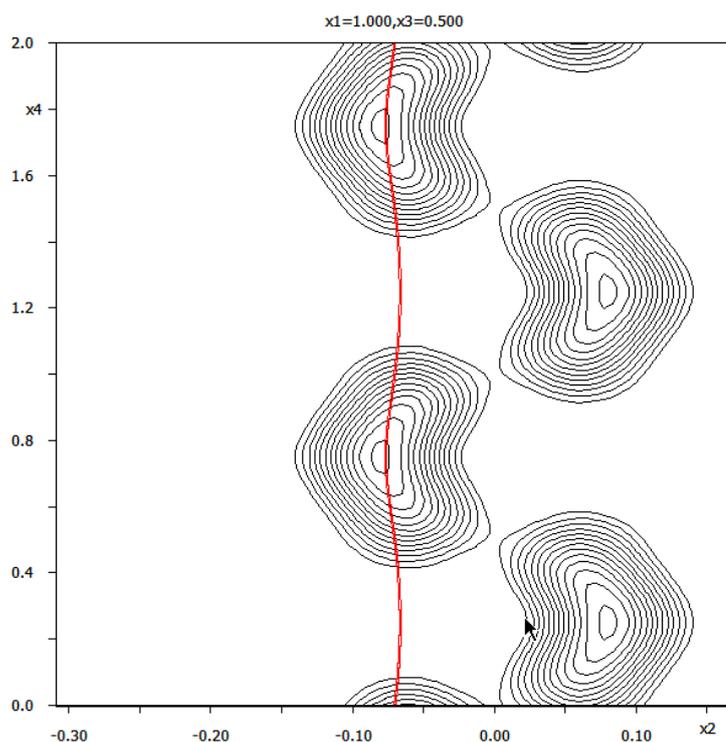


*Oxygen O2 has x2=-0.07, its symmetry equivalent position has x2=+0.07. Therefore we can define a crenel function of the width 0.5 and the centre 0.75 which will be transformed by the symmetry to the crenel function with the same width, the centre 0.25 and x2=+0.07. This will describe "skipping" of the bridging oxygen between two positions separated by the shift in x4.*

Leave Contour, start "Edit atoms"

Edit O2: in "Define" page check "crenel" (it will add one occupation wave)
in "Edit" page press the button "Occupancy", set delta=0.5 and x40=0.75
Leave Edit atoms (save the results)
Plot the same section with Contour (with "Sum ON")
In "Atoms edit" (of Contour) add atoms O2#s4t0,0,0 with color Blue



x1=1.000,x3=0.500
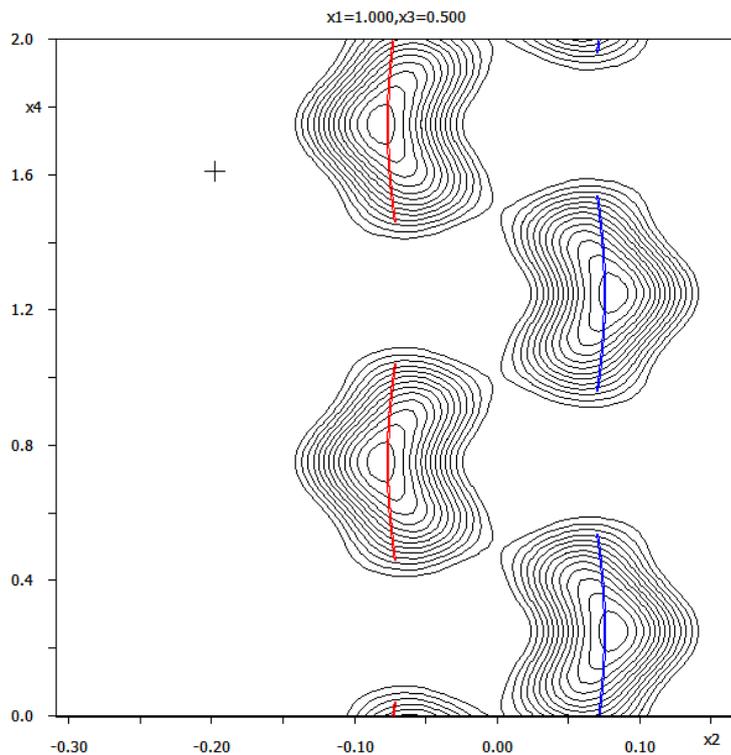
*The Contour plot now shows the two crenel functions related by symmetry operation
x1 -x2 x3 x4+1/2 combined with the position modulation wave found previously with
Superflip*

Using the button "New plot" in Contour plot similar x2-x4 sections for P1

x1=0.809,x3=0.576
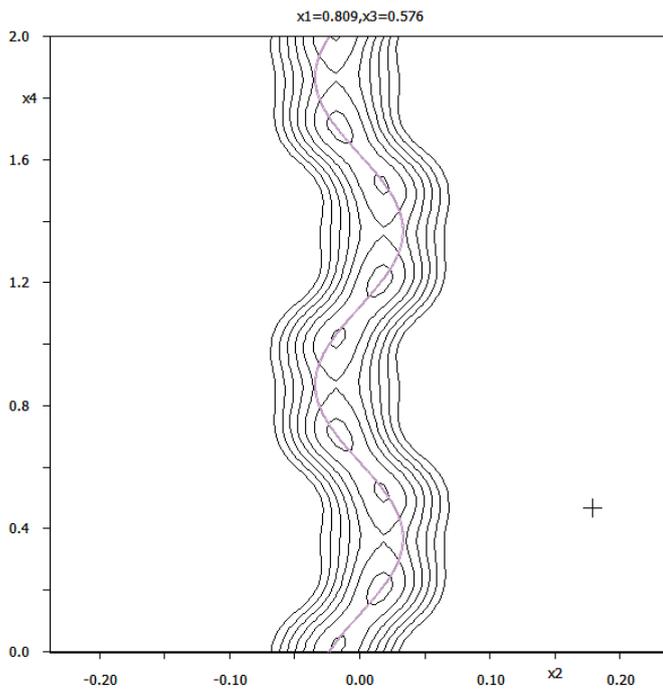
*P1 needs more modulation waves (will be added later)*

Using the button "New plot" in Contour plot similar x1-x4 sections for Cr1



x2=-0.187,x3=0.000
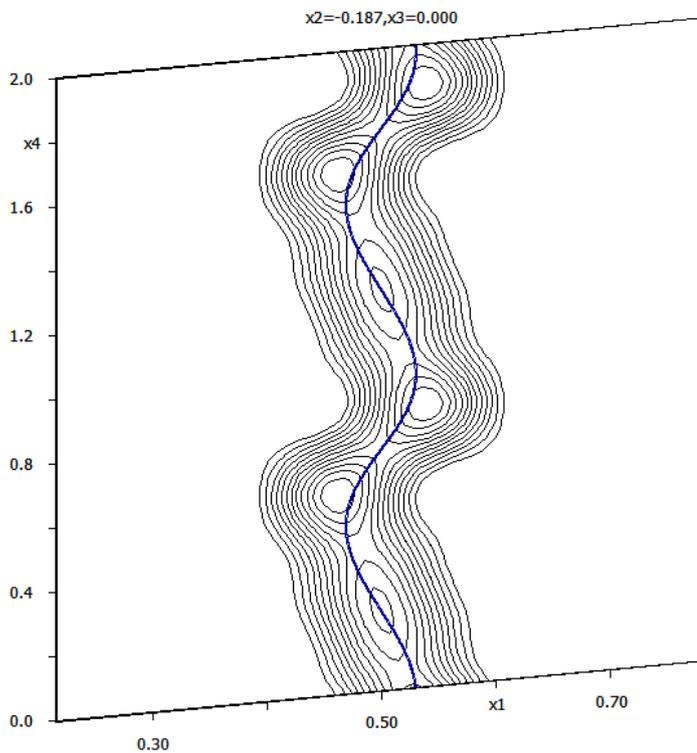
*Cr1 should be described with sawtooth function. Crenel function for Cr1 will have centre 0.25 and width 1.*

Similarly like for O2 define crenel function for Cr1: x40 = 0.25, delta = 1

## Plot the same section with Contour

*The modulation function of Cr1 has the same shape like before, because the crenel function defined in a full interval is combined with position modulation found from Superflip electron density map.Without this combination the modulation function would be s straight vertical line. This line will take the inclination along the Fourier maximum later on after introducing and refining Legendre polynomials.*

## Using the button "New plot" in Contour plot similar x2-x4 sections for O1
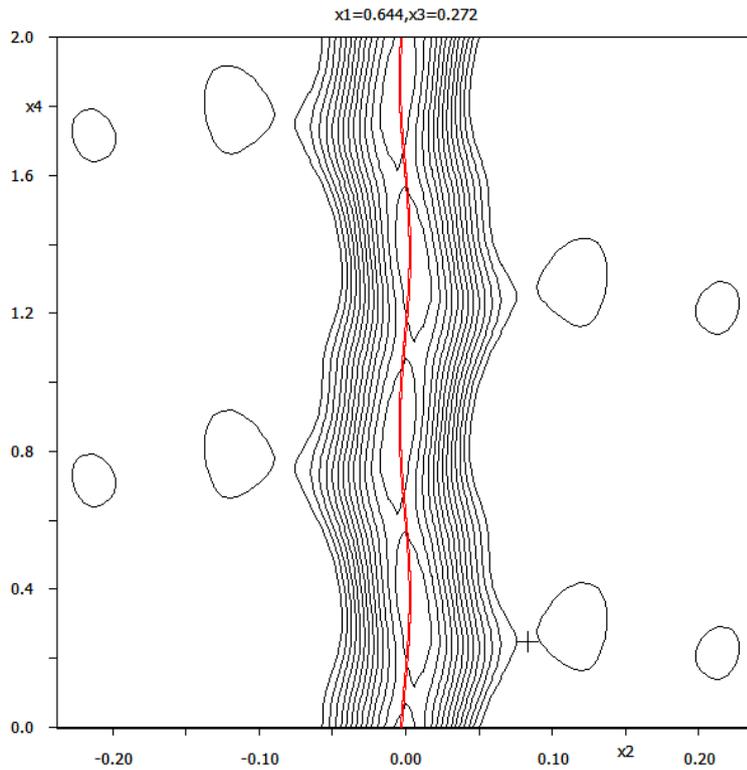


*O1 has no discontinuity*

Using the button "New plot" in Contour plot similar x1-x4 sections for O3
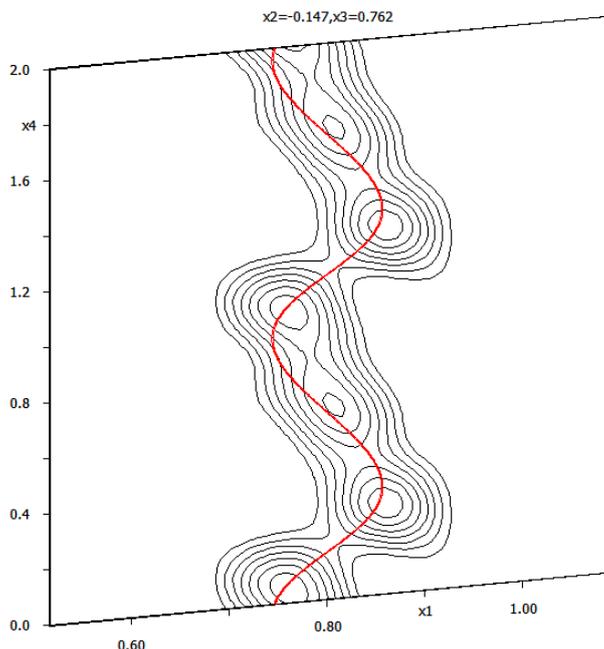


O3 should be described with sawtooth function.
Similarly like for O2 define crenel function for O3: x40 = 0.69, delta = 1



9. **Legendre polynomials**

*With commensurate structures, crenel function can be used but its centre and width cannot be refined because modulation function has only a few definition points.*

*Crenel function refined in a limited interval can be easily combined with position modulation functions expressed by Legendre polynomials. The first three coefficients of such modulation wave describe a straight line; the other coefficients make it wavy.*

*When initial position modulation is already known (in our case it has been found from the Superflip electron density), Jana2006 fits the coefficients of the Legendre polynomials to describe similar shape like the original modulation function. For this fitting centre and width of crenel function must be already known. Thus, we can obtain quite different shape of modulation function when using two different ways of definition of crenel and Legendre: (1) activation of crenel – definition of its centre and width – activation of Legendre (CORRECT); (2) activation of crenel - activation of Legendre - definition of crenel centre and width (INCORRECT). In our case, the centres and widths have been already defined and we can activate Legendre.*

"File → Save As" to make a backup copy
Start "Edit atoms"
Double-click Cr1

Select "Legendre polynomials in crenel interval"
Go to O2; Select "Legendre polynomials in crenel interval"
Go to O3; Select "Legendre polynomials in crenel interval"
OK; OK; YES to save changes
Start "Contour"
Plot the corresponding sections for Cr1, O2 and O3 to see the initial fit of Legendre polynomials
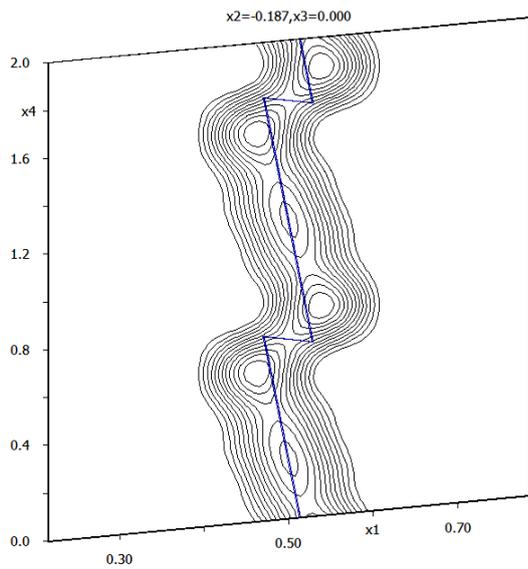


Cr1
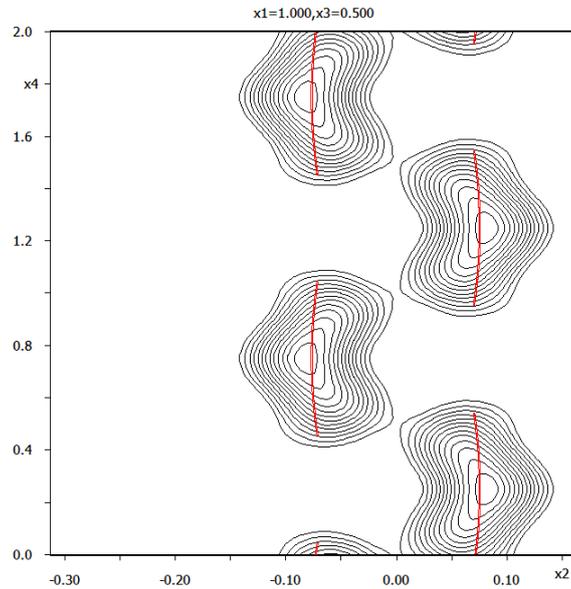


O2
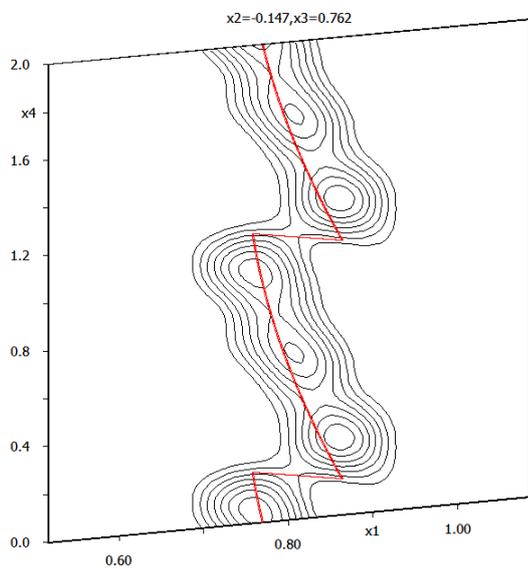


O3

### 10. Refinement

Start "Editm50": check "Commensurate case", supercell 3 1 2, Tzero = 0
Follow wizard for creating the refinement reflection file
Start Refinement commads: 100 cycles, damping 0.25
Refine
*Refinement converges with 21%, 11%, 18%, 47% and 48% for all, main, $1^{st}$ order, $2^{nd}$ order and $3^{rd}$ order. Some Uiso are negative.*
Add the second position modulation wave for all atoms except O2
Refinement commands: damping 0.5
Refine
*Refinement converges with 9%, 5%, 5%, 16% and 46% for all, main, $1^{st}$ order, $2^{nd}$ order and $3^{rd}$ order. All Uiso are now positive.*
Define harmonic ADP for all atoms
Refine
Contour: plot the sections for O2, O3 and Cr1



O2                                    O3                                    Cr1
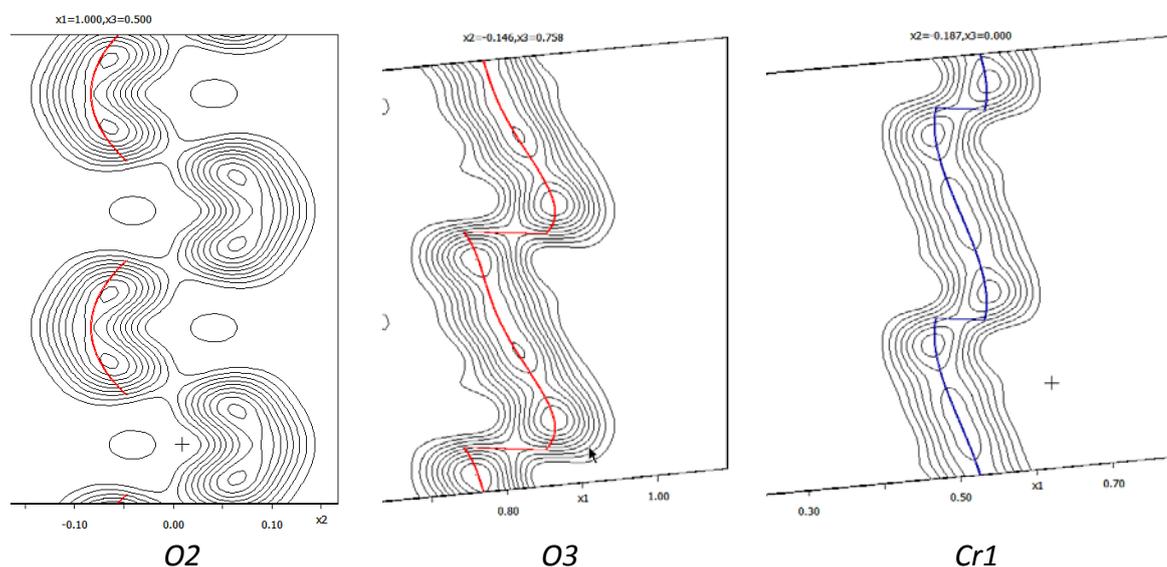
Add second position modulation wave for O2
Refine
At the message about singularity choose "Skip warnings"
Open refinement listing and use Use "Goto → Singularity report"
*For commensurate refinement, the second modulation wave for O2 cannot be used. It would introduce more refinement parameters than the structure would have in a supercell description.*
Delete the $2^{nd}$ position modulation wave for O2
Add the $3^{rd}$ position modulation wave for all atoms except O2
Refine (with skipped warnings)
*Adding the $3^{rd}$ position modulation wave improved significantly the fit!*
Look at the singularity report in the refinement listing
*The list of blocked parameters contains either "cos3" terms (for harmonic modulation) or "ort6" terms (for Legendre modulation). This means that the second halves of the third modulation waves are forbidden (for the same reason given for O2).*

"Refinement commands → Various → Fixed commands"
Use "Set individual" and set "?cos3[*]" to zero
Use "Set individual" and set "?ort6[*]" to zero
*"?" and "*" are wildcards.*
Refine
*Refinement converges without warning messages to 2.7%, 2.5%, 2.7%, 2.7% and 3.6% for all, main, 1st order, 2nd order and 3rd order (72 parameters).*

Add one harmonic ADP modulation wave for all atoms
Refine
*Refinement converges without warning messages to 2.1%, 2.2%, 1.9%, 2.1% and 2.6% for all, main, 1st order, 2nd order and 3rd order (104 parameters).*

"Parameters → Extinction": set isotropic Lorentzian extinction
Refine
*Refinement converges without warning messages to 2.1%, 2.1%, 1.9%, 2.1% and 2.5% for all, main, 1st order, 2nd order and 3rd order.*
*Number of refined parameters: 105*

## 11. Binding t40 of O2 and O3

Start Grapht.
With New/Edit: "Parameter to draw" position – y; "p" from -0.3 to 0.1; t from 0 to 0.2;
Name P1; step in t 0.0001
Press "New Item" and define the same for O2
Press "New Item" and define the same for O3
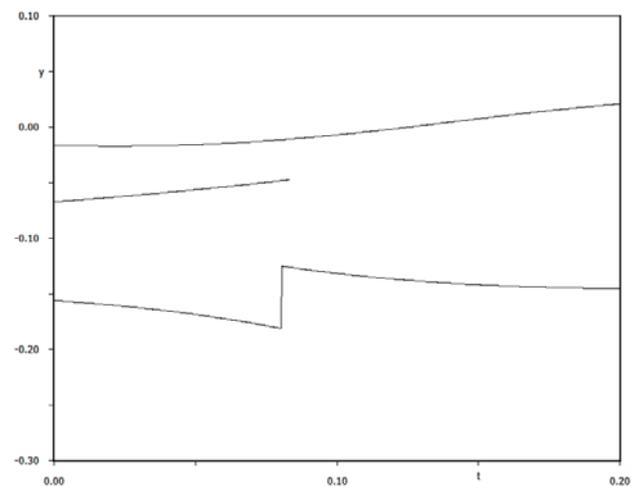


OK to plot

*The discontinuity in O3 occurs at slightly different t then the discontinuity in O2. However, they belong to the same P1 tetrahedron and therefore they must skip in phase.*
Close Grapht


Options for Dist: in "Basic" page set listing "With symmetry code"; in "Select atoms" page set central atom P1, neighbor atoms O2, O3.
Start Dist
Open the listing of Dist
*Atom P1 is coordinated with O2 and O3, both in the basic symmetry position x,y,z*
*The upper limit of the crenel interval should be the same when expressed in t:*
*tmax(O3) = tmax(O2)*
*t40(O3) + delta(O3)/2 = t40(O2) + delta(O2)/2*
*t40(O3) + 0.5 = t40(O2) + 0.25*
*t40(O3) = t40(O2) - 0.25*


Refinement commands: in page "Various" select "Equations" and define
t40[O3]=t40[O2]-0.25
Refine
*The R values are almost unchanged*
*An equivalent solution could be found with lower limits if the crenel interval (t40(O3) = t40(O2) + 0.25)*
Open refinement listing
Look at "Equations defined by user" where the user equation is expanded


Start Grapht and verify that the discontinuity in O2 nad O3 now occurs at the same t
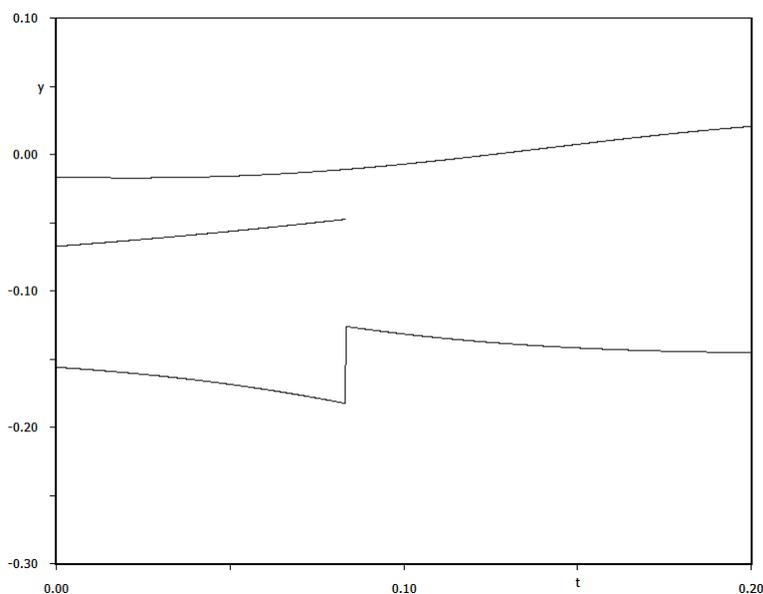
## 12. Transformation to supercell

Start "Tools → Transformations → Go to supercell structure"

Follow the wizard for creating refinement reflection file

Continue with the new (supercell) structure

EditM50: check cell parameters (3x1x2 supercell) and symmetry (I2/c)

Refinement commands: set 0 cycles

Refine

*Refinement (with zero cycles) confirms overall R value found previously in the commensurate model*

*Number of structure parameters is 151. This means we were able to get satisfactory results in commensurate refinement saving 46 parameters.*

*Supercell model can be used for plotting of the structure and for calculation of geometry*

"File → Structure → History": return to the commensurate model

"File → Save As": make a backup copy

Set three ADP modulation waves to all atoms

Refine – skip warnings

*The number of refined parameters is now much larger but no further improvement o R values occurs. By adding modulation waves and fixing forbidden components to zero we should finally reach the same number of structural parameters in the commensurate and supercell model.*

# Example 7.3: PhenanTin

**Commensurate and supercell descripton of a five-fold superstructure.**
**Revised: 5 March 2015**

**Bis(aquachlorotriphenyltin 1,10-phenantroline), $C_{150} H_{125} N_{10} O_5 Cl_5 Sn_5$, Z=4**

Single crystal data measured with Agilent four-cycle diffractometer SuperNova
Input files:
PhenanTin.hkl, PhenanTin.cif_od (diffraction data indexed in the supercell - see later)
phenantroline-no-symmetry.m45 (pattern molecule phenantroline)
phenantroline-no-symmetry.jpg
phenyl-no-symmetry.m45 (pattern molecule phenyl)
phenyl-no-symmetry.jpg
supercell_keep.txt (pre-prepared keep commands for supercell refinement)

Chemical diagram:
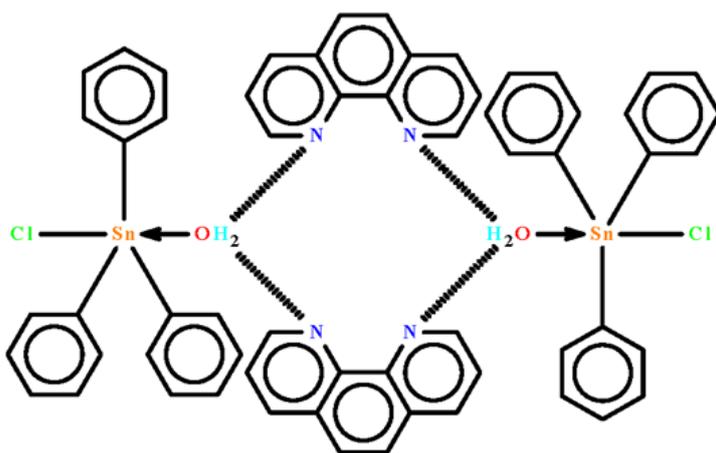


**Introduction**
Structure of this compound has been published in Journal of Science and Technology in the Tropics (2005), 1, 157-163, as a commensurately modulated structure. The data from Nonius KappaCCD diffractometer  contained strong main reflections and weak first and second order satellites with ratio of intensities 1000 : 0.157 : 0.075. Later on the compound has been remeasured with much more intensive source of Agilent's SuperNova. In the new experiment the satellites were strong and the structure could be solved in a five-fold supercell as a classical three-dimensional structure. This example uses data of SuperNova and compares possibilities of the commensurate and supercell structure refinement.
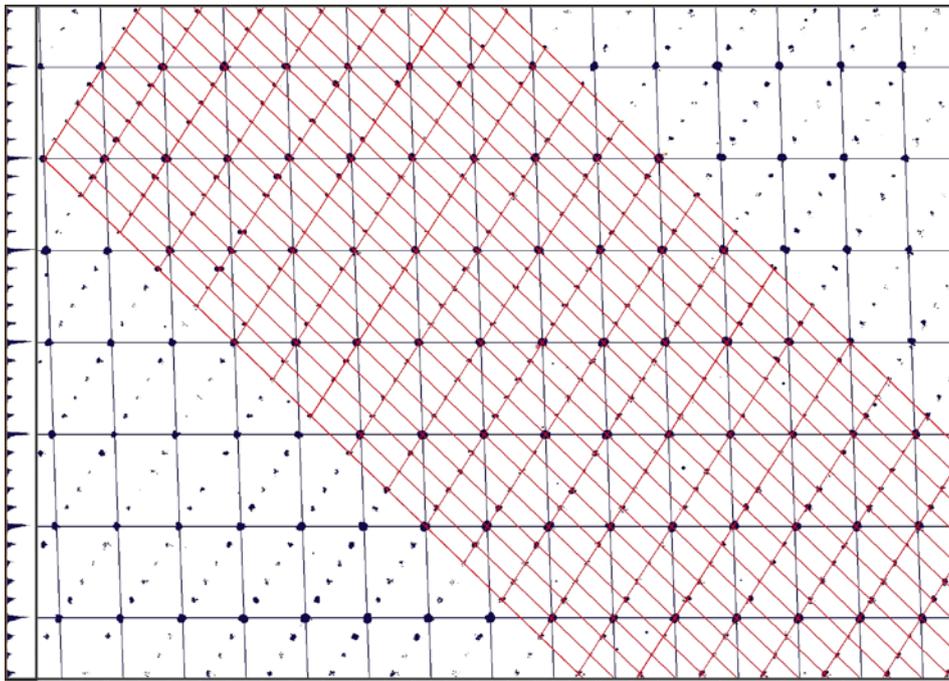
Reciprocal space with peak positions projected along b*. Black: unit cell for commensurate refinement; Red: unit cell for supercell refinement.

Relationship between unit cells in direct space:

$$\mathbf{T}_{comm->sup} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 3 & 0 & -2 \end{pmatrix}; \quad \mathbf{T}_{sup->comm} = \begin{pmatrix} 2/5 & 0 & 1/5 \\ 0 & -1 & 0 \\ 3/5 & 0 & -1/5 \end{pmatrix}$$

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click PhenanTin

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Define basic input file: select Input from "cif_od" file; OK
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *The line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   Use default tolerances for crystal system recognition
   Select monoclinic Laue symmetry
   Select P centering

Select space group P2$_1$/n

*Although it is not first in the list, FOM is almost the same like for P2/n and the button "Details" shows that the discarded reflections are very weak*

Accept the space group transformed into the original cell; FINISH

5. **Creating refinement reflection file**

Follow default steps of the wizard

*Rint ~ 4.8% for 24879 reflections*

6. **Structure solution wizard**

Type the formula C150 H125 N10 O5 Cl5 Sn5, four formula units

*Density should be 1.53 g.cm$^{-3}$*

Select "Superflip" and "Peaks from Jana2006"; "Run solution"

*Superflip converges with R around 20% and confirms the selected space group*

"Accept last solution" to leave the structure solution wizard

Plot the structure
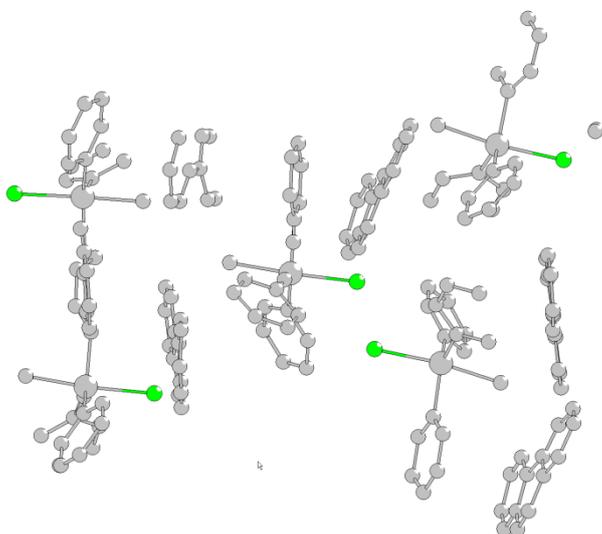


The structure model returned by charge flipping contains most of the expected structure and it could be finished by adding maxima from difference Fourier and possibly by applying geometry constraints imposed during the refinement. However, we would like to make commensurate refinement in order to see its pros and cons.

7. **Data import for commensurate refinement**

*As the structure handled in the 3d supercell cannot be simply transformed in the superspace, we have to re-create the structure. We will use the same job name.*

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click PhenanTin

YES to overwrite the existing job name

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction – CCD"; NEXT

Define basic input file: select Input from "cif_od" file; OK

*[On the screen: Complete/correct experimental parameters]*

Leave all settings unchanged; NEXT

*[On the screen: Define the reference cell/split by twinning]*

Change target dimension to 4

For "1st modulation vector" type 0.2 0 -0.2

*The modulation vector has several possible settings. For instance, the original publication used (0.2,0,0.8). However, the short q-vector as defined here is the most logical selection.*

Press "Define transformation matrix"

*[On the screen: Define the transformation matrix]*

Define the following 4x4 matrix: 2/5 0 1/5 0 ; 0 -1 0 0 ; 3/5 0 -1/5 0 ; 0 0 0 1

OK

*The transformed experimental unit cell parameters should be as follows:*

| Define the reference cell/split by twinning |
| --- |

Cell parameters: 11.8434 12.0277 17.7796  90.008 91.934 89.998

| Target dimension | 4 | | | | Twinning | Twinning matrices | |
| 1st modulation vector | 0.2 0 -0.2 | | | Number of domains | | | |
| 2nd modulation vector | | | | Data related to domain# | | | |
| 3rd modulation vector | | | | Multiply input F(hkl)/I(hkl) by | 1 | | |
| Max. satellite index | 4 | | | | | | |
| Accuracy | 0.001 0.001 0.001 | | | | | | |

Define transformation matrix

Transformatiom matrix applied to input indices:

$$\begin{pmatrix} H \\ K \\ L \\ M \end{pmatrix} = \begin{pmatrix} 2/5 & 0 & 1/5 & 0 \\ 0 & -1 & 0 & 0 \\ 3/5 & 0 & -1/5 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} * \begin{pmatrix} h \\ k \\ l \\ m \end{pmatrix}$$

NEXT

*The wizard transforms indices according to the defined transformation matrix. Resulting integer indices are sorted as main reflections while the others as satellites defined by the q-vector.*

For absorption correction select "None or done before importing"; NEXT

FINISH

OK; YES to accept the data set in the Data repository

## 8. Symmetry Wizard

Use default tolerances for crystal system recognition

Select monoclinic Laue symmetry

Select P centering

Select space group P2$_1$/c

*Although it is not first in the list, FOM is almost the same like for P2/n and the button "Details" shows that the discarded reflections are very weak*

NEXT

Select superspace group P21/c(a0g)0s; NEXT

*In the original publication the superspace group was P21/c(a0g)00. However, q-vector consistent with this symmetry would be (0.2,0,0.8). We prefer using the shortest possible q-vector but both selections are equivalent.*

Accept the superspace group transformed into the original cell; NEXT

## 9. Creating refinement reflection file

<span style="color:blue">Follow default steps of the wizard</span>
*Rint ~ 4.8% for 24879 reflections*

## 10. Structure solution wizard

<span style="color:blue">Type the formula C30 H25 N2 O Cl Sn, four formula units</span>
*Density should be 1.53 g.cm$^{-3}$*
<span style="color:blue">Select "Superflip" and "Peaks from Jana2006";</span>
<span style="color:blue">For "Starting model" select "Patterson superposition map"</span>
<span style="color:blue">"Run solution"</span>
*Superflip converges with R around 22% and confirms the selected superspace group*
<span style="color:blue">"Accept last solution" to leave the structure solution wizard</span>
<span style="color:blue">Start "Plot structure"</span>
<span style="color:blue">Select "Draw average structure" and press "Draw+return" or "Draw+continue"</span>
<span style="color:blue">In Diamont start "Build → Get molecules"</span>



C1
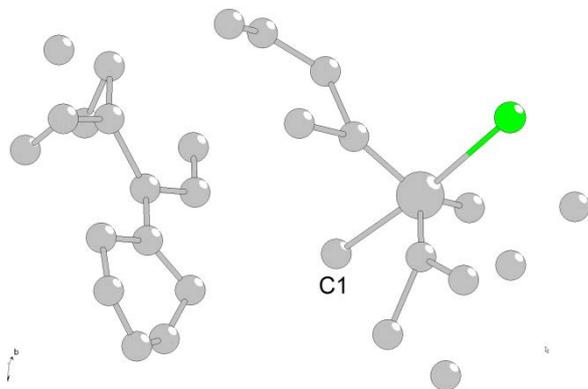
*The structure model obtained from charge flipping contains fragments of phenyls and phenantroline, Sn, Cl and water oxygen assigned as carbon C1. In commensurate description we have only one symmetry independent Sn.*

## 11. Initial commensurate refinement

*As the only special position in the superspace group P2$_1$/c(a0g)0s is the inversion center, which is not compatible with the assumed shape of the molecule, all atoms should be localized in general positions. Thus one atom in the commensurate structure represents five atoms in the supercell structure, i.e. 15 positional and 30 ADP parameters. Therefore, each atom in the commensurate structure can have maximally two positional (12 parameters) and two ADP (24 parameters) modulation waves (each wave of order n represents two periodic components – sin2πnx$_4$ and cos2πnx$_4$), which make together with the basic position and the basic ellipsoid 3+12=15 positional and 6+24=30 ADP parameters.*
*At this stage all atoms from the charge flipping model already have one position modulation wave interpreted from the electron density map provided by Superflip.*

<span style="color:blue">Start "Edit atoms"; change chemical type of C1 (may be also N1) to oxygen and its label to O1;</span>
<span style="color:blue">OK; YES to save changes</span>
<span style="color:blue">Start "EditM50"</span>
<span style="color:blue">Check "Commensurate case"</span>
<span style="color:blue">Clear "Use simple supercell"</span>
<span style="color:blue">Press "Define supercell matrix" and type 1 0 1 ; 0 -1 0 ; 3 0 -2</span>
*This is transformation from commensurate to supercell parameters*

OK
Press "Select supercell group"
*The program lists all supercell space groups, which can be achieved by changing the tzero value. As we know from the preliminary calculations that the symmetry in the supercell should be P21/n, we should select one of the two equivalent possibilities leading to P21/c (P21/n after transformation).*
Select Tzero 0+n/5; OK
OK; YES to rewrite M50; YES to re-create refinement reflection file
Follow steps for merging the reflections; FINISH
*Now we have set up the commensurate refinement. In our case, it means that modulation functions will only have 5 definition points.*
Start refinement
*The refinement converges with $R_{all}\sim38\%$, $R_{main}\sim18\%$ (the number can be different)*
Start "Edit atoms"
Double-click Sn1 and change number of position modulation waves to 2
OK; OK; YES to save changes
Start Refinement options; set 100 refinement cycles; OK; YES+START
*The refinement converges with $R_{all}\sim24\%$, $R_{main}\sim14\%$, $R_{sat1}\sim27\%$ and $R_{sat2}\sim31\%$*
*These numbers can be different because Superflip may have returned different number of carbon atoms. However, if R values at this point are significantly larger, for instance $R_{all} >$ 26% or $R_{sat2} \sim$ 50%, please **do not continue and repeat structure solution (return to the point 10.)**. If nothing helps use the random seed 94958896.*

### 12. Structure completing from difference Fourier

Start Fourier options; select the page "Basic" and "Map type" difference Fourier
OK; YES+START
YES to start procedure for including new atoms
Activate "Skip peaks being too close to existing atom" and set 1.1 Å
Include maxima with reasonable C-C distances named C* (i.e. the next free carbon label).
FINISH; YES to include new atoms
*We don't need a complete structure, just some atomic positions for correct placement of molecules*

### 13. Preparation for rigid body description

*Refinement of a commensurate structure with very strong satellites may be difficult. In this example, the refinement could easily finish in a false minimum with distorted geometry of phenyls and phenantroline. Therefore, for the initial refinement we will use fixed rigid bodies pre-defined in M45 files.*
*Atoms used for definition of a rigid body position must belong to the same fragment without need of symmetry transformation. In the next step we will manage that atoms in M40 are properly transformed.*
Start "Edit atoms"; select all atoms
"Action" → "make symmetry contiguous motifs"
OK; YES to rewrite changes
Start "Plot structure"
Select "Draw average structure"; press "Draw+continue"
In Diamond use "Build → Add all atoms"
*This adds all atoms from the structure model without applying symmetry. This shows that*

*the atoms used for definition of rigid body positions really belong to the same fragment*

Start "Build → Connect atoms"

*The plot may differ for actual solutions but it should display all atoms important for introduction of rigid body of phenyl and phenantroline. In our case, the plot also includes some spurious maxima, but it does not matter.*

For each phenyl and for the phenantroline note labels of three atoms, which will be used for placing complete phenyl and phenantroline templates from m45

In case of phenantroline note also orientation of the fragment because atoms (here) C2 and C3 must fit with proper N1 and N2 of the template
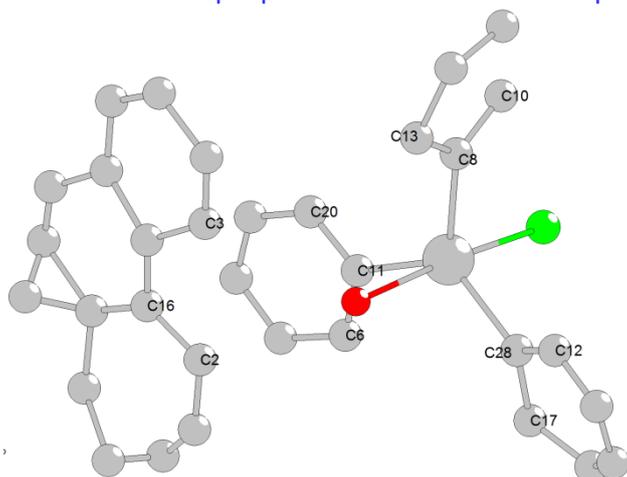


Quit Diamond or let it open for a later reference (depends on style of work)

## 14. *Rigid body templates from M45*

Start "File → Structure → Save As"

Make backup copy of the structure

Start "Parameters → Molecule → New molecule"

Select "Model file"

For "Name of molecule" type "Ph"

Press "Browse" and select "phenyl-no-symmetry.m45"

Keep the default scaling distance

Press the button "Show the model molecule"

*[On the screen: Windows opens jpeg plot of the template in a default viewer. Note that the atom labels of the template phenyl end with "p" in order not to mix with any atoms of the structure. Close the jpeg plot.]*

NEXT

*[On the screen: "Specify atomic types in the model molecule:" dialogue for matching chemical types in the template molecule and in the current structure.]*

Keep the suggested chemical types; NEXT

*[On the screen: Define the molecular reference point]*

Select "Geom. center"; NEXT

*[On the screen: Define and complete molecular position #1]*

Pair the following atoms (your labels will differ!)

C1p with C28

C2p with C12

C6p with C17

For "Maximal coincidence distance" type 0.8

Press "Show coinciding atoms"

*The expected coincidence ratio in our example is 6/11 (in case that all carbon atoms were previously localized from the difference Fourier)*

**Define and complete molecular position # 1:**

☐ Apply inversion

|  | Model atom | Actual position/atom |
|---|---|---|
| 1st point | c1p | c28 |
| 2nd point | c2p | c12 |
| 3rd point | c6p | c17 |

Select the actual atom

Fill by a saved point

**Options for removing of atoms from atomic block coinciding with those generated from molecular position # 1:**

Maximal coincidence distance  0.8    Show coinciding atoms

Calculate molecular parameters

**Molecular parameters:**

Phi = -75.84 Chi = -58.42 Psi = 74.41 determinant = 1

Translation vector : -0.485510 -0.140775 0.275122

Occupancy  1       Coincidence ratio: 6/11

Apply+Next position    Apply+End    Quit

Press "Apply+Next position"

*[On the screen: Define and complete molecular position #2]*

Pair atoms:

C1p with C8

C2p with C10

C6p with C13

*The coincidence ratio (in our example, it may differ) will be 5/11*

Press "Apply+Next position"

*[On the screen: Define and complete molecular position #3]*

Pair atoms:

C1p with C11

C2p with C6

C6p with C20

*The coincidence ratio (in our example, it may differ) will be 6/11*

Press "Apply + End"

*Now we continue with phenantroline*

Start "Parameters → Molecule → New molecule"

Select "Model file"

For "Name of molecule" type "Trol"

Press "Browse" and select "phenantroline-no-symmetry.m45"

Keep the default scaling distance

Press the button "Show the model molecule"

*[On the screen: Windows open jpeg plot of the template in a default viewer. Note that the atom labels of the template phenantroline end with "t" in order not to mix with any atoms of the structure. Close the jpeg plot.]*

NEXT

*[On the screen: "Specify atomic types in the model molecule:" dialogue for matching chemical types in the template molecule and in the current structure.]*

Accept suggested chemical types; NEXT

*[On the screen: Define the molecular reference point]*

Select "Explicit"; type N1t; NEXT

*[On the screen: Define and complete molecular position #1]*

Pair the following atoms (your labels will differ!)

N1t with C3

N2t with C2

C17t with C16

*Be careful with matching the correct orientation of the molecule, interchanging of N1t and N2t would change it*

For "Maximal coincidence distance" type 0.8

Press "Show coinciding atoms"

*The expected coincidence ratio in our example is 14/22 (depends which carbon atoms were previously localized from the difference Fourier)*

Press "Apply+End"

Start "Edit atoms"

Delete all carbon atoms, which are not blue (i.e. carbons out of molecules).

*Be careful not to delete chlorine*

Press "Select all"

The structure should contain 36 atoms

Press "Refresh"; OK; YES to save changes

Plot the structure using "Draw average structure
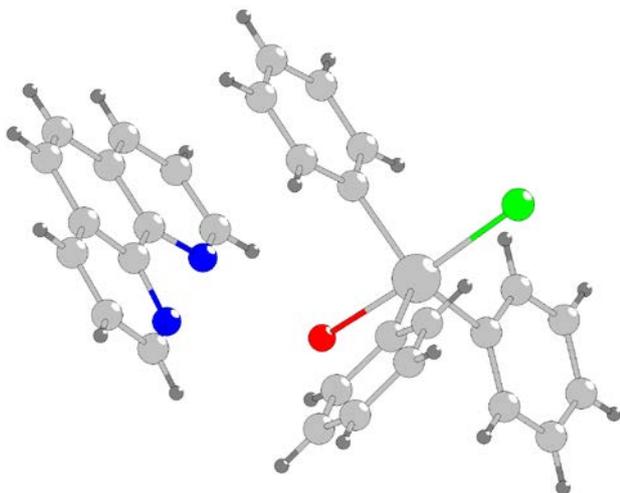
Start :File $\rightarrow$ Structure $\rightarrow$ Save As" and make a backup copy

### 15. Preparing refinement with fixed rigid bodies

Start "Edit atoms"

Select carbons of phenyl, which have hydrogen: C2p, C3p, C4p, C5p and C6p

Start "Action $\rightarrow$ Adding of hydrogen atoms"

Check "generate keep command for Refine"

Check "try automatic run ..."

OK

Repeat procedure for carbon atoms of phenantroline: C7t, C8t, C9t, C11t, C12t, C14t, C15t and C16t

*The procedure for adding hydrogen atoms, applied to already existing hydrogens, generates keep commands, which are necessary for subsequent refinement.*

*After this process number of atoms in the structure must be unchanged, i.e. 36*

Start Refinement options; go to the page "Various"; press "Fixed commands"

Select "All parameters"

For "Atoms/parameters" type "C*p C*t N*t"; Add; OK; OK; YES to save commands without starting Refinement

*This fixes geometry of both phenyl molecules and phenantroline*

### 16. Refinement with rigid bodies

Start "File $\rightarrow$ Structure $\rightarrow$ Save As" and make a backup copy

Start Refinement options; go to the page Basic

Clear "Disable atoms having too large isotropic ADP parameter"

OK; YES+START

*$R_{all}$ will be ~28% for 61 parameters*

Start "Parameters $\rightarrow$ Molecules $\rightarrow$ Edit"

Set 1 position modulation wave for the first position of Ph

Set 1 position modulation wave for the second position of Ph

Set 1 position modulation wave for the third position of Ph

Set 1 position modulation wave for the first position of Trol
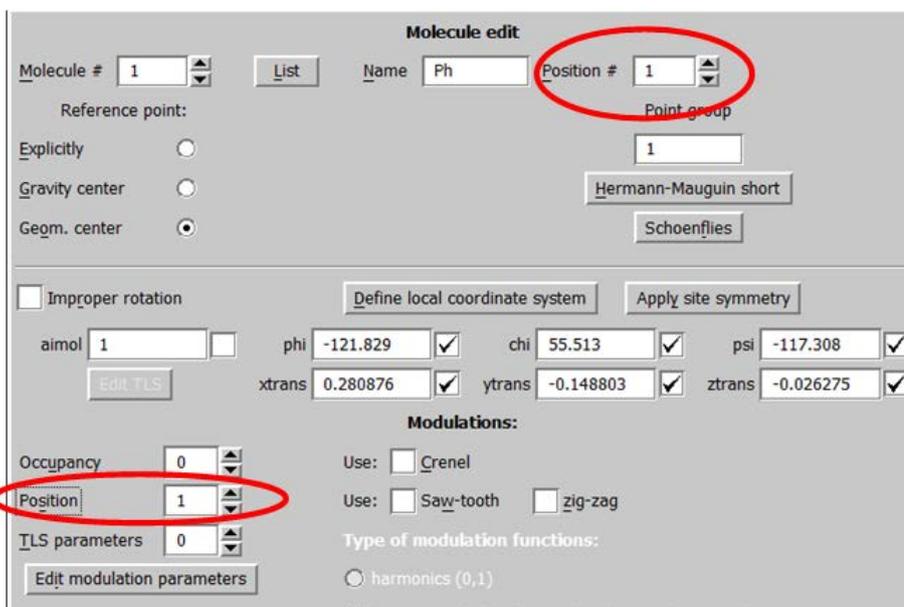
Run refinement

*$R_{all}$ will be ~22% for 109 parameters*

Start "Edit atoms"

For Sn1 set harmonic ADP

For Cl1 and O1 set 2 position modulation waves and harmonic ADP

Run refinement

*$R_{all}$ will be ~20% for 136 parameters*

Start Refinement options; go to the page "Various"; press "Fixed commands"

Disable the command "fixed all C*p C*t N*t "

OK; OK; YES+START

*The refinement converges with $R_{all}$~19%, $R_{main}$~11%, $R_{sat1}$~22% and $R_{sat2}$~27% for 204 parameters*

Start "Edit atoms"

Set harmonic ADP for carbons and nitrogens of both molecules

OK; OK, YES to save changes

Start "Parameters → Molecules → Edit"

Set 2 position modulation wave for the first position of Ph

Set 2 position modulation wave for the second position of Ph

Set 2 position modulation wave for the third position of Ph

Set 2 position modulation wave for the first position of Trol

Run refinement

*The refinement converges with $R_{all}$~9%, $R_{main}$~6%, $R_{sat1}$~11% and $R_{sat2}$~10% for 352 parameters*

Start "Edit atoms"

Set one ADP modulation wave for Sn1, Cl1 and O1

Start "Parameters → Molecules → Edit"

Set one ADP modulation wave (modulation of TLS parameters) for three positions of Ph and one position of Trol

Run refinement

*The refinement converges with $R_{all}$~8%, $R_{main}$~6%, $R_{sat1}$~10% and $R_{sat2}$~10% for 548 parameters*

Start "Edit atoms"
Set another one ADP modulation wave for Sn1, Cl1 and O1
Start "Parameters → Molecules → Edit"
Set another one ADP modulation wave for three positions of Ph and one position of Trol
Run refinement
*The refinement converges with $R_{all}$~8%, $R_{main}$~6%, $R_{sat1}$~10% and $R_{sat2}$~9% for 744 parameters*
*This is the final structure model with molecules*

## 17. Analysis of results
*Considering very good data quality, the results are still not satisfactory. Here we are looking for problems in the structure model*
Start "Edit/View → View of Refine"
*There are no serious warnings*
Plot the supercell structure
*The program does not use the transformation to five-fold supercell. Instead, it expands the structure to 5x1x5 supercell.*
*Geometry seems to be correct.*
Calculate difference Fourier map
YES to start procedure for including new atoms
*Do not include any maxima but look at their distances to atoms of our structure model. The largest difference maxima are close to atoms of phenantroline and phenyl, indicating some problem with the rigid body description.*
Start options for "Dist"
Press "Planes"
For "Atoms defining the best plane" type: C1pa C2pa C3pa C4pa C5pa C6pa; Add
For "Atoms defining the best plane" type: C1pb C2pb C3pb C4pb C5pb C6pb; Add
For "Atoms defining the best plane" type: C1pc C2pc C3pc C4pc C5pc C6pc; Add
*The second and third line can be created with help of the button "Clone"*
OK
Go to the page "Modulation"
Check "Make coordination t-tables"
OK, YES+START
Start "Edit/View → View of Dist"
"Go to" → "List dihedral angles"

```
Dihedral angle between plane#1 and plane#2 - Average : 60.1(2), Minimum : 56.7(2), Maximum : 68.4(2)

    t        Angle     t        Angle     t        Angle     t        Angle     t        Angle     t
  0.000     57.5(2)  0.200     56.7(2)  0.400     68.4(2)  0.600     58.1(2)  0.800     59.9(2)

Dihedral angle between plane#1 and plane#3 - Average : 42.4(2), Minimum : 21.9(2), Maximum : 59.8(2)

    t        Angle     t        Angle     t        Angle     t        Angle     t        Angle     t
  0.000     35.2(2)  0.200     59.8(2)  0.400     21.9(2)  0.600     52.2(2)  0.800     42.7(2)

Dihedral angle between plane#2 and plane#3 - Average : 66.5(2), Minimum : 55.9(2), Maximum : 89.2(3)

    t        Angle     t        Angle     t        Angle     t        Angle     t        Angle     t
  0.000     69.4(2)  0.200     58.6(2)  0.400     89.2(3)  0.600     55.9(2)  0.800     59.3(2)
```

*Each "t" value indicates one of the defined commensurate sections, which is realized as one configuration in the five-fold superstructure. We can see that changes of angles between the planes #1, #2 and #2, #3 reach 30 degrees, which cannot be reliably described by rigid body modulation function as used in Jana2006.*

Start "Grapht"
Press "New/edit"
For "Parameter to draw" set "plane"
For "p" set limits from 0 to 90
For "Plane #1" type "C1pa C2pa C3pa C4pa C5pa C6pa"
For Plane #2" type "0 0 1"

*Grapht now displays angle between the plane through the first position of Ph and the axis c.*

Press "Options"; check "Indicate commensurate t sections"; OK

*Grapht now also displays the sections, for which the structure is defined. The orientation of the single plane changes by ~40 degrees. Again, this cannot be reliably described by rigid body modulation function as used in Jana2006.*
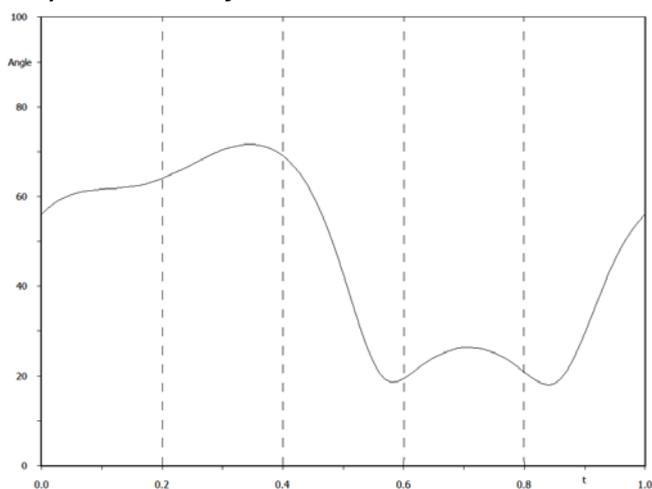


*Actual value of t-sections is connected with the origin selection made automatically during solution by Superflip. Also the phenyl molecules na be placed in different order comparing with this manual. Thus the actual plot will differ.*

### 18. Creating structure model without phenyl molecules

Start "File → Structure → Save As" and make a backup copy
Start "Edit atoms"; Select atoms *p
Start "Action → Atoms from molecule to atomic part"

*The three molecular position have been transformed to atoms with suffixes "a", "b" and "c"*

Select H*pa, H*pb and H*pc (it can be also done with H*p?)
Start "Action → Edit/Define"
Set isotropic ADP
OK; OK; YES to save changes
Start Refinement options
Go to the page "Various"; press "Keep commands"; press "Edit"
Using the text editor:
- change labels *p to *pa
- duplicate the commands and change *pa to *pb
- create the same commands for *pc
OK
Go to the page "Basic"; set Damping factor 0.5
OK; YES+START
Run refinement

*The refinement converges with $R_{all}$~5%, $R_{main}$~4%, $R_{sat1}$~6% and $R_{sat2}$~6% for 1176 parameters.*

**19.** Creating structure without phenantroline molecules
Start "Edit atoms"; Select atoms *t
Start "Action → Atoms from molecule to atomic part"
*The molecular position have been transformed to atomic part without adding suffix "a", because the molecule had only one position. For this reason keep commands are still valid.*
Select H*t
Start "Action → Edit/Define"
Set isotropic ADP
OK; OK; YES to save changes
Run refinement
*The refinement converges with $R_{all}$~2.7%, $R_{main}$~2.3%, $R_{sat1}$~3.2% and $R_{sat2}$~2.9% for 1576 parameters*

**20. Geometry of the atomic model**
*The atomic model has excellent R factors. However, we have to ensure that the phenyls are planar and not distorted.*
Start "File → Structure → Save As" and make a backup copy
Start Refinement options
Go to the page "Various"; press "Keep commands"
Select "Geometry" and "Plane"
For "List of atoms" type C1pa C2pa C3pa C4pa C5pa C6pa; Add
For "List of atoms" type C1pb C2pb C3pb C4pb C5pa C6pb; Add
For "List of atoms" type C1pc C2pc C3pc C4pc C5pc C6pc; Add
OK; OK; YES+START
*Change in R values should be very small*
Start Dist
*Commands for best planes prepared previously are still valid*
Start "Edit/View → View of Dist"
"Go to" → "List of best planes"
*Here we can see that the phenyls are almost exactly planar*
Start Grapht
Press "New/Edit"
For "Parameter to draw" select "ADP parameter"
For "p" define "0" as Minimum and "0.1" as Maximum
For type of parameter to plot, select "U(max)"
For Central atom type "N1t"
OK
*[On the screen: plot of U(max) for N1t]*
Press "Options"
Select "Indicate commensurate t sections"; OK
*Now the plot shows the section where the structure is defined*
Press "New/Edit"
Press "New Item"; for "Central atom" type "N2t"
Press "New Item"; for "Central atom" type "C7t"
Press "New Item"; for "Central atom" type "C8t"

Add New items for C8t - C18t
OK
*[On the screen: cumulative plot of U(max) for all atoms of the phenantroline]*
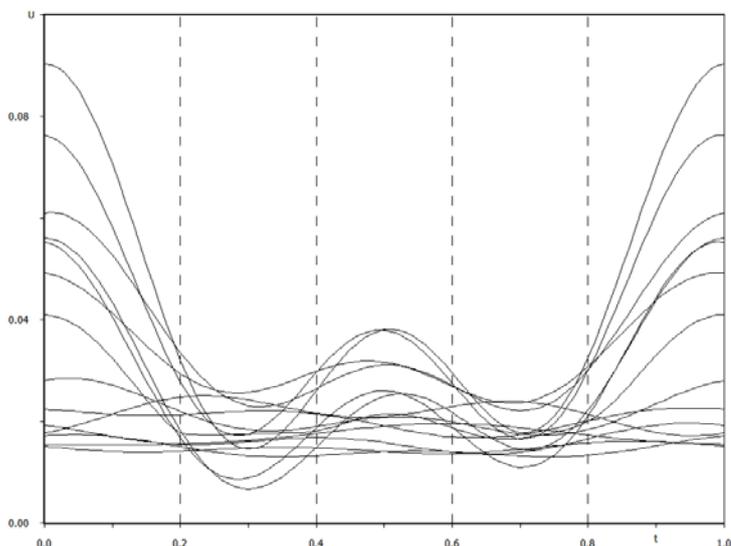


*The plot indicates that for one of the sections (here for t=0; its actual value is connected with the origin selection made automatically during solution by Superflip) some of the phenantroline atoms are strongly disordered, while the other not. This could not be described with the rigid body model.*
Quit Grapht
Draw the average structure, select only the phenantroline molecule
*For this Ctrl-M keyboard shortcut of Diamond can be used, which selects molecule belonging to a selected atom*
Note atoms N1t, C18t, C17t and N2t.
Phenantroline is often twisted and we will calculate torsion angle of these atoms
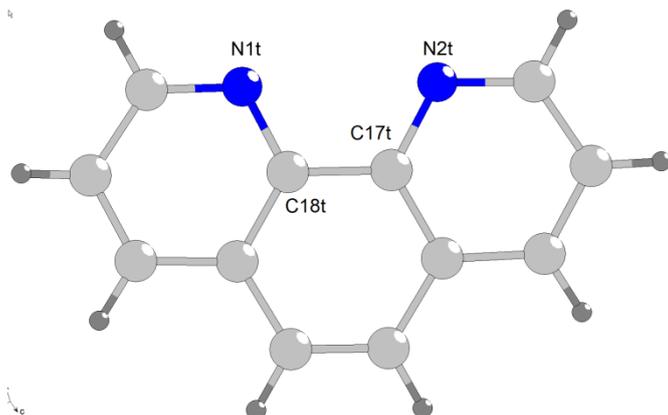


Start Dist options
Press "Torsion angles"
For atoms type N1t, C18t, C17t and N2t; Add
OK; OK; YES+START
Open listing of Dist
"Go to" → "List of torsion angles"

```
*************************
* List of torsion angles *
*************************

N1t-C18t-C17t-N2t : 5.58(13)

Individual values:
 0.000 12.59(17)  0.200 -4.11(17)  0.400 -1.82(16)  0.600 10.82(17)  0.800 10.99(17)
Average : 5.69(17), Minimum : -4.11(17), Maximum : 12.59(17)
```

*Here we can see that for five commensurate sections the torsion angle fluctuates between -4 and +12 degrees. This torsion could not be described by the molecular model.*

*The same torsion angle can be visualized in Grapht:*
*(Note that only the indicated sections are defined)*
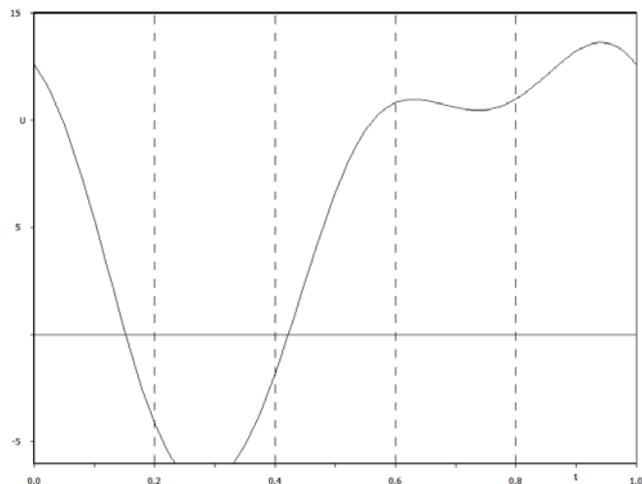


## 21. *Water*

*The last missing atoms in our structure model are hydrogens of the water molecule*
Start Fourier options
For "Map type" select difference Fourier
Check "Apply sin(th)/lambda limits
define "max" as 0.5
OK; YES+START
YES to start procedure for including new atoms
Add two difference maxima (probably the first two ones) 0.82Å close to O1 and name them H1O1 and H2O1
Start "Parameters → Molecules → New molecule"
Select "Atomic part" and "water" as a name; Next
Select O1, H1O1 and H2O1; OK
For the reference point select "Explicit" and use O1; NEXT
Apply+End
Start "Edit atoms"
Delete all modulation waves for O1, H1O1 and H2O1; OK; YES to save changes
Start "Parameters → Molecules → Edit"
Set one position modulation wave for "water"; OK; YES to save changes
Start Refinement options
In page "Various" define  distance restraint 0.82Å for O1-H1O1 and O1-H2O2
In page "Various" define keep command for ADP of hydrogens H1O1, H2O1, to be 1.2 multiple of Ueq(O1).

Run refinement

Add another position modulation wave for the molecule "water"

Run refinement

In "Edit atoms" set one ADP modulation wave for O1

Run refinement

*The refinement converges with $R_{all}$~2.7%, $R_{main}$~2.2%, $R_{sat1}$~3.0% and $R_{sat2}$~2.8% for 1584 parameters*

*The first ADP modulation wave improved only slightly R values. Therefore, we will not add the second wave - this is the principle of saving parameters in commensurate refinement comparing with refinement in the supercell.*

In the final step introduce isotropic extinction

Run refinement

*The refinement converges with $R_{all}$~2.6%, $R_{main}$~2.1%, $R_{sat1}$~3.0% and $R_{sat2}$~2.8% for 1585 parameters*

*This is the final commensurate model*

## 22. Transformation to supercell

*The final commensurate model can be transformed to the supercell*

Start "Tools → Transformations → Go to supercell structure"

For Name type "sup"; OK

OK to transform molecules

Follow steps of the data processing wizard

YES to continue with the new structure

Set **zero** refinement cycles

Run refinement (skip warnings)

*The R value will be 2.6%, because both descriptions are equivalent*

*In order to refine the supercell structure, keep commands for hydrogens must be re-created.*

*The supercell structure contains 15 independent phenyls:*
```
C1pa-1, C2pa-1, C3pa-1, C4pa-1, C5pa-1, C6pa-1
....
C1pa-5, C2pa-5, C3pa-5, C4pa-5, C5pa-5, C6pa-5
C1pb-1, C2pb-1, C3pb-1, C4pb-1, C5pb-1, C6pb-1
....
C1pb-5, C2pb-5, C3pb-5, C4pb-5, C5pb-5, C6pb-5
C1pc-1, C2pc-1, C3pc-1, C4pc-1, C5pc-1, C6pc-1
....
C1pc-5, C2pc-5, C3pc-5, C4pc-5, C5pc-5, C6pc-5
```

*Five independent phenantroline molecules:*
```
N1t-1, N2t-1, C7t-1, C8t-1, C9t-1, C10t-1, C11t-1, C12t-1,
C13t-1, ..., C17t-1, C18t-1
....
N1t-5, N2t-5, C7t-5, C8t-5, C9t-5, C10t-5, C11t-5, C12t-5,
C13t-5, ..., C17t-5, C18t-5
```

*Five independent water molecules:*
```
O1a-1; O1a-2; O1a-3; Oa-4; O1a-5
```

*Keep commands can be easily expanded and edited according to the above mentioned labels, however, they can be also copied from the pre-prepared file supercell_keep.txt.*

Start Refinement options

Go to the page "Various"; press "Keep commands"

Press "Edit"

Replace content of the file with content of the supercell_keep.txt

Save and close the text editor

OK

*Number of keep commands should be 235*

Press "Distance restraints"

Restrain the following distances to 0.82Å: O1a-1 H1O1a-1; O1a-1 H2O1a-1; O1a-2 H1O1a-2; O1a-2 H2O1a-2; O1a-3 H1O1a-3; O1a-3 H2O1a-3; O1a-4 H1O1a-4; O1a-4 H2O1a-4; O1a-5 H1O1a-5; O1a-5 H2O1a-5;

*Some keep commands and distance restraints may be invalid because the atomic positions may be transformed during the commensurate-to-supercell transformation. Such commands would need symmetry codes.*

Start "Edit atoms"

Press "Select all"

Start "Action" $\rightarrow$ "create symmetrically contiguous motifs"

*After this the keep commands can use labels without symmetry codes*

Start refinement (still with zero cycles)

*The R value will be 2.6%*

Start "File $\rightarrow$ Structure $\rightarrow$ Save As" and make a backup copy

Set 100 refinement cycles, damping factor 0.5, and run refinement

*Refinement uses 1611 parameters, which is more than in comensurate refinement, because we did not use full set of parameters for water molecules. However, the resulting R value is still 2.58%*

### 23. Back to the rigid body description

*Now we can introduce phenyl molecule in 15 positions, which was not possible in the commensurate refinement due to too large rotations. For phenantroline, we can try to use rigid body description using two halves of the phenantroline as independent pattern molecules, in order to describe the torsion of phennatroline. Finally, we can model the disordered phenantroline molecule by partially occupied molecules. All this is routinne job, which will not be presented here.*

### 24. Conclusions

Commensurate refinement can help to find solution of very large structures, it allows to save parameters by using less than the full set of modulation parameters, and it facilitates interpretation of a superstructure through calculation of various parameters as a function of t. However, commensurate refinement may be difficult when satellites are too strong, because strength of satellites indicates large displacements, which must be described by modulation functions defined only in few points. Despite of this, commensurate refinement was possible for our structure and it helped to understand its geometry. On the other hand, saving parameters through defining the phenyl rigid body could be only possible in the supercell refinement, as well as the full description of the one disordered phenantroline molecule.

# Example 8.1: TerBut

**Application of rigid body groups for disordered parts of crystal structure**
**Revised: 4 March 2015**

**N-(3-nitrobenzoyl)-N',N''-bis(tert-butyl)phosphoric triamide**
**Chemical formula: $C_{90}H_{150}N_{24}O_{24}P_6$**
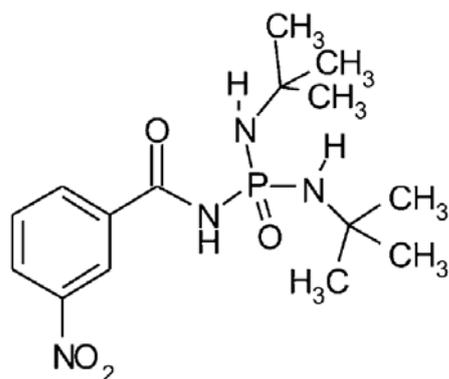


Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: TerBut.hkl, TerBut.cif_od
Frame scaling, absorption correction: done with software of the diffractometer

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click TerBut

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data Repository*
   *Each line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   *[On the screen: "Information" about symmetry wizard]*

NEXT

*[On the screen: "Tolerances for crystal system recognition".]*

Leave all settings default; NEXT

[On the screen: Select Laue symmetry]

Select Triclinic; NEXT

Select primitive unit cell; NEXT

*[On the screen: Select space group]*

Select P-1; NEXT

Accept the space group; FINISH

## 5. *Creating refinement reflection file*

NEXT to confirm threshold 3sigma

*[On the screen: settings for merging of reflections]*

Leave all settings default; NEXT

Press "Accept the new DatBlock and calculate coverage"; FINISH

## 6. *Structure Solution Wizard*

*[On the screen: "Information" about Structure solution tool]*

OK

*[On the screen: window of Structure solution]*

In "Formula" textbox type list of chemical elements for TerBut: C15 N4 O4 P H25;

Set "Formula units" to 2 and calculate density;

*[On the screen: Calculated density: 0.4242 g/cm$^3$]*

*This is unrealistic value which indicates that the structure can contain more independent structural motifs. As the density should be larger than 1 the most probable number of independent structural motifs is 6.*

Set "Formula units" to 6;

Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"

Close listing of Superflip

Press Accept last solution" to leave the structure solution wizard

## 7. *Verification of the structure solution*

Start "Plot structure", use either "Draw+return" or "Draw+continue"

*[On the screen: window of Diamond]*

Start "Build → Get molecules" or use ⬡ on the bottom toolbar

Rotate the molecule (✛ and ↻ on the bottom toolbar) to get an optimal view

*[On the screen: plot of the three independent, probably incomplete molecules]*

*Assignment of chemical types need not be correct and some atoms may be missing. Chemical types will be corrected later on.*

*The three iindependent molecules are combined with the inversion center. This confirms Z=6 as estimated previously from the density. Correct Z helps the program to offer proper number of maxima from difference Fourier.*

Quit Diamond;

## 8. *Refinement*

*[On the screen: basic window of Jana]*

Right-click the icon of Refine.

*[On the screen: Refinement commands]*
Define 100 of cycles; OK
Choose "YES+START"
*Refinement converges with R(obs) value about 20-22%*

9. **Completing the structure – difference Fourier synthesis**
   *[On the screen: basic window of Jana]*
   Right-click the icon of Fourier.
   *[On the screen: Fourier commands]*
   For "Map type" select difference Fourier, make sure that "Weighting of reflections" is checked and "Apply sin(th)/lambda limits" unchecked
   OK; YES+START to save commands and run the difference Fourier;
   YES to start the procedure for including of new atoms;
   *[On the screen: parameters for inserting/replacing of atoms]*
   Use default parameters; OK
   *[On the screen: the form for inserting of new atoms]*
   Go through the list of maxima and include all peaks having reasonable distances (i.e. similar to C-C distance) to already localized atoms. Skip short distances. Do not attempt including H atoms.
   After pressing the button "Include selected peak" the form for completing of the new atom appears. For the "Name of the atom" type C*. For more information what C* means press the "Info" button.
   Repeat the points 8 and 9 till no new atoms are localized. The structure should have 72 non-H atoms
   FINISH; YES to include new atoms
   Repeat refinement
   *Finally R(obs) value should be between 16 and 17%*

10. **New verification of the structure solution**
    Start "Plot structure", "Draw+continue" or "Draw+return"
    *[On the screen: window of Diamond]*
    Start "Build → Get molecules" or use ⬡ on the bottom toolbar
    Rotate the molecule ( ⊕ and ↻ on the bottom toolbar) to get an optimal view
    *[On the screen: plot of the three independent molecules]*
    Activate atom labels
    *[On the screen: plot of the molecule with atom labels]*
    Compare the plot with the chemical scheme at the beginning of this Cookbook chapter and note labels of atoms which chemical types need to be changed.
    *(For Diamond started by "Draw + return" the changes can be done immediately in Jana2006 running alongside.)*
    Use M ▾ at the bottom toolbar of Diamond to see temperature ellipsoids.
    *The large spheres derived from Uiso values for the terminal carbon atoms indicate positional disorder of some tertiary butyl groups.*

11. **Assignment of correct chemical types**
    *[On the screen: basic Jana window]*

Start "Edit atoms"

*[On the screen: list of atoms]*

Highlight one of the atoms you are going to modify

Make left double-click or Start "Action → Edit/define"

Change "Type" to the desired one

Rename the atom. Here you can use again the wild character * which prevents duplication of atom names.

Repeat this procedure till all atoms have correct chemical types.

*Note: alternatively you can select more atoms and change the chemical type of the selected group. After returning to the list of atoms in Atom/Edit the atoms are still selected and they can be automatically renamed with "Action → Rename selected atoms".*

Check again the chemical types with Diamond

Check number of atoms with "Edit atoms", using the textbox close to "Select advanced", which accepts wildcards as "C*". The structure contains 3P, 12O, 12N and 45C; 72 atoms altogether.

## 12. Refinement

*[On the screen: basic window of Jana]*

Double-click the icon Refine.

*Refinement converges with R(obs) value about 16%*

Start "Edit atoms"

[On the screen: list of atoms]

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms.* OK, OK, YES to save changes

Double-click the icon Refine.

*Refinement converges with R(obs) value about 9%*

## 13. Formula check

*[On the screen: basic window of Jana]*

Run EditM50;

Go to the tab "Composition" and press button "Formula from M40".

*The derived formula should be correct for all atom types except hydrogen.*

## 14. Unifying atom labels

*To follow easily the cookbook we need to re-label the atoms. It would be tedious work and therefore we will used pre-prepared files with correct labelling.*

Start "File → Structure → Copy in", select the structure "TerBut-simple-atomic" and in the next dialogue select files m40 and m50 for the copy.

Double-click the icon Refine.

*Refinement should converge to R(obs) value about 9.4%*

*The labeling of atoms of the first independent molecule is shown in the following figure:*
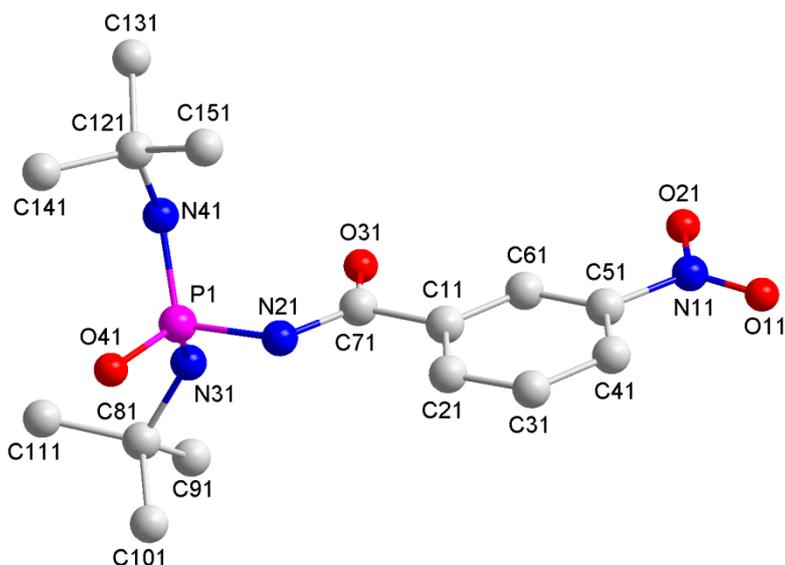
*The last digit in each label is the identifier of the molecule (replaced by 2 and 3 for the second and third independent molecule, respectively).*


## 15. Search for split atom positions

Double-click the icon Contour; Click the button "New plot"
*[On the screen: options for defining of new maps]*
In "New map to draw" select "Fourier map";
Select "Calculate new ones" and "Draw a general section"; OK
*[On the screen: Fourier commands – page Basic]*
Set "Map type" to "F(obs) – Fourier";
Clear "Omit not-matching reflections";
Clear "Apply sin(th)/lamba limits";
Select "Use weighting of reflections"; OK
*[On the screen: Plane/Volume]*
For 1st, 2nd and 3rd atom use C91, C101 and C111;
Keep interpolation step 0.1 Å;
Define scope of the section: 5 5 0 and "1st point to" 1.5 1.5 0; OK
*You should see the following figure:*
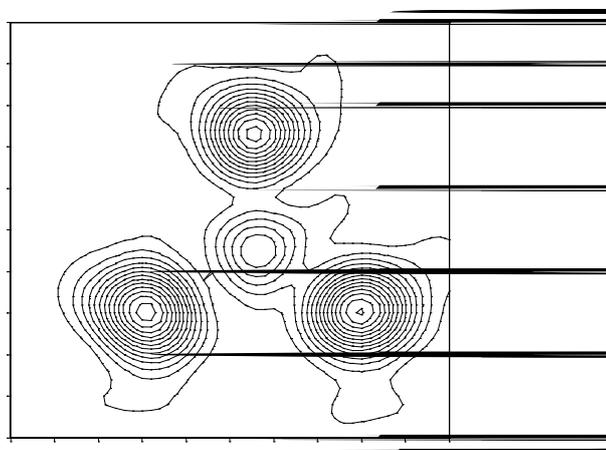
Click the button "New plot"

*(The definition of the plane has been automatically saved as Plane#1)*

*[On the screen: options for defining of new maps]*

Select "Use old maps" and "Draw a general section" (i.e. default values); OK

*[On the screen: Plane/Volume]*

Select "Use old"

Rewrite 1st, 2nd and 3rd atom by C92, C102 and C112;

*You should see similar figure like for the previous figure*

Repeat the procedure for C93, C103 and C113;

*Again no clear splitting of atomic positions*

Repeat the procedure for C131, C141 and C151.

*The last map indicates clearly splitting for two atoms:*
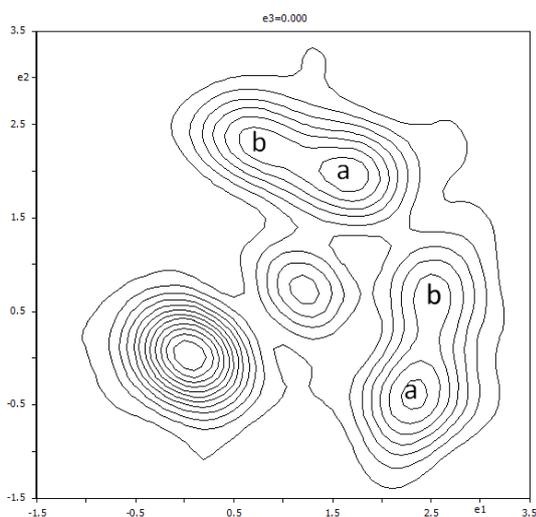


Locate the split positions by clicking at corresponding points of the section and save them for future use by "Save the selected point for future use" button.

*points close to C141 ~ (0.2795, 1.102,0.2494) and (0.2995,1.1158,0.1820)*
*(they can be named C141a and C141b)*
*points close to C151 ~ (0.2455,1.111,0.1117) and (0.1869,1.0974,0.1017)*
*(they can be named C151a and C151b)*

Make the same for the second molecule (the section C132, C142, C152). *Here the splitting of atoms C142 and C152 is less pronounced, however we only need some points for initial orientation of rigid bodies.*
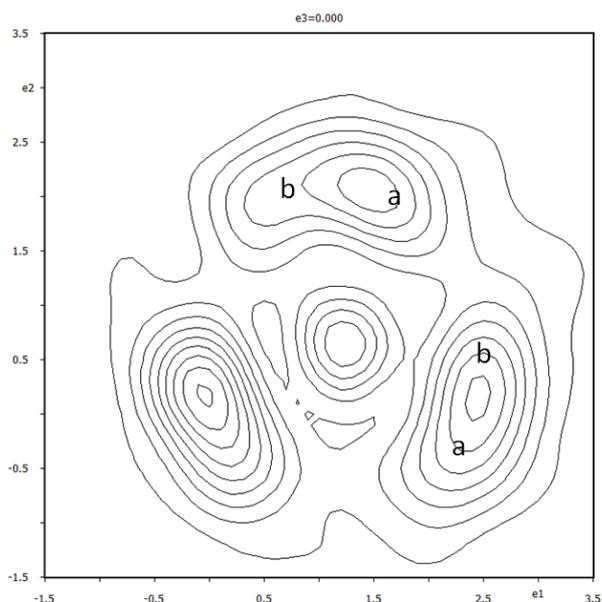
*points close to C142 ~ (0.7732, 0.3731,0.4747) and (0.8239,0.4088,0.4588)*
*(they can be named C142a and C142b)*
*points close to C152 ~ (0.8695,0.4942,0.5074) and (0.8356,0.5156,0.5715)*
*(they can be named C152a and C152b)*

Make the same for the third molecule (the section C133, C143, C153)*. Here all positions are clearly split but we only need two pairs of points..*
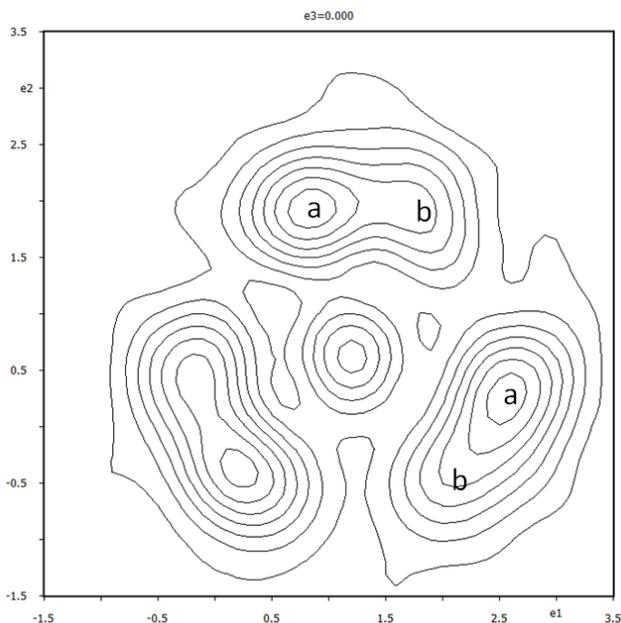


*points close to C143 ~ (-0.1854, 0.7837,0.1733) and (-0.1759,0.7836,0.1320)*
*(they can be named C143a and C143b)*
*points close to C153 ~ (-0.0588,0.8945,0.1860) and (-0.1022,0.8639,0.2186)*
*(they can be named C153a and C153b)*

*The split positions localized during preparation of this example were also written to the file "TerBut-points.txt" and can be later to pasted to Jana2006 textboxes.*

Quit Contour

YES to save new points in M40 (this does not change structure model)

*The points have been stored in M40 in the "Saved points" section*

## 16. Defining of rigid-body groups

*First we will create a model where one pattern "molecule" – tertiary butyl – is used to create three non-split positions related to N3i, C8i, C9i, C10i, C11i fragments and another six split positions related to N4i, C12i, C13i, C14i and C15i fragments (i=1,2,3).*

Start "File → Structure → Save As" and **create a backup copy** "before_rigid" but **do not continue** with the new structure.

Start "Parameters → Molecules → New molecule";

*[On the screen: Wizard for new molecule]*

Select "Atoms of the new molecule from" - "Atomic part";

For "Name of the molecule" type, for instance, "Tb"; NEXT;

*[On the screen: Select atoms for the molecule]*

Select atoms to be used as a *pattern* (elsewhere called *model*) molecule – N31, C81, C91, C101 and C111;OK

*[On the screen: Define the molecular reference point]*

Select "the molecule reference point" as "Explicit" defined by the atom C81; NEXT

*[On the screen: Form for completing of the molecular position #1];*

*The "Coincidence ratio" says that five atoms of the molecular position #1 coincide with five atoms in the atomic part of M40. This should be true because the pattern molecule is created from five atoms in M40 and the first position coincides with the pattern molecule.*

Use the default value for occupancy; Press "Apply+Next Position";

*[On the screen: Form for completing of the molecular position #2];*

*For the position #2 and all consecutive ones we have to define where to put the pattern molecule to get the new actual position. This means that actual positions of three atoms of the pattern molecule, not lying in a line, are to be specified.*

Fill "Model atoms" column with N31, C101 and C111 and the fill the "Actual position/atom" column with N32, C102 and C112. Press the button "Calculate molecular parameters".

*The coincidence ratio should be 5/5. It says that five atoms of the pattern molecule coincide in its actual position with five already existing atoms of the structure. After finishing the molecular position the coinciding atoms will be deleted from the atomic part – for this reason it is important that all of them are recognized by the program. The coincidence can be controlled by the "Maximal coincidence distance".*

Press the button "Apply+Next Position";

Repeat the procedure for the third non-split tertiary group (i.e. N33, C103 and C113 for Actual positions); press "Apply+Next position"

*[On the screen: Form for completing of the molecular position #4];*

For actual positions use N41, % C141a and %C151a. The character "%" refers to saved points.

Press the button "Calculate molecular parameters".

If the "Coincidence ratio" is not 5/5, change the "Maximal coincidence distance" to 0.8 and press again "Calculate coincidence distance"

If the "Coincidence ratio" is still not 5/5, replace the points for the 2nd and 3rd actual position and press again "Calculate coincidence distance"

*The reason for this step is that the selected saved points may define by mistake contradicting rotations of the pattern molecule. This cannot happen when the "a" and "b"*

*labels have been used as indicated in the plots.*
*Finally, the "Coincidence ratio" should be 5/5*
For "Occupancy" type 0.5.
Press "Apply+Next position";
*[On the screen: Form for completing of the molecular position #5];*
For actual positions use the same atom N41 and another two split positions % C141b and
%C151b.
Press the button "Calculate molecular parameters" and check that the "Coincidence ratio"
is 5/5;
Change the occupancy to 0.5;
Press the button "Apply+Next Position";
Repeat the process for the second and third split tertiary butyl:
*Position #6: N42, %C142a, %C152a*
"Apply+Next Position"
*Position #7: N42, %C142b, %C152b*
"Apply+Next Position"
*Position #8: N43, %C143a, %C153a*
"Apply+Next Position"
*Position #9: N43, %C143b, %C153b*
"Apply+**End**"
*The total number of molecular positions is 9.*

17. **Verification**
    Use Diamond for verification of proper geometry: each molecule should have one single
    and one disordered tertiary group.
    Use Parameters → Molecules → Edit for verification that positions #4 – #9 have occupancy
    (i.e. the parameter "aimol") 0.5
    Use "EditM50", page "Composition", button "Formula from M40"
    *If occupancy of molecular positions has been properly defined and the coincidence ratio has*
    *been always 5/5 the formula should be C15 N4 O4 P H0 (for Z=6)*
    Use "Edit atoms" to see changes in the atomic part of M40
    *Black atoms are the ones not used in molecular description*
    *Blue atoms are the ones defining the pattern molecule*
    Start "File → Structure → Save As" and create a backup copy "rigid_ini" but **do not**
    **continue** with the new structure.

18. **Refinement**
    *[On the screen: basic window of Jana]*
    Right-click the icon of Refine.
    *[On the screen: Refinement commands]*
    Change the damping factor to 0.5;
    OK, "YES+START"
    *Refinement converges with R(obs) value about 10.4%*

19. **Refinement of the molecular occupancies**
    Start "Parameters → Molecules → Edit";
    *[On the screen: molecule edit]*
    Allow refinement of the molecular occupancies (aimol) for the positions #4, #6 and #8;

OK; YES to save changes
Right-click the icon of Refine; select tab "Various";
*[On the screen: Refinement commands]*
Press the button "Restrictions";
*[On the screen: The tool for defining and editing of restriction commands]*
Write into the textbox "Atoms/molecules": "Tb#4 Tb#5"
Deselect "Coordinates"
Select "Occupancies: Keep overall sum"
Select "ADP parameters"
Press the button "Add";
*This restriction means that the molecular positions #4 and #5 have independent coordinates, the same ADP and complementary occupation*
Select the line: restric Tb#4 Tb#5;
Press the button "Clone" and then "Load" and modify the string to "Tb#6 Tb#7"
Press the button "Rewrite";
Press the button "Clone" and then "Load" and modify the string to "Tb#8 Tb#9"
Press the button "Rewrite";
OK; OK; Yes+Start;
*Refinement converges with R(obs) value about 10.3% with 475 parameters*

## 20. Refinement of the molecular TLS tensors

Start "Edit atoms";
*[On the screen: tool for selection of atoms]*
Select all atoms of the pattern molecule (before selection they are indicated by blue color).
Double-click; Select "Use TLS";
OK; OK; Rewrite changes
*This change means that individual ADP parameters of the pattern molecule are suppressed. Instead, for each actual position independent TLS tensors will be refined.*
Run refinement
*Refinement converges with R(obs) value about 8.6% with 565 parameters*

## 21. Adding hydrogen atoms

Start "Edit atoms";
*[On the screen: tool for selection of atoms]*
Select all carbon atoms and nitrogen atoms N21, N22 and N23
Press the button "Action"
Select the procedure "Adding of hydrogen atoms"
*[On the screen: parameters for adding hydrogen atom]*
Use default options (i.e. automatic procedure for C and manual procedure for N);
For N21, N22 and N32 select the trigonal coordination with two neighbors (P and C). Then only one H atom will be added.
*Total number of hydrogen atoms in Atoms edit should be 24*
OK; Save changes
Use Diamond for verification that all hydrogen atoms have been correctly placed
Run refinement
*Refinement converges with R(obs) value about 6%*

### 22. Drawing of the refined model

Start "Plot structure"

In Diamond, start "Build → Get molecules" or use ⬡ on the bottom toolbar

Use **M ▾** at the bottom toolbar of Diamond to see temperature ellipsoids. For plotting H atoms without ellipsoids switch to "Table of atom groups", select all H atoms and use **M ▾** again.

*The large temperature ellipsoids for the terminal carbon atoms indicate that there is probably some additional positional splitting of tertiary butyls N3, C8, C9, C10, C11 and also of some oxygen atoms. For teaching purposes, we can stop at this stage, as introducing of additional splitting does not bring any new.*

Quit Diamond

Start "File → Structure → Save as" and save the result as "TerBut_final_1" but **do not continue** with the new structure.

### 23. Reset the structure into the atomic model

Start "File → Structure → Copy in", select the structure "before_rigid" and copy in the m40 and m50 file.

### 24. Defining of rigid-body groups from a known model saved in M45

*M45 may contain coordinates of a rigid-body group. Syntax of M45 is explained in the example 2.3.2-MagCag, where steps how to create M45 from a template found in CSD are shown. Library of frequently used rigid bodies for Jana2006 is under development, see the directory "Molecular patterns" in Jana2006 installation path.*

Start "Parameters → Molecules → New molecule";

*[On the screen: Wizard for new molecule]*

Select "the new molecule from a model file";

Define "Name of the molecule" Tb;

Define "Model filename" TerButyl-no-symmetry.m45;

Keep the default scaling distance

*With this number the whole object can be shrunk or expanded*

Press "Show the model molecule"

*This will display the pre-prepared figure from the file TerButyl-no-symmetry.jpg*

NEXT

*[On the screen: specify atomic types in the model molecule]*

Keep the default atomic types; NEXT

*[On the screen: Define the molecular reference point]*

Select "the molecular reference point" as explicit defined by the atom C81; NEXT

*[On the screen: Form for completing of the molecular position #1];*

*For creating molecular parameters from a model file we have to specify also the actual coordinates of the first position. Starting from the position #2 we can repeat instructions from the point 16 and 17. Because the pattern molecule contains hydrogen atoms which are not present in the atomic part, the coincidence ratio will be 5/14 or higher for the split positions. This is due to the fact that some hydrogen atoms of the split positions can be close to average carbon positions. This should not have any effect as this message has only informative character.For coincidence lower than 5 please change the "Maximal coincidence distance" to 0.8.*

*As follows from the point 16 and 17, the atoms N31, C101 and C111 of the pattern molecule will be associated with the following actual positions present in the atomic part of M40 or from the saved points:*

*1. N31 C101 C111 (occupancy 1)*
*2. N32 C102 C112 (occupancy 1)*
*3. N33 C103 C113 (occupancy 1)*
*4. N41 %C141a %C151a (occupancy 0.5)*
*5. N41 %C141b %C151b (occupancy 0.5)*
*6. N42 %C142a %C152a (occupancy 0.5)*
*7. N42 %C142b %C152b (occupancy 0.5)*
*8. N43 %C143a %C153a (occupancy 0.5)C101*
*9. N43 %C143b %C153b (occupancy 0.5)*

*Resulting number of atoms: 42 in atomic part (here hydrogens are still missing); 14 in the pattern molecule.*

## 25. Refining of the structure with fixed ideal geometry

Start "Parameters → Molecules → Edit";
*[On the screen: molecule edit]*
Allow refinement of the molecular occupancies (aimol) for the positions #4, #6 and #8;
OK; YES to rewrite files;
Right-click the icon of Refine;
*[On the screen: Refinement commands]*
Change number of cycles to 100 and the damping factor to 0.5;
Select tab "Various";
*[On the screen: Refinement commands]*
Press the button "Restrictions";
*[On the screen: The tool for defining and editing of restriction commands]*
Write into the textbox "Atoms/molecules": "Tb#4 Tb#5"
Deselect "Make identical coordinates";
Select: "Occupancies: Keep overall sum"
Select: "ADP parameters"
Press the button "Add";
*This restriction means that the molecular positions #4 and #5 have independent coordinates, the same ADP and complementary occupation*
Select the line: restric Tb#4 Tb#5;
Press the button "Clone" and then "Load" and modify the string to "Tb#6 Tb#7"
Press the button "Rewrite";
Press the button "Clone" and then "Load" and modify the string to "Tb#8 Tb#9"
Press the button "Rewrite"; OK
*[On the screen: Refinement commands]*
Press the button "Fixed commands";
Select "Coordinates"; Fill textbox "Atoms/parameters" with
N31 C81 C91 C101 C111 H?c91 H?c101 H?c111
*This fixes coordinates of the pattern molecule. For library molecule we expect correct geometry.*
Press the button "Add"; OK

*[On the screen: Refinement commands]*
Select "Keep commands";
Select "ADP", "Riding";
Central atom: C91; Number of hydrogen atom 3;
Fill hydrogen textboxes by: H1C91, H2C91 and H3C91;
*For this button "Select hydrogens" can be used.*
Add;
Repeat the process for C101 and C111;
OK; OK; Yes+Start
*Refinement converges with R(obs) value about 10.2% for 441 parameters.*

### 26. Refining of the structure with anisotropic ADP for tertiary butyls
Start "Edit Atoms";
*[On the screen: tool for selection of atoms]*
Select non-hydrogen atoms of the pattern molecule.
Double-click; Select "Harmonic ADP";
OK; OK; Rewrite changes
Start refinement;
*Refinement converges with R(obs) value about 9.4% for 466 parameters*

### 27. Refining of the structure with TLS tensors for tertiary butyls
Start "Edit Atoms";
*[On the screen: tool for selection of atoms]*
Select **all** atoms of the pattern molecule.
Select "Use TLS" using double-click;
OK; OK; Rewrite changes
Start refinement;
*Refinement converges with R(obs) value about 7.5% for 556 parameters*

### 28. Adding remaining hydrogen atoms
Start "Edit Atoms";
*[On the screen: tool for selection of atoms]*
Select all individual (black) carbon atoms and nitrogen atoms N21, N22 and N23
*It is important that carbon atoms of the molecule are not selected. Here the geometric keep commands would contradict with setting of the local symmetry, which will be done later on*
Press the button "Action"
Select the procedure "Adding of hydrogen atoms"
*[On the screen: parameters for adding hydrogen atom]*
Use default (i.e. automatic run);
For N21, N22 and N32 select the trigonal coordination with the neighbors (P1, C71), (P2 C71) and (P3, C73), respectively.
OK; Save changes
Repeat refinement
*Refinement converges with R(obs) value about 6.6% for 556 parameters. This result can be compared with the previously obtained model TerBut_final_1, where the shape of the pattern molecule was refined, yielding R value 5.8 for 565 parameters.*
Start "File → Structure → Save as" and save the result as "TerBut_final_2" but do not continue with the new structure.

### 29. Introducing of the local symmetry

*The tertiary butyl has in an ideal case the point symmetry $31m$. Application of the local symmetry can considerably reduce the number of independent atoms. The point group generated by Jana2006 has its three-fold axis directed along the z-axis and the normal of the mirror plane directed along x-axis. As the atoms N31 and C81 are localized at the three-fold axis of the molecule the vector from the central point C81 to N31 can be used to define the z axis. The second x-axis is to be perpendicular to the z axis and it can be located at the plane N31-C81-C91.*

Start "Parameters → Molecules → Edit";
Define the point group 31m; TAB
A dialog window for defining the local coordinate system for the pattern molecule will appear.

*The model imported from the m45 file fulfills already the 31m symmetry in the setting as described above and therefore the local coordinate system need not be modified.*

OK to close the dialog window; OK; YES to save changes

*This process is irreversible because atoms in the pattern molecule are deleted if they become duplicit with respect to the introduced point group*

### 30. Check atoms of the model tertiary butyl

Start "Edit Atoms";
*The number of independent atoms is now only 5.*
Select the first atom of the model tertiary butyl and make double-click;
Switch to Edit to see the site occupancy;
You should get:
N31    0.166667
C81    0.166667
C91    0.500000
H1c91  0.500000
H2C91  1.000000

### 31. Refinement of the structure with local symmetry 31m – atomic positions of the tertiary butyl fixed

Start the refinement;
*Refinement converges with R(obs) value about 6.6% for 556 parameters, i.e. the same value like before, because the shape of the pattern molecule is still fixed.*

### 32. Refinement of the structure with local symmetry 31m

Right-click the icon of Refine; select tab "Various";
*[On the screen: Refinement commands]*
Press the button "Fixed commands";
Disable the fixed command; OK
Start the refinement;
*Refinement converges with R(obs) value about 6.5% for 564 parameters.*

# Example 8.2: Dinitros

**Application of rigid body groups for disordered parts of crystal structure**
**Revised: 3 March 2015**

**(3aRS,7aRS )-1,3-dinitrosooctahydro-1H-benzimidazole**
**Chemical formula: $C_7H_{12}N_4O_2$**
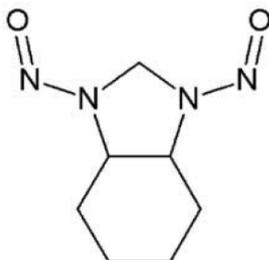


Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: dinitros.hkl, dinitros.cif_od
Frame scaling, absorption correction: done with software of the diffractometer

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click dinitros

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. ***Data Repository***
   *Each line in data repository window corresponds to one data set.*
   OK; YES to accept the data set

4. ***Symmetry Wizard***
   *[On the screen: "Tolerances for crystal system recognition".]*
   Leave all settings default; NEXT
   *[On the screen: Select Laue symmetry]*
   Select Monoclinic; NEXT
   Select primitive unit cell; NEXT
   *[On the screen: Select space group]*
   Select P2/c; NEXT

Accept the space group; FINISH
*[On the screen: define space group window]*
OK to accept the space group P2/c

5. ***Creating refinement reflection filed***
NEXT to confirm threshold 3sigma
*[On the screen: settings for merging of reflections]*
Leave all settings default; NEXT
Accept the data block and calculate coverage; FINISH

6. ***Structure Solution Wizard***
*[On the screen: window of Structure solution]*
In "Formula" textbox type list of chemical elements for Dinitros: C7 H12 N4 O2;
Set "Formula units" to 4 and calculate density;
*The density 1.393 g/cm³ looks reasonably so probably Z=4 is correct*
Select "use Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"
Close listing of Superflip
*Superflip converges with R value 16% and confirms symmetry P2/c*
Press "Accept last solution" to leave the Structure solution wizard

7. ***Verification of the structure solution***
Start "Plot structure"; "Draw + Continue"
*[On the screen: window of Diamond]*
Start "Build → Get molecules" or use ⬡ on the bottom toolbar
Rotate the molecule (✛ and ↻ on the bottom toolbar) to get an optimal view
*[On the screen: plot of the two independent molecules]*
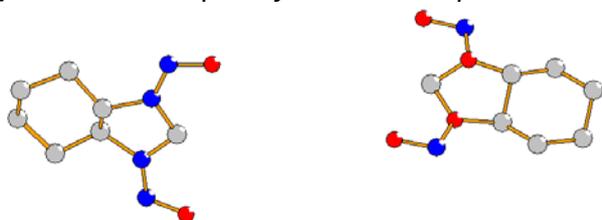


*The results may be slightly different for each run of Superflip, because it starts from random phases.*
Draw rectangle to select all atoms of the molecule or press Ctrl-A
Right-click on one of the selected atoms, choose "Add → Atom labels"
*[On the screen: dialogue of Diamond for atom labeling]*
Note incorrect chemical types (using the chemical diagram above);
Quit Diamond;
Run "Edit atoms";
Correct the improper chemical types;
Rename atoms according to chemical types;
Make symmetry contiguous motifs;
Quit "Edit atoms", save the changes
*For this structure making the symmetry contiguous motifs is very important. To make sure the motifs have been correctly created:*

Return to Diamond;

Use ⊞ or "Build → Add all atoms";

Connect atoms with bonds

*This will plot symmetry independent atoms of the structure model without any symmetry transformation. They should create motifs:*



*If these motifs are not created the atoms must be put to the motif manually using symmetry transformations in "Edit atoms".* **Without proper motifs this example will not work!**

Quit Diamond

8. **Refinement**

*[On the screen: basic window of Jana]*

Right-click the icon of Refine.

*[On the screen: Refinement commands]*

Define 100 of cycles; OK

Choose "YES+START"

*Refinement converges with R(obs) value about 13%*

Plot the structure

It should be the same like before

Start "Edit atoms" and change ADP of all atoms to "harmonic"

Repeat refinement

*Refinement converges with R(obs) value about 9.4%*

Plot the structure

Activate ADP ellipsoids using "Picture → Model and Radii"

*One of the molecules has very large ellipsoids for carbon atoms:*
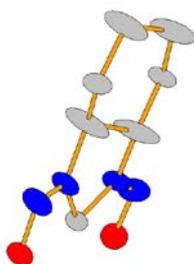


9. **Labeling**

*At this point we would need some more practical labeling of atoms. Jana2006 doesn't include tools for graphical renaming. The labels and their changes must be planned in Diamond, noted and realized in "Edit atoms" tool or by direct editing of M40*
*The desired labeling for the molecule with large ADP's (starts from C1) and the one with smaller ADP's (starts from C5):*

0.75C21C4'
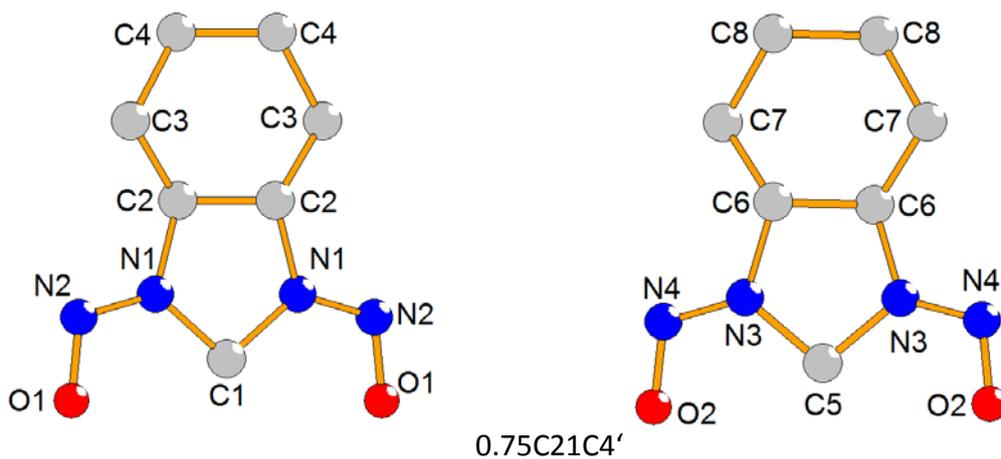
*(The molecule with large ADP's starts from C1)*

Plot the molecules in Diamond; activate atom labels;

EITHER note the desired changes and Quit Diamond;

OR rename atoms in Jana2006 running parallel with Diamond (Diamond started with "Draw+continue")

*(You may also keep Diamond window open and type the new labels directly to Edit atoms tool of Jana2006)*

Start "Edit atoms"; select all atoms and choose "Rename the selected atoms manually"

Plot the structure and verify the labels

## 10. Splitting positions with large ADP

The largest ADP have been found for atoms C2 and C4

Start "Edit atoms" and split positions of C2 and C4, using default options for splitting
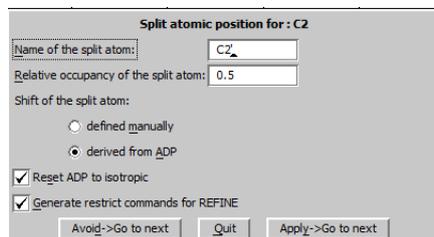


*The splitting procedure created pairs C2-C2' and C4-C4', their ADP are isotropic and the same for each pair, partial occupations are ½ and the sum of occupancies for each pair is kept by a Restriction for the case it would be refined*

Run refinement

*Refinement converges with R(obs) value about 10%*

Start "Edit atoms" and activate refinement of occupancy for C2 and C4

Run refinement

*Refinement converges with R(obs) value about 8.4%*

*The refined occupancies in both pairs are in the ratio 1:3, i.e. one of the split atom in each pair is much weaker.*

Plot the structure; distinguish by colors the weakly occupied carbon atoms

Activate plotting of ADP ellipsoids and plotting of labels
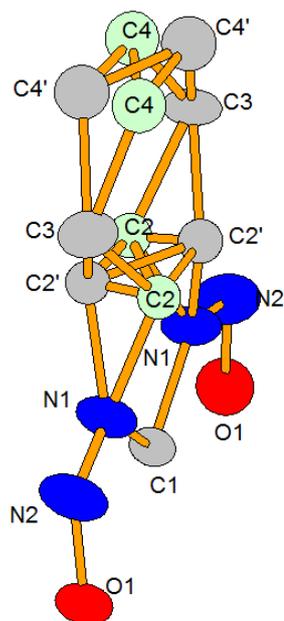
*In the plot C4, C2 have occupancy ~0.25; C4', C2' have occupancy ~0.75, the other atoms have a full occupancy. We can distinguish two chairs: C4-C4-C3-C2-C2-C3 and C4'-C4'-C3-C2'-C2'-C3, the latter having stronger occupation.*

***Warning****: splitting of atomic positions was automatic process. In particular solution it may happen that the labels of the strongly and weakly occupied atoms (i.e. atoms with and without comma) will be exchanged. In such a case we recommend relabeling the atoms according to this plot in order to follow easily the cookbook.*

## 11. Rigid body description

*Refinement of the weakly occupied positions is unreliable because ¼ of carbon is an electron density comparable with hydrogen. In this part we will describe the disorder with a rigid body. For model molecule we will take the stronger version of the molecule.*

Start "File → Structure → Save As" and **create a backup copy**
Start "Parameters → Molecules → New molecule"
Choose the name for the molecule, e.g. "molec"
Select "Atomic part"; NEXT
*[On the screen: Select atoms for the molecule]*
Select O1, N1, N2, C1, C2',C3,C4'
OK
*The selected atoms will be removed from the atomic part of the structure model, and they will be used as a pattern molecule. This pattern molecule will be later on transformed to the actual places in the crystal structure by a translation vector and three rotations*
*[On the screen: Define the molecular reference point]*
*Reference point of the molecule is used for calculation of symmetry restrictions. In our case C1 is located in a special position while the other atoms not. Therefore C1 should be the reference point*
Select "Explicit"; for "Reference point" type C1; NEXT
*[On the screen: complete molecular position #1]*
*For the placement of the model molecule to the first actual position the program shows*

*zero rotations and zero translation. This is because the model molecule has been taken from the existing atoms in the atomic part of the structure model. "Coincidence ratio 7/7" means that 7 atoms of the model molecule placed to the actual position #1 coincides with existing seven atoms in the atomic part. This is correct - the 7 atoms have been used for the model molecule.*
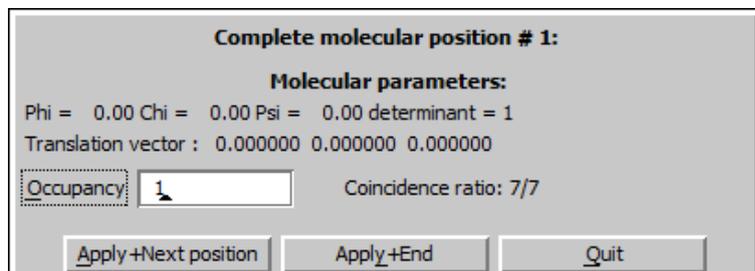


For "Occupancy" type 0.75;
"Apply + Next position"

*[On the screen: Define and complete molecular position #2]*
*In this dialogue we will define rotations and a translation vector for placing the model molecule to the second actual position. This is done by defining three atoms of the model molecule and three atoms in the atomic part of the structure model, which should coincide. In order to get correct placement of the second position the split atom positions must be used.*

Use C1, C2', C4' as model atoms and C1, C2 and C4 for the actual position
Press "Show coinciding atoms"
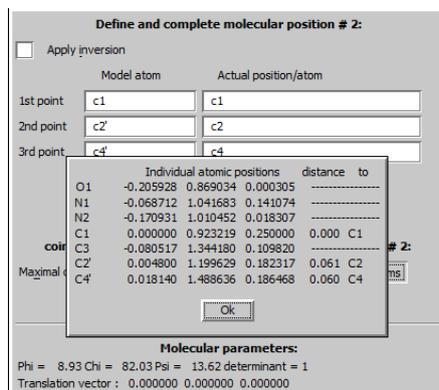


*We expected that the 7 atoms in the actual position will coincide with 7 atoms in the atomic part. However, we obtained only 3 coinciding atoms .*
OK to quit information window
Select "Apply inversion"; Press "Show coinciding atoms"

**Define and complete molecular position # 2:**

☑ Apply inversion

|  | Model atom | Actual position/atom |
|---|---|---|
| 1st point | c1 | c1 |
| 2nd point | c2' | c2 |
| 3rd point | c4' | c4 |

| Individual atomic positions | | | distance | to |
|---|---|---|---|---|
| O1 | 0.160020 | 0.847047 | 0.138719 | 0.155 O1 |
| N1 | 0.060140 | 1.033941 | 0.189811 | 0.193 N1 |
| N2 | 0.139442 | 0.991804 | 0.135700 | 0.108 N2 |
| C1 | 0.000000 | 0.923219 | 0.250000 | 0.000 C1 |
| C3 | 0.093749 | 1.333709 | 0.175734 | 0.096 C3 |
| C2' | 0.004800 | 1.199629 | 0.182317 | 0.061 C2 |
| C4' | 0.018140 | 1.488636 | 0.186468 | 0.060 C4 |

Ok

**Molecular parameters:**
Phi = 179.52 Chi = -53.10 Psi = -0.70 determinant =-1
Translation vector : 0.000000 0.000000 0.000000

Occupancy | 1 | Coincidence ratio: 3/7

*Now we have seven coinciding atoms. Thus to get the second position the rotation must be combined with inversion. The inversion centre is the reference point.*

For "Occupancy" type 0.25

"Apply + End"

Start "Edit atoms"

*The atoms of the model molecule are blue*

Rename C2' to C2 and C4' to C4

Change occupancy of C2 and C4 to 1 (the model molecule has the full occupancy)

Change ADP of C2, C4 to "harmonic"

Quit "Edit atoms"

Plot the structure

*Before starting Diamond Jana transforms the molecular positions back to the atomic part. Atoms of the first position will obtain the suffix "a", the second position has the suffix "b"*
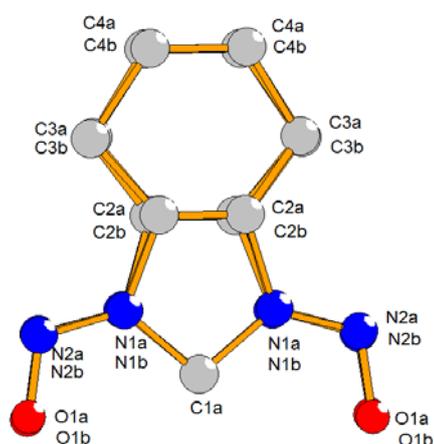


*Note that all positions except C1 are now more or less split. Close positions in the rigid body model are not problematic because the individual atomic parameters will be refined only once for the model molecule.*

Start "Parameters → Molecules → Edit"

Select refinement of "aimol" (this is occupancy of the molecular position)

OK; YES to save changes

Start Refinement options

In page "Various" go to "Restrictions" and delete two existing commands

*The deleted restrictions concerned the split atomic positions and they are no more needed*

In the same form define a new restriction command between Molec#1 and Molec#2: coordinates and ADP parameters will not be restricted but molecular occupancies will

keep the overall sum.
OK; OK; Yes+Start
*Refinement converges with R(obs) value about 8%*
*The R value is still rather high but in a light structure missing hydrogen atoms may play an important role*

## 12. *Local coordinate system*

*Atoms in the atomic part are generated according to the space group symmetry. In order to generate atoms within a model molecule, we have to define local symmetry of the molecule. After the placement of the model molecule to the final position in the unit cell, the local symmetry and the space group symmetry are combined.*

*In our case, if we define the local symmetry 1, still keeping only one half of atoms in the model molecule, the molecule would be completed after correct placement on a two-fold crystallographic axis. However, we could not keep hydrogens of the carbon C1 in geometrically expected positions because the keep command applies to the model molecule and hydrogen positions need to be generated by symmetry. For this reason, we have to define the local symmetry.*

*In our case, the model molecule has a two-fold axis along **b** and its point group will be 2. Because the internal definition of the point group expects rotation along **c** we have to define the point group 2 and change the local coordinate system.*

Start "Parameters → Molecules → Edit"
For "point group" type "2"; TAB
Check "use local system" and define "1 0 0" for x and "0 1 0" for z
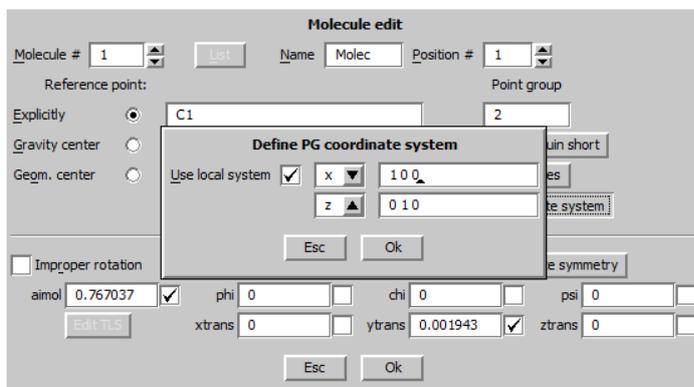


OK; OK; YES to save changes
Run refinement – the results should be the same like without the local symmetry

## 13. *Hydrogen atoms*
Start "Edit atoms"
Select all carbon atoms including the ones of the model molecule
Add hydrogen atoms in automatic mode
Verify by plotting placement of hydrogen atoms
*For suppressing one of the disordered positions its molecular occumapcy can be temporarily set to zero through "Parameters → Molecules → Edit". In such case, do not forget to set it back after the plotting.*
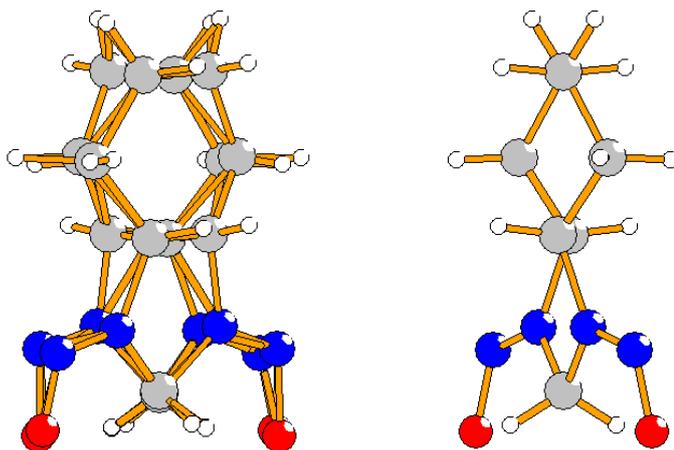
Run refinement
R value drops to *3.9%, GOF=2.6.*

Start EditM50
Go to the page "Composition"
Press "Formula from M40"
*It should print C7 H12 N4 O2 for Z=4*
Start Refinement options, page Basic
Change Instability factor from 0.01 to 0.02
Run refinement
*Refinement converges with R(obs)=3.9%, GOF=2.0.*
*Ideally, the instability factor should be determined for a given instrument. In the practice we know that it ranges between 0.01 and 0.02.*
*GOF about 2.0 may indicate that disorder is not described exactly. It may also indicate that the data contains information about bonding effects.*
Start Fourier options
In page Basic define "Map type" "Fobs-Fcalc difference Fourier"
Run difference Fourier
In the listing of Fourier check list of maxima and minima
*The residua are small like for fully solved structure*
*Last step, which is skipped in this example would be comparison of the molecular model with a model built from split atom positions. The resulting R value would be very similar to that of the molecular model.*

# Example 9.1: L9A

**Getting familiar with the output of Superflip. Some useful tricks.**

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: L9A.m40, L9A.m50, L9A.m90, L9A.m95

The purpose of this exercise is to understand the log-file of Superflip, point out the most important information to check, and to learn some basic tricks for the case Superflip does not converge with default parameters. The structure used for the exercise is an organic structure with symmetry P$na2_1$.

1. *Load the structure*

   *The structure is already prepared in Jana format for your convenience.*
   Start Jana2006;
   "File → Structure → Open" opens a file manager;
   Left pane: locate directory with input files;
   Right pane: double-click L9A;

   *Plot the structure, if you wish, check EditM50 to see the composition and symmetry.*

2. *Run Superflip.*

   Double click the icon Structure solution

*[On the screen: Structure solution]*



<span style="color:blue">Select "use Superflip";</span>
<span style="color:blue">Start "Run Solution";</span>

*Superflip starts, and after a few moments you will see the Superflip's log-file open in the window of Jana. It should be very similar to the commented file below. It will not be exactly the same, because the iteration starts from random starting point, but the differences should be minor. Please take your time to go through the text below, read the comments, try to understand the listing both in this exercise and on your screen. Are the two listings different in any important manner?*

*The first part is the header of the file, with information about the version. If you encounter strange behavior of Superflip, make sure in http://superflip.fzu.cz you have the newest version.The executable of Superflip downloaded from this web page should be copied to the SUPERFLIP directory of Jana2006 installation.*

```
***************************************************************
                      Superflip
                Version: 12/04/13  7:57
Palatinus, L. & Chapuis, G.(2007): J. Appl. Cryst. 40, 786-790
            http://superspace.epfl.ch/superflip
***************************************************************
```

*Next part is a review of input parameters and crystallographic information. Superflip currently writes only the matrix-vector representation of the space group, and not the space group symbol.*

```
----------------------------------------------
Start of the calculation: 28.JAN 2014, 14:29:49
----------------------------------------------


##############################################################
# Following data were read from the input file or set as default: #
##############################################################

Job title: L9A

-----------------------
```

```
Information about files:
-----------------------
Name of the input file: L9A.inflip
Density will be writen in following files:
   L9A.m81, with type jana
   L9A.m80, with type m80
Warning: If the outputfile exists, it will be overwritten by the new density.
Logfile will contain only basic information about the calculation.
Logfile will contain information about the data coverage.


---------------------------
Crystallographic information:
---------------------------
Superspace dimension:          3
Dimension of the physical space: 3
Direct cell parameters:       15.3079  9.2915  13.8059  90.0000  90.0000  90.0000  Volume:   1963.65942
Reciprocal cell parameters:    0.0653   0.1076   0.0724  90.0000  90.0000  90.0000  Volume:      0.00051
Wilson plot will be based on this composition: C84H104N8O16
4 symmetry operations found, their list follows:

   1:   1  0  0    0.0000   2:  -1  0  0    0.0000   3:   1  0  0    0.5000
        0  1  0    0.0000        0 -1  0    0.0000        0 -1  0    0.5000
        0  0  1    0.0000        0  0  1    0.5000        0  0  1    0.0000

   4:  -1  0  0    0.5000
        0  1  0    0.5000
        0  0  1    0.5000


The structure is non-centrosymmetric.


------------------------
Settings of the algorithm:
------------------------
Number of voxels:              40    24    36   Total:     34560
Number of voxels for polishing: 80    48    72   Total:    276480
The density modification method will be charge flipping.
Delta will be determined automatically.
The iteration will be stopped when the convergence is detected or after ***** cycles.
After the regular iteration   5 cycles of "density polishing" will be applied.
The random number generator will be initialized automatically.

Random initial phases will be assigned to the structure factors.
Isotropic Debye-Waller factor:    0.000
Proportion of reflections to be treated as weak:    0.000
All reflections with sin(th)/lambda < 0.400 not present in the input data set will be treated a missing.
The amplitudes of the missing reflections will be left unconstrained.

The resulting density will be shifted and averaged according to the symmetry operations given above.
Following symmetry operations will be used to locate the origin of symmetry:   3   4
```

*Most of the information above is just diagnostic and is not important for ordinary user. However, the number of reflections treated as weak might be changed, if Superflip does not converge with default parameters. See below for more discussion on this parameter.*

*Next part is an overview of reflection import. "Number of reflections treated as missing" is the number of low-resolution reflections that are not present in the input data. By default, Superflip lets their value vary freely during the iteration. However, if this number is large (say more than 10% of all reflections), the iteration may fail. In such a case a more sophisticated treatment of reflections (or a more complete dataset) may be necessary. See manual of Superflip, keyword* `missing` *for more information.*

```
################################
# Information about reflections: #
################################

Number of reflections in the input file:   1624


------------------------
Averaging of reflections:
------------------------
Redundancy   : 1.000
Rint         : -----

Maximum indices in expanded reflection set:  17  10  15

Number of reflections treated as missing:      6
```

*Wilson plot is always a useful indicator of the data quality and consistency. If you encounter problems with your structure, do not forget to check the Wilson plot and make sure it does not show anomalies. The value Biso is the Wilson-plot based estimate of the average Debye-Waller factor. If it is larger than 2, a correction of the input data might be needed. We will learn how to make this correction later in this exercise.*

```
------------
Wilson Plot:
------------

circles: <I>/SUM(f^2)
dots   : linear fit y =   1.5450 +   -3.480 * [sin(theta)/lambda]^2

   4.15377-|     o o
          -|        . . o
 Scale^2 -|   o      o . o                      o
          -|        o       o .            o
          -|            .         o       o o
   2.99073-|          o   . .     o o
          -|          o     . .            o
          -|                 . .          o
          -|          o          . .
          -|           o o           . .
   2.15334-|                         . . o
          -|                       . o
          -|                         o o
          -|                              .
          -|                         o . .
   1.55041-|                            . .
          -|                       o       . . o
          -|                        o o
          -|                          o        .
          -|                           o
   1.11630-|                            o
          I------------------I------------------I------------------I----------
          0.00              0.10              0.20              0.30
                         [sin(theta)/lambda]^2

Scale (F_obs = K * F_abs):     2.165
Biso:                          1.740
```
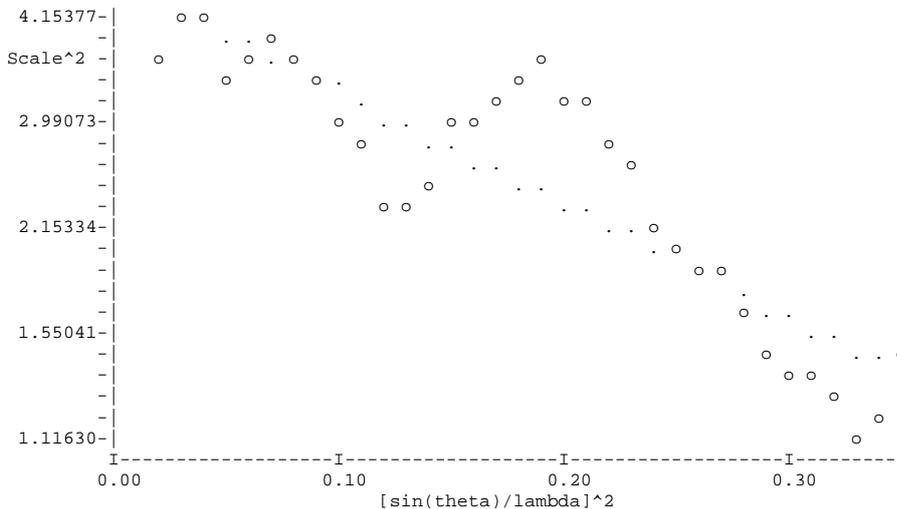
*Coverage statistics shows the coverage as a function of resolution. The coverage should be high (optimally more than 90%) up to a reasonable resolution ($d_{min}<1.1$ or better). If one of these conditions is not fulfilled, Superflip may fail. Very low coverage at low resolution is especially dangerous.*

```
-----------------------------------------------------------
Coverage statistics of the expanded reflections by shells:
-----------------------------------------------------------
Resolution (sin(th)/l):   0.050   0.100   0.150   0.200   0.250   0.300   0.350   0.400
Resolution (d_min):      10.000   5.000   3.333   2.500   2.000   1.667   1.429   1.250
Obs. refl. in shell:          0      25      69     139     238     349     515     655
Total refl. in shell:         0      27      73     139     238     349     515     655
Coverage in shell:         0.0%   92.6%   94.5%  100.0%  100.0%  100.0%  100.0%  100.0%
Commulative coverage:      0.0%   92.6%   94.0%   97.5%   98.7%   99.3%   99.6%   99.7%

Resolution (sin(th)/l):   0.450   0.500   0.550   0.575
Resolution (d_min):       1.111   1.000   0.909   0.870
Obs. refl. in shell:        876    1093    1323     708
Total refl. in shell:       876    1093    1323     730
Coverage in shell:       100.0%  100.0%  100.0%   97.0%
Commulative coverage:     99.8%   99.8%   99.9%   99.5%
```

*Iteration record shows some most important quantities during the iteration process. At the beginning the program tries to estimate the value of delta automatically. This procedure is very reliable, and only in very rare cases a manual selection of delta is necessary. The four quantities shown in every line are as follows:*

- *R: The R-value between the observed structure-factor amplitudes, and the amplitudes calculated after flipping. This value usually lowers at the convergence.*
- *Charge: Total charge in the current density. This value progressively lowers during the whole iteration, but drops down abruptly at the convergence*
- *Peaks: The third central moment of the density – a measure of "peakiness" of the density. This value grows at the convergence.*
- *Score: A combined "Figure of merit" calculated from the three quantities above as well as from their derivatives. If the score grows above 0.8, Superflip considers the iteration as converged.*

  *Note: An automatic detection of convergence is an extremely difficult task, because it must cover a wide range of cases. Therefore, despite of a substantial effort invested into the detection, Superflip occasionally fails to detect convergence. It is therefore always worth checking whether the structure is solved, even if the iteration does not seem to converge.*

```
#############
# Iteration #
#############

Estimated delta:  2.2715
Random seed:     131727704

Searching for a proper delta:
Current delta =     2.27153  (k_ed =   1.00000)
Total/flipped ratio =     1.021. Increasing delta.

Current delta =     2.43053  (k_ed =   1.07000)
Total/flipped ratio =     0.856.
Criterion for delta fulfilled, continuing iteration.
   20  R: 49.925  Charge:    1220.10  Peaks: 1.26  Score:   ---
   30  R: 48.103  Charge:    1149.05  Peaks: 1.36  Score:   ---
   40  R: 49.758  Charge:    1128.06  Peaks: 1.47  Score:   ---
   50  R: 49.224  Charge:    1120.09  Peaks: 1.53  Score:   ---
   60  R: 49.160  Charge:    1067.55  Peaks: 1.58  Score:   ---
   70  R: 49.279  Charge:    1092.28  Peaks: 1.62  Score:   ---
   80  R: 48.642  Charge:    1088.73  Peaks: 1.70  Score:   ---
   90  R: 48.457  Charge:    1063.52  Peaks: 1.74  Score:   ---
  100  R: 48.313  Charge:    1065.67  Peaks: 1.74  Score:   ---
  200  R: 46.931  Charge:    1057.27  Peaks: 1.89  Score:   ---
  300  R: 38.686  Charge:     972.57  Peaks: 2.09  Score:  0.15

Calculation successfully converged after   390 cycles.
Last iteration record:
  390  R: 23.891  Charge:     878.59  Peaks: 2.23  Score:  0.91

     5 cycles of noise suppression follow:
    5  R: 14.793  Charge:       0.00  Peaks: 2.71
```

*At this moment the calculation is converged (or the maximum number of iteration cycles was reached). Superflip has the capacity to check the resulting density for symmetry. It is advisable to always check this part of the log-file, and to make sure that the detected symmetry corresponds to your expectations. Derived space group P1 in cases where higher symmetry is expected usually indicates that the structure is not solved.*

*Superflip lists all symmetry operations compatible with the lattice. Each line in the listing corresponds to one symmetry operation. The symbol of the operation is followed by a one-line representation as used in International Tables for crystallography. Next is the "symmetry agreement factor". This number indicates quantitatively, how well the operation is present in the electron density. Numbers below 10 indicate a very good match, number between 10 and 25 are still probable symmetry operations of the density, and numbers above 25 usually mean that the corresponding symmetry operation is not present. In the*

*example below the n-glide, a-glide, and two-fold screw axis have agreement factors below 0.1, indicating an excellent agreement. All the rest of the list has a far too high value. The rows of XXXXXX after the symmetry agreement factor are just a graphical representation of the agreement factor, and serve as a quick guide for eye.*

```
#####################################
# Checking the density for symmetry #
#####################################

Symmetry operations compatible with the lattice and centering:
                    Symmetry operation            agreement factor
    n(1,0,0):        -x1      1/2+x2    1/2+x3     0.022    XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
    a(0,1,0):      1/2+x1       -x2        x3      0.072    XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
  2_1(0,0,1):        -x1        -x2     1/2+x3     0.090    XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
    m(0,0,1):         x1         x2       -x3     74.885    XXXXXXXXXXXXX
  2_1(0,1,0):        -x1      1/2+x2      -x3     74.894    XXXXXXXXXXXXX
  2_1(1,0,0):      1/2+x1       -x2       -x3     74.907    XXXXXXXXXXXXX
    m(1,0,0):        -x1         x2        x3     78.690    XXXXXXXXXXX
    2(0,0,1):        -x1        -x2        x3     78.739    XXXXXXXXXXX
    2(0,1,0):        -x1         x2       -x3     80.683    XXXXXXXXXX
        -1:          -x1        -x2       -x3     80.741    XXXXXXXXXX
    b(0,0,1):         x1      1/2+x2      -x3     84.318    XXXXXXXX
    n(0,0,1):      1/2+x1     1/2+x2      -x3     91.302    XXXX
    2(1,0,0):         x1        -x2       -x3     91.311    XXXX
    a(0,0,1):      1/2+x1        x2       -x3     91.487    XXXX
    b(1,0,0):        -x1      1/2+x2       x3     92.258    XXXX
    c(0,1,0):         x1        -x2     1/2+x3    104.952    X
    m(0,1,0):         x1        -x2        x3    107.481    X
    c(1,0,0):        -x1         x2     1/2+x3    120.115    X
    n(0,1,0):      1/2+x1       -x2     1/2+x3    135.532    X
```

*An experienced crystallographer can "see" the space group already in the list of the symmetry operations, but Superflip can analyze the list automatically. The default threshold for accepting a symmetry operation is the symmetry agreement factor below 25. All such operations are combined together, and a final space group is printed as Herman-Mauguin symbol, Hall symbol, Fingerprint, and a list of symmetry operations. The "Fingerprint" is an internal space-group symbol used by Superflip for a database search, and currently does not have any other use.*

```
-----------------------------------------------
Space group derived from the symmetry operations:
-----------------------------------------------
    HM symbol:     Pna21
    Hall symbol:   P 2c -2n
    Fingerprint:   3300223}240qY3 (3/4,3/4,0)
    Symmetry operations:
           1:          x1         x2        x3
  2_1(0,0,1):         -x1        -x2     1/2+x3
    n(1,0,0):      1/2-x1     1/2+x2    1/2+x3
    a(0,1,0):      1/2+x1     1/2-x2       x3
```

*As the density is reconstructed in P1, the origin is arbitrary. To allow for further processing, the density must be shifted to the standard origin of the space group, and averaged to have the desired symmetry exactly. The lines below show the record of this process.*

*Important note: The "Check for symmetry" described above is just indicative, and does not have any impact on further symmetry processing (unless you force it explicitly in the input file of Superflip – see manual, keyword derivesymmetry for details). Thus, the output symmetry will be the symmetry indicated in the input file. If you call Superflip from Jana with default parameters, this is the symmetry recorded in m50.*

*"Agreement factors of individual generators" show agreement factors for the generators of the input space groups. These generators are used to locate the origin of the space group. If the input space group is incorrect, or the solution did not converge, these agreement factors will be high (more than 25). Low values of the agreement factors are another reliable indicator that the structure was correctly solved.*

```
############################################
# Search for the origin of the space group #
############################################


Position of the origin in the CF map:
  0.6641  0.6559  0.0000
Agreement factors of individual generators:
Number smb agreement
    3    a       0.07
    4    n       0.02

Overall agreement factor:   0.06
```

*These are the final notes in the log file with information about the file with the output:*

```
You can obtain more information about the reconstructed reflection phases by using 'expandedlog yes'.

Electron density written to file L9A.m81.


-------------------------------------------
End of the calculation: 18.JAN 2010, 13:17:29
-------------------------------------------
Superflip version: 07/16/09 09:12
```

Press "Close" to close the listing and return to the Structure solution dialogue

3. ***View the output of Superflip and resulting structure model***

*[On the screen: Structure solution]*
*After closing the listing of Superflip, Jana2006 automatically interprets the resulting density in terms of atomic positions and types. For chemical types, only the ones available in "Formula" are considered.*
Press "Draw structure" to visualize structure model interpreted by Jana2006 from the density provided by Superflip
*Note that the structure model has the symmetry originally det by the user. If the symmetry suggested by Superflip is different and you want to use it, it must be set by the "Change the space group" button, and the interpretation of the density map or complete charge flipping must be repeated.*
*"Return to previous" loads the previous structure model. Note that there is only one step back possible.*

*If everything goes well, the structure model correctly describes the density produced by Superflip. However, in some cases this can lead you to the wrong impression that this is what Superflip produces. In case of problems (typically disorder or wrong chemical types in the formula) viewing the density may be very helpful.*

Press "Draw 3d map" to view the 3D isosurface representation of the raw density produced by Superflip
*The crystallographic (not only) viewer VESTA must be installed on your computer and enabled it in Jana. If not, consult the installation notes and install the program first. Jana passes the volumetric data to VESTA along with the structure model. VESTA shows an overlay of both, with the density represented by isosurfaces, and atoms by spheres. In this case the density shows nice spherical maxima at the positions of atoms. All maxima are "occupied" by an atom. Thus, the structure model is likely to be complete and ready to be refined.*

*By default, the density from Superflip is saved in the file jobname.m81. That means that you can directly view it even after quitting the Structure solution dialogue as long as you do not overwrite it by calculating another Fourier map. M81 can be viewed with Contour program.*

*By default, the structure factors from Superflip are saved in the file jobname.m80. That means the Fourier map can be recalculated by Jana2006 as long as m80 is not overwritten by refinement.*

4. ***Modify the default settings for Superflip***
*The default settings passed to Superflip by Jana are applicable to most standard cases. However, under some circumstances the change is necessary. The most useful changes will be listed here.*

*Hint 1: use normalized intensities:*
For more difficult structures using normalized intensities helps enormously.
Check the checkbox next to Use local normalization: 

*Hint 2: Run Superflip several times with a limited number of cycles:*
Check the checkbox "Repeat Superflip: number of runs"

You may select a different number of repetitions than the default 10.
If necessary, modify the maximum number of cycles per run, for example to 5000:

*This option may help if the solution appears unstable or if it gets trapped in a local minimum. Some of the repeated runs may escape from the local minimum. Superflip selects the best of all attempts for the output.*

*Hint 3: Use a non-random starting model*
Select the option "Patterson superposition map" from the list named "Starting model":

*With this option Superflip first calculates a Patterson superposition map and then uses this map as a starting model for the iteration. Very often this option speeds up the convergence, and sometimes it makes the difference between solved and non-solved structure. However, sometimes – especially for simpler structures – the convergence is so rapid that it cannot be detected and Superflip keeps running. This option saves time only for larger structures, ideally with at leas one non-light atom.*

*Hint 4: use the AAR algorithm:*
Select the AAR iteration scheme from the list of options at the bottom of the window:

*The AAR algorithm appears to perform better than the standard algorithm for very incomplete data or for low-resolution data. However, it is less stable than the standard algorithm and it is more difficult to detect its convergence. AAR is the default algorithm for electron diffraction data.*

*Try one or more of the above hints and see how they affect the speed of convergence. You should come to the conclusion that for this simple structure there is hardly any difference between the options, but most of them speed up the convergence., However, combination AAR + local normalization is too aggressive and does not lead to the solution.*

*Superflip offers a large number of other options, which are described in detail in the manual. If you want to use any of these advanced options, then:*
Check the checkbox "Allow manual editing of the command file before start:
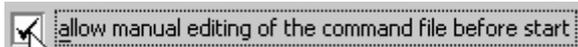


Click Run solution

*Before Superflip starts, the input file opens in a text editor and you may edit the file and include whatever additional options you wish.*

*The price to pay for faster convergence is the increased noise in the result, and sometimes more difficult detection of convergence. Because the default parameters work usually quite well and yield the best densities, we recommend using them for first attempts. Only if the iteration does not converge, try modifying the parameters according to the hints described above.*

Press "Quit" to close the Structure solution tool
*Note that there is no "escape" option. The original M40 which might be present before starting this tool is being overwritten after each "Run solution" process and the only way how to retain it is to use in proper time the "Return to previous" button.*

## 5. Integration of Superflip to Jana2006

The following scheme shows how Superflip communicates with the rest of Jana2006. M95 contains raw data; M90 is refinement reflection file (merged reflections without extinct reflections); M40 is structure model; M50 is basic crystal information; M80 are structure factors from refinement or charge flipping; M81 is density map
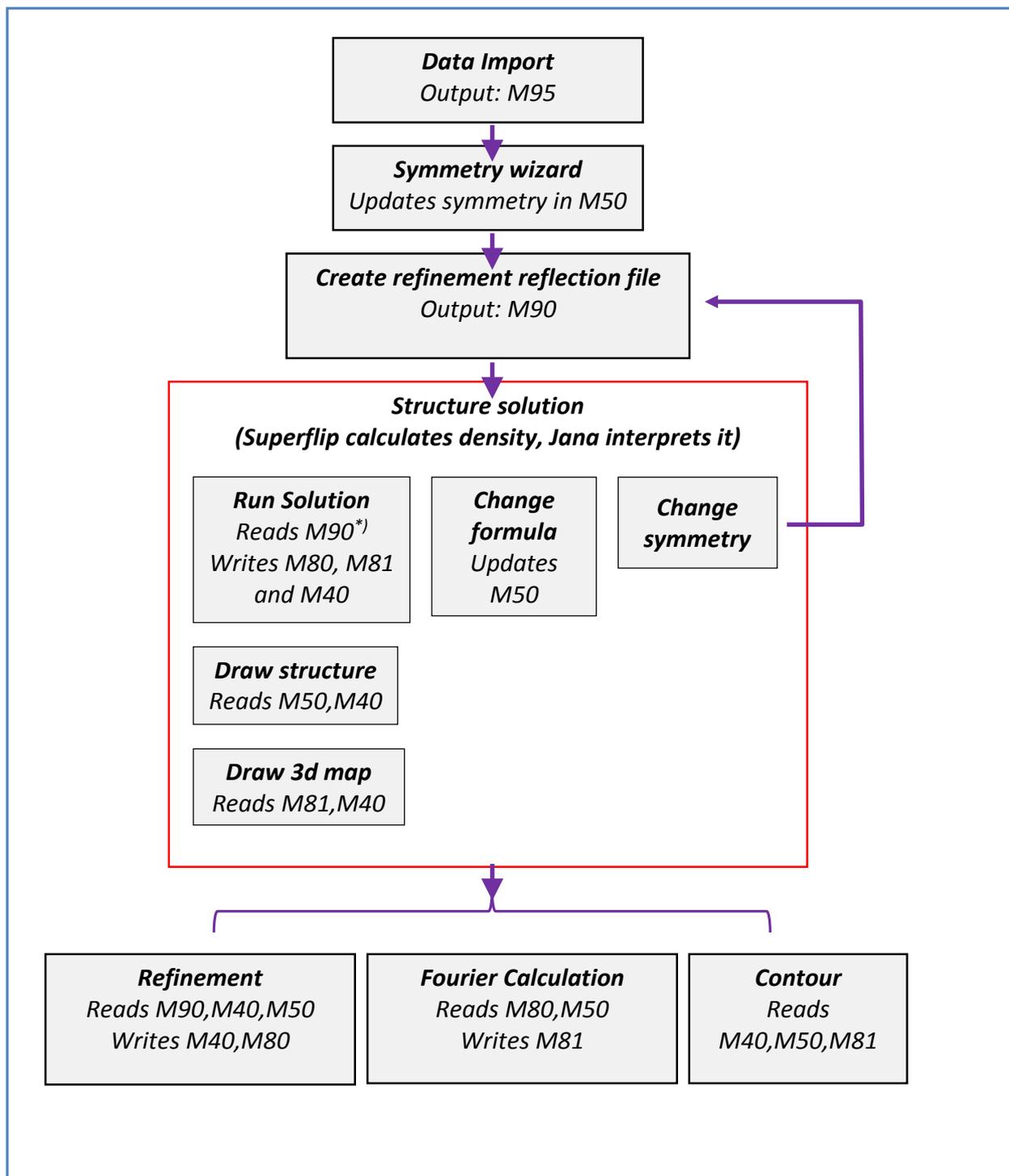


*) Superflip expands M90 to P1 symmetry. However, its results are to some extent influenced by the symmetry set by the user with the Symmetry wizard, because M90 contains merged reflection and systematically extinct reflections are omitted

# Example 9.2: pArNO2

**Solving the centro-noncentro ambiguity with Superflip**

This relatively simple structure illustrates the advantages of using Superflip to determine the space group.

**Revised: 16 September 2014**

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: pArNO2.hkl, pArNO2.cif_od

1. ***Create new structure***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click pArNO2

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Leave all settings unchanged; NEXT
   OK to confirm the name of the basic input file
   Leave all settings unchanged (note the cell parameters and thus the probable crystal system); NEXT
   Finish the import wizard with all settings default

3. ***Symmetry Wizard***
   *[On screen: Information about the symmetry wizzard.]*
   NEXT to start the wizard;
   Leave all settings default; NEXT; OK;
   *[On screen: Select Laue symmetry]*
   *Jana2006 suggests orthorhombic symmetry based on $R_{int}$. In this case the choice appears clear.*
   Keep the suggested selection; NEXT
   Select primitive unit cell; NEXT
   *[On screen: Select space group]*
   *You are now offered a list of candidate space groups sorted by their likelihood. Note that the first two space groups Pnma and Pn2$_1$a differ only by the presence of inversion center and they have the same FOM:*

| Select space group | | | |
|---|---|---|---|
| Space group | obs/all | ave(I/sig(I)) | FOM |
| Pnma | 33/1780 | 4.720/0.530 | 0.00174 |
| Pn21a | 33/1780 | 4.720/0.530 | 0.00174 |
| Pmma | 19/1193 | 4.345/0.458 | 0.00201 |
| Pm2a | 19/1193 | 4.345/0.458 | 0.00201 |
| P21ma | 19/1193 | 4.345/0.458 | 0.00201 |
| Pnmm | 14/587 | 5.229/0.675 | 0.00802 |
| Pnm21 | 14/587 | 5.229/0.675 | 0.00802 |
| Pn21m | 14/587 | 5.229/0.675 | 0.00802 |
| P21212 | 3/46 | 6.782/1.041 | 0.04581 |

*Jana by default does not use the distribution of E-values to estimate, if the structure is centrosymmetric or not. The main reason is that the same information can be obtained from Superflip with higher reliability. At this point the space group choice can be made either randomly or based on chemical knowledge. The choice of one of the two space groups has no impact on the structure solution by Superflip.*

Select Pnma; NEXT
Accept the space group; FINISH


4. **Creating refinement reflection file**
   Proceed with the creation of refinement reflection file, leaving all settings default until you see the following screen:

> **INFORMATION**
> In the next step the program will open a tool for starting different programs for solution of the structure. The most universal one, applicable for powder or single crystals data, is Superflip.
>
> Ok
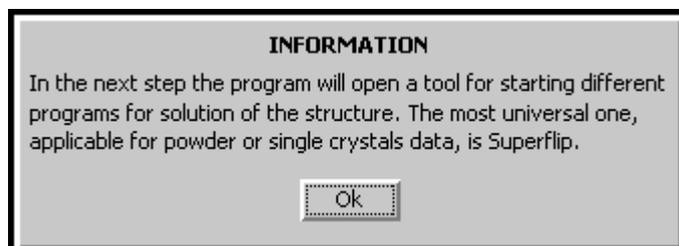
5. **Consulting the intensity statistics**
   *At this point we will interrupt the standard flow of the solution process to check the E-statistics and estimate the presence or absence of the inversion center.*
   OK; Quit to escape the structure solution dialog.
   *[On screen: Main window]*
   *First we have to define the chemical composition.The crystallized molecule has sum formula C42 H43 N1 O6 S4 (see the end of the exercise for the picture of the molecule), number of molecules per unit cell: 8. The solvent was acetonitrile – we do not know the number of solvent molecules per formula unit, but we may ignore the solvent contribution for now.*

   Double click the icon EditM50
   Select the page "Composition"
   Enter "C42 H43 N O6 S4" in the first field;

Keep 8 for the number of formula units; OK; Yes;

*[On screen: Main window]*

Go to Run → Intensity statistics

*[On screen: Wilson plot]*

Check the Wilson plot. Click anywhere in the plot to continue;

Yes to open the listing;

*[On screen: listing of intensity statistics]*

*This listing contains a large number of statistics related to intensity normalization. We will focus only on the following table (found around the middle of the listing):*

| | | | | | Experimental | | Theoretical | |
|---|---|---|---|---|---|---|---|---|
| Value | All data | hkl | 0kl | h0l | hk0 | Acentric | Centric | Hypercen. |
| mod(E) | 0.801 | 0.804 | 0.779 | 0.499 | 0.867 | 0.886 | 0.798 | 0.718 |
| E**2 | 1.000 | 1.003 | 1.086 | 0.473 | 1.095 | 1.000 | 1.000 | 1.000 |
| E**3 | 1.690 | 1.694 | 2.131 | 0.630 | 1.773 | 1.329 | 1.596 | 1.916 |
| E**4 | 3.556 | 3.570 | 5.127 | 0.997 | 3.433 | 2.000 | 3.000 | 4.500 |
| E**5 | 8.781 | 8.832 | 13.989 | 1.728 | 7.628 | 3.323 | 6.383 | 12.260 |
| E**6 | 24.409 | 24.611 | 41.363 | 3.164 | 18.939 | 6.000 | 15.000 | 37.500 |
| **mod(E**2-1)** | **0.983** | **0.981** | **1.177** | **0.905** | **0.985** | **0.736** | **0.968** | **1.145** |
| (E**2-1)**2 | 2.556 | 2.565 | 3.955 | 1.051 | 2.244 | 1.000 | 2.000 | 3.500 |
| (E**2-1)**3 | 15.740 | 15.908 | 28.239 | 0.592 | 10.922 | 2.000 | 8.000 | 26.000 |

*This table shows the numbers typically used to estimate the centrosymmetry. If you compare the column All data with the theoretical values, you can see that all numbers indicate a centric or hypercentric distribution. Our guess* Pnma *thus appears to be strongly supported by the statistics*

Click the button "Close" to close the listing and return to the main window.


6. *Structure Solution*

Double click the icon Structure solution

*[On screen: window of Structure solution]*

Leave all settings default;

Click the button "Run solution" to start Superflip

*Superflip converges smoothly and the listing of the solution procedure opens in Jana.*

*[On screen: listing of Superflip]*

Locate the symmetry analysis in the listing. It should look very similar to this (rows of XXXX are omitted here to save space):

```
####################################
# Checking the density for symmetry #
####################################

Symmetry operations compatible with the lattice and centering:
                  Symmetry operation                 agreement factor
        a(0,0,1):      1/2+x1           x2          -x3     0.229
        n(1,0,0):         -x1       1/2+x2      1/2+x3     0.651
      2_1(0,1,0):         -x1       1/2+x2         -x3     0.714
      2_1(0,0,1):         -x1          -x2      1/2+x3    51.947
             -1:         -x1          -x2         -x3    52.037
        2(0,0,1):         -x1          -x2          x3    66.366
```

```
       m(0,1,0):             x1            -x2            x3    71.723
    2_1(1,0,0):          1/2+x1            -x2           -x3    72.620
       c(0,1,0):             x1            -x2         1/2+x3   72.643
       2(0,1,0):            -x1             x2           -x3    78.403
       m(1,0,0):            -x1             x2            x3    78.485
       2(1,0,0):             x1            -x2           -x3    78.709
       n(0,1,0):          1/2+x1            -x2         1/2+x3   78.768
       m(0,0,1):             x1             x2           -x3    82.199
       b(1,0,0):            -x1          1/2+x2            x3    82.308
       a(0,1,0):          1/2+x1            -x2            x3    83.217
       c(1,0,0):            -x1             x2         1/2+x3   89.079
       n(0,0,1):          1/2+x1          1/2+x2          -x3   126.255
       b(0,0,1):             x1          1/2+x2          -x3   131.166


   --------------------------------------------------
   Space group derived from the symmetry operations:
   --------------------------------------------------
      HM symbol:     Pn21a
      Hall symbol:   P -2ac -2n
      Fingerprint:   33002241Y40qY3 (3/4,0,3/4)
      Symmetry operations:
              1:             x1             x2            x3
       a(0,0,1):          1/2+x1             x2         1/2-x3
       n(1,0,0):          1/2-x1          1/2+x2         1/2+x3
     2_1(0,1,0):            -x1          1/2+x2           -x3
```

*Look at the table. You can see that the first three operators belonging to the Pn2₁a space group have very low agreement factors (less than 1%) indicating a very good match. All other operators have agreement factors above 50%, which is very poor. In particular the mirror plane perpendicular to **b** has agreement factor 71.7%. It is thus clearly absent in the structure. The space group is without doubt Pn2₁m.*

6. **Insert the correct space group and solve the structure**
   *Although the solution by Superflip is correct, the space group in Jana is still wrong, and the solution is thus not usable. We have to set the correct space group and rerun Superflip.*
   Close the view of the log file;
   Click "Change the space group" in the "Structure solution" form;
   Type "Pn21a" in the upper left box; OK; YES;
   *As the symmetry changed, the refinement reflection file must be recreated. Create the new file with default settings.*
   Press "Run solution" to start Superflip again with the correct symmetry;
   *Superflip starts, and should again converge smoothly to a solution.*
   Close the log-file viewer;
   Click "Draw 3D map";
   *View the resulting electron density and the interpreted model. The structure is correctly solved, but quite a few peaks have not been assigned an atom. We know the expected composition and we may thus use the alternative peak-interpretation option – use of an external program EDMA:*
   Close VESTA;
   Select the radiobutton "EDMA – fixed composition":

Check the checkbox "Use old solution and reinterpret it:



Click "Run solution" to interpret the previous solution with the new setting.
*A new screen appers with the run-time information from EDMA: When EDMA finishes, a listing of Superflip opens.*
Close the listing and return to the structure solution dialog
Double click "Draw 3D map"
*This time you sould see all maxima in the map occupied by an atom. Most atoms should have a correctly assigned atomic type, although carbon, nitrogen and oxygen may be occasionally swapped.*
*Here is the correct molecule for reference (hydrogens omitted for clarity):*
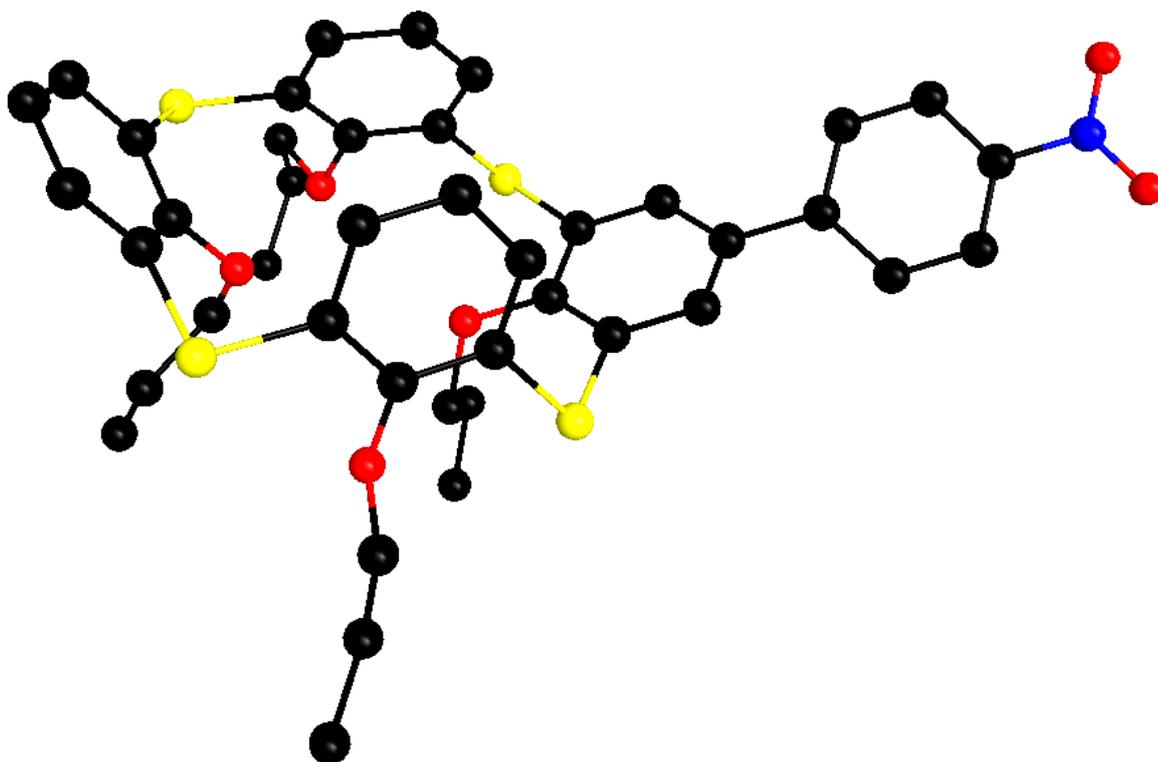
# Example 9.3: flo19

**A challenging case of difficult symmetry and difficult convergence detection**

**Revised: 18 February 2014**

Input files: flo19.cif, flo19.hkl. The structure is an organic molecule built by four aromatic rings bridged by one or two nitrogen atoms.

1. ***Load the structure from CIF***
   Start Jana2006;
   "File → Structure → New";
   Locate the input files, and double click the name flo19 in the right pane;
   Select the radiobutton "Structure: from CIF"; NEXT; OK to confirm the file flo19.cif
   OK to the warning that the CIF does not contain symmetry information;
   *At this moment you loaded the basic crystallographic information. You can check the composition and unit cell dimensions by double clicking the EditM50 icon and consulting the card Cell and Composition.*

2. ***Import the reflection file***
   "File → Reflection file → Import/modify the reflection file"
   Select "Single crystal: reflection file corrected for LP and absorption"; NEXT;
   Check that the filename is flo19.hkl and that the file type is SHELX on I; NEXT;
   2x NEXT for the two following screens; OK; Finish; OK; YES to finish the import wizard

3. ***Estimate the symmetry***
   *When the reflection import finishes, you are automatically offered the symmetry determination form[1].*
   NEXT to start the wizard;
   NEXT to confirm the default settings of the test;
   OK to the information about no higher metric symmetry;
   *On the screen with Rint for different Laue groups make sure you understand Jana's choice of the mmm Laue group.*
   NEXT;
   *On the screen with centering statistics make again sure that you understand the meaning of the numbers and the choice Jana2006 made.*
   NEXT;
   *At this moment you are presented with the list of possible space groups. The upper part of the list looks like this:*

---

1. [1] *If you accidentally close the wizard or if you want to repeat the test, you can access the symmetry determination procedure through the EditM50 icon, card Symmetry.*

| Space group | | obs/all | | ave(I/sig(I)) | | FOM | |
|---|---|---|---|---|---|---|---|
| P21221 | \| | 3/48 | \| | 3.993/0.820 | \| | 0.03190 | \| |
| P2221 | \| | 3/43 | \| | 3.993/0.886 | \| | 0.03891 | \| |
| P212121 | \| | 4/50 | \| | 5.722/1.015 | \| | 0.04050 | \| |
| P22121 | \| | 4/45 | \| | 5.722/1.100 | \| | 0.05127 | \| |
| P2122 | \| | 0/5 | \| | 0.000/0.252 | \| | 0.16973 | \| |
| Pmmn | \| | 8/41 | \| | 5.230/1.644 | \| | 0.79129 | \| |
| Pm21n | \| | 8/41 | \| | 5.230/1.644 | \| | 0.79129 | \| |
| P21mn | \| | 8/41 | \| | 5.230/1.644 | \| | 0.79129 | \| |
| P21212 | \| | 1/7 | \| | 10.911/1.804 | \| | 0.94732 | \| |
| Pmmm | \| | 0/0 | \| | 0.000/0.000 | \| | 1.00000 | \| |
| Pm2m | \| | 0/0 | \| | 0.000/0.000 | \| | 1.00000 | \| |
| P2mm | \| | 0/0 | \| | 0.000/0.000 | \| | 1.00000 | \| |
| Pmm2 | \| | 0/0 | \| | 0.000/0.000 | \| | 1.00000 | \| |
| P222 | \| | 0/0 | \| | 0.000/0.000 | \| | 1.00000 | \| |

Select the space group P21221 and click "Details";
*In the listing you can find basic information about the space group and the list of observed reflections that violate the rules for systematic absences. Check the details for several space groups. Which space groups would you consider possible and which would be the most likely?*

*Because the solution in Superflip is not sensitive to the choice of the space group symmetry, we will choose just one of the space groups without any systematic absences to keep the solution unbiased.*

Select the space group *Pmmm*; NEXT; FINISH; OK; YES to finish the space group selection
*We selected the space group Pmmm not because it is the most likely choice, but because it does not induce any systematic absences. We will now process the reflections, and ask Superflip to estimate the space group. If we selected a space group with systematic absences, some reflections would be excluded from the reflection file, and the result from Superflip could be biased.*

4. *Create refinement reflection file*
   *When the space group determination finishes, you are automatically offered the "Create refinement reflection file" tool. If you accidentally exit it, you can always return to it through "File → Reflection file → Create refinement reflection file"*
   NEXT; OK; NEXT; OK; FINISH to create the refinement reflection file with all settings default

7. *Run Superflip.*
   *Next Jana offers you the dialog for structure solution. If you want to open this dialog later, just double click the icon "Structure solution" in the main window of Jana.*
   Make sure Superflip is selected;
   Leave other settings default; Click Run solution;
   *Superflip starts and runs for many thousand cycles. No convergence is detected.*
   Press "Interrupt" to stop Superflip;
   *The log file of Superflip opens. Check the symmetry determination part. You will see that no symmetry operation has agreement factor lower than 25% and thus the derived space group is P1. Because we expect higher symmery (although we do not know the exact space group), it is a sign that the calculation did not converge.*

*Inspection of the log file does not reveal any serious problem, but a series of hints shows that the structure can be difficult to solve. The potential problems are that the coverage starts dropping already at $d_{min} \approx 1.1$ Å, and that the coverage at low resolution is very low (only 21% at $d_{min} \approx 5$ Å). It can be assumed that quite a few strong reflections are missing in the dataset. The first change to try is to use normalized intensities. When using normalized intensities, Superflip also automatically treats the missing reflections in a special way that improves the performance in case of data with missing low-order reflections.*

Close the view of the log file;
Check the checkbox "local normalization"
Click "Run solution"

*Superflip starts and probably runs again for many thousand cycles without detecting convergence[2].*
*If you look at the evolution of the convergence indictors, you will most probably see behavior similar to this[2,3]:*

```
  20  R: 56.175  Charge:     20.84  Peaks:  1.11  Score:    ---
  30  R: 57.537  Charge:     20.13  Peaks:  1.16  Score:    ---
  40  R: 58.291  Charge:     19.03  Peaks:  1.15  Score:    ---
  50  R: 58.075  Charge:     19.08  Peaks:  1.22  Score:    ---
  60  R: 57.460  Charge:     18.65  Peaks:  1.22  Score:    ---
  70  R: 59.161  Charge:     18.79  Peaks:  1.32  Score:    ---
  80  R: 57.279  Charge:     18.88  Peaks:  1.33  Score:    ---
  90  R: 59.624  Charge:     18.89  Peaks:  1.39  Score:    ---
 100  R: 56.954  Charge:     18.29  Peaks:  1.41  Score:    ---
 200  R: 55.838  Charge:     18.37  Peaks:  1.29  Score:   0.15
 300  R: 57.292  Charge:     18.12  Peaks:  1.35  Score:   0.15
 400  R: 55.889  Charge:     17.89  Peaks:  1.32  Score:   0.15
 500  R: 55.456  Charge:     18.50  Peaks:  1.32  Score:   0.15
 600  R: 55.902  Charge:     18.88  Peaks:  1.22  Score:   0.15
 700  R: 53.192  Charge:     18.50  Peaks:  1.24  Score:   0.15
 800  R: 53.102  Charge:     18.23  Peaks:  1.27  Score:   0.15
 900  R: 50.902  Charge:     17.41  Peaks:  1.23  Score:   0.15
1000  R: 45.968  Charge:     18.16  Peaks:  1.19  Score:   0.15
2000  R: 43.139  Charge:     18.59  Peaks:  1.12  Score:   0.15
3000  R: 42.466  Charge:     18.12  Peaks:  1.11  Score:   0.15
4000  R: 43.158  Charge:     19.33  Peaks:  1.16  Score:   0.15
5000  R: 43.369  Charge:     18.80  Peaks:  1.11  Score:   0.15
6000  R: 44.689  Charge:     18.11  Peaks:  1.12  Score:   0.15
```

*Note the bold part. We can see a clear drop in R-value accompanied by no change in the charge and a small decrease (instead of expected increase) of the Peaks indicator. Although the change in R-value is clearly visible, together with the decrease in Peaks it is not enough to trigger automatic convergence detection. However, it is likely that the iteration converged.*

Press "Interrupt" to stop Superflip;
In the log file locate the symmetry determination part.
*You will see a listing similar to this:*

---

[2] Occasionally it may detect convergence, but in most cases it does not.
[3] Rarely the calculation does not converge even after several thousand cycles. In that case interrupt Superflip and run it again.

```
#####################################
# Checking the density for symmetry #
#####################################


Symmetry operations compatible with the lattice and centering:
                         Symmetry operation          agreement factor
     2_1(0,0,1):       -x1        -x2      1/2+x3    1.072   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
        2(0,1,0):      -x1         x2        -x3     2.753   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     2_1(1,0,0):     1/2+x1       -x2        -x3     3.190   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
        2(1,0,0):      x1         -x2        -x3    40.793   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     2_1(0,1,0):      -x1       1/2+x2       -x3    40.914   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
        m(1,0,0):      -x1         x2         x3    65.397   XXXXXXXXXXXXXXXXX
        n(0,1,0):     1/2+x1       -x2      1/2+x3   67.329   XXXXXXXXXXXXXXXX
        c(0,1,0):      x1         -x2      1/2+x3    70.126   XXXXXXXXXXXXXXX
            -1:        -x1        -x2        -x3     74.273   XXXXXXXXXXXXX
        m(0,0,1):      x1          x2        -x3     77.273   XXXXXXXXXXX
        n(0,0,1):     1/2+x1     1/2+x2       -x3    79.068   XXXXXXXXXX
        b(0,0,1):      x1       1/2+x2       -x3     83.217   XXXXXXXX
        m(0,1,0):      x1         -x2         x3     84.501   XXXXXXXX
        2(0,0,1):      -x1        -x2         x3     93.289   XXX
        a(0,0,1):     1/2+x1       x2        -x3     94.046   XXX
        c(1,0,0):      -x1         x2      1/2+x3    98.050   X
        n(1,0,0):      -x1       1/2+x2     1/2+x3  101.107   X
        a(0,1,0):     1/2+x1      -x2         x3    112.158   X
        b(1,0,0):      -x1       1/2+x2        x3   133.710   X


-----------------------------------------------
Space group derived from the symmetry operations:
-----------------------------------------------

   HM symbol:     P21221
   Hall symbol:   p 2ac 2ac
   Fingerprint:   3300223}040qW1 (0,0,1/4)
   Symmetry operations:
            1:        x1          x2         x3
     2_1(0,0,1):    1/2-x1       -x2      1/2+x3
     2_1(1,0,0):    1/2+x1       -x2      1/2-x3
        2(0,1,0):     -x1         x2        -x3
```

*Go carefully through the list, and make sure you understand, why Superflip suggests the space group P2₁22₁. Note also that the space group has nothing to do with the Pmmm space group used as input. This confirms that the symmetry derivation by Superflip is indeed independent from the input space group.*

*Note also that the space group found by Superflip is the same as the most likely space group suggested by Jana2006 on the basis of systematic absences. Thus, in this case the two indications agree. However, the analysis of systematic absences was not conclusive, while the result of Superflip leaves no doubt about the correct space group.*

8. **Insert the correct space group and solve the structure**
   *Although the solution by Superflip is correct, the space group in Jana is still wrong, and the solution is thus not usable. We have to set the correct space group and rerun Superflip.*
   Close the view of the log file;
   Click "Change the space group" in the "Structure solution" form;
   Type "P21221" in the upper left box; OK; YES;
   *As the symmetry changed, the refinement reflection file must be recreated. You will be guided through the process. Repeat it as you did in step 4 of this exercise.*

Press "Run solution" to start Superflip again with the correct symmetry;

*Superflip starts, and should again converge smoothly to a solution. You may again need to interrupt the iteration, when you see the drop of the R-value. Check that the derived symmetry is again P2$_1$22$_1$.*

Close the log-file viewer;

Double click "Plot structure"; Draw+continue

In Diamond click the "Get molecules directly" ⬡ button in the bottom toolbar. The molecule should look like this, possibly with a few carbon and nitrogen atom types interchanged:
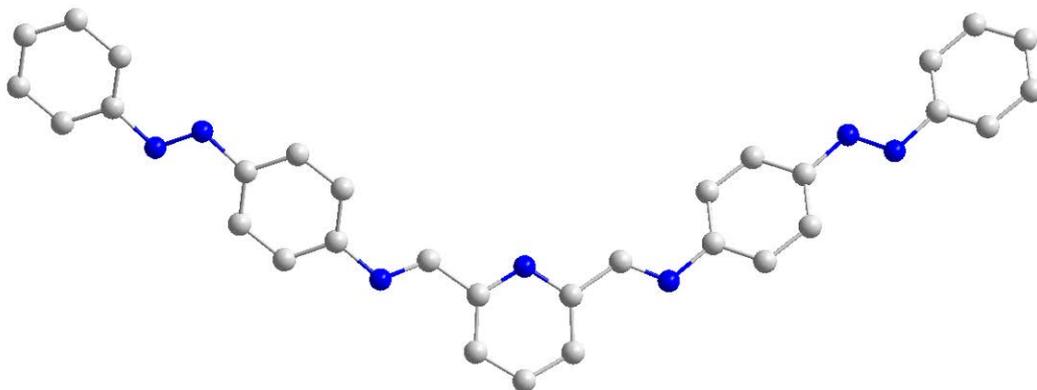


Close Diamond;

Double click the icon "Refine"

*The refinement will converge to an R-value around 10% or less depending on the number of incorrectly identified atoms. The structure is solved. Now the atoms must be correctly assigned to chemical types, and the structure refined in the standard manner.*

# Example 9.4: MnVPO

**A difficult case for symmetry determination**
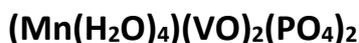
## $(Mn(H_2O)_4)(VO)_2(PO_4)_2$

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: MnVPO.m50, MnVPO.m95

1. ***Opening the structure***
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ Open" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click MnVPO_start

   *You opened a structure which contains crystal information about the compound and hkl-data. There is no structural information present yet. To preserve the original files, save the structure under another name:*

   "File $\rightarrow$ Structure $\rightarrow$ Save as" opens a file manager
   Type "MnVPO" in the line under the right pane and press Enter
   "YES" to the question if you want to continue with the new structure

2. ***Symmetry Wizard***
   "File $\rightarrow$ Reflection file $\rightarrow$ Make space group test"
   *Proceed with the space group test. Check the table of the Laue groups, and note $R_{int}$ for Laue groups 4/m and 4/mmm. Continue until the screen with the title "Select space group". You should see this output:*

   | Select space group | | | |
   |---|---|---|---|
   | Space group | obs/all | ave(I/sig(I)) | FOM |
   | I4/m | 0/0 | 0.000/0.000 | 1.00000 |
   | I-4 | 0/0 | 0.000/0.000 | 1.00000 |
   | I4 | 0/0 | 0.000/0.000 | 1.00000 |
   | I41 | 2/3 | 19.872/13.855 | 798.18793 |

   *In this case it is impossible to determine the space group only from systematic absences.*
   Select the space group I4/m, NEXT, FINISH

3. ***Creating refinement reflection file***
   Answer YES to the question if you want to create refinement reflection file
   Leave all settings default; NEXT; OK; NEXT; OK;
   Accept the data block; FINISH

## 4. Structure Solution

Click the icon "Structure solution" in the main window of Jana

Make sure that the formula is H8 Mn O14 P2 V2 with Z=2
Leave other settings default; Click the button "Run solution"
*[On the screen: listing of Superflip]*
*Superflip converges rapidly. The symmetry determination part of the log-file looks like this:*

```
Symmetry operations compatible with the lattice and centering:
                         Symmetry operation        agreement factor
      m(0,0,1):        x1         x2       -x3     1.186   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     -4(0,0,1):        x2        -x1       -x3     1.661   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     -4(0,0,1):       -x2         x1       -x3     1.746   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      4(0,0,1):        x2        -x1        x3     2.166   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      4(0,0,1):       -x2         x1        x3     2.247   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      m(1,0,0):       -x1         x2        x3     2.559   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     2(1,-1,0):       -x2        -x1       -x3     2.748   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      2(0,0,1):       -x1        -x2        x3     2.827   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      m(0,1,0):        x1        -x2        x3     3.320   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      m(1,1,0):       -x2        -x1        x3     3.373   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      2(1,1,0):        x2         x1       -x3     3.640   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      2(0,1,0):       -x1         x2       -x3     3.755   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
           -1:       -x1        -x2       -x3     4.235   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
     m(1,-1,0):        x2         x1        x3     4.281   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      2(1,0,0):        x1        -x2       -x3     4.569   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
      a(0,0,1):     1/2+x1         x2       -x3    69.893   XXXXXXXXXXXXXXXX
     d(1,-1,0):     3/4+x2     3/4+x1    1/4+x3    72.263   XXXXXXXXXXXXXX
   4+_1(0,0,1):       -x2         x1    1/4+x3    73.130   XXXXXXXXXXXXXX
   4-_1(0,0,1):        x2        -x1    1/4+x3    73.576   XXXXXXXXXXXXXX
     d(1,1,0):     3/4-x2    1/4-x1     1/4+x3    75.666   XXXXXXXXXXXXX
      a(0,1,0):     1/2+x1        -x2        x3    83.970   XXXXXXXXX
      b(1,0,0):       -x1     1/2+x2        x3    98.870   X

-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
   HM symbol:       I4/mmm
   Hall symbol:     -I 4 2
   Fingerprint:     33123070n{01xQ03}20 (0,0,0)
   Centering vectors:
     0.000   0.000   0.000
     0.500   0.500   0.500
   Symmetry operations:
           1:        x1         x2        x3
     4(0,0,1):       -x2         x1        x3
     2(1,0,0):        x1        -x2       -x3
          -1:       -x1        -x2       -x3
     2(0,0,1):       -x1        -x2        x3
    2(1,-1,0):       -x2        -x1       -x3
     2(1,1,0):        x2         x1       -x3
    -4(0,0,1):        x2        -x1       -x3
     m(1,0,0):       -x1         x2        x3
     4(0,0,1):        x2        -x1        x3
     2(0,1,0):       -x1         x2       -x3
     m(0,0,1):        x1         x2       -x3
    m(1,-1,0):        x2         x1        x3
     m(1,1,0):       -x2        -x1        x3
    -4(0,0,1):       -x2         x1       -x3
     m(0,1,0):        x1        -x2        x3
```

*Superflip suggests the space group I4/mmm. This space group is incompatible with the detected Laue group (Check your notes with Rint of the Laue groups 4/m and 4/mmm). It is a supergroup of all three possible space groups suggested by the symmetry wizard. This is an indication that the structure is peculiar in some respect.*

Close listing of Superflip
Quit the Structure solution dialog

*Note: Superflip suggests a different space group, but it does not use this space group to produce the final density. The final result has always the symmetry defined in EditM50. If you want to accept the symmetry suggested by Superflip, you have to change the symmetry and rerun Superflip to get new solution.*

"Parameters → Atoms → Edit"

*Check that the list of atoms contains one Mn, V and P atom and three oxygens. The peak search sometimes does not assign all atoms at once. In practice the missing atom would be located among the Fourier peaks. For the purposes of this example, however, make sure the solution contains 6 atoms immediately to keep your files compatible with the rest of the exercise. If it does not, rerun Superflip again.*

5.  **View the structure**

    Double click the icon "Plot structure"; Answer NO to question about Fourier peaks;

    In Diamond click the button for filling one unit cell ⬦ and for filling coordination spheres
    ◉;

    *You should get a view similar to this:*
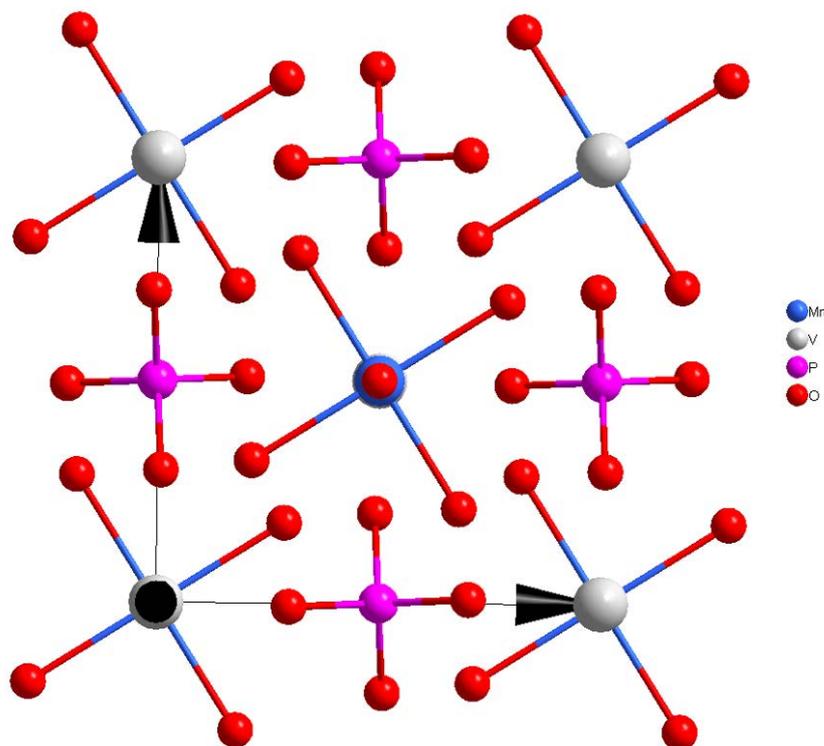


*The structure looks correct. To convince yourself that the cations have correct coordinations, rotate the structure and increase the accepted V-O bond length to 2 ("Build → Connectivity"). Try to understand, why Superflip suggested a wrong space group before you go to the next page and read the solution.*

*The reason Superlip gets confused by this structure is the strong pseudosymmetry. All atoms except for one oxygen (the in-plane oxygen coordinated to Mn) obey the I4/mmm symmetry. The contribution of the oxygen to the total density is not sufficiently strong to indicate the deviation from the higher symmetry.*

*If you look closely at the list of symmetry operators and their agreement factors, you will see indeed that the symmetry operators of the space group I4/m are all at the beginning of the list with the lowest agreement factors. But the difference in agreement factors between the true opeators and the remaining operators of the I4/mmm space group is too small to be detected by the program.*

## 6. Refine the structure

Run Refine by double clicking the icon Refine
*Refinement should immediately converge to an R-value around 5%*
"Parameters → Atoms → Edit → Select all → Action → Edit/Define atoms → harmonic"
*Change the type of displacement parameters of all atoms from isotropic to harmonic*
Run Refine again
*Refinement should converge to an R-value around 3.8%*

*This exercise demonstrates that the best approach to determining the space group is to combine the information from diffraction pattern and the symmetry determination of Superflip. In most cases the two approaches yield the same result. If the results differ, the structure or data usually exhibit some non-standard features. It can be a strong pseudosymmetry (as in this example), problem in the evaluation of systematic absences, or twinning. The two approaches are complementary, and have different weaknesses. Their combination gives the best result.*

## 7. Additional exercises

a) *Try to solve and refine the structure in I4/mmm. Apart from the high $R_{int}$, would you be able to recognize that something is wrong with the structure model? What R-value do you get?*

b) *For training purposes you can try to finish off the structure – check for the presence of hydrogen atoms, define them and refine.*

# Example 9.5: 8rings

**Very large structure – use of non-random starting point in Superflip**

**Revised: 12 February 2014**

Input files: 8rings.hkl, 8rings.p4p. This is a huge organometallic structure with three eight-membered and one three-membered ring containing chromium, nickel, iron and cobalt. Cell volume 67312 $\text{Å}^3$.

Refrence: G. F. S. Whitehead, F. Moro, G. A. Timco, W. Wernsdorfer, S. J. Teat and R. E. P. Winpenny, Angewandte Chemie International Edition, 2013, 52, 9932-9935.

1.  ***Load the data***
    Start Jana2006;
    "File → Structure → New";
    Locate the input files, and double click on the green name 8rings in the right pane;
    Select the radiobutton "known diffractometer formats"; NEXT;
    Select the format Bruker-CCD; OK
    OK to skip the warning about incomplete information;
    Continue with the data import wizard, leaving all setting default, until the screen with the information about the symmetry wizard
    *At this moment you loaded the basic crystallographic information and intensity data.*

2.  ***Determine the symmetry***
    *When the reflection import finishes, you are automatically offered the symmetry determination form. If you accidentally close this card, you can access the same functions through the EditM50 icon, card Symmetry.*
    NEXT to start the wizard;
    NEXT to confirm the default settings of the test;
    OK to the information about no higher metric symmetry;
    *On the screen with Rint for different Laue groups make sure you understand Jana's choice for the 6/m Laue group.*
    NEXT;
    *On the screen with centering statistics make again sure that you understand the meaning of the numbers and the choice Jana2006 made.*
    NEXT;
    *At this moment you are presented with the list of possible space groups. Based on the analysis of systematic absences Jana suggests the space group P65. You may click the button "Details" to get a detailed listing with the absent reflections. In this case there is little doubt that the correct space group is indeed $P6_1/P6_5$.*

3.  ***Create refinement reflection file***
    *Now you will filter and merge the raw reflection ata to produce the final reflection file ready for solution and then refinement. In this case all settings can be left default:*

### 4. Structure Solution

*As the next step the wizard suggests starting the structure solution. When you accept the suggestion, a form with options for structure solution opens.*

*This is a large structure, and normalizing the intensities is most likely necessary.*
Check the checkbox "Use local normalization".

*It is also necessary to give some composition. It is not used for solution but for interpretation. It is sufficient to enter just a list of present atoms. Iron, cobalt and nickel will most probably be indistinguishable in the solution, but we may enter them anyway, so that we do not have to add them later during the refinement process. The same holds for hydrogen.*
In the files Composition enter "Cr Fe Co Ni C H F N O"
Leave other settings default.
Click "Run solution"

*Superflip starts and tries to solve the structure with default options for the charge flipping algorithm. You may let the iteration run for a few hundred cycles and you will see that there are no signs of convergence in the three indicators (R-value, total charge and peakiness).*
*There is still a chance that the structure is solved – sometimes the convergence is just not visible. We will interrupt the iteration and check the result.*
In the window of Jana click the button "Interrupt"

*Superflip finishes the calculation and the log-file opens in the main window of Jana. Check the symmetry analysis. The final part will look like this:*

```
-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
    HM symbol:      P1
    Hall symbol:    P 1
    Fingerprint:    33001041a0 (0,0,0)
    Symmetry operations:
             1:            x1            x2            x3
```

*It is most unlikely that the structure really has symmetry P1. Together with the lack of indicators of convergence this means that the structure is not solved.*

*The structure contains moderately heavy atoms. It is thus sensible to start the iteration with Patterson superposition map instead of the random map.*
Click the button "Close" in the upper row to close the viewer of the log file;
In the selection list labeled "Starting model" select the radiobutton "Patterson superposition map":

Starting model:  ○ Random phases
                 ● Patterson superposition map

Run the solution again

*Typically the iteration converges within a few hundred cycles. The space group determination part of the log file looks like this:*

```
-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
    HM symbol:      P61
    Hall symbol:    P 61
    Fingerprint:    3300163Xx01 (0,0,0)
    Symmetry operations:
               1:           x1          x2          x3
    6+_1(0,0,1):         x1-x2          x1      1/6+x3
    3+_1(0,0,1):           -x2       x1-x2      1/3+x3
     2_1(0,0,1):           -x1          -x2      1/2+x3
    3-_2(0,0,1):        -x1+x2          -x1      2/3+x3
    6-_5(0,0,1):            x2       -x1+x2      5/6+x3
```

*This time the solution has the correct symmetry and it is a strong indication that the structure is solved.*

Close the log-file viewer;
Wait until Jana performs the peak search (be patient, it is a large structure…)
Click the button "Draw 3D map" to view the resulting electron density

*The density and the interpreted model are shown overlaid in VESTA. The structure is large and it is not easy to understand the density. Nevertheless, after a while it becomes clear that the structure is correctly solved and the main expected motifs are well visible. It is also visible that some of the peaks present in the electron density were not interpreted as atoms by the peak-seaching routine. These peaks are saved as "Fourier maxima" in Jana and you may change them to regular atoms when you go to Parameters → Atoms → New → Peaks from the last Fourier calculation. To see which maxima are interesting, we will plot the strongest peaks together with the structure:*

Close VESTA;
Click the button "Draw structure";
In the next dialog click "Add Fourier peaks";
*A dialog with a long list of maxima opens. First about 100 maxima are deselected, because they represent existing atoms. Then a large number of maxima are selected (typed in red).*
OK to include all maxima;

*The structure-plotting program (typically Diamond) opens and you may view the structure.The added maxima are shown as the lightest element from the element list. In this case it is hydrogen. You can see that a large number of these maxima are just artifacts close to the heavy atoms, but among the added maxima you can also find most of the missing atoms. This illustrates the fact that often the raw solution – the electron density – is more complete and informative than the structure interpretation, and it is worth checking the electron density after the solution, if the interpreted structure appears incomplete or otherwise wrong.*

*Here is for reference the image of the two chemically different entities found in the structure:*

*The three-ring with mixed iron-cobalt sites:*
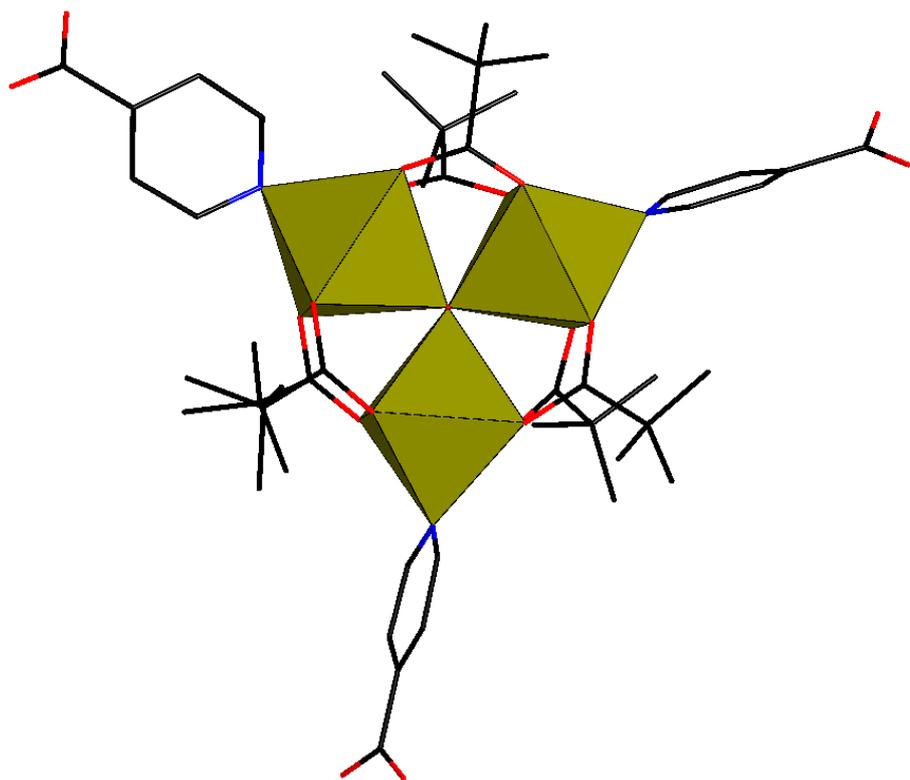


*The eight-ring with chromium and nickel:*
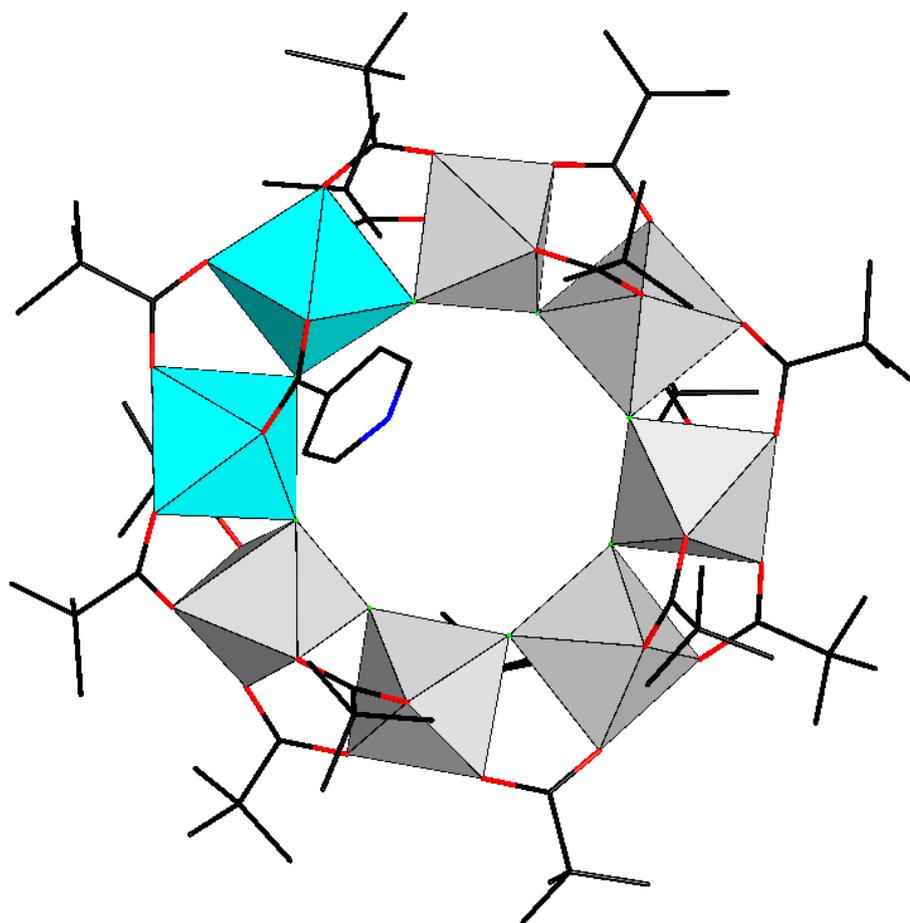
# Example 10.1: AgSbS

**Refinement of anharmonic ADPs in Jana2006.**

**Chemical formula: $Ag_3SbS_3$**

**Reference:** F. Laufek, J. Sejkora & M. Dušek (2010). Journal of Geosciences, 55, 161–167

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: agsbs.hkl, agsbs.cif_od
Frame scaling, absorption correction: done with software of diffractometer

*In this example we shall need installation of VESTA for visualization of electron density associated with anharmonic ADP. VESTA is supplied as a zip archive which can be unpacked to arbitrary location (with simple path – not to Desktop). Then the path to VESTA.exe must be defined in "Parameters → Programs".*

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click agsbs
   *Right pane detects possible Jana files and shows one jobname for each group of files*

2. *Import Wizard*
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Select "Input from "cif_od" file"; OK
   *The used diffractometer software splits reflection file and another information (cell parameters, wavelength …). There are several output formats for both cases.*
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   *The program reads 11948 reflections from hkl file*
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. *Data RepositoryOK;*
   *Each line in data repository window corresponds to one data set converted to Jana format. In our case we use only one data set.*
   OK; YES to accept the data set

4. *Symmetry Wizard*
   *[On the screen: "Tolerances for crystal system recognition".]*
   *Symmetry wizard can be started separately by "File → Reflection file → Make space group test.*
   Leave all settings default; NEXT
   *[On the screen: Select Laue symmetry]*

Select Trigonal -3m1 Laue symmetry; NEXT
Select R-obverse cell; NEXT
*[On the screen: Select space group]*
Select *R3c*; NEXT
*Selecting the non-centrosymmetric space group is a shortcut. It will be explained at "Verification of structure solution".*
Accept the space group transformed into the original cell; FINISH
*Symmetry is saved in file agsbs.M50.*

5. **Creating refinement reflection file**
   *In this step program creates file agsbs.M90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*
   NEXT to confirm threshold 3sigma
   *[On the screen: settings for merging of reflections]*
   Leave all settings default; NEXT
   *The program reports Rint 1.88% for 430 observed reflections merged from 3577 observed reflections.*
   Accept the new data block and calculate coverage; FINISH

6. **Structure Solution Wizard**
   *[On the screen: window of Structure solution].*
   In "Formula" textbox type list of chemical elements: Ag Sb S
   Select "Use Superflip", "Peaks from Jana2006";
   Select "Use a specific random seed" and use "222"
   *Fixing the random seed to 222 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. Otherwise each run of Superflip may return different equivalent origin. For normal work random seed should be automatic because the convergence of charge flipping is not guaranteed for every value of random seed.*
   Leave other settings default; OK
   *[On the screen: window of Superflip replaced after reaching the convergence with listing of Superflip]*
   *Superflip converges (after noise suppression) with R value (after noise suppression) 16%.*
   Press CLOSE to leave the listing
   Press "Accept the result"

7. **Verification of the structure solution**
   Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"
   *It displays formula Ag3 Sb S3 (for Z=6). This is the same as expected composition.*
   *[On the screen: Information about formula]*
   OK; YES for updating the formula.
   *In next steps we shall verify with Superflip that centre of symmetry is not present.*
   Start "File → Structure → Save As"
   Save the structure with jobname "testspg"
   YES to continue with the new structure
   Start "Run → Solution"
   Select "Use Superflip" and press button "Change the space group"

For the "Space group" type R-3c; OK; YES to rewrite M50

Follow steps for creating the refinement reflection file

*Merging the data yields Rint 2.11% and the program returns to the structure solution wizard*

*[On the screen: Structure solution wizard]*

OK to start structure solution

*[On the screen: listing of Superflip]*

*At the end of the listing we can see unsatisfactory agreement factor for the symmetry operator "2". This indicates the space group is probably wrong.*

Press "Accept the result"

Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"

*It displays formula Ag0 Sb S6 (for Z=6) which is also wrong*

Return to the basic window of Jana2006

Start "File → Structure → History" and open the previous structure (with space group R3c)

## 8. Refinement

*[On the screen: basic window of Jana]*

Right-click the icon of Refine.

*[On the screen: refinement options]*

Define 100 of cycles, damping factor 0.5; OK

Choose "YES+START"

*Refinement converges with R value about 12%*

Start "Edit atoms"

*[On the screen: list of atoms]*

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms.* OK, OK, Yes to save changes

Double-click the icon Refine.

*Refinement converges with R value about 4%.*

## 9. Extinction correction

*The results seem to be OK, but:*

*[On the screen: basic window of Jana2006]*

Open listing of Refine (by "Edit/View → View of Refine")

Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement"

*R value should decrease with increasing intensity or with lowering the diffraction angle. Here the R value for the strongest reflections as well as for the low angle reflections is higher than in the previous shell. This suggests that extinction correction is required.*

Close the refinement listing

"Parameters → Extinction"

Select "Isotropic"; OK

*Refinement of extinction coefficient is enabled by default*

Double-click Refine and refine the final structure

*Refinement converges with R factor 3.67 %.*

Check the extinction coefficient through "Parameters → Extinction"

View listing of Refine; Go to "Statistics"; check improved R value for strongest reflections.

## 10. Anharmonic refinement

Run Contour, start "New plot" – "Calculate new ones" +" Draw maps as calculated".
*Here no previous map exists and therefore "Calculate new ones" will be disabled*
*[On the screen: Fourier commands]*
In Basic thumbnail select "F(obs)-F(calc) – difference Fourier"; leave other settings default In
screenshot; OK
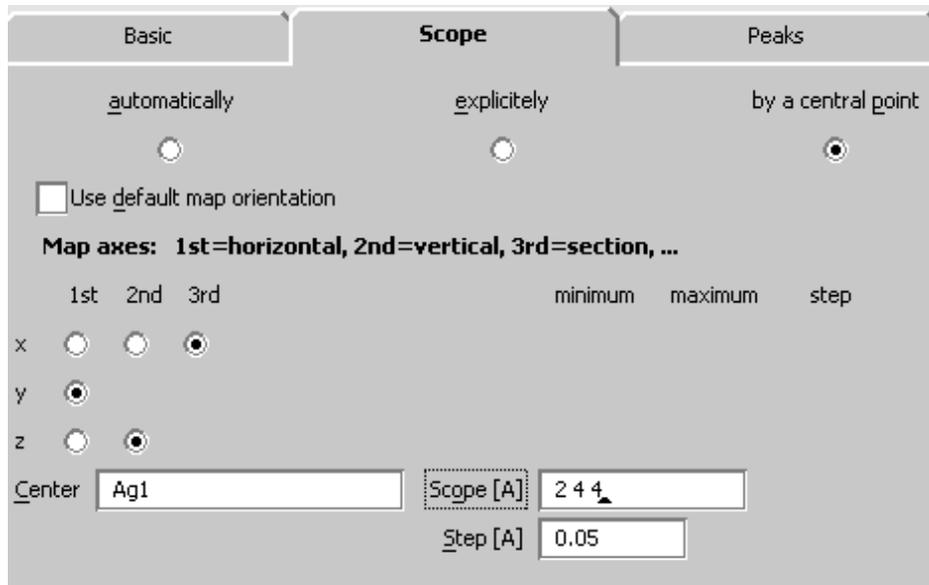


*[On the screen: contour plot of the first section]*
In "Contours" define both positive and negative contours to 0.1 e⁻/Å³;
In "Atoms edit" add Ag1;
Examine the sections using "M+" and "M-"

x=0.363
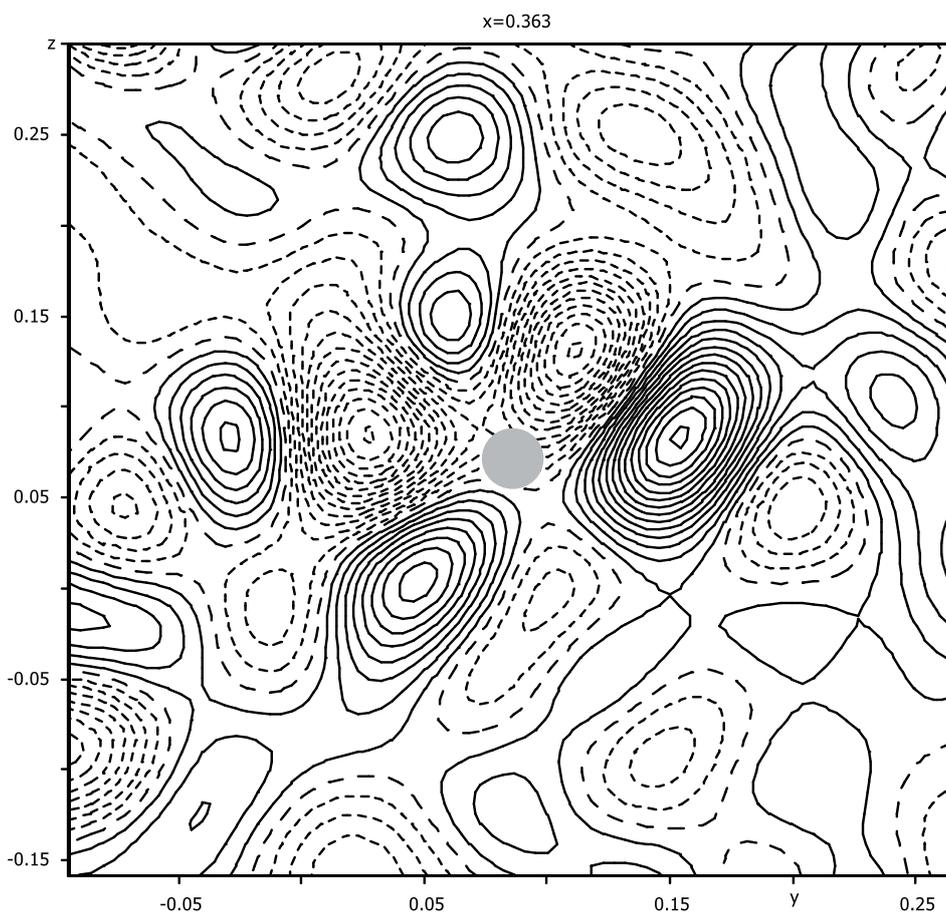
*We can see residua of positive density in the vicinity of the Ag atom.*

Quit Contour

Run "Edit atoms" and select Ag1.
"Action → Edit/define atoms": check "Anharmonic ADP", third order;
Run Refine
*Refinement converges with R factor 1.14 %.*
In Contour draw the same difference Fourier section as previous (calculate new maps). Use the same limits for contours.
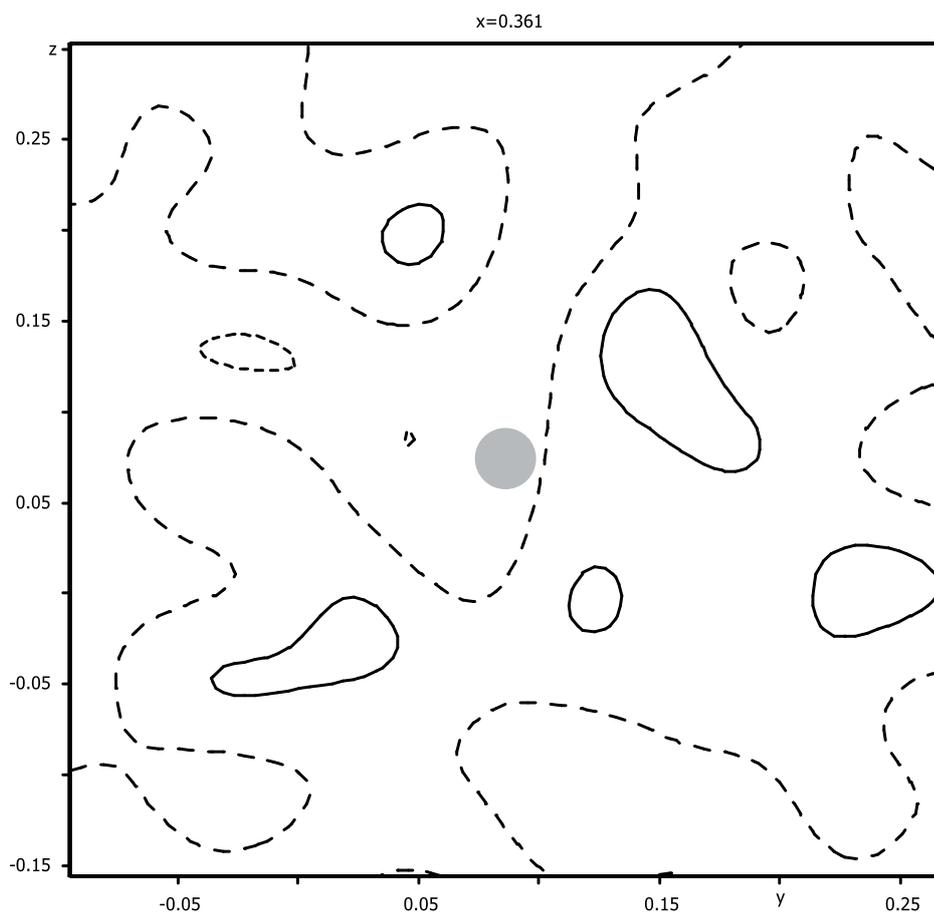
*The residua have significantly decreased.*

**11. Density modeling using the joint probability density function**
Run Contour, start "New plot" – select j.p.d.f.
*[On the screen: Select atoms and basic parameters for j.p.d.f]*
Select Ag1 and S1; Next
*[On the screen: Plane/Volume]*
For 1$^{st}$ atom use Ag1; for the 2$^{nd}$ and 3$^{rd}$ atom use difference to 1$^{st}$ 1 0 0 and 0 1 0, respectively;
Define scope of the section: 6 6 6 and "1st point to" 3 4 2.5;
Use cutoff distance for atoms 4 Å; NEXT

*[On the screen: Select individual atoms for j.p.d.f]*

Select Ag1, and all symmetry related sulphur atoms close to Ag1 and note their symmetry codes (i.g. S1#s5c3t0,-1,-1); NEXT



In "Atoms Edit" of Contour define the Ag1 atom and all four S1 atoms using their symmetry codes.

Press "Run 3d maps"

*Jana2006 will call an external program for drawing isosurfaces, previously defined in "Tools → Programs", in our case VESTA*

Setting drawing options:

In "Edit → Bonds" define bond between Ag and S; maximal distance 3.15 Å,

In "Objects → Structural model" select "Stick",

In "Properties" check "Do not show unit cell".
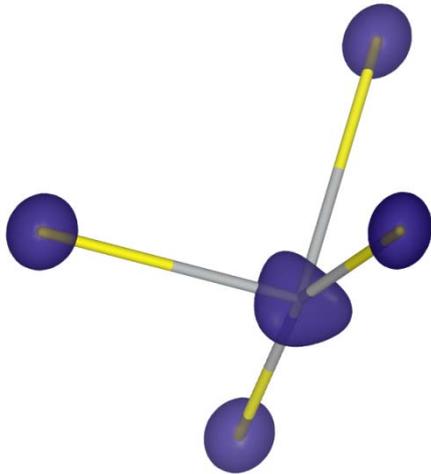
The application of non-harmonic parameters led to the triangular shape of the electron density centered in Ag1 position. The electron density is extended in directions between of Ag-S bonds.

## 12. Drawing one particle potential curve

Sulphur and Silver form spirals defined by short Ag-S bonds. The possible exchange paths for silver atoms within and between the spirals can be tested with help of one particle potential along a proposed path. One of proposed paths is shown in the following figure where it goes along sides of the indicated triangle:
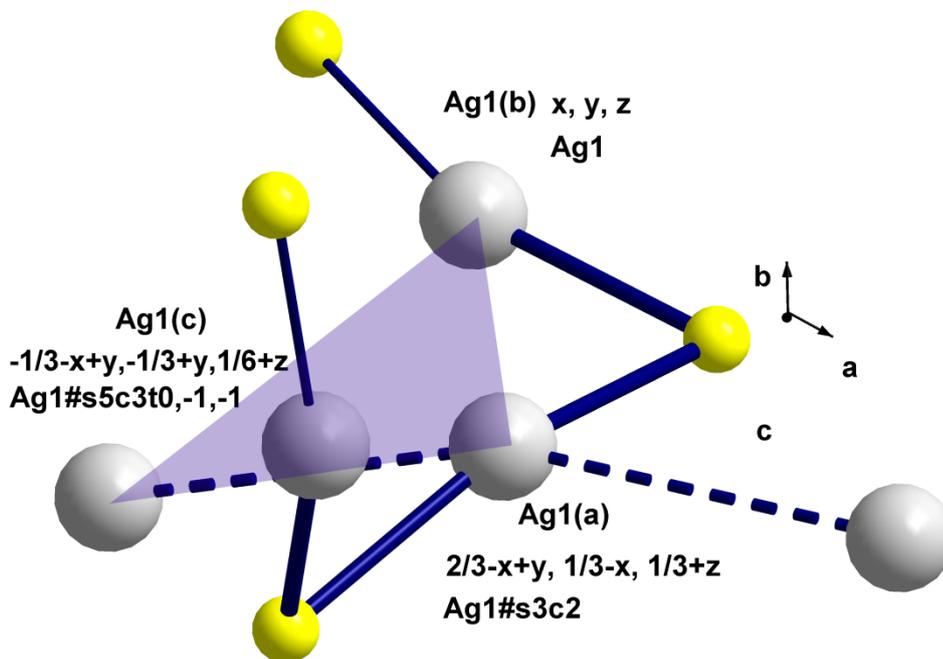
Run Contour, start "New plot" – select j.p.d.f.

[On the screen: Select atoms and basic parameters for j.p.d.f]

*Select Ag1; Next*

[On the screen: Plane/Volume]

Define the displayed volume according to the following screenshot; OK

| | Atom | Coordinates | Difference to 1st |
|---|---|---|---|
| 1st | Ag1#s3c2 | .391859 -0.028111 0.40688 | |
| 2nd | Ag1 | 361444 0.086636 0.073547 | 30415 0.114747 -0.333333 |
| 3rd | Ag1#s5c3t0,-1,-1 | 58525 -0.246697 0.240214 | 33333 -0.218587 -0.166667 |

**Scope**

| Interpolation step | Scope of section | 1st point put to |
|---|---|---|
| 0.05 | 7 7 2 | 2 2 1 [Ang] |

Adjust

Cutoff distance for atoms  4  [Ang]

Select Ag1#s3c2, Ag1#s5c3t0,-1,0 and Ag1; NEXT

**Select individual atoms for j.p.d.f.**

| Atom | Distance | Symmetry code |
|---|---|---|
| Ag1 | 1.800 | -x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1 |
| Ag1 | 2.121 | -x+y+2/3,-x+1/3,z+1/3#s3c2 |
| Ag1 | 2.308 | x,y,z |
| Ag1 | 4.097 | x-1/3,x-y-2/3,z-1/6#s6c2t-1,-1,-1 |
| Ag1 | 4.353 | -y+1/3,-x+2/3,z+1/6#s4c3t0,0,-1 |
| Ag1 | 4.367 | -y+1/3,x-y-1/3,z-1/3#s2c3t0,-1,-1 |
| Ag1 | 4.374 | -y,-x,z+1/2#s4 |

In "Curves" "Use mouse to define polyline" and draw the line Ag1(a)—P—Ag1(b)—P—Ag1(c)—P—Ag1(a) by mouse (2nd mouse button quits the selection). You can also fill in these points directly in the textboxes of the "Curves" dialogue. Fractional coordinates of the point P are approximately 0.267 -0.63 0.235. Ag atoms should be written with corresponding symmetry codes, i.e. Ag1#s3c2.
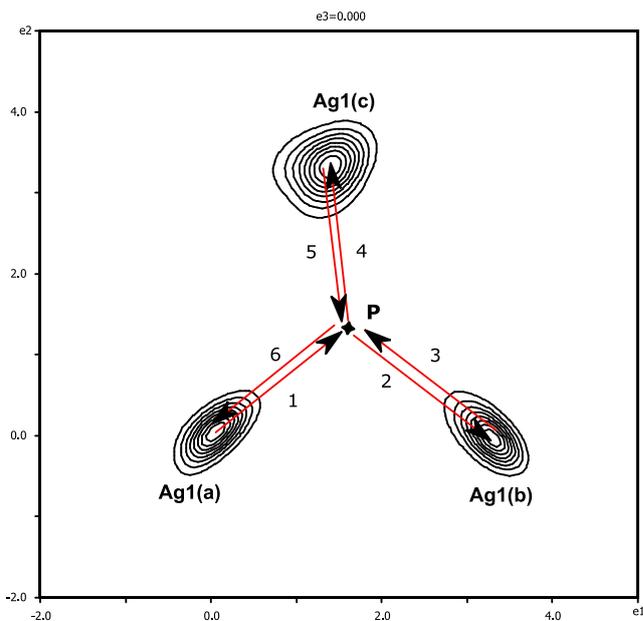
In the first plot we can see an electron density curve. The maximal electron density is located in Ag1 atoms.
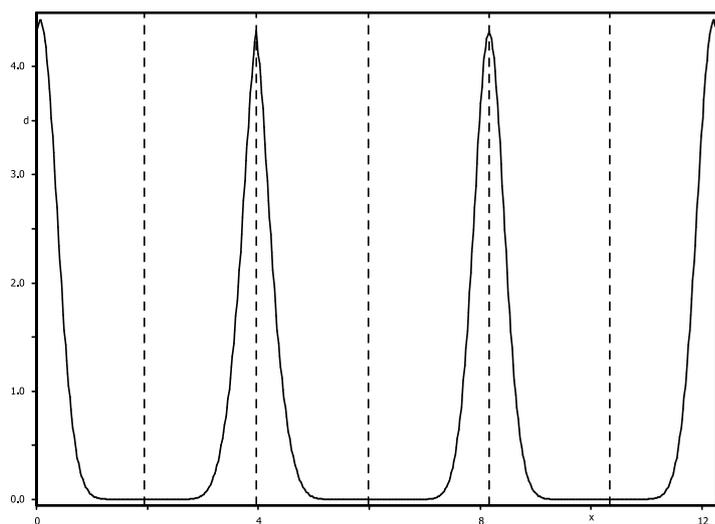
*The resulting curve is one particle potential path. The peaks represent the potential barrier between Ag1 atoms when the exchange path runs through the point P. These values suggest that the silver transfer within and between neighboring Ag–S–Ag spirals is possible.*
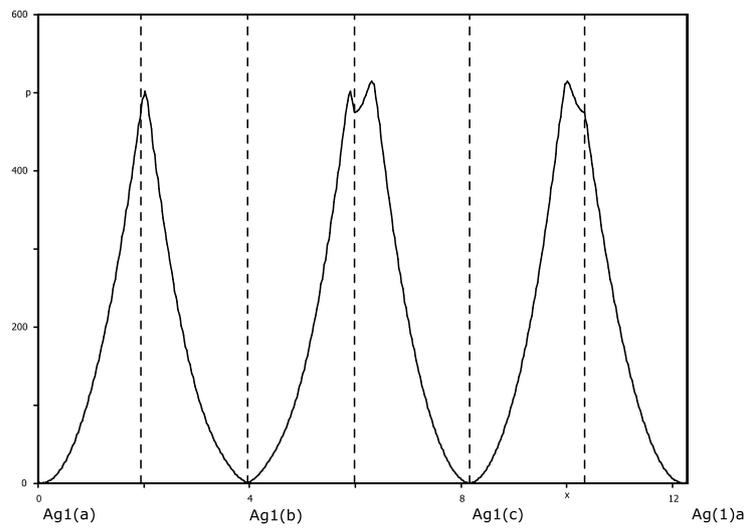
# Example 10.2: Oxa

**multipole refinement**

X-ray data from an oxalic acid sample measured at 110K to a high resolution limit. The crystal contains also crystal water: $C_2O_4H_2.2H_2O$

Input files: oxa.m40, oxa.m50, oxa.m90 and oxa.m95 – Jana files from a conventional refinement

1. ***Drawing density map based on the regular refinement***
   *[On the screen: Basic Jana window]*
   Start Jana2006
   "File → Structure → Open": open structure "oxa"
   *This is result of conventional structure refinement*
   Run refinement
   *Refinement converges in 1 cycle to R(obs)=2.74%*
   *[On the screen: Basic Jana window]*
   Double-click the icon Contour; Press the button "New plot"
   Select "Draw a general section"; OK;
   *[On the screen: Fourier commands]*
   In "Basic" page for "Map type" select "F(obs) – Fourier"
   clear "Omit non-matching reflections"
   select "Use weighting of reflections"
   clear "Apply sin(th)/lambda limit"
   In "Scope" page select "automatically", "Independent parallelepiped" and "Use default map orientation"
   Change the step to 0.05 Å
   OK
   *[On the screen: Plane/Volume]*
   This form defines the general section to be drawn from the calculated map.
   Define: 1st atom C1; 2nd atom C1#s3; 3rd atom O1
   *#s3 encodes symmetry operation (the third one in the list in EditM50)*
   Set the "Interpolation step" to 0.05 Å, "Scope of section" 6 6 0; 1st point to 2 3 0
   OK;
   *After calculation the density section through oxalic acid molecule will appear:*
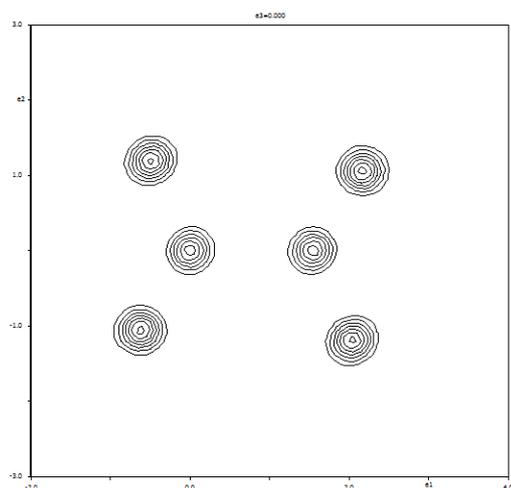
*Atomic positions can be included into the map by clicking the pointer at different locations and selecting atoms close to the given location. The following atomic position should be selected: C1, O1, H1, O2, C1#s3, O1#s3, H1#s3; O2#s3.*
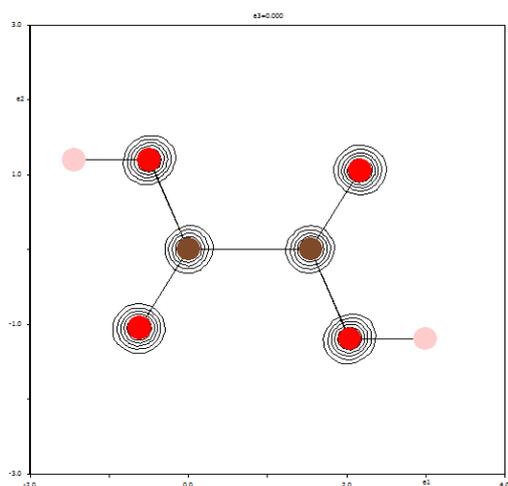


Quit; Save it as Plane#1; OK
*[On the screen: Basic Jana window]*
*Now we shall visualize the difference map.*
Double-click the icon Contour; Press the button: "New plot"
Select "Calculate new ones" and "Draw a general section"; OK;
*[On the screen: Fourier commands]*
In "Basic" page for "Map type" select "F(obs)-F(calc) – difference Fourier"
Keep all remaining settings unchanged; OK;
*[On the screen: Plane/Volume]*
Select "Use old"; OK
*[On the screen: Difference Fourier map through the oxalic acid]*
Press the button "Atoms ON"
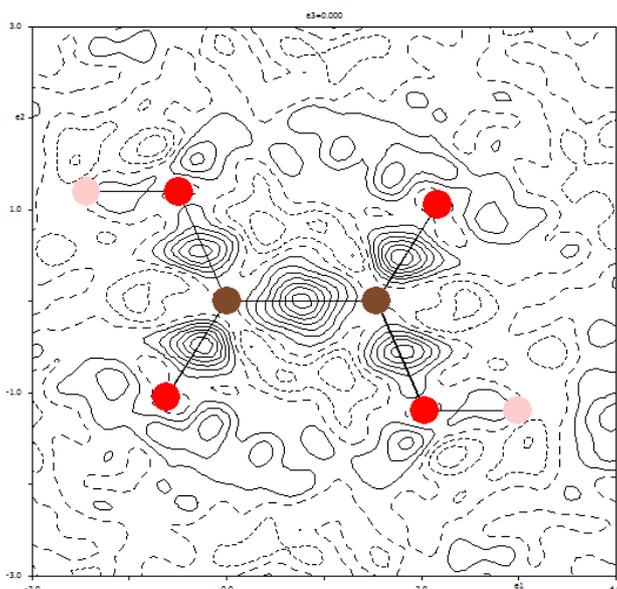
Press the button "Contours" to see contour interval. The value should be about 0.05 e⁻/Å³.

*The positive density clouds are in vicinities of possible bonds. This indicates that the multipole model can reflect real charge densities in this crystal.*

Quit Contour

2. ***Kappa refinement***

*[On the screen: Basic Jana window]*

*We shall keep backup copy of the conventional refinement. Refinement will now continue with new job name.*

Start "File → Structure → Save As"

Save structure as "Oxa-Kappa"

Continue with the new structure

*[On the screen: Basic Jana window]*

Double-click the icon EditM50

In page "Composition" define multipoles "MOLLY";

In page "Multipole parameters" define orbital populations; for O and C atoms keep the default values; for H atom select "Slater form factor" with the default values for H-N and H-Dzeta;

OK; YES to rewrite M50

*[On the screen: Basic Jana window]*

Double click the icon "Edit atoms";

Select all atoms; Choose "Action → Edit/define" or double click on the selected atoms;

*[On the screen: Atom edit]*

In the column "Multipole parameters" select "kappa"; OK; OK;

Yes to rewrite the changed files

*[On the screen: Basic Jana window]*

Right click on the icon "Refine";

In the "Various" page press "Equations" and define the following equations:

pv[H3]=pv[H2]

kappa[H2]=kappa[H1]

kappa[H3]=kappa[H1]

OK; OK; Yes+start

*Refinement converges to R(obs)=2.69%*
*The kappa refinement made only small improvement. This is in accordance with the difference Fourier map in which strong asphericity has been visible.*

### 3. Distance and angular restrains for H atom

*Way how hydrogen atoms are described is a delicate point for charge density refinement. Generally hydrogen electron can be related to any reference point. In order to have reasonable deformation maps it is worthwhile to fix the reference positions of hydrogen atoms close to its ideal values. For the oxalic acid we can use the distance and angular restrains to values refined against neutron diffraction data. For distance H1-O1 this value is 1.07 Å with angle H1-O1-C1 113° and for O3-H2 and O3-H3 0.97 Å with angle H2-O3-H3 about 106°.*

*[On the screen: Basic Jana window]*
Right click on the icon "Refine";
In the page "Various" define the following "Distance restrains":
O1 H1; Value 1.07; s.u. 0.001;
O3 H2; Value 0.97; s.u. 0.001;
O3 H3; Value 0.97; s.u. 0.001;
OK;
In the page "Various" define the following "Angle restrains":
H1 O1 C1; Value 113; s.u. 0.01;
H2 O3 H3; Value 106; s.u. 0.01;
OK
In the page "Various" define the following "Keep commands":
ADP; Riding; Central O1; Extension 1.2; One hydrogen: H1;
ADP; Riding; Central O3; Extension 1.2; Two hydrogens: H2, H3;
OK; Yes+start;
Use all to "significant discrepancies";
*Refinement converges to R(obs)=2.74%*

### 4. Multipole refinement

*For defining of multipole parameters it is convenient to select a local coordinate systems for each atom. The following figure shows a recommended choice for atoms C1, O1, O2 and H1:*
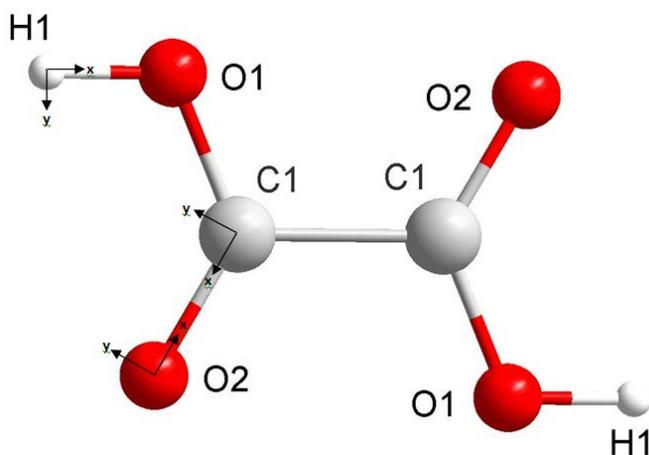
*The axis **x** is oriented along the bond from the central atom to one of non-hydrogen atoms (here called "first atom"). Our choice of "first atom" for central atoms C1, O1, O2 and H1 is O2, C1, C1 and O1, respectively. According to the definition in Jana2006, the second axis (here **y**) is perpendicular to the axis **x** and it lies in the plane defined by the central, first and second atom in such a way that the angle between the axis **y** and vector from the central atom to the second one is smaller than 90°. Our choice of "second atom" for central atoms C1, O1, O2 and H1 is O1, O2, C1 and C1, respectively. Note that second atoms need not make bonds with the central atom.*

*The similar choice can also be used for the molecule of crystal water.*

*[On the screen: Basic Jana window]*

In order to save the result of the kappa refinement a new structure will be opened:

Start "File → Structure → Save As"

*[On the screen: File manager for saving structure]*

In File manager focus the right-bottom textbox and define a new name for testing of the kappa refinement i.e. "Oxa-Multipole"; OK

Yes to continue with the new structure

*[On the screen: Basic Jana window]*

Run "Edit atoms";

Double click the first atom – C1; switch from "kappa" to "order"

Change multipole parameters to order 3 and define the coordinate system x → O2 and y → O1.
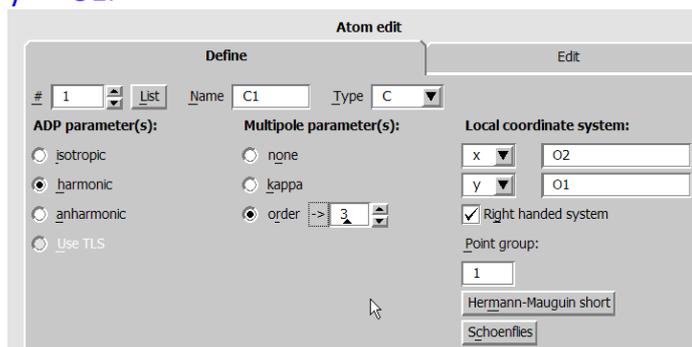


Using the list box on the top left corner go to the next atom – O1.

Change multipole parameters to order 3 and define the coordinate system x → C1 and y → O2. Go to the next atom – O2.

Change multipole parameters to order 3 and define the coordinate system x → C1 and y → O1. Go to the next atom – O3.

Change multipole parameters to order 3 and define the coordinate system x → H2 and y → H3. Go to the next atom – H1.

Change multipole parameters to order 1 and define the coordinate system x → O1 and y → C1. Go to the next atom – H2.

Change multipole parameters to order 1 and define the coordinate system x → O3 and y → H3. Go to the next atom – H3.

Change multipole parameters to order 1 and define the coordinate system x → O3 and y → H2.

OK; OK; Yes to the question "Do you want rewrite changed files?"

*[On the screen: Basic Jana window]*

Right click on the icon "Refine";

In the page "Basic" select the number of cycles 100 and damping factor 0.1;

In the page "Various" press "Fixed commands" and fix the following parameters:

"Set individual", P00[*], "Set to" 0;
"Individual", kappa'[*];
*[*] stands for all atoms. P000 wil be zero for all atoms while kappa' will be fixed to the current value.*
OK; OK; YES+Start
*Refinement converges to R(obs)=1.75%.*

5. **Multipole refinement including kappa' parameters**
   *[On the screen: Basic Jana window]*
   Right click on the icon "Refine";
   In the "Various" fix the following parameters:
   Delete or disable "Individual", kappa'[*];
   In the "Equation" define two equations for H atoms;
   kappa'[H2]=kappa'[H1]
   kappa'[H3]=kappa'[H1]
   OK; OK; Yes+start;
   *Refinement converges to R(obs)=1.69%.*
   *It may happen that at this point R value is higher, around 1.75%. That means water molecule is in a false minimum. In such case: change number of multipoles for O3, H2 and H3 to zero; fix kappa'; repeat refinement; change number of multipoles back to 3,1,1 (for O3, H2, H3); repeat refinement; release kappa', repeat refinement*

6. **Fourier maps**
   *[On the screen: Basic Jana window]*
   Double-click the icon Contour; Press the button "New plot"
   Select "Calculate new map" and "Draw a general section";OK;
   *[On the screen: Fourier commands]*
   In "Basic" use default setting i.e. Map type F(obs)-F(calc) – difference Fourier;
   Keep all remaining parameters unchanged; OK;
   *[On the screen: Plane/Volume]*
   Select "Use old";OK
   *[On the screen:* Difference Fourier map through the oxalic acid*]*
   Press the button "Atoms ON".
   Press the button "Contours" and modify the positive and negative contours to 0.05 e$^-$/Å$^3$
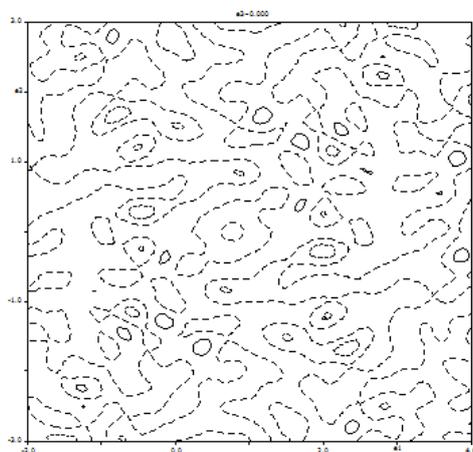


*The map does not show any clear positive or negative maxima which means that the model explain the experimental density adequately.*

## 7. Interpretation of multipole parameters – map visualization

*[On the screen: Basic Jana window]*
Double-click the icon Contour; Instead of "Fourier maps" select "Charge density maps";OK
*[On the screen: Define atoms and basic parameters for charge density maps]*
Select all atoms; Calculate "deformation density";NEXT;
*[On the screen: Plane/Volume]*
Select "Use old"; NEXT
*[On the screen: Select individual atoms for charge density]*
Select all atoms; NEXT
Press the button "Atoms ON";
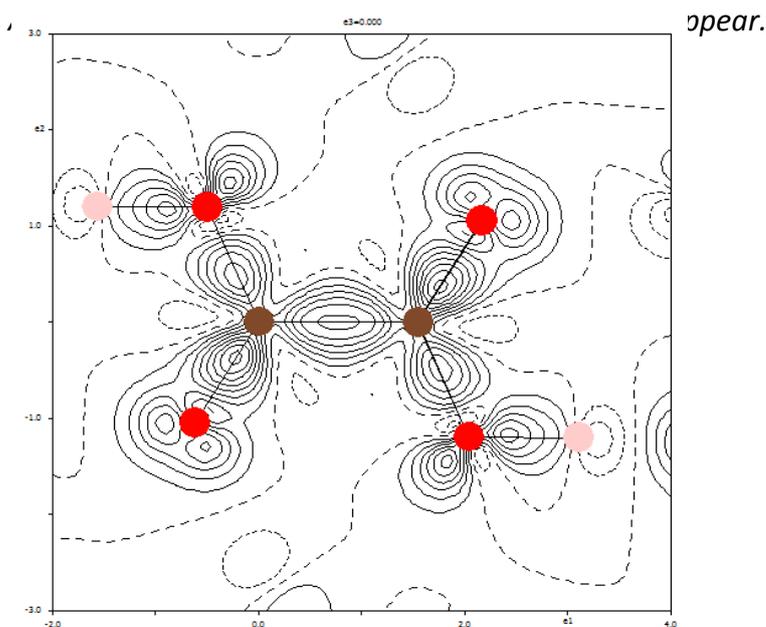


## 8. Topological analysis – critical points

*[On the screen: Basic Jana window]*
Run "Tools → Topological analysis → Find critical points"
*[On the screen: Define parametrs for CP search]*
Select "Type of search" "between all bonds within interval";
For all other parameters keep in default values;
OK;
*[On the screen: Select atoms for distance check]*
Select all; OK
*[On the screen: Basic Jana window]*
Run "Edit/View → View of CP report";
*[On the screen: Viewer for critical points]*
The listing contain information about critical point along all important bonds in the molecule.

| Bond | Fractional coordinates | | | $\rho$ | Laplacian | Hess eigenvalues | Ellipsity |
|------|------|------|------|------|------|------|------|
| | x | y | z | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C1-C1[-x,-y,-z] | 0.0000 | 0.0000 | 0.0000 | 1.77 | -13.55 | -13.59 | -11.04 | 11.08 | 0.23 |
| C1-O1 | 0.0011 | 0.0187 | 0.0875 | 2.50 | -31.96 | -22.99 | -20.38 | 11.41 | 0.13 |
| C1-O2 | -0.1076 | 0.1228 | 0.0465 | 2.97 | -36.60 | -30.34 | -25.97 | 19.71 | 0.17 |
| O1-H1 | 0.0331 | -0.0015 | 0.2065 | 1.62 | -22.14 | -22.47 | -22.34 | 22.66 | 0.01 |
| O3…H1 | 0.0041 | 0.0592 | 0.2493 | 0.54 | 5.16 | -3.86 | -3.36 | 12.38 | 0.15 |
| O3-H2 | 0.0499 | 0.1790 | 0.3755 | 2.21 | -49.22 | -36.74 | -35.88 | 23.40 | 0.02 |
| O3-H3 | -0.1228 | -0.0092 | 0.3421 | 2.30 | -61.79 | -43.69 | -42.49 | 24.39 | 0.03 |

9.  ***Topological analysis – Basin integration***

*[On the screen: Basic Jana window]*

Run "Tools → Topological analysis → Basin integration"

*[On the screen: Select atoms for basic integration]*

Select all; OK

*[On the screen: Define parameters for integration]*

Use default values; OK

*Calculation can take some time …*

Run "Edit/View → View of Inb report";

*The integrated values for individual atoms should be:*

| Atom | Number of electrons | Charge |
|---|---|---|
| C1 | 5.147 | 0.853 |
| O1 | 9.124 | -1.124 |
| O2 | 8.773 | -0.773 |
| O3 | 9.378 | -1.378 |
| H1 | 0.396 | 0.604 |
| H2 | 0.407 | 0.593 |
| H3 | 0.419 | 0.581 |

# Example 11.1: bezcox

**Composite structure**

**Sr$_{1.272}$CoO$_3$**
**Revised: 28 April 2014**
Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: bezcox.hkl, bezcox.cif_od
Frame scaling, absorption correction: done by diffractometer software

1. ***Creating new jobname***
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click bezcox

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   *[On the screen: "Define basic input file:"]*
   Select "Input from cif_od file"; file name "bezcox.cif_od"; OK
   *[On the screen: "Complete/Correct experimental parameters"]*
   Leave all settings unchanged; NEXT
   *[On the screen: "Define the reference cell/split by twinning"]*
   Leave all settings unchanged; NEXT
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. ***Data Repository***
   OK; YES to accept the data set
   *[On the screen: "Information about starting symmetry wizard"]*
   NEXT

4. ***Symmetry Wizard***
   *[On the screen: "Tolerances for crystal system recognition".]*
   *Symmetry wizard can be started separately by "File $\rightarrow$ Reflection file $\rightarrow$ Make space group test".*
   Leave all settings default; NEXT
   *[On the screen: Select Laue symmetry]*
   Select Trigonal -3m1 Laue symmetry; NEXT
   *[On the screen: Select cell centering]*
   *In the list we can see that R-reverse centering is almost fulfilled.*
   Click on "Details" and examine strongest reflections contradicting R-reverse centering
   *The most of printed reflections follow the rule -h+k+l=3n. Similarly, reflections contradicting R-obverse centering follow the rule h-k+l=3n. This can be a sign of obverse/reverse twinning.*
   Return back to the page with tolerances and check there "Introduce twin laws in case of subgroup"

Follow steps of the symmetry wizard, select -3m1 Laue symmetry, NEXT

*Now, only 128 reflections contradicts the R (obverse or reverse) centering*

Select R-reverse; NEXT

*Before introducing the twinning, R-reverse centering was better fulfilled. This indicates that the major twin domain has R-reverse centering.*

Select R-3m; NEXT

*[On the screen: Select superspace group]*

R-3m(00g)0s

*[On the screen: Final step of the superspace test]*

Accept the superspace group in the standard setting: R-3m(00g)0s;

Accept twinning matrices induced by the space group test; FINISH; OK

Continue with creation of reflection file with default options;

*[On the screen: Structure solution]*

Press "Quit";

## 5. *Define W-matrix*

*Using Tools → Reciprocal space viewer we can clearly distinguish the composite subsystems. This compound has the simplest W matrix, which only exchanges the "l" and "m" index. Than means that "h k l m" are reflections of the first subsystem while "h k m l" are reflections of the second subsystem.*

Open "Edit M50", change number of composite parts to 2 and define W-matrix for the second subsystem: ( 1 0 0 0 | 0 1 0 0 | 0 0 0 1 | 0 0 1 0 )

```
                  Induced cell parameters:
 9.505   9.505   3.990   90.00   90.00   120.00     Volume:     360.468
                  Induced modulation vector(s):
                      0.0000   0.0000   1.5770

         Do you want to accept the composite matrix?
                    Yes          No
```
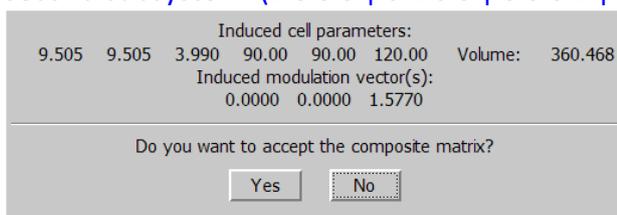
*"Induced cell paramemeters" are parameters of the second subsystem, as follow from the W matrix*

## 6. *Structure Solution*

Double-click the icon "Structure solution".

*[On the screen: window of Structure solution]*

In "Formula" textbox type list of chemical elements for $Sr_{1.272}CoO_3$ : Sr Co O

Select "use Superflip"; "**Peaks from Jana2006 but first run Fourier**"

Select "Use a specific random seed" and type value "111"

Press "Run solution";

*The option "Peak from Jana2006 but first run Fourier" in necessary for proper interpretation of Fourier map for composite structure because we need to look for bot subsystems*

*Superflip converges (after noise suppression) with R value 20%. It confirms the symmetry R-3m(00g)0s.*

*Fixing the random seed to 111 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. For this example finding proper solution would require many attempts with Superflip.*

Press "Quit" to leave the structure solution wizard

## 7. *Verification of the structure solution*

Double click on the icon "Edit atoms";

Select oxygen atoms if present and delete them;
*At this stage found oxygen positions are not reliable;*
Double click on the Co1 atom and check its coordinates;
*Co1          0.333333 0.666667 0.166667  - in the first subsystem*
Move to the Co2 atom;
*Co2          0.000000 0.333333 0.250000 – in the second subsystem*
*The solution program cannot distinguish at this stage between chemical types of heavy atoms because both atoms are placed in different subsystem and we cannot compare their electron densities directly.*
OK;OK; Yes to save the changes;

Double click on the icon "Contour";
Press "New plot"; Select "Calculate new ones" and "Draw maps as calculated"; OK;
*[On the screen: window of Fourier commands]*
On the page "Basic" define Composite part no. 1;
Map type "F(obs) – Fourier";
On the page "Scope" select the central point Co1;  select the x3-x4 section; scope 1 1 2; OK
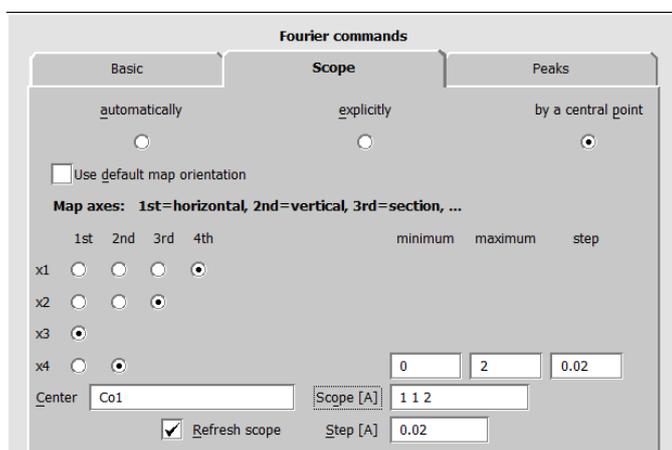
Repeat the procedure for Co2;
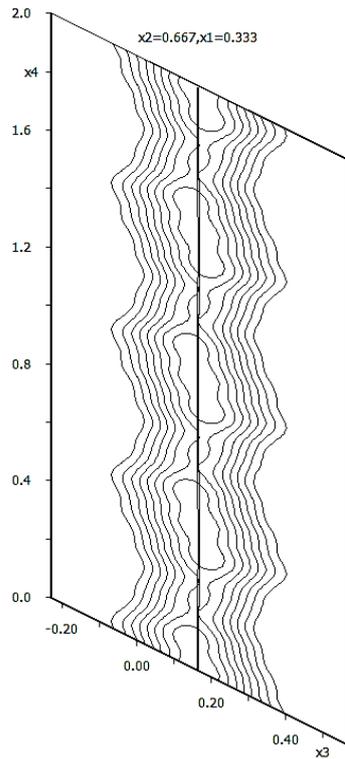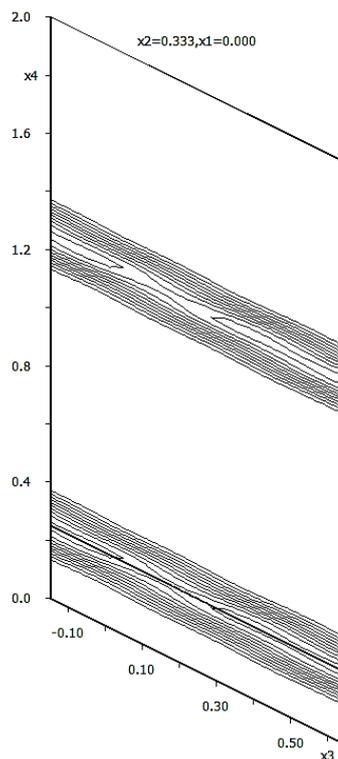


x3-x4 section for Co1                    x3-x4 section for Co2

*Note: Both maps are summed over x1 and x2.*
Press "New plot"; Select "Calculate new ones" and "Draw maps as calculated"; OK;
*[On the screen: window of Fourier commands]*
On the page "Basic" define Composite part no. 2;
Repeat map calculations for both atoms.
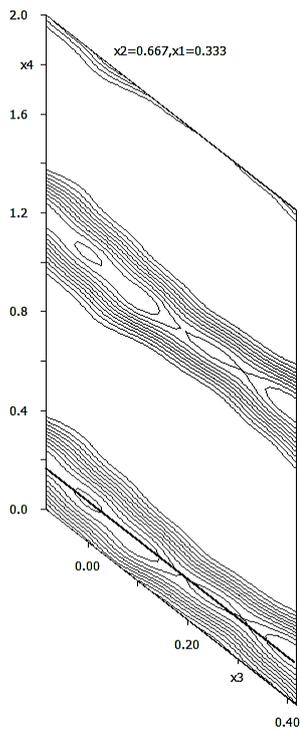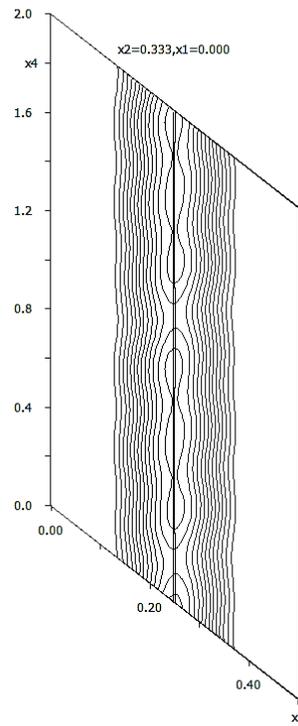
*x3-x4 section for Co1*        *x3-x4 section for Co2*

Start "Parameters → Twin fractions" and change the twin fraction to 0.5

Activate refinement of twin fraction

In Refinement options change number of cycles to 100

Run refinement

*Refinement converges with R values 34%, 24%, 41%, 58%, 67% and 97%*

Start "Edit/View → View of Refine" and read information following the header "Composite part #2".

*Here we can see unit cell and symmetry of the second composite subsystem. Note that the second subsystem has also different centering because centering vectors are also transformed by W matrix.*

```
Composite part #2

           | 1.000  0.000  0.000  0.000|
     W(2) = | 0.000  1.000  0.000  0.000|
           | 0.000  0.000  0.000  1.000|
           | 0.000  0.000  1.000  0.000|

Cell parameters      :    9.5050    9.5050    3.9899    90.000    90.000   120.000    Volume :     312.2
Reciprocal parameters :  0.121483  0.121483  0.250632    90.000    90.000    60.000    Volume :  0.003203

Modulation vector q(1):   0.000000  0.000000  1.577038

Centrosymmetric super-space group: X-3c1(00g)000

List of centring vectors:

  0.000000  0.000000  0.000000  0.000000
  0.666667  0.333333  0.000000  0.333333
  0.333333  0.666667  0.000000  0.666667

Symmetry operators:

    x1       x2       x3       x4
   -x2      x1-x2     x3       x4
  -x1+x2    -x1       x3       x4
    x2       x1     -x3+1/2  -x4
   x1-x2    -x2     -x3+1/2  -x4
   -x1     -x1+x2   -x3+1/2  -x4
   -x1      -x2      -x3      -x4
Refinement program                                                          page=  3
structure :                                                           19:21:28 17-01-11

    x2     -x1+x2    -x3      -x4
   x1-x2    x1       -x3      -x4
   -x2      -x1      x3+1/2    x4
  -x1+x2    x2       x3+1/2    x4
    x1     x1-x2     x3+1/2    x4
```

Double click on the icon "Edit atoms"; Double click on the atom Co2;

*The "Edit" page shows that the parameter Uiso is negative. It indicates that atom type is Sr.*

Go the "Define" page and change the atom type to Sr and rename it to Sr1;

Run refinement

*Refinement converges with R values 32%,21%, 40%, 58%, 70% and 97% and the isotropic ADP parameters become positive.*

8. **Making results compatible with Acta Cryst. (1999), B55, 841-848**

Start "Tools → Transformation → Origin shift" and move origin to the position of Co1.

Position of Sr1 changes to -1/3, -1/3, 1/4.

Start Edit atoms, select Sr1, Action: Transform selected atoms

Select symmetry operator –x2 x1-x2 x3 x4

Run Refinement

R factors of the previous refinement are exactly repeated

Now we are compatible with published positions of Co1 and Sr1.

9. **Oxygen**

Run refinement to obtain input for Fourier

Run difference Fourier for composite part No 1, with Scope="automatically", default map orientation, independent parallelepiped

*We use composite part 1, because we expect oxygen belonging to Co coordination*

YES to start procedure for including atoms

Locate the strongest maximum with reasonable distance to Co (probably Max2)

Include this maximum as O1 in position about 0.17, 0.04, 0.5

Start Contour and plot section x3-x4 through O1, scope 1 1 2, difference Fourier, using summation of x1, x2 over 1 Å;
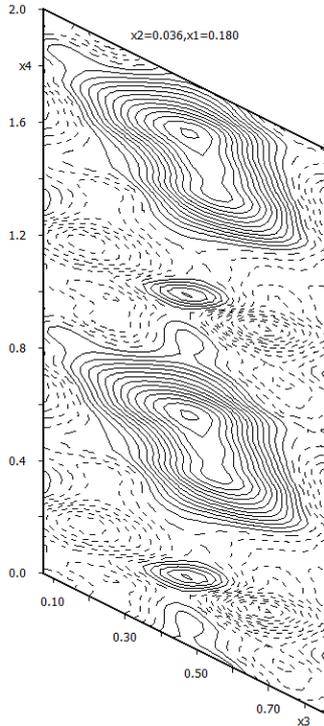
*section x3-x4 of O1*

*The section reveals O1 should be described with crenel function, x40=0.75, delta=0.5*

Plot section x1-x2, difference Fourier, x4 from 0 to 1, scope 5 5 0, step 0.5A, center 0 0 0.5
*The section x1-x2 with center at (0,0,1/2) with scope about 5 Å as a function x4 shows the character of the modulation*



:

x4=0.240,x3=0.500

Run "Movie" to see the discontinuous character of the modulation.

*The three oxygen positions are generated by the three fold axis. From the above figure on epossibility for oxygen position is about (0.157,0.157,0.5) (as indicated by the arrow) with crenel of length 0.5 with x4 center 0.25.*

Start Edit atoms and double-click O1

Define the crenel function for O1 and delete its position modulation wave

In page Edit press Occupancy and set x40=0.25 and delta=0.5 (page "Edit").

In page Edit modify the atomic position of O1 to the one found in the difference Fourier and reset size occupancy (it should be 0.5).

Finally in the page "Define" define type of modulation functions – Legendre polynomials.

Run refinement

*Refinement converges with R values 26%,13%, 36%, 58%, 66% and 88%*

Set harmonic ADP for all atoms

Repeat refinement

*R values are almost unchanged*

## 10. *More modulation waves*

Add one by one more position and ADP modulation waves.

Co: 4 for position, 4 for ADP

O1: 4 for position, 2 for ADP

Sr1: 4 for position, 4 for ADP

The last *refinement will converge with R values 4.3%,2.5%, 4.2%, 9.2%, 21.5% and 59% With fourth order satellites it is doubtful if we could achieve better results because they are almost completely unobserved. However, the fit for $2^{nd}$ and $3^{rd}$ order satellites is not yet satisfactory*

## 11. *Sawtooth for Sr1*

Start Contour and plot x3-x4 section (observed and difference Fourier) for Co1, O1 and x2-x4 section for Sr1. Use 1 Å summation. Do not forget to switch composite subsystem in the Basic page of Fourier commands.
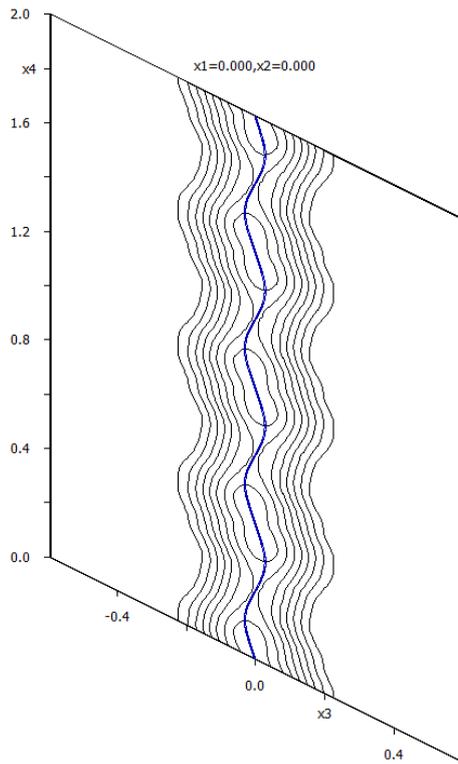
x3-x4 section for Co1
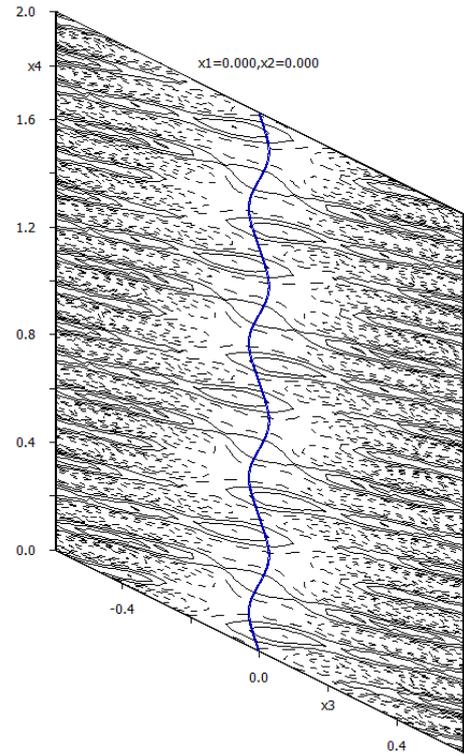
difference section, contour step 0.2
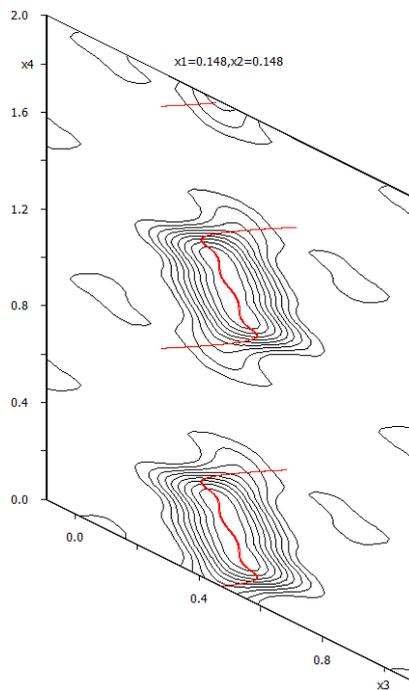


x3-x4 section for O1
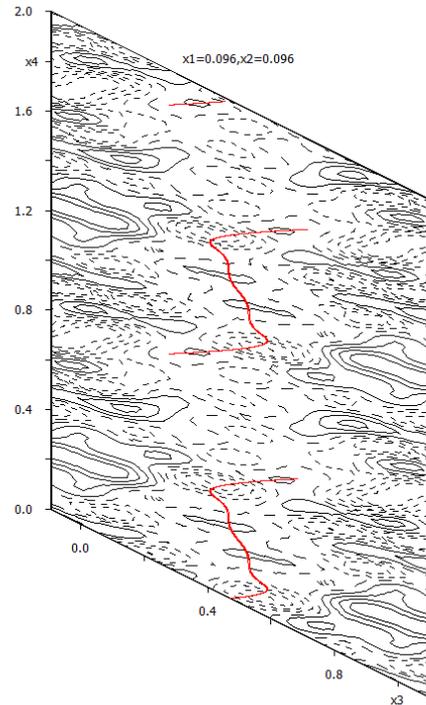
difference section, contour step 0.2
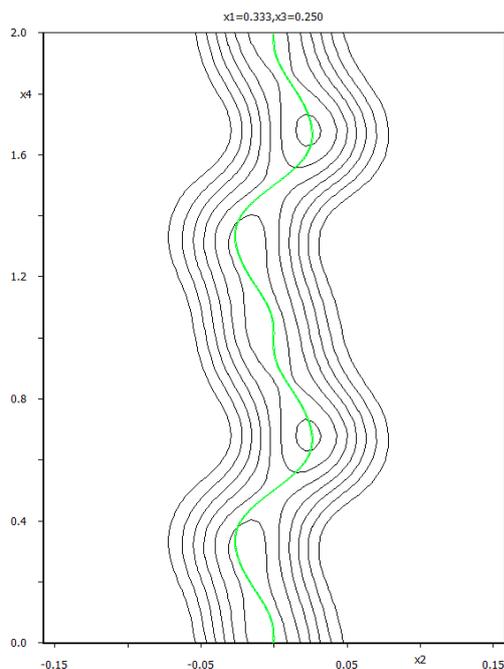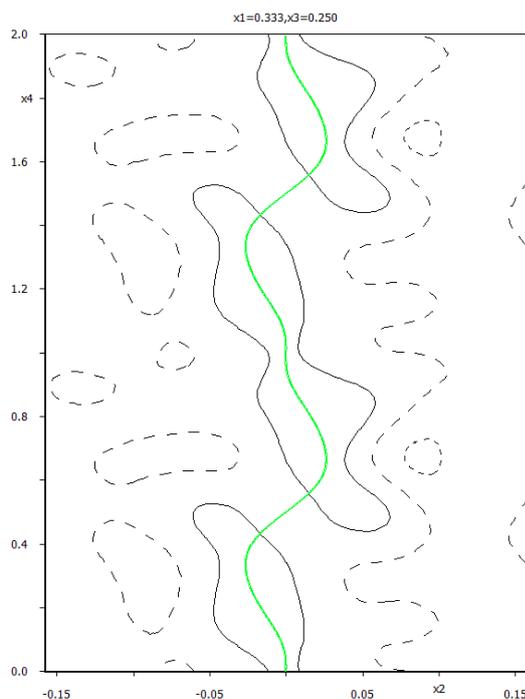
x2-x4 section for Sr1          difference section, contour step 0.2

*The largest different peaks are around Sr1 position. Now we shall attempt to describe modulation function of Sr1 with Lagrange polynomials, with crenel defined at x40=0 with delta=1*

Make backup copy (File → Structure → Save As)

Start Edit atoms

Remove all ADP and position modulation waves of Sr1 except the first position modulation wave;

Activate in the Crenel for Sr1 and the the edit page set x40=0 and delta=1. Keep x40 and delta fixed

In the page "Define" Parameters activate Legendre polynomials

In refinement commands set Damping factor 0.1

Run refinement

During the refinement change Damping factor to 0.5

*Refinement converges with R values 10.3%, 4.0%, 9.3%, 37.7%, 46% and 53%*

Add one by one position and ADP modulation waves for Sr1 up to three position waves and three ADP waves.

*The last refinement will converge with R values 3.7%, 1.9%, 3.6%, 8.2%, 18.7% and 55%. This is significant improvement comparing with the structure model without sawtooth function.*


**Anharmonic ADP for Co1**

"Start Contour → New plot → Calculate new ones"

In Basic page select Difference Fourier and Composite part no. 1

In Scope select central point Co1, section x1-x2, scope 6 6 1

OK

In Contour make summation only along x3 (not x4)





x3=0.000,x4=0.000

*x1-x2 section through Co1, contour step 0.05, x4=0*

x1-x2 section through Co1, contour step 0.05, x4=0.26

The neighborhood of Co1 is changing from octahedron to trigonal prisma (check it with drawing program). The trigonal coordination induces a slightly triangular shape of ADP.

However, the region in x4 in which the effect is detectable is very narrow and the number of modulation waves for ADP's of the order 3 would be very large to describe such abrupt change.

The atom Co1 should therefore be split into two positions by crenel – the first one Co1 (x40=0, delta=0.45) and the second one Co1' (x40=0.25, delta 0.05). After adjusting of occupancies to  ai=1/6 for both atoms the two Legendre waves for position and harmonic ADP Co1 should be used.

For the Co1' only average parameters for position and ADP up to the third order.

Final R values : 3.2%, 1.8%, 3.0%, 7.3%, 13.9% and 55%

# Example 12.1: Ba5Co5

**Simple magnetic structure**
**Revised: 28 November 2014**

### $Ba_5Co_5ClO_{13}$

Powder data measured with the ILL neutron source at 1.4 K
For more details: Mentré, O., Kauffmann, M., Ehora, G., Daviero-Minaud, S., Abraham F. & Roussel, P. (2008). *Solid State Sciences* **10**, 471-475.

Input files:      Ba5Co5.dat (powder profile data)
                  Ba5Co5_nuclear.cif (nuclear structure)

In order to facilitate work with magnetic structures Jana2006 offers special wizards and protects the basic file - the parent structure. However, for experienced users of Jana, all operations offered by wizards can be also done manually by starting the tools directly from the basic user interface. The standard work with magnetic structures based on powder data follows this scheme:

```
┌─────────────────────────────────────────────────────────────┐
│     Reading of powder profile and parent structure model     │
└─────────────────────────────────────────────────────────────┘
                              ↓
┌─────────────────────────────────────────────────────────────┐
│    Wizard for le Bail refinement of powder profile parameters │
│   Leaving this wizard automatically fixes all profile         │
│          parameters except the background                     │
└─────────────────────────────────────────────────────────────┘
                              ↓
┌─────────────────────────────────────────────────────────────┐
│    Wizard for Rietveld refinement of the parent structure     │
│   Leaving this wizard automatically locks the parent          │
│   structure in order to prevent its accidental refinement     │
└─────────────────────────────────────────────────────────────┘
                              ↓
┌─────────────────────────────────────────────────────────────┐
│       Wizard for selection of the magnetic symmetry           │◄─┐
└─────────────────────────────────────────────────────────────┘  │
                              ↓                                    │
┌─────────────────────────────────────────────────────────────┐  │
│  Magnetic structure refinement using the selected magnetic    │  │
│  symmetry                                                     │  │
│  This runs under different jobname in order to keep the parent│  │
│  structure unchanged. Each magnetic symmetry should be tested │  │
│  under a unique jobname.                                      │  │
└─────────────────────────────────────────────────────────────┘  │
                              ↓                                    │
┌─────────────────────────────────────────────────────────────┐  │
│  Loading the parent structure for testing another magnetic    │──┘
│  symmetry                                                     │
└─────────────────────────────────────────────────────────────┘
```

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click Ba5Co5
   *[On the screen: Specify type of the file to be imported]*
   Select "Magnetic parent structure: nuclear model from CIF"; NEXT
   *[On the screen: Select input CIF file]*
   Right pane: select (by the button with arrow) the input file Ba5Co5_nuclear.cif; OK

2. ***Define magnetic propagation vector and form factors***
   *[On the screen: Define magnetic propagation vector and form factors]*
   For "Atom type" select "Co"; check "Use as a magnetic atom"
   For "Magnetic formfactor <j0>" select Co4+; NEXT; Finish
   *The parent structure has been created*

3. ***Import the reflection file***
   *[On the screen: Specify type of the file to be imported]*
   Select "Powder data - Various CW formats"; NEXT
   Check that the name of the input file is "Ba5Co5.dat" and the format is "Free format of 2th, I, [sig(I)]"; NEXT
   *[On the screen: Complete/correct experimental parameters];*
   For "Wave length" type 2.52; NEXT; Finish
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

   ***Refining of profile parameters by le Bail technique.***
   *[On the screen: Information]*
   NEXT;
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *As common for powder neutron data the background is strongly varying with the diffraction angle. It is recommended to estimate it manually and use just a few additional parameters.*
   Manual background: "Create new"; Use default parameters; OK
   *The automatic procedure has created a first estimation of the manual background, which can be modified manually: the points can be dragged by the left mouse button; dragging a point to the position of neighboring point deletes the point; clicking between two points creates a new point.*
   Using "X+", "Y+", enlarge the profile plot
   Modify background point at high and low angles as indicated in the next figures:
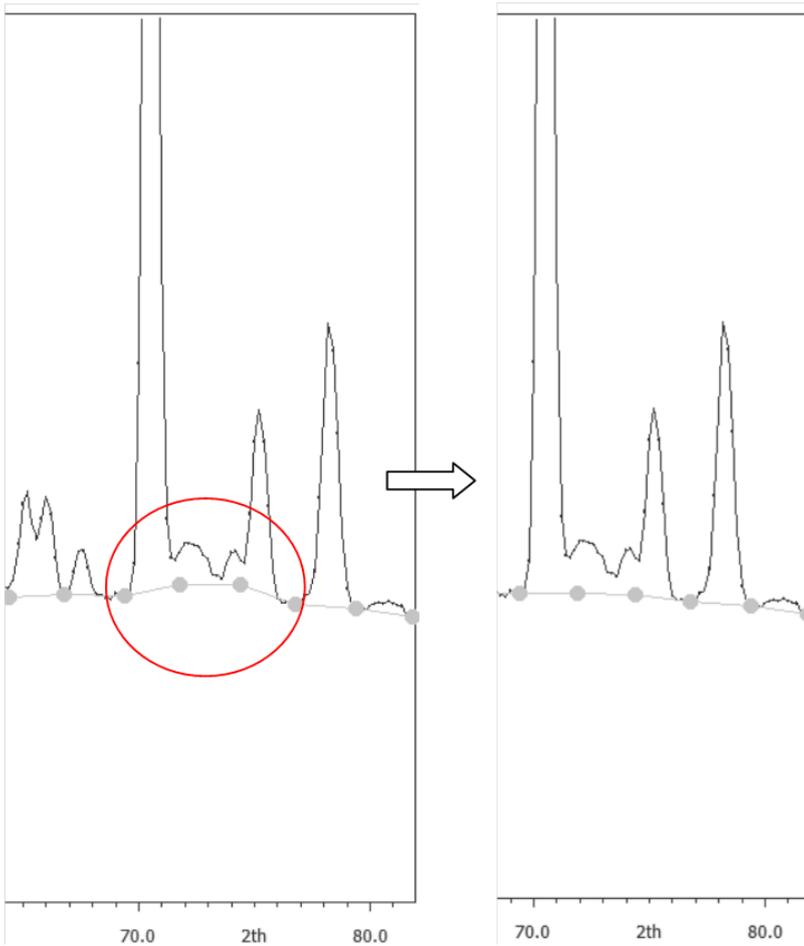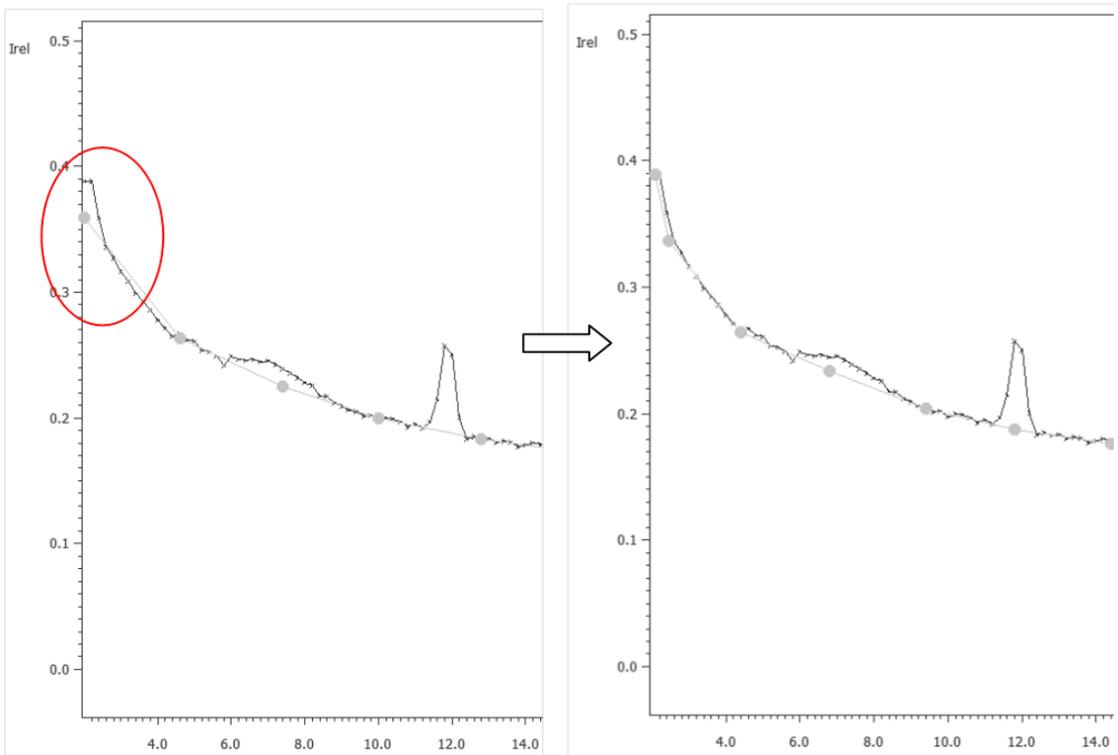
"QUIT"; Select "Accept the new manual background" and "Reset polynomial coefficients to zeros"; OK

*This means that the polynomial background will be refined and combined with the manual background*
"Edit profile parameters";
*[On the screen: Powder options]*
In the page "Cell" activate refinement of a and c parameters;
In the page "Profile" change the starting value of GW to 50 and activate its refinement;
In the page "Corrections" activate refinement of "shift" parameter; OK; YES to save changes
"Run Refine";
*The refinement should converge to Rp~2.7%.*
"Edit profile parameters";
*[On the screen: Powder options]*
In the page "Profile" change activate refinement of GU and GV; OK; YES to save changes
"Run Refine";
*The refinement should converge to Rp~2.1%.*
"Show powder profile" to see the fit of the calculated profile; QUIT
NEXT;
YES to "Do you really want to leave the form for le Bail refinement?"
*Now we will refine the scale parameter for the nuclear structure*
*[On the screen: Refinement of the nuclear structure by the Rietveld method]*
"Edit refinement commands"; On the page "Various" select "Fixed commands;
Fix all parameters for all atoms ("*" for "Atoms/Parameters" textbox );
Press "Add";
*The command will appear in the panel as "fixed all *"*
OK; OK;
"Run Refine";
*The refinement should converge to Rp~3.4%.*
NEXT;
YES to "Do you really want to leave the form for Rietveld refinement?"
NEXT to accept the Information

4. ***Testing different irreps to get the best single irrep model***
   *[On the screen: Representation analysis]*
   This window has an informative character. You can see here all irreps leading to non-paramagnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.
   Press "Display representations" and look at the representation "mGM5-".
   Individual 2x2 representation matrices of each of 24 operations:

```
Jana2006
 Find   Find next   Go to   Print   PgTop   Open in editor   Close
Representation: mGM5-  Dimension: 2
-----------------------------------

Symmetry operator      Symbol      Matrix       Character

(x,y,z)                  1    |  1.000  0.000|    2.000
                              |  0.000  1.000|    2.000

(-y,x-y,z)               3    | -0.500  0.866|   -1.000
                              | -0.866 -0.500|   -1.000

(-x+y,-x,z)              3    | -0.500 -0.866|   -1.000
                              |  0.866 -0.500|   -1.000

(-x,-y,z+1/2)           21    |  1.000  0.000|    2.000
                              |  0.000  1.000|    2.000

(y,-x+y,z+1/2)          63    | -0.500  0.866|   -1.000
                              | -0.866 -0.500|   -1.000

(x-y,x,z+1/2)           63    | -0.500 -0.866|   -1.000
                              |  0.866 -0.500|   -1.000

(y,x,-z)                 2    | -0.500  0.866|    0.000
                              |  0.866  0.500|    0.000

(x-y,-y,-z)              2    | -0.500 -0.866|    0.000
                              | -0.866  0.500|    0.000

(-x,-x+y,-z)             2    |  1.000  0.000|    0.000
                              |  0.000 -1.000|    0.000

(-y,-x,-z+1/2)           2    | -0.500  0.866|    0.000
                              |  0.866  0.500|    0.000

(-x+y,y,-z+1/2)          2    | -0.500 -0.866|    0.000
                              | -0.866  0.500|    0.000

(x,x-y,-z+1/2)           2    |  1.000  0.000|    0.000
                              |  0.000 -1.000|    0.000

List of irreducible representations                              page= 13
structure :                                                 16:32:47 07-01-14

(-x,-y,-z)              -1    | -1.000  0.000|   -2.000
                              |  0.000 -1.000|   -2.000

(y,-x+y,-z)             -3    |  0.500 -0.866|    1.000
                              |  0.866  0.500|    1.000

(x-y,x,-z)              -3    |  0.500  0.866|    1.000
                              | -0.866  0.500|    1.000

(x,y,-z+1/2)             m    | -1.000  0.000|   -2.000
```

Close the window; NEXT;
*[On the screen: List of kernels and epikernels]*



List of kernels and epikernels:

| Shubnikov space group | Axes | Origin shift | Representation |
|---|---|---|---|
| P63/mmc | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM1+ |
| P63/m'm'c' | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM1- |
| P63/mm'c' | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM2+ |
| P63/m'mc | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM2- |
| P63'/m'mc' | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM3+ |
| P63'/mm'c | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM3- |
| P63'/m'm'c | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM4+ |
| P63'/mmc' | (1,0,0|0,1,0|0,0,1) | (0,0,0) | mGM4- |
| Cm'c'm | (1,0,0|1,2,0|0,0,1) | (0,0,0) | mGM5+ |
| Cmcm | (1,0,0|1,2,0|0,0,1) | (0,0,0) | mGM5+ |
| Cmcm' | (1,0,0|1,2,0|0,0,1) | (0,0,0) | mGM5- |
| Cm'c'm' | (1,0,0|1,2,0|0,0,1) | (0,0,0) | mGM5- |

Show details

**Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.**

Back    Next    Cancel

Select e.g. magnetic group Cmcm' and press "Show details".
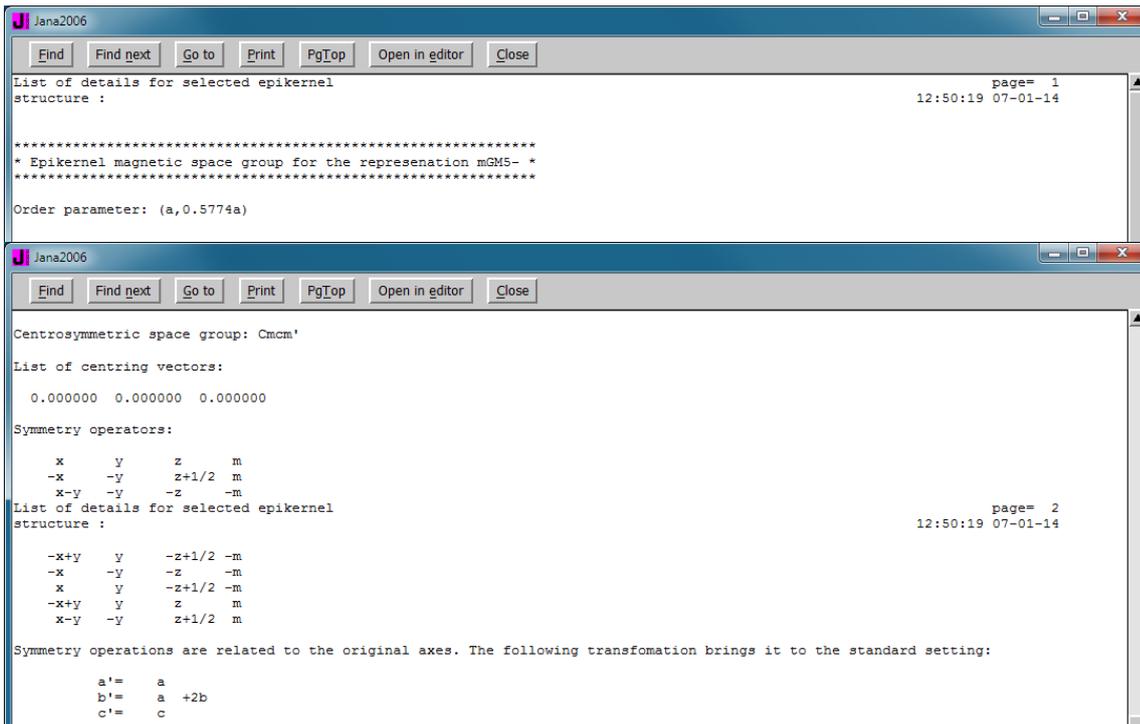


*It shows symmetry operators of the selected magnetic group, transformation to the standard setting and the relevant order parameter.*

Close;
Select one of the hexagonal magnetic space groups; NEXT
*This will pass all present hexagonal magnetic space groups to further testing.*
*[On the screen: Select magnetic space group]*
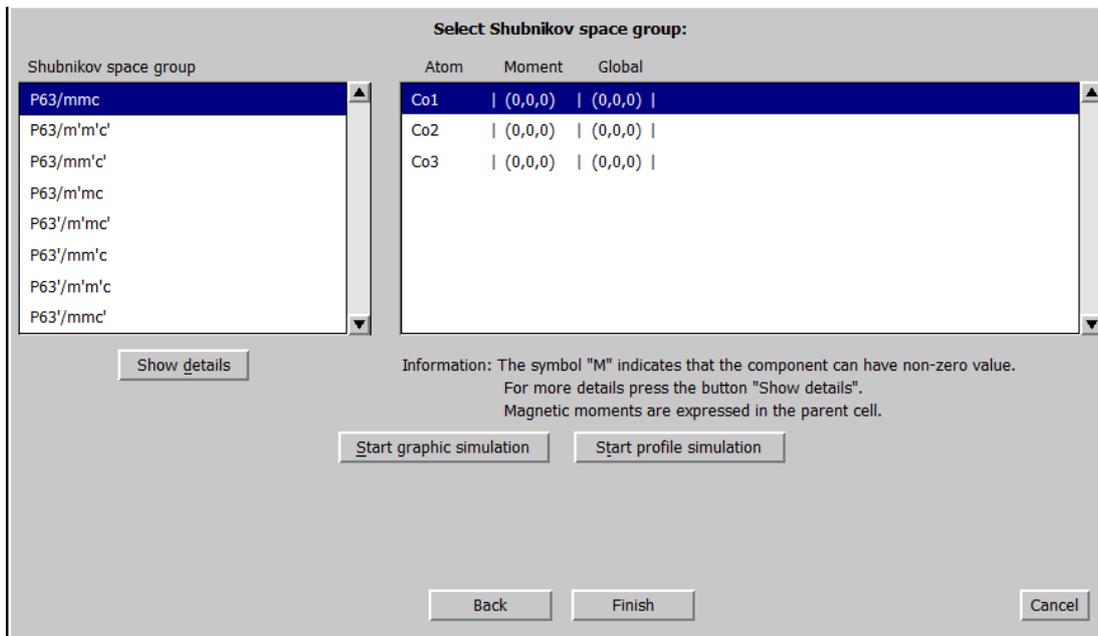


*For an individual Shubnikov space group the tool shows components of the magnetic vector of all magnetic atoms in the structure. The button "Show details" gives analysis that is more*

*detailed. In our case only two Shubnikov space groups – P6₃/mm'c' and P6₃'/m'm'c – allow magnetic ordering for all Co atoms. Note that for the first of them the global magnetic moment for is generally non-zero, which means that this arrangement allows a ferromagnetic ordering. As ferromagnetism has not been detected for this compound, the first model can be excluded from the analysis. However, we shall test all models to check if such a decision can also be based of the diffraction experiment.*

Select the Shubnikov space group *P6₃/mm'c'* and press "Start profile simulation". Use "Go to 2th/hkl" textbox and find position of the reflection  2 -1 3 . Click on the tick corresponding to the reflection 2 -1 3:
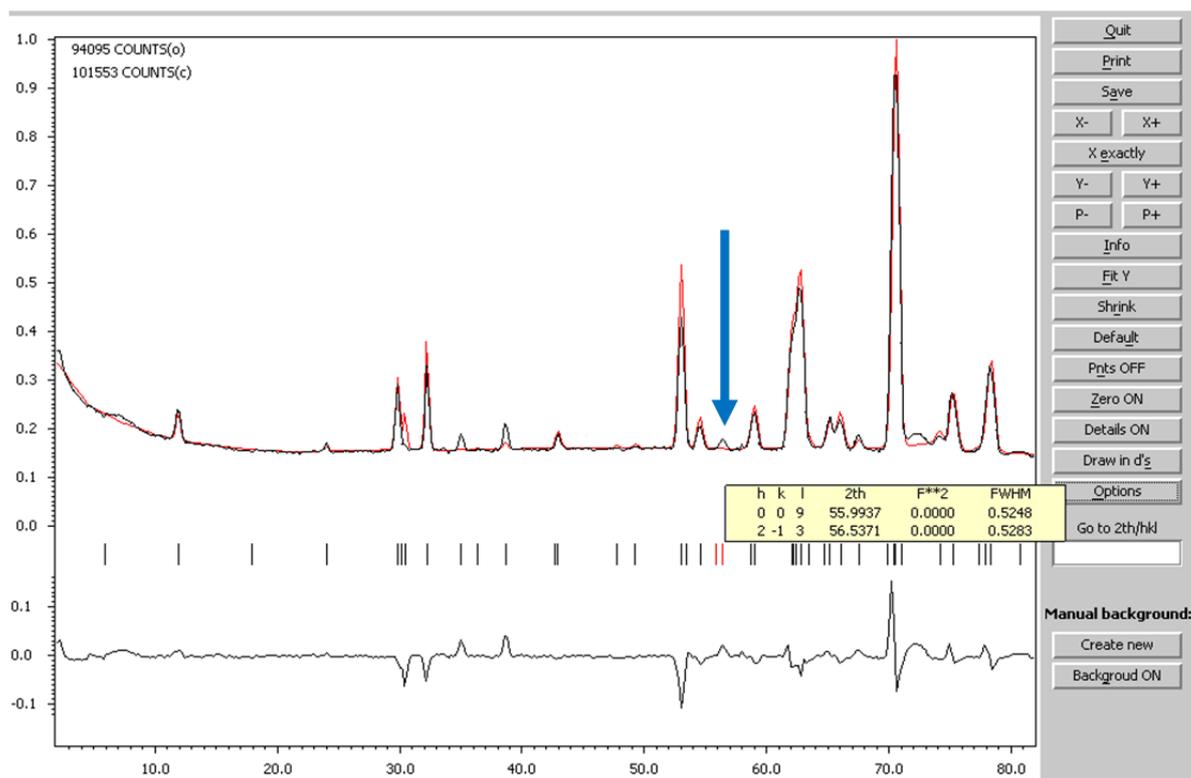


*Although the peak is clearly visible, the calculated structure factor is zero.*

ESC
Press "Quit" and the select Shubnikov space groups *P6₃'/m'm'c* and investigate again the reflection 2 -1 3:
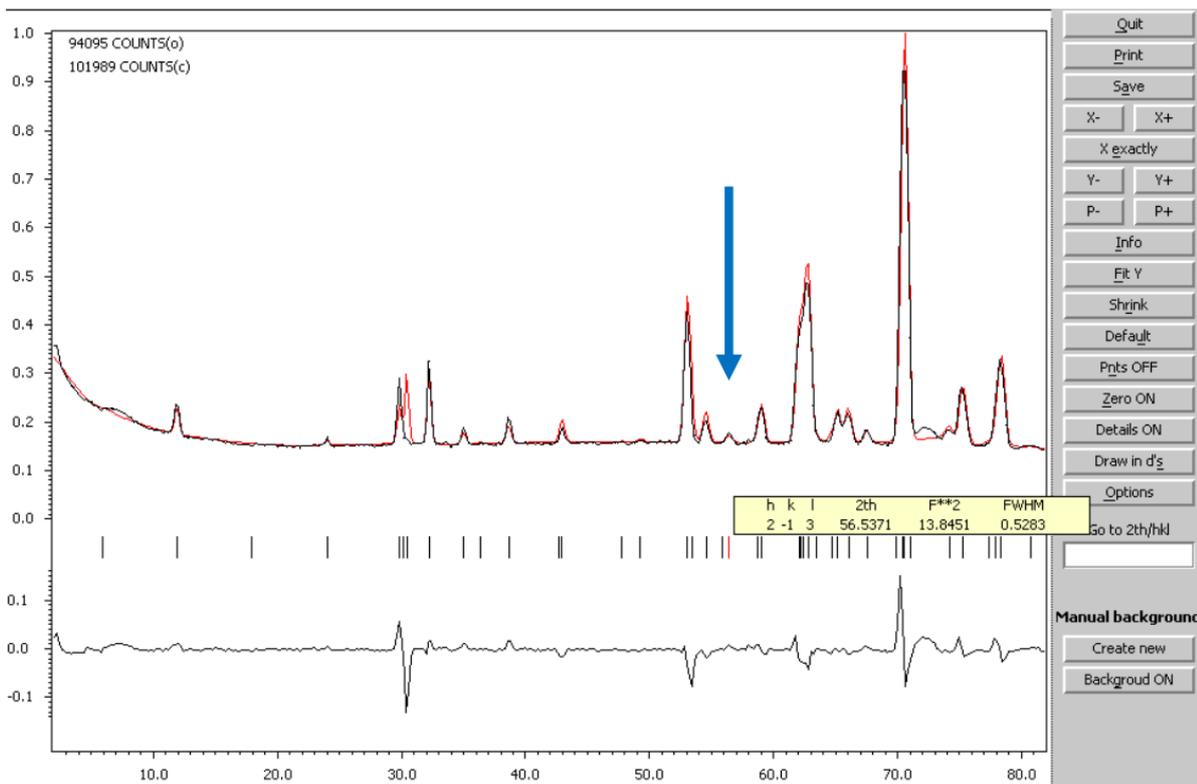
For this Shubnikov space group the intensity of (2 -1 3) is non-zero in accordance with the diffraction pattern. As this reflection is systematically absent for the nuclear structure (c glide plane), this is clear that it originates from magnetic scattering. As apparent from the the Shubnikov space group test all magnetic moments are directed along the z-axis. This leads to the systematic extinctions $l = 2n + 1$ for reflections $(2h, -h, -h, l)$ but only in the case that the glide plane "c" is combined with the time inversion operation. The fact that the peak 2 -1 3 is clearly detectable gives us another support for the Shubnikov space group P6₃'/m'm'c.

Select again the Shubnikov space group *P6₃/mm'c'* and press "Start graphic simulation";
Select "Use Vesta to draw the magnetic structure";
Press "Draw+return" or "Draw+continue";
In the VESTA program you can modify the length of the displayed vectors by "Edit→Vectors…"

*You can see that in this case the magnetic moments, which are in the simulation chosen identical for the independent magnetic atoms, are not compensated in the unit cell.*

Repeat this procedure for *P6₃'/m'm'c*
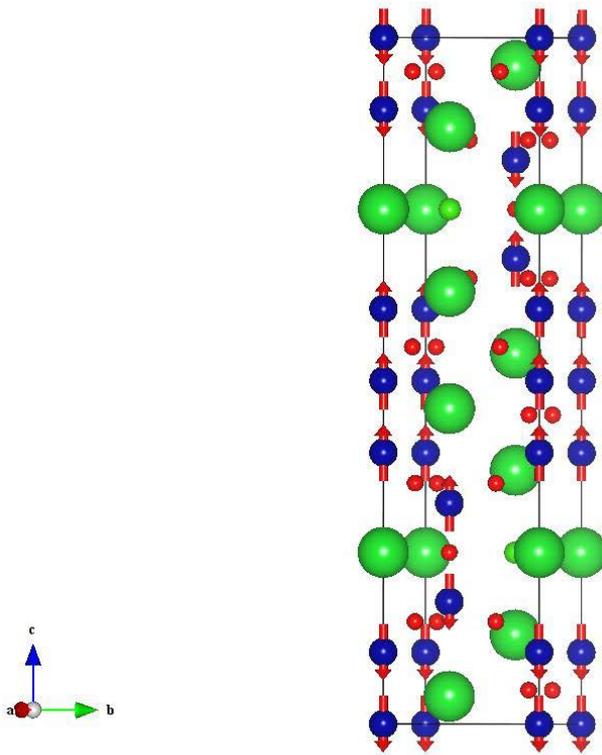


5. **Refinement of the magnetic structure in P6₃/mm'c'(GM2+)**

   *[On the screen: Select Shubnikov space group]*

   Select the Shubnikov space group *P6₃/mm'c'*; Finish; YES to the question "Do you want to continue with the last kernel/epikernel?";

   *[On the screen: Select structure name]*

   Use the default name "Ba5Co5_01"; OK

   *The test will be done under the new job name in order to keep the parent structure unchanged*

   *[On the screen: Basic window]*

   Right-click the icon of Refine and select the page "Various".

   Click "Fixed commands" and make sure the coordinates of all atoms are fixed:

   ` fixed xyz * `

   Click "Restrictions" and make sure ADP parameters all atoms are restricted to be the same:

   ` restric * 12 `

   *The "Fixed commands" and "Restrictions" are created automatically by the program when preparing the testing structure.*

   OK; select the page "Basic"

   Change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

   OK; Start refinement;

   *Refinement converges with Rp~3.3%, R(obs)~8.4%.*

6. **Refinement of the magnetic structure in P6₃'/m'm'c (GM4+)**

   *[On the screen: Basic window]*

   "File → Structure → History" and select the parent structure Ba5Co5; OK;

   *[On the screen: Basic window]*

"Tools → Special tools → Representation analysis for magnetic structures";
*[On the screen: Representation analysis]*
NEXT; Select one of hexagonal Shubnikov space groups; NEXT; Select *P6₃'/m'm'c*; Finish;
YES to the question "Do you want to continue with the last kernel/epikernel?";
*[On the screen: Select structure name]*
Use the default name; OK
*[On the screen: Basic window]*
Right-click the icon of Refine and select the page "Various".
Click "Fixed commands" and make sure the coordinates of all atoms are fixed:

| fixed xyz * |

Click "Restrictions" and make sure ADP parameters all atoms are restricted to be the same:

| restric * 12 |

OK; select the page "Basic"
Check that the "Number of cycles" is 100 and the "Damping factor" to 0.1;
OK; Start refinement;
*Refinement converges with Rp~3%, R(obs)~6%.*

7.  ***Drawing of the magnetic structure***
    *[On the screen: Basic window]*
    Double click on the icon "Plot structure";
    Press "Draw+return" or "Draw+continue";
    Select "Objects→Structural models" and choose "Polyhedral"
    Select "Edit→Bonds"; New; Define A1 as Co, A2 as O and Max.length 2.3; Apply;OK;
    Select "Objects→Properties→Polyhedra";
    Choose new polyhedral style and reduce the opacity to 50:
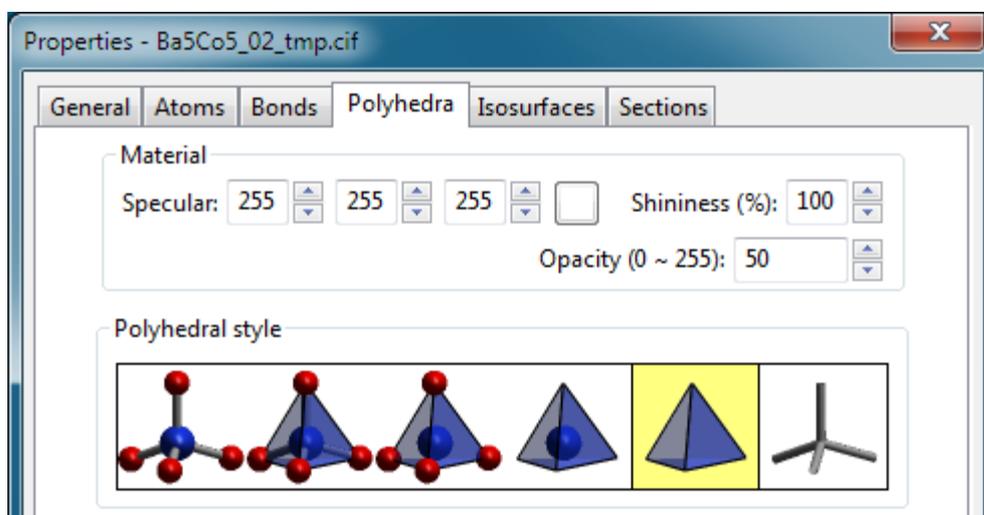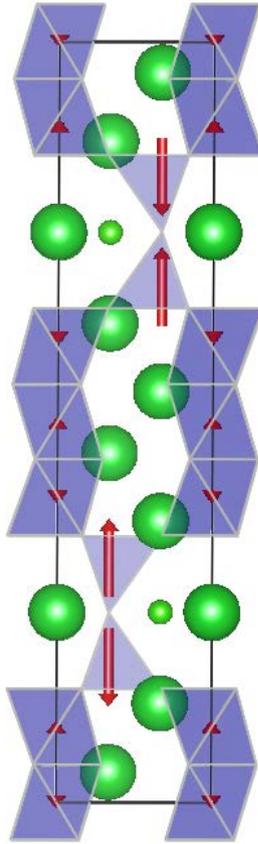
*The magnetic moments of atoms Co4 and Co5 are negligible. The atom Co6 is tetrahedrally coordinated by O atoms while the others have octahedral coordination.*

# Example 12.2: Ba6Co6

**Commensurate magnetic structure – modulation (propagation) vector (0,0,1/2)**
**Revised: 28 November 2014**

## Ba$_6$Co$_6$ClO$_{16}$

Powder data measured with the ILL neutron source at 1.4 K

For more details: Mentré, O., Kauffmann, M., Ehora, G., Daviero-Minaud, S., Abraham F. & Roussel, P. (2008). *Solid State Sciences* **10**, 471-475.

Input files:  Ba6Co6.dat (powder profile data)
  Ba6Co6_nuclear.cif (nuclear structure)

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click Ba6Co6

2. *Import Wizard*
   Select "Magnetic: nuclear model from CIF"; NEXT
   Right pane: select the input file Ba6Co6_nuclear.cif; OK

3. *Define magnetic propagation vector and form factors*
   *[On the screen: Define magnetic propagation vector and form factors]*
   Check "Use non-zero magnetic propagation vector" and fill its value: 0 0 1/2
   Select atom type Co; check "Use as a magnetic atom"; select "Magnetic formfactor <j0>"
   Co4+; NEXT; FINISH
   *The parent structure is created*

4. *Import the reflection file*
   *[On the screen: Specify type of the file to be imported]*
   Select "Various CW format"; NEXT;
   Check that the name of the input file is "Ba6Co6.dat" and the data format is "Free format of 2th, I, [sig(I)]"; NEXT
   *[On the screen: Complete/correct experimental parameters];*
   Fill used wavelength 2.394; NEXT; FINISH
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

5. *Refining of profile parameters by the le Bail technique.*
   *[On the screen: Information]*
   NEXT
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *Although the background is often strongly varying with the diffraction angle for powder*

*neutron data, in this case it is relatively smooth and it can be described without introducing a manual background.*

"Quit"; "Edit profile parameters";

*[On the screen: Powder options]*

In page "Cell" activate refinement of a and c parameters;

In the page "Profile" change the starting value of GW to 50 and activate its refinement;

In the page "Corrections" activate refinement of "shift" parameter; for background enlarge the number of used Legendre polynomials to 10

OK; YES to save the changes

"Edit refinement commands"; In the page "Basic" change the number of cycles to 100; OK

"Run Refine";

*The refinement should converge to Rp~9.3%.*

"Edit profile parameters";

*[On the screen: Powder options]*

In the page "Profile" change activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LY

OK; YES to save the changes

"Run Refine"

*The refinement should converge to Rp~5.5%.*

NEXT; YES to leave the form for le Bail refinement

6. ***Refinement of the scale parameter for the nuclear structure***

*[On the screen: Refinement of the nuclear structure by the Rietveld method]*

"Edit refinement commands"; On the page "Various" select "Fixed commands";

Fix all parameters for all atoms (wild character *); "Add"; OK; OK

"Run Refine"

*The refinement should converge to Rp=9.7%, R(obs)=6.5%*

NEXT; YES to leave the for for Rietveld refinement

7. ***Testing different irreps to get the best single irrep model***

*[On the screen: Information]*

NEXT

*[On the screen: Representation analysis]*

**Representation analysis:**

| Representation | Dimension | Shubnikov space group | Axes | Origin shift | |
|---|---|---|---|---|---|
| Tau1 | 1 | P[c]-6m2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,0) | Details |
| Tau2 | 1 | P[c]-6c2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,0) | Details |
| Tau3 | 1 | P[c]-6c2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,1/4) | Details |
| Tau4 | 1 | P[c]-6m2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,1/4) | Details |
| Tau5 | 2 | P[b]m | (0,1,0\|0,0,2\|1,0,0) | (0,1/4,0) | Details |
| Tau6 | 2 | P[b]m | (0,1,0\|0,0,2\|1,0,0) | (0,0,0) | Details |

Display representations

Back — Next — Cancel

*This window has an informative character and shows all irreps leading to non-paramagnetic ordering. The "Details" buttons provides more information about an individual irrep. There are four highest symmetrical hexagonal Shubnikov space groups; two of them differ only in the origin position, but this may lead to different solutions in commensurate cases.*
NEXT
*[On screen: List of kernels and epikernels]*



**List of kernels and epikernels:**

| Shubnikov space group | Axes | Origin shift | Representation |
|---|---|---|---|
| P[c]-6m2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,0) | Tau1 |
| P[c]-6c2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,0) | Tau2 |
| P[c]-6c2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,1/4) | Tau3 |
| P[c]-6m2 | (1,0,0\|0,1,0\|0,0,2) | (0,0,1/4) | Tau4 |
| A[a]ma2 | (0,0,2\|1,1,0\|-1,1,0) | (0,0,0) | Tau5 |
| A[a]mm2 | (0,0,2\|1,1,0\|-1,1,0) | (1/4,0,0) | Tau5 |
| A[a]mm2 | (0,0,2\|1,1,0\|-1,1,0) | (0,0,0) | Tau6 |
| A[a]ma2 | (0,0,2\|1,1,0\|-1,1,0) | (1/4,0,0) | Tau6 |
| P[b]m | (0,1,0\|0,0,2\|1,0,0) | (0,1/4,0) | Tau5 |
| P[b]m | (0,1,0\|0,0,2\|1,0,0) | (0,0,0) | Tau6 |

Show details

**Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.**

Back — Next — Cancel

**Select one of the hexagonal Shubnikov groups; NEXT**
*This will pass all present hexagonal Shubnikov groups to further testing.*
*[On the screen: Select Shubnikov space group]*
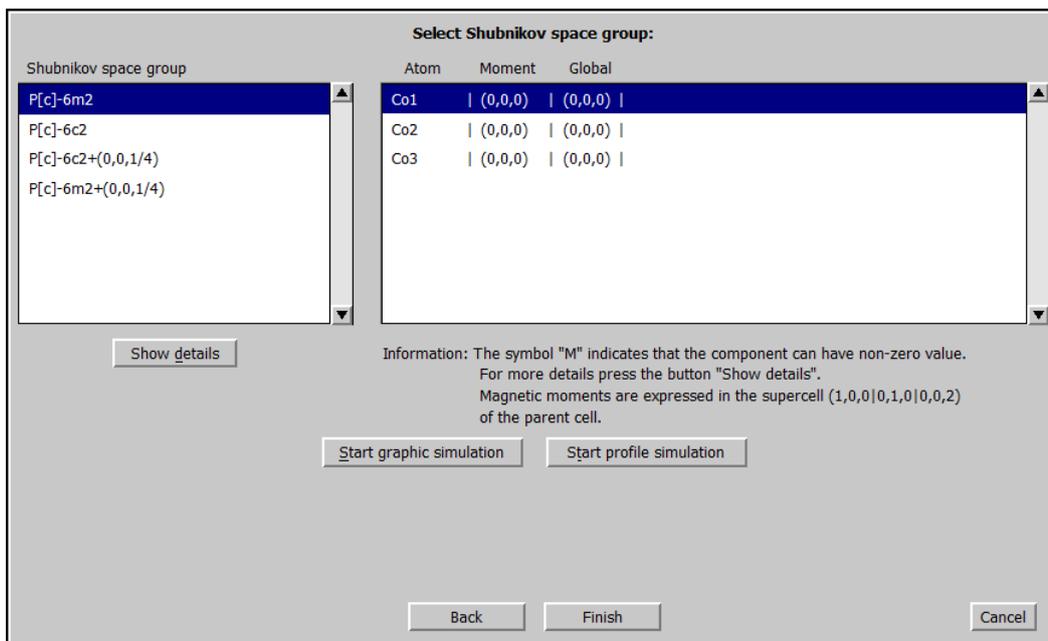
*Only the second and the third Shubnikov group allows for non-zero magnetic moments for Co atoms.*

Select the second Shubnikov group: *P[c]-6c2*
Press "Start profile simulation";
Press "X exactly" and focus the region 18-40 degrees; Press "Fit Y":
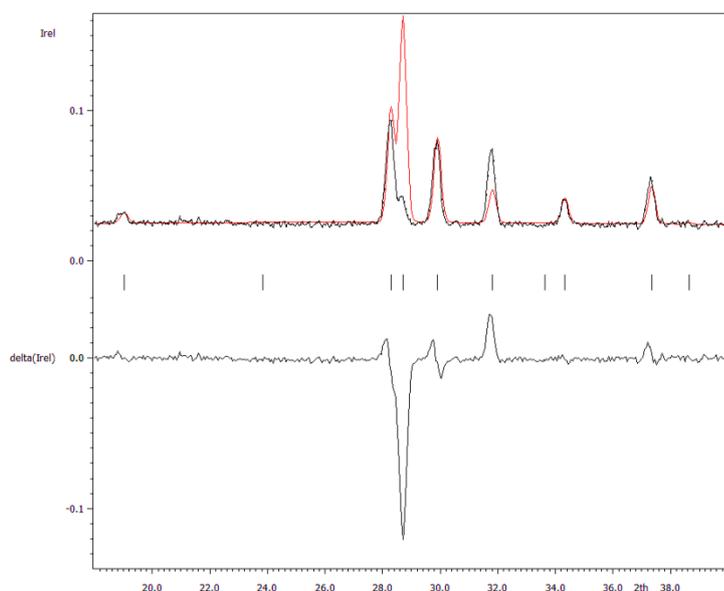


Press "Quit" and repeat this procedure for the next magnetic Shubnikov group *P[c]-6c2 with origin shifted by (1/4,0,0), which is listed in the third line*:
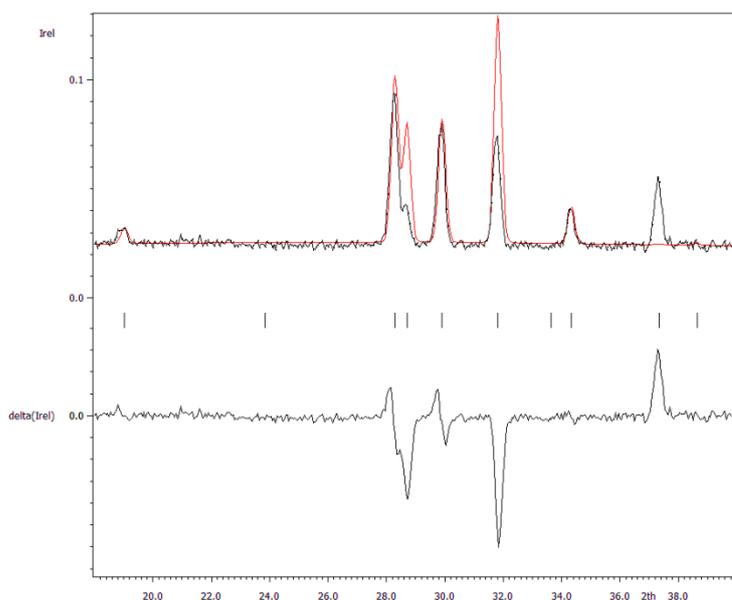
*At this stage none of them can be excluded.*

8. **Refinement of the magnetic structure – P[c]-6c2**
*[On the screen: Select Shubnikov space group]*
Select the Shubnikov space grou*p P[c]-6c2* from the second line of the list
FINISH; YES to the question "Do you want to continue with the last kernel/epikernel?";
*[On the screen: Select structure name]*
Use the default name; OK
*[On the screen: Basic window of Jana2006]*
Right-click the icon of Refine and select the page "Various"
Use the button "Restrictions" and ensure that all atoms (i.e. *) have been restricted to have identical ADP parameters.
*The restriction "restric * 12" has been set automatically when the program created the testing structure. To see the meaning of the restriction focus it by mouse and press "Load". "Load" opens the restriction for editing. Make sure that "Coordinates" and "Modulations" boxes are cleared and press "Rewrite" to close the editing mode.*
OK
Select the page "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz *").
OK
Select the page "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1; OK; Start refinement
*Refinement converges with Rp~8.8%, R(obs)~ 6.5%, 6.5%, 6.5% for all, nuclear and magnetic reflections, respectively.*


9. **Drawing the resulting magnetic structure**
*[On the screen: Basic window]*
Double click on the icon "Plot structure"
Select "Use Vesta to draw the magnetic structure"
Press "Draw+return" or "Draw+continue"
Select "Objects→Structural models" and choose "Polyhedral"

Select "Edit→Bonds"; New; Define A1 as Co, A2 as O and Max.length 2.3; Apply;OK;
Select "Objecs→Properties→Polyhedra";
Choose new polyhedral style and reduce the opacity to 50:
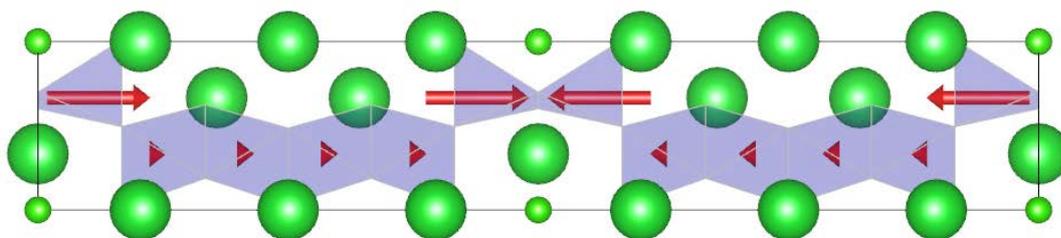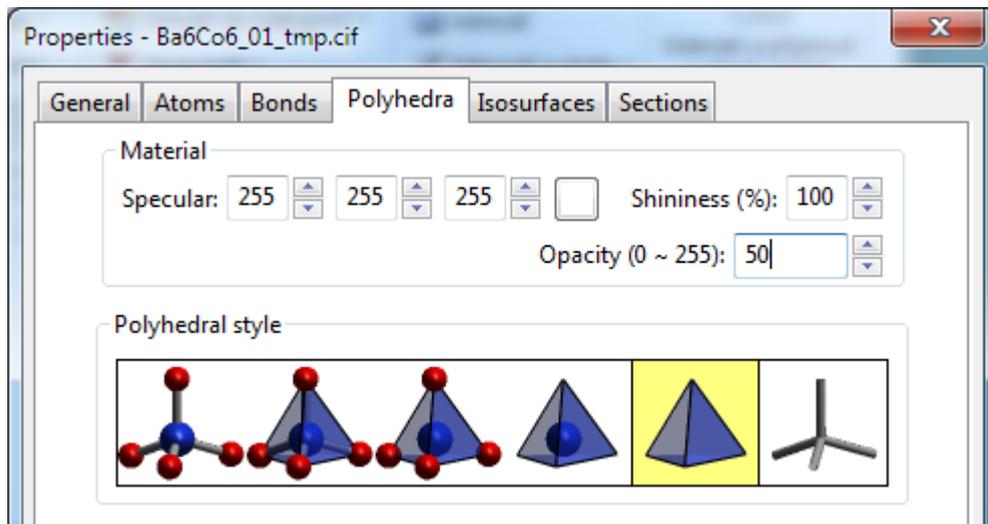




## 10. Refinement of the magnetic structure – P[c]-6c2 origin shifted by (0,0,1/4)

[On the screen: Basic window]

"File → Structure → History" and select the parent structure Ba6Co6; OK;

[On screen: Basic window]

"Tools → Special tools → Representation analysis for magnetic structures";

[On the screen: Representation analysis]

NEXT; Select one of hexagonal magnetic groups; NEXT; Select the third Shubnikov space group; FINISH

YES to the question "Do you want to continue with the last kernel/epikernel?";

[On the screen: Select structure name]

Use the default name; OK

[On the screen: The following transformation can bring the structure to the standard setting]

NO to refuse the suggested origin shift

[On the screen: Basic window]

Right-click the icon of Refine and select the page "Various".

Similarly like in the previous test ensure (under "Restrictions") that all atoms are restricted to have identical ADP and ensure (under "Fixed commands") that coordinates of all atoms

are fixed.
Select the page "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1; OK; Start refinement;
*Refinement converges with Rp~8.9%, R(obs)~ 6.6%, 6.5%, 7.7% for all, nuclear and magnetic reflections, respectively.*

## 11. Comparing of two different results
*[On screen: Basic window]*
Double click on the icon "Plot structure";
Select "Use Vesta to draw the magnetic structure"; OK
Press "Draw+return" or "Draw+continue"
In VESTA select "Objects→Structural models" and choose "Polyhedral"
Select "Edit→Bonds"; New; Define A1 as Co, A2 as O and Max.length 2.3; Apply;OK;
Select "Objecs→Properties→Polyhedra";
Choose new polyhedral style and reduce the opacity to 50;
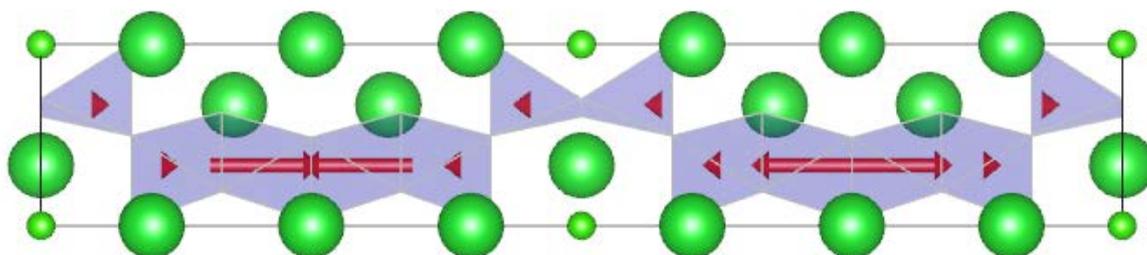


*The models are very different. In the first model the only significant magnetic moment was localized at the tetrahedrally coordinated Co atom while in the second one the significantly non-zero magnetic moment was localized at the octahedrally coordinated site.*

*The first structure model has better R values. Moreover, the presence of magnetic moments at the tetrahedral site corresponds to the result in Example 12.1*

# Example 12.3: PrSrMnO

**Commensurate magnetic structure – modulation (propagation) vector (1,0,0)**

**Revised: 28 November 2014**

Powder data measured the ILL neutron source at 10 K

For more details: K. Knížek, J. Hejtmánek, and Z. Jirák, C. Martin, M. Hervieu, and B. Raveau, G. André and F. Bourée, Chemistry of Materials, (2004), 1104-1110.

Input files:   PrSrMnO.dat (powder profile data)
   PrSrMnO_nuclear.cif (nuclear structure)

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click PrSrMnO

2. *Import Wizard*
   Select "Magnetic: nuclear model from CIF"; NEXT
   [On the screen: Select input CIF file]
   Right pane: select the input file PrSrMnO_basic.cif; OK

3. *Define magnetic propagation vector and form factors*
   *[On the screen: Define magnetic propagation vector and form factors]*
   Check "Use non-zero magnetic propagation vector" and fill its value: 1 0 0
   For "Atom type" select "Mn"; check "Use as a magnetic atom"
   For "Magnetic formfactor <j0>" select Mn3+; NEXT; FINISH
   *The parent structure is created*

4. *Import the reflection file*
   *[On the screen: Specify type of the file to be imported]*
   Select "Various CW format"; NEXT
   Check that the name of the input file is "PrSrMnO.dat" and the format is "ILL D1A/D2B (Rietveld-Hewat format)"; NEXT
   *[On the screen: Complete/correct experimental parameters];*
   For "Wave length" type 1.227; NEXT; FINISH
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

5. *Refining of profile parameters by le Bail technique.*
   *[On the screen: Information]*
   NEXT;
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *The background is relatively smooth and it can be described without introducing manual background.*

"Quit";

"Edit profile parameters";

*[On the screen: Powder options]*

In page "Cell" activate refinement of a, b and c parameters;

In the page "Profile" change the starting value of GW to 50 and activate its refinement;

In the page "Corrections" activate refinement of "shift" parameter and change the number of used Legendre polynomials to 10

OK; YES to rewrite the changes

"Edit refinement command"; In the page "Basic" change the number of cycles to 20

OK; "Run Refine";

*The refinement should end with Rp~7.8%.*

"Edit profile parameters";

*[On the screen: Powder options]*

In the page "Profile" activate refinement of GU and GV; Change the peak-shape function to pseudo-Voigt and activate refinement of LY; OK; YES to the question about rewriting;

"Run Refine"

*The refinement should converge to Rp~5.9%.*

"Show powder profile"; Select the region 2θ from 7 to 22 degs – use the button "X exactly".
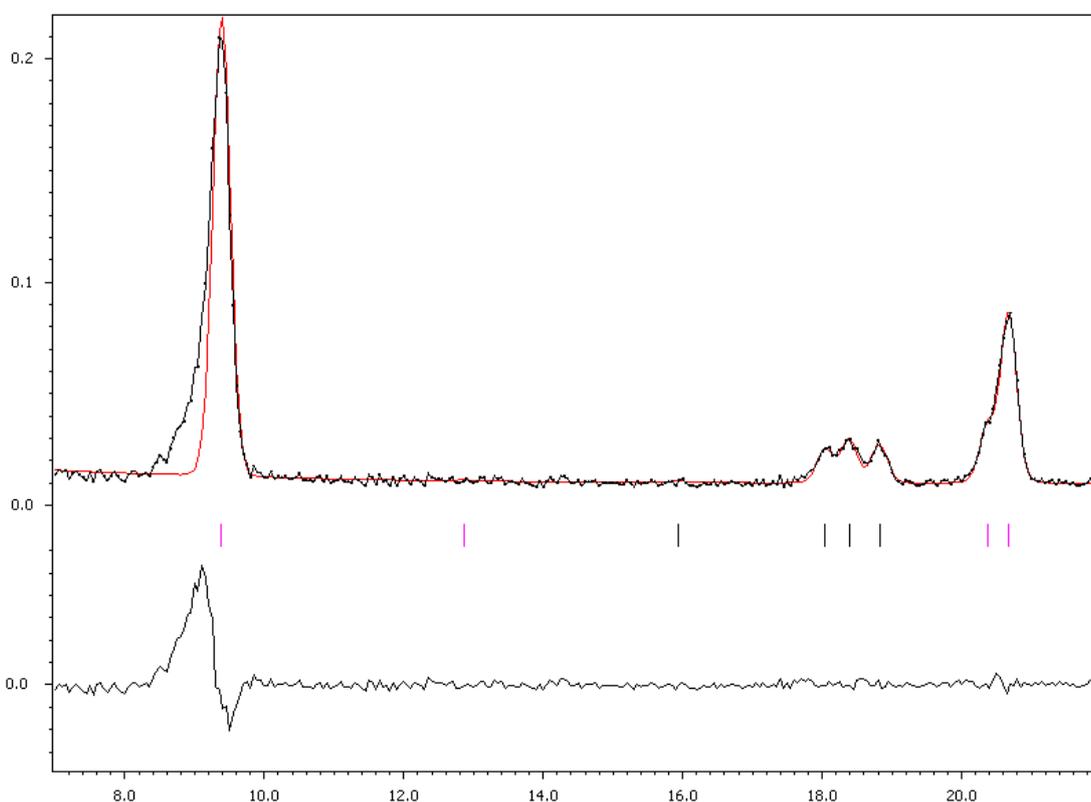


*The first peak has a strong asymmetry. For neutron and synchrotron cases, such asymmetry can be described by the correction for divergence as introduced by Finger-Cox-Jephcoat, J. Appl. Cryst. (1994).* **27, 892-900.**

"Quit"

"Edit profile parameters"

*[On the screen: Powder options]*

In the page "Asymmetry" select "correction by divergence"

*Activate refinement of HpS/L and HmS /L keeping their default values*
OK; YES to save changes
"Run Refine";
*The refinement should end with Rp~4.7%.*
"Show powder profile"; Select the region 2θ from about 7 to 22 degs.
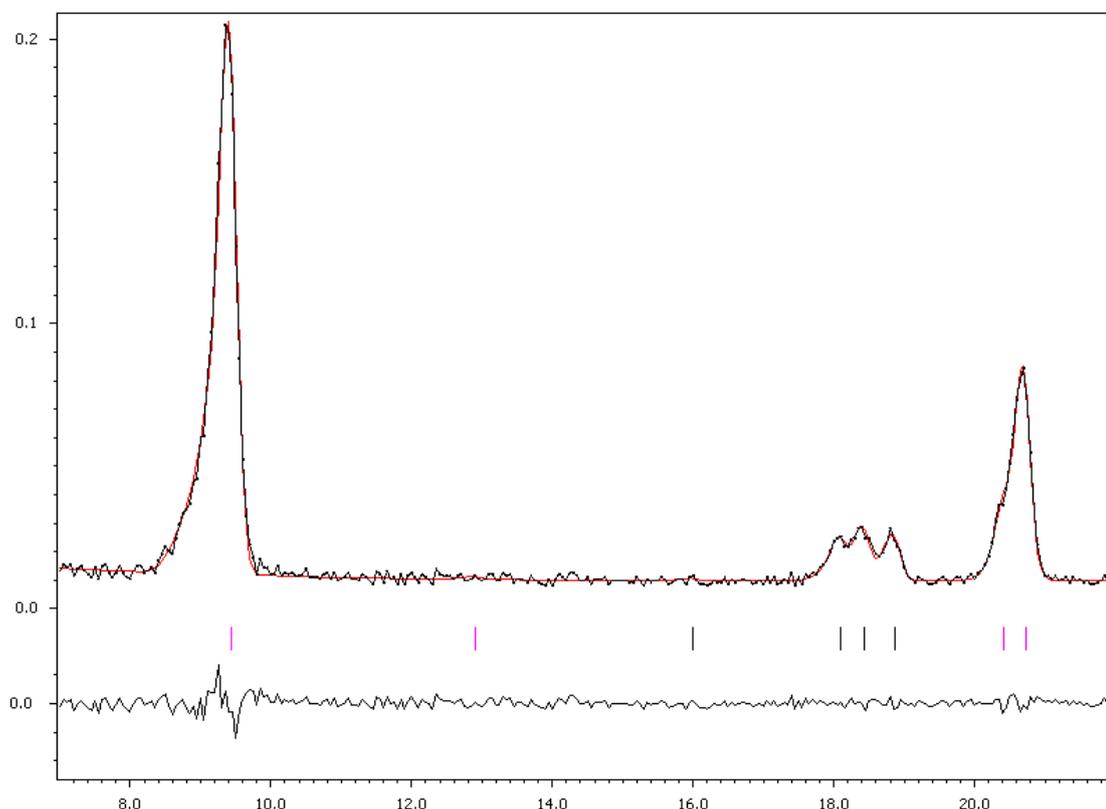


*The correction considerably improved the profile*
"Quit"; NEXT; YES to leave the form for le Bail refinement

6. ***Refinement of the scale parameter for the nuclear structure***
*[On the screen: Refinement of the nuclear structure by the Rietveld method]*
"Edit refinement commands"; On the page "Various" select "Fixed commands";
Fix all parameters for all atoms ("*" for "Atoms/Parameters" textbox ); "Add"; OK; OK;
*The command will appear in the panel as "fixed all *"*
"Run Refine"
*The refinement should converge to Rp~11.6%, R(obs)~3.6%.*
NEXT; YES to leave the form for Rietvel refinement

***Testing different irreps to get the best single irrep model***
*[On the screen: Information]*
NEXT
*[On the screen: Representation analysis]*
*This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.*

## Representation analysis:

| Representation | Dimension | Shubnikov space group | Axes | Origin shift | |
|---|---|---|---|---|---|
| Tau1 | 1 | C[B]mmm | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Details |
| Tau2 | 1 | C[B]cce | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Details |
| Tau3 | 1 | C[B]mce | (0,0,1\|0,1,0\|-1,0,0) | (0,0,0) | Details |
| Tau4 | 1 | C[B]mcm | (0,1,0\|0,0,1\|1,0,0) | (0,1/4,1/4) | Details |
| Tau5 | 1 | C[B]mce | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Details |
| Tau6 | 1 | C[B]mcm | (0,0,1\|0,1,0\|-1,0,0) | (0,1/4,1/4) | Details |
| Tau7 | 1 | C[B]ccm | (0,1,0\|0,0,1\|1,0,0) | (1/4,1/4,0) | Details |
| Tau8 | 1 | C[B]mme | (0,1,0\|0,0,1\|1,0,0) | (0,1/4,1/4) | Details |

Display representations

Back    Next    Cancel

NEXT

*[On the screen: List of kernels and epikernels]*

## List of kernels and epikernels:

| Shubnikov space group | Axes | Origin shift | Representation |
|---|---|---|---|
| C[B]mmm | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Tau1 |
| C[B]cce | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Tau2 |
| C[B]mce | (0,0,1\|0,1,0\|-1,0,0) | (0,0,0) | Tau3 |
| C[B]mcm | (0,1,0\|0,0,1\|1,0,0) | (0,1/4,1/4) | Tau4 |
| C[B]mce | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Tau5 |
| C[B]mcm | (0,0,1\|0,1,0\|-1,0,0) | (0,1/4,1/4) | Tau6 |
| C[B]ccm | (0,1,0\|0,0,1\|1,0,0) | (1/4,1/4,0) | Tau7 |
| C[B]mme | (0,1,0\|0,0,1\|1,0,0) | (0,1/4,1/4) | Tau8 |

Show details

**Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.**

Back    Next    Cancel

NEXT

*[On the screen: Select Shubnikov space group]*
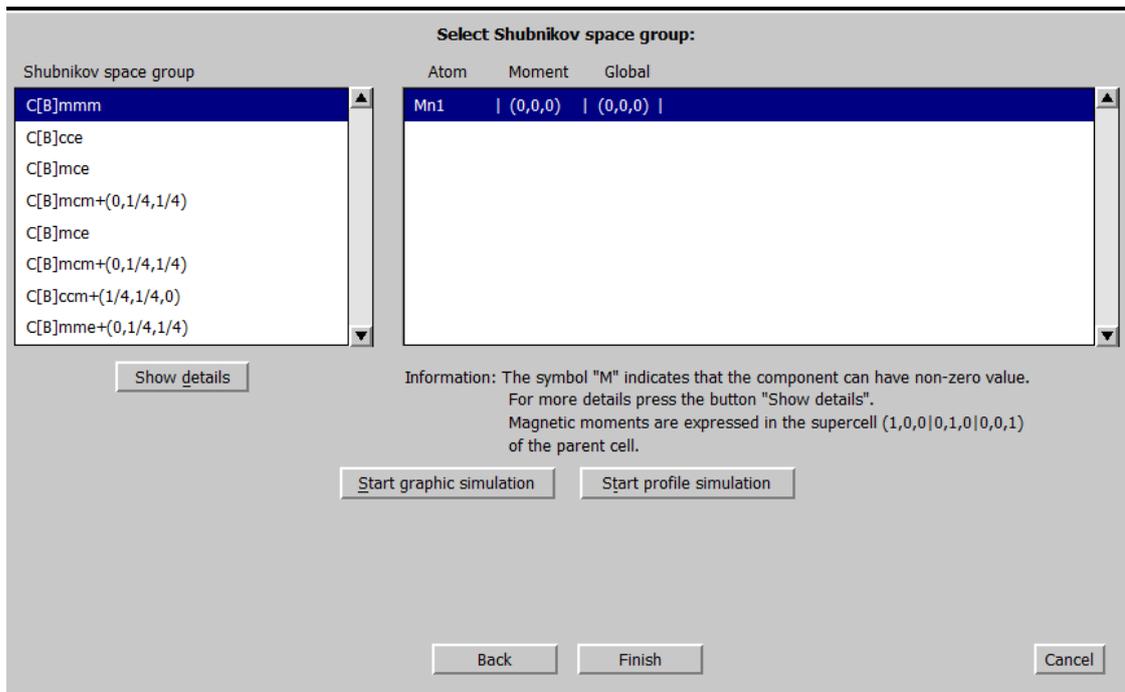
This form shows that only for Shubnikov space group **№ 2, № 4, № 6 and № 8** allows non-zero magnetic moment for the Mn1 atom.In the following we shall test all four possibilities. *Pr1 Sr1*

7. **Refinement in the Shubnikov space group C[B]cce  (№ 2 in the list)**
   [On the screen: Select Shubnikov space group]
   Select the second line in the left panel; FINISH
   YES to the question "Do you want to continue with the last kernel/epikernel";
   [On screen: Select structure name]
   Use the default name i.e. PrSrMnO_01; OK
   After selection of the actual Shubnikov group you can use either the cell and origin selection as follows from the setting of the parent structure or you can apply transformation to get a standard setting.
   **NO** to the question "Do you want to apply this transformation?".
   Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;
   Select the page "Various" and use the button "Restrictions"
   Check that all atoms are restricted to have identical ADP parameters and not restricted occupancies;
   Restrict atoms Pr1 and Sr1, occupying the same position in the nuclear structure: identical Coordinates ADP parameters and "keep overall sum" for occupancies; Add;
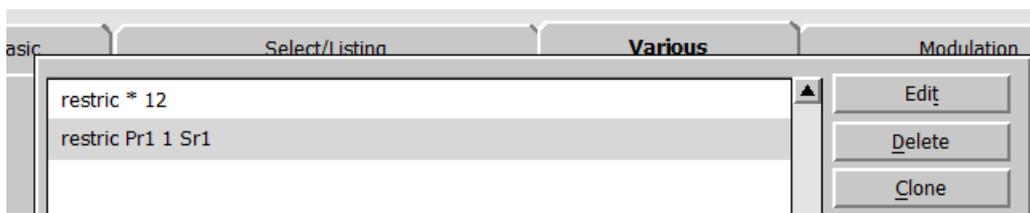


OK; "Yes+start";

*Refinement converges with Rp~10.1%, R(obs)~3.7%.*
*This refinement is very unstable.*

Double click on the icon "Plot structure" and select Vesta to draw the structure:
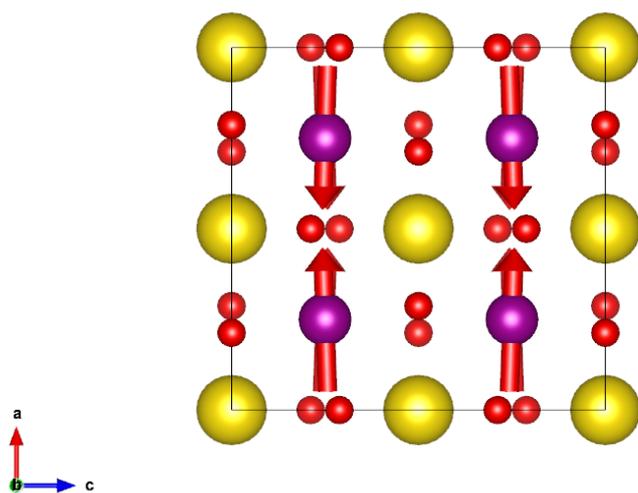


Use "Tools → Powder → Profile viewer" and check fit of the calculated powder profile:
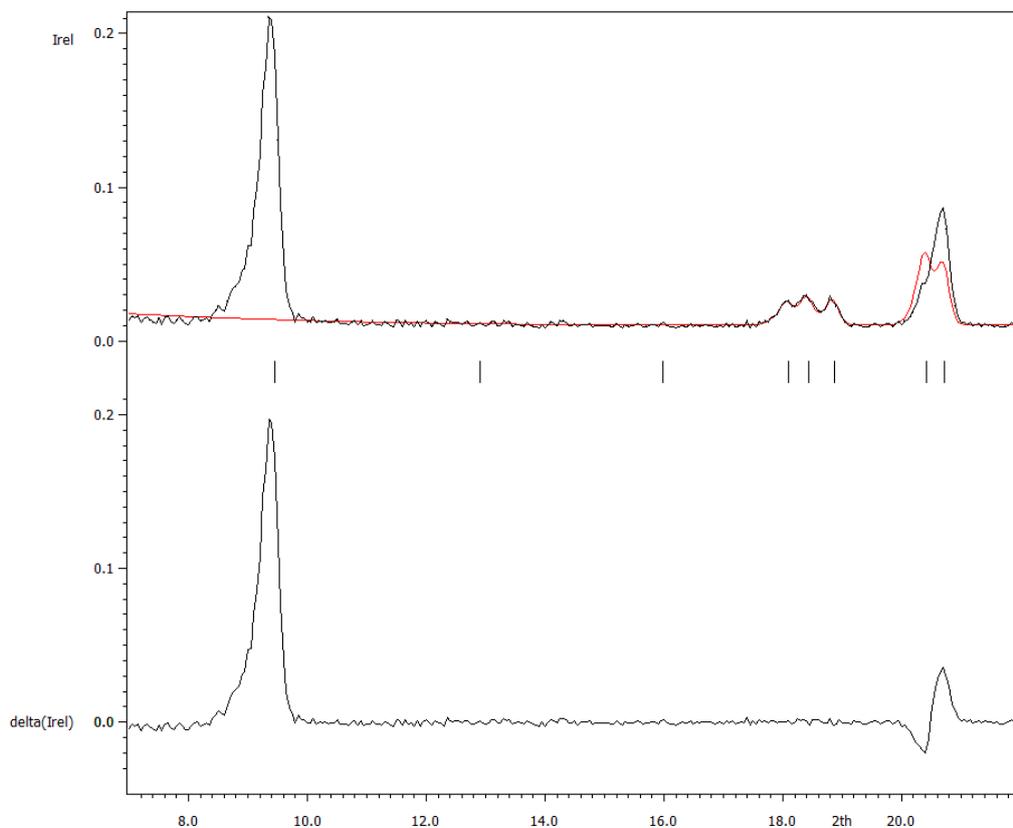


The model cannot explain the peak at (1,0,0)
"Quit"

**8. Refinement in the Shubnikov superspace group C[B]mcm with the origin shift (0,1/4,1/4) (№ 4 in the list)**

*[On screen: Basic window]*

"File → Structure → History" and select the parent structure PrSrMnO; OK;

*[On screen: Basic window]*

"Tools → Special tools → Representation analysis for magnetic structures";

*[On screen: Representation analysis]*

NEXT; NEXT; Select the fourth Shubnikov superspace group "*C[B]mcm+(0,1/4,1/4)*"; FINISH

YES to the question "Do you want to continue with the last kernel/epikernel?";

*[On screen: Select structure name]*

Use the default name i.e. PrSrMnO_02; OK

No to the question "Do you want to apply this transformation".

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various" and use the button "Restrictions"

Check that all atoms are restricted to have identical ADP parameters and not restricted occupancies;

Restrict atoms Pr1 and Sr1, occupying the same position in the nuclear structure: identical Coordinates ADP parameters and "keep overall sum" for occupancies; Add;

OK; OK; "Yes+start";

*Refinement converges with Rp~6.0%, R(obs)~3.2%.*

Double click on the icon "Plot structure" and select Vesta to draw the structure::
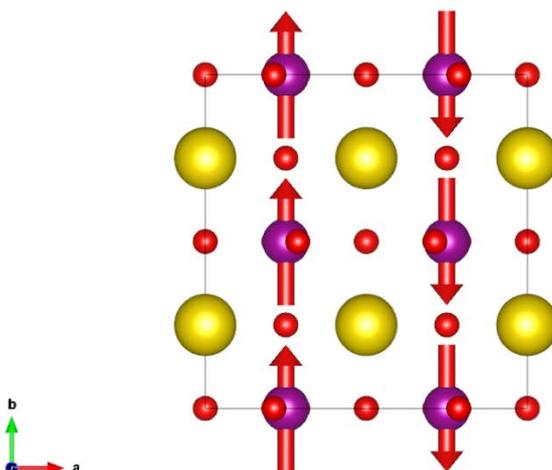


Use "Tools → Powder → Profile" viewer and check fit of the calculated powder profile:
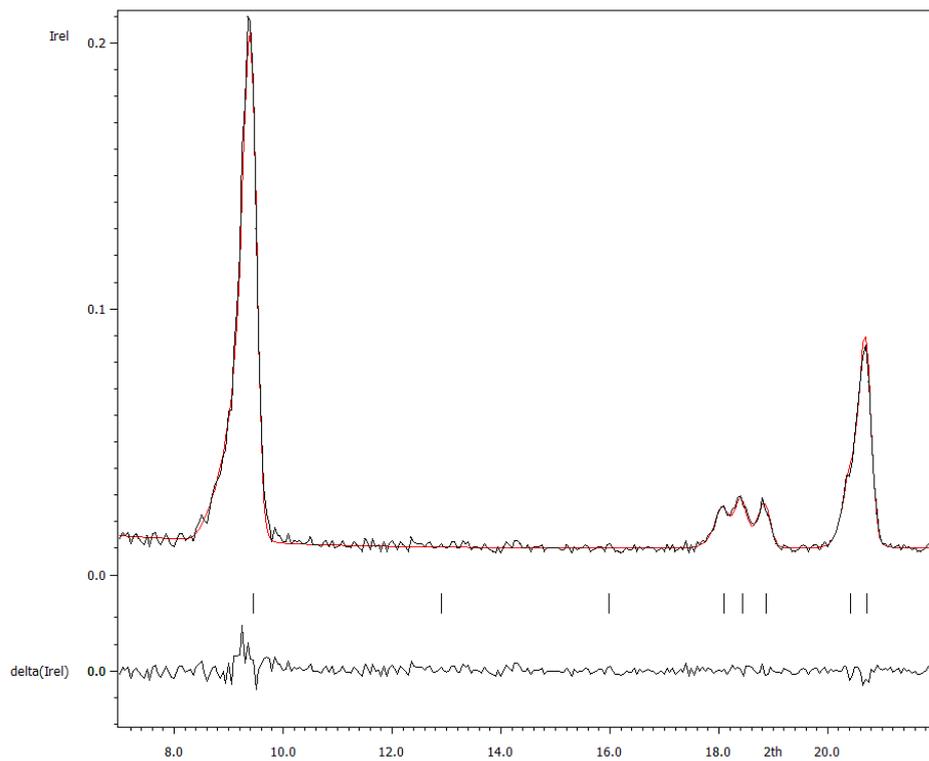
The profile fit is very good.

9. **Refinement in the Shubnikov superspace group C[B]mcm with the origin shift (0,1/4,1/4) (№ 6 in the list)**
*The symbol in the table is the same as for the № 4 but both epikernels are generally different. Compare details for both. The first one has in the original setting the symbol A[C]mma and the second one A[C]mam. Both give the same symbol when transformed to the standard setting.*
Make the same steps and calculation as in the previous test.

*Rp~8.1%, R(obs)~ 3.9%.*
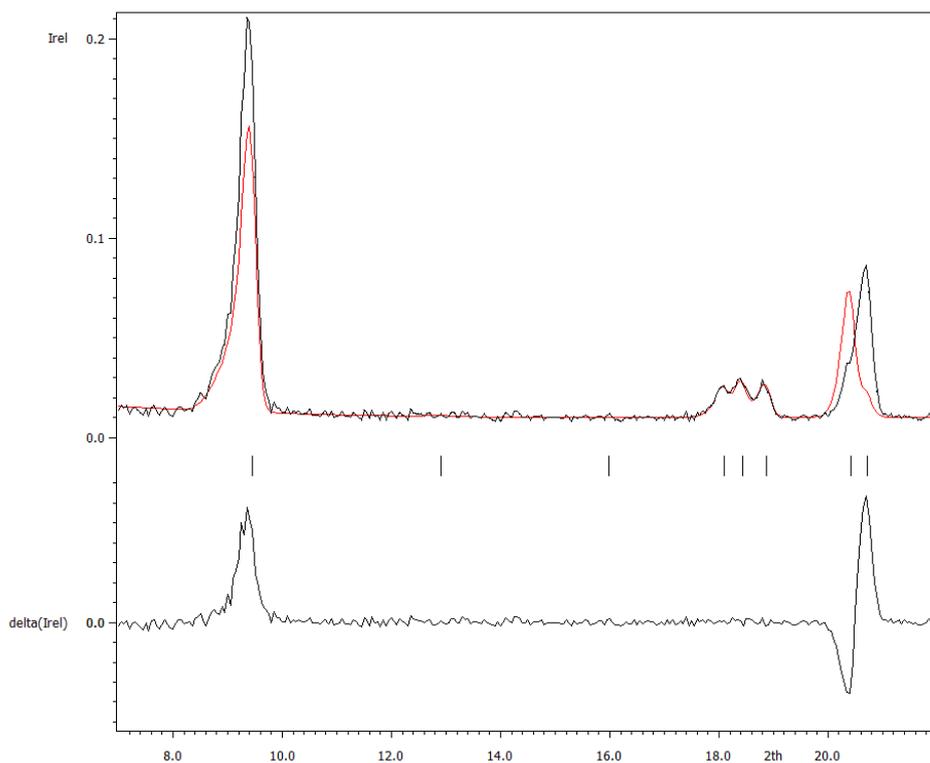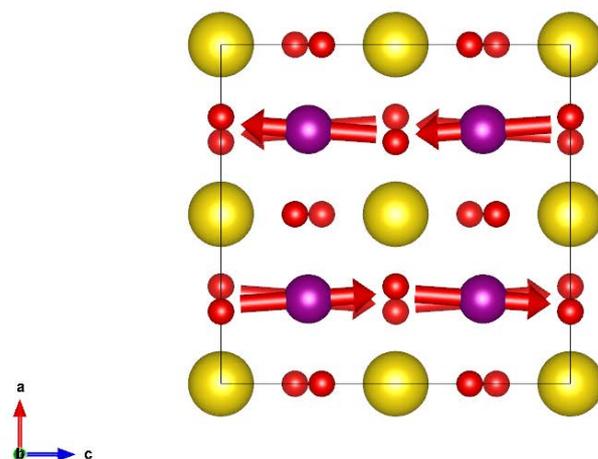
**10. Refinement in the Shubnikov superspace group C[B]mme+(0,1/4,1/4) (№ 8 in the list)**
Make the same calculation for the last Shubnikov superspace group with sin wave (Line eight in "Select Shubnikov space group" dialogue).

*Rp~11.5%, R(obs)~ 3.1%.*

*This refinement is very unstable.*
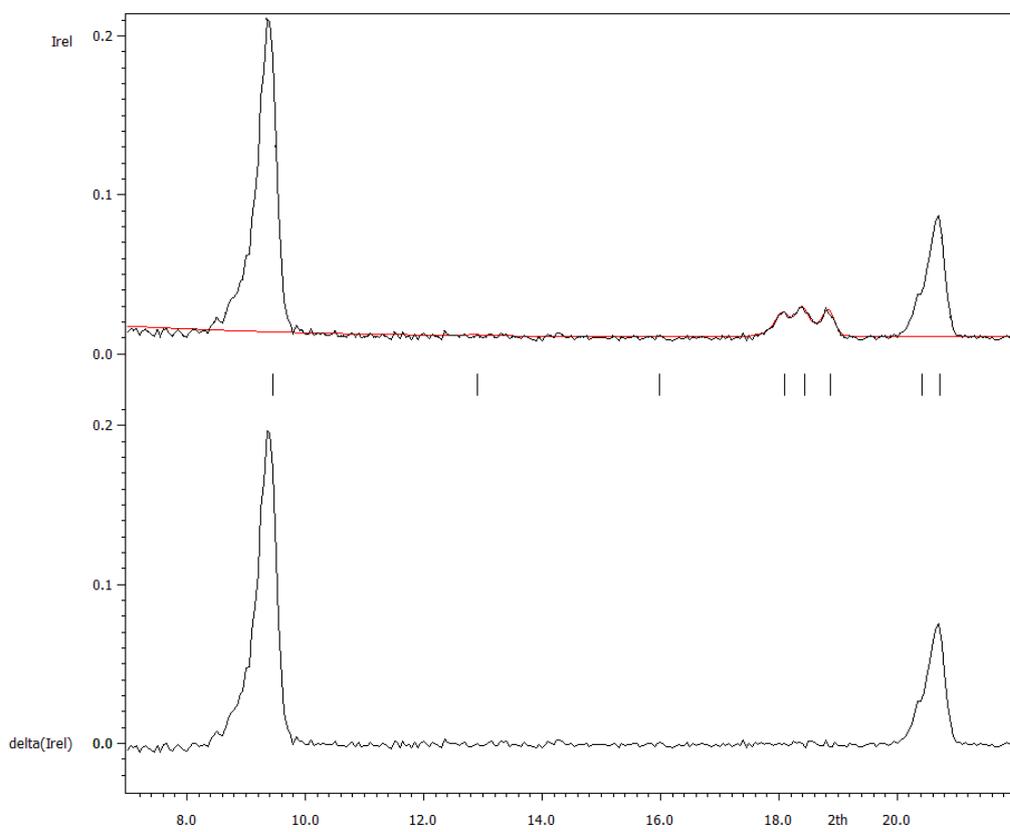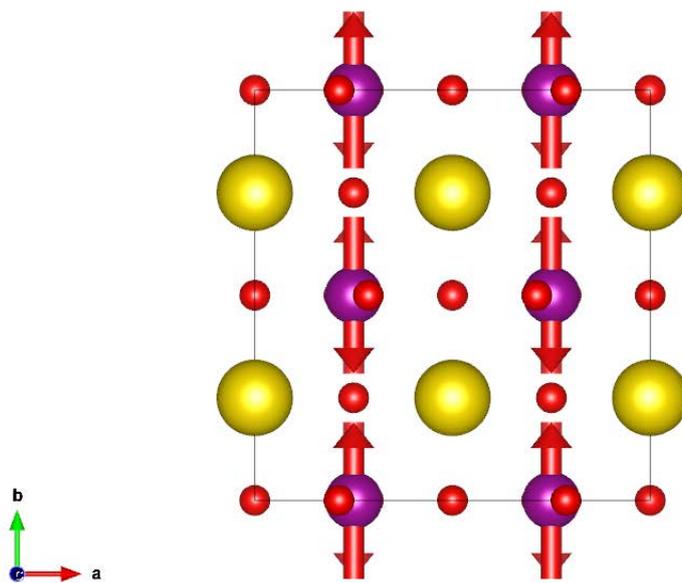
# Example 12.4: MnWO₄

**Incommensurate magnetic structure**

**Revised: 28 November 2014**

Powder data measured the ILL neutron source at 10 K

For more details: L. Meddar, M. Josse, P. Deniard, C. La, G. Andre, F. Damay, V. Petříček, S. Jobic, M.H. Whangbo, M. Maglione & C. Payen: *Effect of Nonmagnetic Substituents Mg and Zn on the Phase Competitionin the Multiferroic Antiferromagnet MnWO₄*
Chemistry of Materials, **21**, (2009), 5203-5214.

Input files:  MnWO4.dat (powder profile data)
  MnWO4_nuclear.cif (nuclear structure)

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click MnWO4

2. ***Import Wizard***
   Select "Magnetic: nuclear model from CIF", NEXT
   Right pane: select the input file MnWO4_nuclear.cif

3. ***Define magnetic propagation vector and form factors***
   *[On the screen: Define magnetic propagation vector and form factors]*
   Check "Use non-zero magnetic propagation vector" and fill its value: -0.209 0.5 0.453
   Select atom type Mn; check "Use as a magnetic atom"; select "Magnetic form factor <j0>"
   Mn2+; NEXT; FINISH
   *The parent structure is created*

4. ***Import the reflection file***
   *[On the screen: Specify type of the file to be imported]*
   Select "Various CW format"; NEXT;
   Check that the name of the input file is "MnWO4.dat" and the data format is "Free format of 2th, I, [sig(I)]"; NEXT
   *[On the screen: Complete/correct experimental parameters]*;
   Fill used wavelength 2.4226; NEXT; FINISH
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

5. ***Refining of profile parameters by the le Bail technique.***
   *[On the screen: Information]*
   NEXT
   *[On the screen: Refinement of the powder profile by the le Bail algorithm]*
   "Show powder profile"
   *The background is relatively smooth and it can be described without introducing manual*

*background.*

"Quit"; "Edit profile parameters";

*[On the screen: Powder options]*

In page "Cell" activate refinement of a, b, c parameters and beta angle;

Activate refinement of component q1 and q3 of the modulation vector. The q2 component is fixed for planar monoclinic superspace groups to 0.5;

Check that the maximal satellite index is set to 1;

In the page "Profile" change the starting value of GW to 50 and activate its refinement;

In the page "Corrections" activate refinement of "shift" parameter and enlarge the number of used Legendre polynomials to 20

OK; YES to save the changes

"Edit refinement commands"; In the page "Basic" change the number of cycles to 100 and the damping factor to 0.5; OK

"Run Refine";

*The refinement should converge to Rp~5.2%.*

"Edit profile parameters";

*[On the screen: Powder options]*

In the page "Profile" change activate refinement of GU and GV

Change the peak-shape function to pseudo-Voigt and activate refinement LY

OK; YES to save the changes

"Run Refine"

*The refinement should converge to Rp~3.4%.*

NEXT; YES to leave the form for le Bail refinement

6. ***Refinement of the scale parameter for the nuclear structure***

*[On the screen: Refinement of the nuclear structure by the Rietveld method]*

"Edit refinement commands"; On the page "Various" select "Fixed commands";

Fix all parameters for all atoms (wild character *); "Add"; OK; OK

"Run Refine"

*The refinement should converge to Rp=12.8%, R(obs)=5.5%.*

NEXT; YES to leave the form for Rietveld refinement

7. **Testing different irreps to get the best single irrep model**

*[On the screen: Information]*

NEXT

*[On the screen: Representation analysis]*

*This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.*

| | | Representation analysis: | | | |
|---|---|---|---|---|---|
| Representation | Dimension | Shubnikov superspace group | Axes | Origin shift | |
| mG1 | 2 | P2/c.1'(a1/2g)00s | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) | Details |
| mG2 | 2 | P2/c.1'(a1/2g)0ss | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) | Details |

NEXT

*[On the screen: List of kernels and epikernels]*

NEXT

*[On the screen: Select Shubnikov superspace group]*

**Select Shubnikov superspace group:**

| Shubnikov superspace group |
|---|
| P2/c.1'(a1/2g)00s |
| P2/c.1'(a1/2g)0ss |

| Atom | Moment | Global | sin#1 | cos#1 |
|---|---|---|---|---|
| Mn1 | (0,0,0) | (0,0,0) | (M,M,M) | (M,M,M) |

Show details

Information: The symbol "M" indicates that the component can have non-zero value.
For more details press the button "Show details".
Magnetic moments are expressed in the parent cell.

Start graphic simulation          Start profile simulation

Back          Finish          Cancel

Notice that for both SSG's there are non-zero amplitudes for sine and cosine waves. However only three amplitudes are independent as can be found from "Details":

```
****************************************************************
* List of relationships between magnetic moments of individual atoms *
****************************************************************

Atom: Mn1
=========
mx0=0                    mxsin1 ... free        mxcos1=1.6787*mxsin1
my0=0                    mysin1 ... free        mycos1=-0.59571*mysin1
mz0=0                    mzsin1 ... free        mzcos1=1.6787*mzsin1
```

The cosine amplitudes have generally non-zero values but they are related with the sine amplitudes. However the coefficients are functions of y coordinate of the Mn1 atom, which means that these restrictions are non-linear. Later we shall see how these restrictions can be simplified.

In this case, both possibilities yield similar diffraction patterns and we cannot decide at this stage which solution makes a better fit.

Note: The presence of a rational non-zero modulation vector component $q_y$ = 0.5 leads to a specific problem of the origin selection. While for the space group $P2/c$ the c glide planes

*located at y=0 and y=1/2 are equivalent, in the SSG $P2/c.1'(\alpha 1/2\gamma)00s$ they are not. In this SSG the first glide plane is connected with zero shift along the internal space while the second one with 1/2 shift. This means that the origin selection used for the starting structure model solved and refined from the main reflections, must be reconsidered for solution of modulated structure. Here two models shifted by 1/2 in y must be tested. Another possibility is to use non-standard SSG symbol $P2/c.1'(\alpha 1/2\gamma)0ss$, which would generate reverse order of c glide planes. The second method is used in this example.*

8. **Refinement in the first Shubnikov superspace group – P2/c.1'(a1/2g)00s**
   *[On the screen: Select Shubnikov space group]*
   Select the first line in the left panel; FINISH
   YES to the question "Do you want to continue with the last kernel/epikernel";
   *[On screen: Select structure name]*
   Use the default name i.e. MnWO4_01; OK
   Right click on the icon "Refine"; Select the page "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;
   Select the page "Various". Use the button "Restrictions". All atoms are restricted to have identical ADP parameters;
   Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical Coordinates + Modulations + ADP parameters and "keep overall sum" for occupancies
   Use button "Fixed commands" and fix all coordinates and delete or disable fixing of ADP's (if present).
   OK; OK; "Yes+start";
   *The refinement should end with Rp~4.9% and Bragg R factors R(obs)=5.3%, 2.9% and 9.1% for all, main and satellite reflections, respectively.*
   Use "Tools → Powder → Profile" viewer and check fit of the calculated powder profile and focus to the interval (38.5,47):
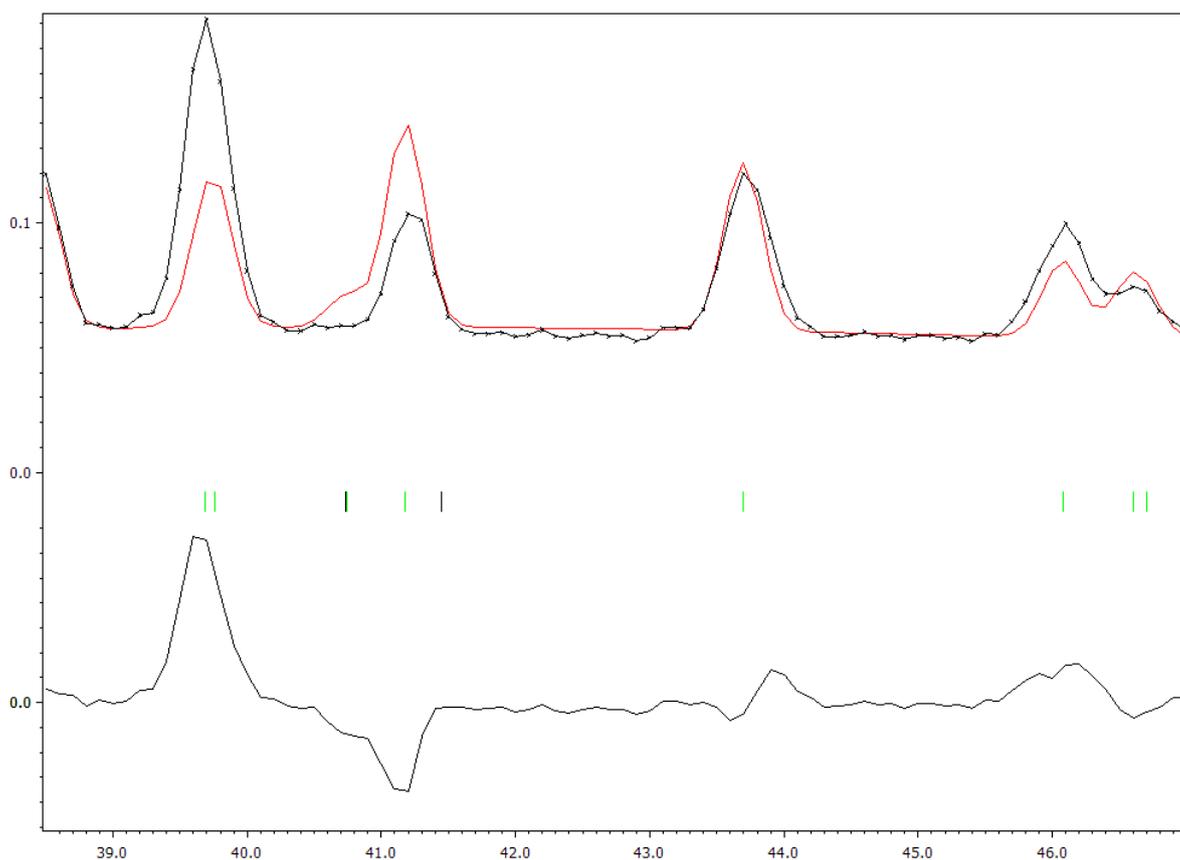
*Quit*

9. ***Refinement in the second Shubnikov superspace group – P2/c.1'(a1/2g)0ss***

*[On the screen: Basic window]*

"File → Structure → History" and select the parent structure MnWO4; OK;

*[On screen: Basic window]*

*"Tools → Special tools → Representation analysis for magnetic structures";*

*Continue with representation analysis; OK;*

*[On the screen: Representation analysis]*

*NEXT; NEXT; Select P2/c.1'(a1/2g)0ss; FINISH;*

*YES to the question "Do you want to continue with the last kernel/epikernel?";*

*[On the screen: Select structure name]*

*Use the default name; OK*

*[On the screen: Basic window]*

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various". Use the button "Restrictions". All atoms are restricted to have identical ADP parameters;

Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical Coordinates + Modulations + ADP parameters and "keep overall sum" for occupancies

Use button "Fixed commands" and fix all coordinates and delete or disable fixing of ADP's (if present).

OK; OK; "Yes+start";

*The refinement should end with Rp~4.3% and Bragg R factors R(obs)=3.8%, 2.3% and 5.5%*

*for all, main and satellite reflections, respectively.*

Use "Tools → Powder → Profile" viewer and check fit of the calculated powder and focus to the interval (38.5,47):
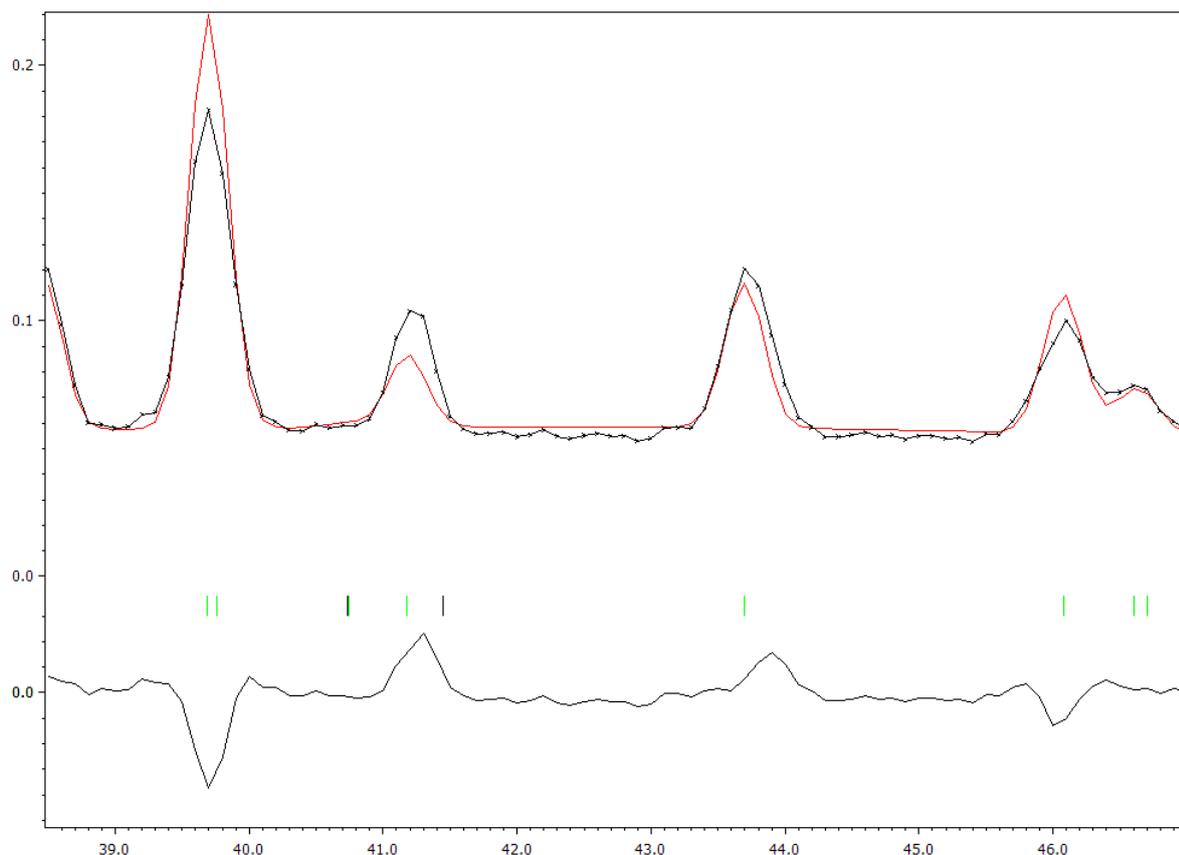


*The second solution gives significantly better profile fit and also better Bragg R values.*
*Quit*

## 10. Transforming the final solution to the supercentered cell.
*[On the screen: Basic window]*
"Tools→Transformation→Transform to the X-centered cell";
Create new structure e.g. "MnWO4_02_X";
YES to the question "Do you want to continue with the new structure?";

## 11. Refinement in the supercentered setting
*[On the screen: Basic window]*
Run EditM50, go to "Symmetry"; Check the new SSG symbol; "X" stands for the supercentered setting. For more details about centering vectors expand the list of centering symbols at "cell centering" and re-select the symbol X
*The generated supercell centering (0,1/2,0,1/2) is in accordance with the values from "findSSG" (except that the monoclinic axis is now "b")*
ESC; ESC;
Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;
Select the page "Various"; Use the button "Restrictions" and restrict all atoms to have identical ADP parameters and not restricted occupancies; Add;
Restrict atoms Zn1 and Mn1, occupying the same position in the nuclear structure: identical

Coordinates + Modulation + ADP parameters and "keep overall sum" for occupancies;
Add; OK
Use button "Fixed commands" and fix coordinates for all atoms, i.e. *.
OK; OK; "Yes+start";
*The refinement should finish with Rp~5.0% and Bragg R factors R(obs)=4.3%, 3.0% and 6.4% for all, main and satellite reflections, respectively.*
YES to the question "Open the listing"; Check the symmetry restrictions:

```
 Find    Find next   Go to    Print    PgTop    Open in editor    Close

Equations induced by symmetry :

x[Zn1]=0.5
z[Zn1]=0.25
x[Mn1]=0.5
z[Mn1]=0.25
mx0[Mn1]=0
my0[Mn1]=0
mz0[Mn1]=0
mysin1[Mn1]=0
Refinement program                                              page=
structure :                                            10:35:54 16-09

mxcos1[Mn1]=0
mzcos1[Mn1]=0
x[W1]=0
z[W1]=0.25
alpha=90
gamma=90
```

*Now the y component of the sine wave and x and z components of the cos wave are fixed to zero values. This setting makes a full separation of internal and external space (before the transformation some wave components depended on the y coordinate).*

# Example 12.5: HoNi

**Magnetic structure refined from single crystal data – k=(0,0,1)**

**Revised: 28 November 2014**

Single crystal data

For more details: not yet published

Input files:     HoNi.hkl (powder profile data)
               HoNi_nuclear.cif (nuclear structure)

1. ***Creating new jobname***
   Start Jana2006
   "File $\rightarrow$ Structure $\rightarrow$ New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click HoNi

2. ***Import Wizard***
   Select "Magnetic: nuclear model from CIF", NEXT
   Right pane: select the input file HoNi_nuclear.cif

3. ***Define magnetic propagation vector and form factors***
   *[On the screen: Define magnetic propagation vector and form factors]*
   Check "Use non-zero magnetic propagation vector" and fill its value: 0 0 1
   Select atom type Ho; check "Use as a magnetic atom"; select "Magnetic form factor
   <j0>+c<j2>" Ho3+; NEXT; FINISH
   *The parent structure is created*

4. ***Import the reflection file***
   *[On the screen: Specify type of the file to be imported]*
   Select "reflection file corrected for LP and absorption"; NEXT;
   Check that the name of the input file is "HoNi.hkl" and the data format is "General file on I";
   Type in the "Input format:" (3i5,2f10.2); NEXT
   *[On the screen: Complete/correct experimental parameters]*;
   Fill used wavelength 0.794 Å ; NEXT; NEXT; FINISH
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

5. **Testing different irreps to get the best single irrep model**
   *[On the screen: Information]*
   NEXT
   *[On the screen: Representation analysis]*
   *This window has an information character. You can see here all irreps leading to non-paramagnetic ordering. The "details" buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.*

**Representation analysis:**

| Representation | Dimension | Shubnikov space group | Axes | Origin shift | |
|---|---|---|---|---|---|
| Tau1 | 1 | P[I]4mm | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Details |
| Tau2 | 1 | P[I]4nc | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Details |
| Tau3 | 1 | P[I]42mc | (1,0,0\|0,1,0\|0,0,1) | (0,1/2,0) | Details |
| Tau4 | 1 | P[I]42nm | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Details |
| Tau5 | 2 | P[I]21 | (0,1,0\|0,0,1\|1,0,0) | (1/4,0,1/4) | Details |

Display representations

Back    Next    Cancel

NEXT
*[On the screen: List of kernels and epikernels]*



**List of kernels and epikernels:**

| Shubnikov space group | Axes | Origin shift | Representation |
|---|---|---|---|
| P[I]4mm | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Tau1 |
| P[I]4nc | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Tau2 |
| P[I]42mc | (1,0,0\|0,1,0\|0,0,1) | (0,1/2,0) | Tau3 |
| P[I]42nm | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Tau4 |
| C[B]mc21 | (1,1,0\|-1,1,0\|0,0,1) | (0,1/4,0) | Tau5 |
| P[I]mn21 | (0,1,0\|1,0,0\|0,0,-1) | (0,1/4,0) | Tau5 |
| P[I]21 | (0,1,0\|0,0,1\|1,0,0) | (1/4,0,1/4) | Tau5 |

Show details

**Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.**

Back    Next    Cancel

Select one of the tetragonal Shubnikov space groups; NEXT
*This will pass all present tetragonal Shubnikov space groups to further testing.*
NEXT

6.  ***Testing tetragonal Shubnikov space groups***
    *[On the screen: Select Shubnikov superspace group]*
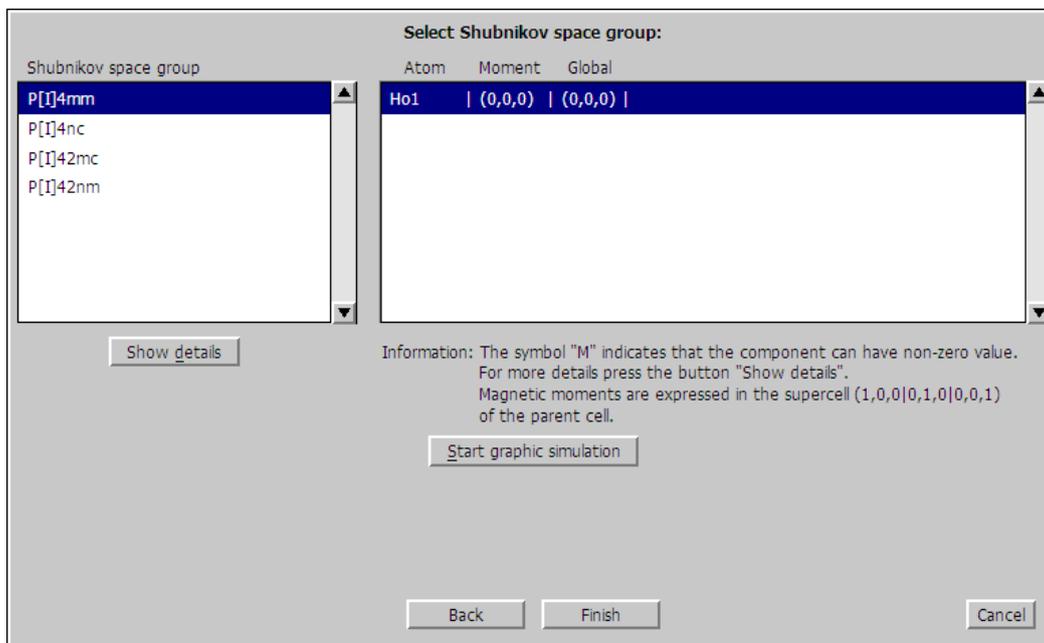
Note that only the second ShSG P[I]4nc allows for a non-zero magnetic moment.
Select it and press FINISH button;
YES to the question "Do you want to continue with the last kernel/epikernel?";
*[On the screen: Select structure name]*
Use the default name "HoNi_01"; OK

7. ***Refinement in the tetragonal Shubnikov space group – P[I]4nc***
*[On the screen: Basic window]*
Start refinement;
*Refinement converges with R(obs)~ 20.8%, 12.8%, 40.8% for all, nuclear and magnetic reflections, respectively.*
*[On the screen: Basic window]*
"Parameters → Extinction"
*[On the screen: Extinction model]*
Start "Parameters → Extinction"
Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes
Run refinement
*Refinement converges with R(obs)~ 17.4%, 8.2%, 40.8% for all, nuclear and magnetic reflections, respectively.*
Right click on the icon "Refine";
Select the page "Various" and use the button "Restrictions";
Disable the command "restrict * 12" which keeps ADP's of all atoms identical. OK;
Use the button "Fixed" and disable the command "fixed xyz *" which fixes coordinates of all atoms. OK; OK; Yes+start;
*Refinement converges with R(obs)~ 16.7%, 7.7%, 39.4% for all, nuclear and magnetic reflections, respectively.*
*[On the screen: Basic window]*
Double click on the icon "Plot structure"; Use the Vesta program to draw the structure;
Press "Draw+return" or "Draw+continue";

In Vesta enlarge the boundaries in z direction:
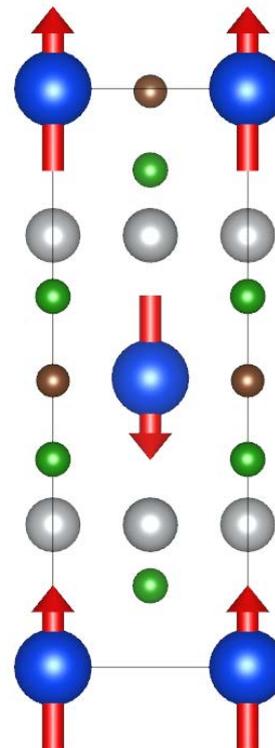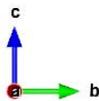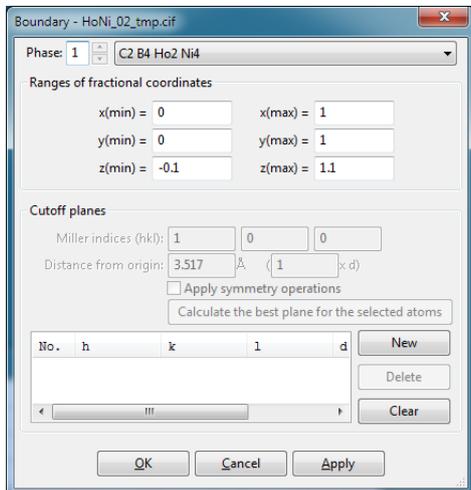


## 8. Testing orthorhombic Shubnikov space group C[B]mc21

*[On the screen: Basic window]*

"File → Structure → Opeen" and select the parent structure HoNi; OK;

*[On screen: Basic window]*

"Tools → Special tools → Representation analysis for magnetic structures";

*[On the screen: Representation analysis]*

Select one of two orthorhombic Shubnikov space groups: C[B]mc21; NEXT

*This space group also allows for a non-zero magnetic moment*

FINISH

YES to the question "Do you want to continue with the last kernel/epikernel?";

*[On the screen: Select structure name]*

Use the default name "HoNi_02"; OK

NO to the question "Do you want to apply this transformation?";

*[On the screen: Basic window]*

Start refinement;

*Refinement converges with R(obs)~ 12.8%, 12.3%, 14.3% for all, nuclear and magnetic*

*reflections, respectively.*

*[On the screen: Basic window]*

"Parameters → Extinction"

*[On the screen: Extinction model]*

Start "Parameters → Extinction"

Select Isotropic, Type1, Gaussian; OK; Yes to rewrite changes

*[On the screen: Basic window]*

Run refinement

*Refinement converges with R(obs)~ 9.6%, 7.8%, 14.6% for all, nuclear and magnetic reflections, respectively.*

Right click on the icon "Refine";

Select the page "Various" and use the button "Restrictions";

Disable the command "restrict * 12" which keeps ADP's of all atoms identical. OK;

Use the button "Fixed" and disable the command "fixed xyz *" which fixes coordinates of all atoms. OK; OK; Yes+start;

*Refinement converges with R(obs)~ 8.4%, 6.7%, 13.0% for all, nuclear and magnetic reflections, respectively.*

Start "Parameters → Twin fractions";

*[On the screen: Edit twin fraction]*

*Selection of the orthorhombic Shubnikov space group represents a lowering symmetry from the original one (parent symmetry. This can create different magnetic domains related by the lost symmetry operations. The lost symmetry operation has been automatically created by the program as a twinning operation. The default value of the relative fraction was 0.5 which means 1:1 ratio. In the final stage this value can be refined.*

Press the button "Show twinning matrix".

*[On the screen: Twinning matrix #2]*

*As expected the twinning operation is the four-fold axis, which was present in the tetragonal description but it is missing in the orthorhombic description.*

OK;

*[On the screen: Edit twin fraction]*

Change the volume fraction to zero and activate the refinement key for the volume fraction.

OK; Yes to the question "Do you want to rewrite changed files?".

*[On the screen: Basic window]*

Run refinement

*Refinement converges with R(obs)~ 8.3%, 6.7%, 12.6% for all, nuclear and magnetic reflections, respectively.*

*[On the screen: Basic window]*

Start "Parameters → Twin fractions";

*[On the screen: Edit twin fraction]*

*Check that the volume fraction return to the value close to 0.41.*

*[On the screen: Basic window]*

Double click on the icon "Plot structure"; Use the Vesta program to draw the structure;

Press "Draw+return" or "Draw+continue";

In Vesta enlarge the boundaries in z direction (like in the previous plot):
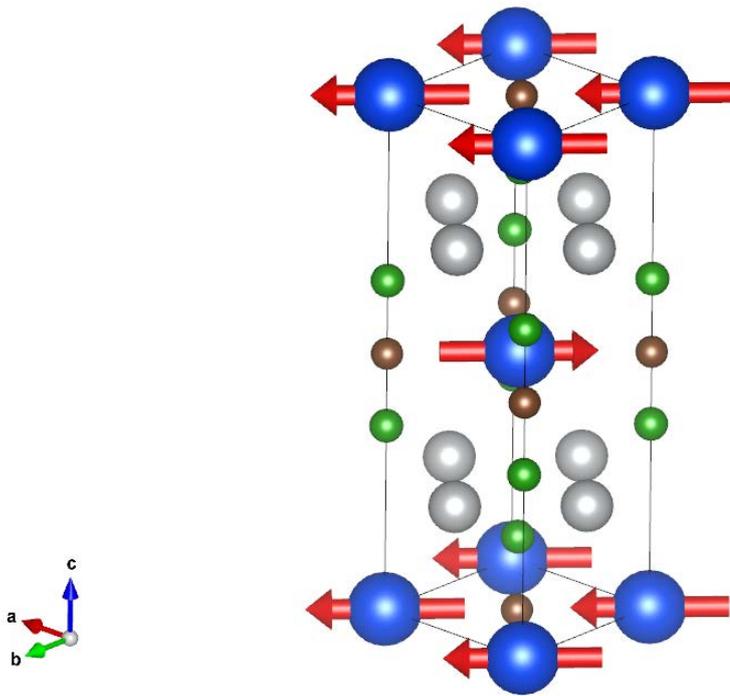
9. **Testing orthorhombic Shubnikov space group P[I]mn21**

   *[On the screen: Basic window]*

   Repeat the procedure form the previous point but now for the Shubnikov space group P[I]mn21.

   *Refinement converges with R(obs)~ 8.8%, 7.4%, 12.4% for all, nuclear and magnetic reflections, respectively.*
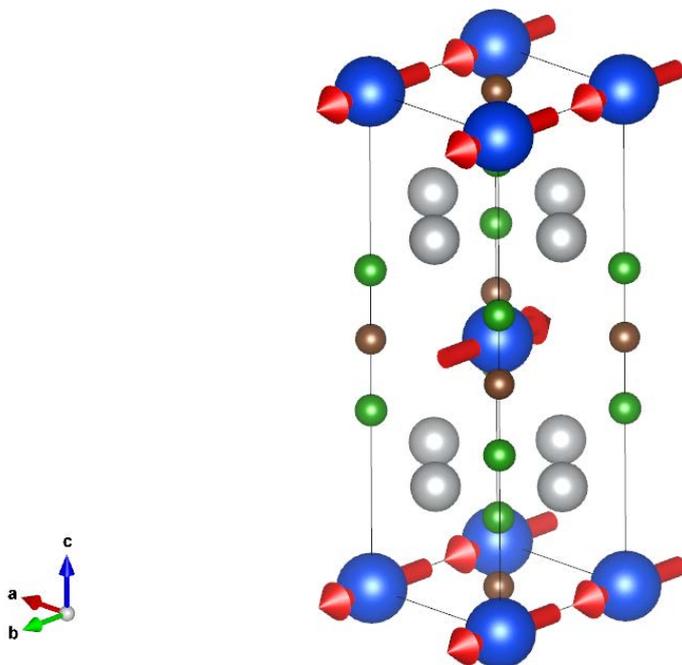
# Example 12.6: ISODISTORT

**Practical introduction to Jana2006-ISODISTORTcommunication**

**Revised: 28 November 2014**

Input files:     Ba5Co5.m40, Ba5Co5.m41, Ba5Co5.m50, Ba5Co5.m90

## 1. *Creating CIF file from the parent structure*

*[On the screen: Basic window]*

Start Jana2006

Start "File → Structure → Open" and open the structure Ba5Co5;

"File → CIF utilities → Make CIF file";

*[On the screen: Select Hermann-Mauguin symbol to be used:]*

Select the short symbol P63/mmc;

## 2. *Start ISODISTORT home page*

*[On the screen: Basic window]*

"Tools → Connect through internet to → Stokes, Campbell & Hatch ISODISTORT";

Your Internet default browser should open the page:

http://stokes.byu.edu/iso/isodistort.php



Browse for the CIF file created in the previous step; OK

*[On the screen: ISODISTORT search]*

## ISODISTORT: search

Reading CIF file...
Done.
Space Group: 194 P6_3/mmc D6h-4, Lattice parameters: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, Cl1 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063, z=-0.14926, O3 12k (x,2x,z), x=-0.14584, z=0.04948,
O4 2d (1/3,2/3,3/4)

---

**Graphical display of parent**  OK  ⊘

Atomic radius (Angstroms): 0.4    Maximum bond length (Angstroms): 1.91    Applet width (pixels): 1024

---

**Types of distortions to be considered**  Change  ⊘

Strain: ☑
Displacive: all☐ none☐ Ba☑ Co☑ Cl☑ O☑
Order:      all☐ none☐ Ba☐ Co☐ Cl☐ O☐
Magnetic:  all☐ none☐ Ba☐ Co☐ Cl☐ O☐

**Important: You must click on Change to implement any changes in the above type of distortions to be considered.**

---

**Method 1: Search over all special *k* points**  OK  ⊘

Crystal system(s): triclinic☐ monoclinic☐ orthorhombic☐ tetragonal☐ trigonal☐ hexagonal☐ cubic☐
Space-group symmetry: no choice ▾   Conventional lattice: no choice ▾   Primitive lattice: no choice ▾   Maximal subgroups only☐

---

**Method 2: General method - search over specific *k* points**  OK  ⊘

Specify *k* point: GM, k16 (0,0,0) ▾  a=____  b=____  g=____  # of incommensurate modulations= 0

Change number of superposed IRs: 1    Change  ⊘

**Important: You must click on Change to implement any changes in the number of superposed IRs.**

---

**Method 3: Search over arbitrary *k* points for specified space group and lattice**  OK  ⊘

Select either space group symmetry: Not selected ▾  or point group (crystal class): Not selected ▾
◉ Specify a real-space sublattice of the parent lattice with Default◉ P◯ A◯ B◯ C◯ I◯ F◯ R◯ centering.
◯ Specify a primitive reciprocal-space superlattice
Choose a representative basis:
a' = 1  a + 0  b + 0  c
b' = 0  a + 1  b + 0  c
c' = 0  a + 0  b + 1  c

---

**Method 4: Mode decomposition of a distorted structure**  OK  ⊘

Upload distorted structure from CIF file: [_____]  Browse...
☐ Read old mCIF format

---

**Space-Group Preferences**  Change  ⊘

These preferences apply to subsequent distortions but do not affect your parent structure):
Monoclinic axes: a(b)c◉ c(-b)a◯ ab(c)◯ ba(-c)◯ (a)bc◯ (-a)cb◯
Monoclinic cell choice: 1◉ 2◯ 3◯
Orthorhombic axes: abc◉ ba-c◯ cab◯ -cba◯ bca◯ a-cb◯
Trigonal axes: hexagonal◉ rhombohedral◯
Origin choice: 1◯ 2◉
Superspace group setting: standard (IT-C)◉ basic (IT-A)◯

**Important: You must click on Change to implement any changes in the above preferences.**

---

## Define distortions to be considered:
*In our case we are interested just in magnetic ordering;*

**Types of distortions to be considered** [Change] ⑦

Strain: ☐
Displacive: all☐ none☐ Ba☐ Co☐ Cl☐ O☐
Order:      all☐ none☐ Ba☐ Co☐ Cl☐ O☐
Magnetic:  all☐ none☐ Ba☐ Co☑ Cl☐ O☐

**Important: You must click on Change to implement any changes in the above type of distortions to be considered.**

Press Change;
In the box for "Method 2" select GM k16(0,0,0), which means k=(0,0,0):

**Method 2: General method - search over specific *k* points** [OK] ⑦

Specify *k* point:  GM, k16 (0,0,0)  ▾   a=☐   b=☐   g=☐   # of

incommensurate modulations= 0

Change number of superposed IRs: 1   [Change] ⑦

**Important: You must click on Change to implement any changes in the number of superposed IRs.**

Press OK;
*Select irreducible representation*
*[On the screen: ISODISTORT irreducible representation ]*

# ISODISTORT: irreducible representation

. . . . . . . . . . . . . .

Next choose an IR:  mGM2+, mk16t3  ▾  ⑦ [OK]

| mGM2+, mk16t3 |
| mGM4+, mk16t7 |
| mGM5+, mk16t11 |
| mGM6+, mk16t9 |
| mGM1-, mk16t2 |
| mGM3-, mk16t6 |
| mGM5-, mk16t12 |
| mGM6-, mk16t10 |

*Comparing with "Representation analysis" list of Jana2006, only irreducible representations allowing non-zero magnetic moments are listed. In the next step we will demonstrate two dimensional irreducible representation mGM5+.*
Select the representation mGM5+ and press OK;

*Represantation analysis of Jana2006 (for comparison):*

**Representation analysis:**

| Representation | Dimension | Shubnikov space group | Axes | Origin shift | |
|---|---|---|---|---|---|
| mGM1+ | 1 | P6₃/mmc | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM1- | 1 | P6₃/m'm'c' | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM2+ | 1 | P6₃/mm'c' | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM2- | 1 | P6₃/m'mc | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM3+ | 1 | P6₃'/m'mc' | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM3- | 1 | P6₃'/mm'c | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM4+ | 1 | P6₃'/m'm'c | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM4- | 1 | P6₃'/mmc' | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | Deta |
| mGM5+ | 2 | P2₁/m | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Deta |
| mGM5- | 2 | P2₁/m' | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Deta |
| mGM6+ | 2 | P2₁'/m | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Deta |
| mGM6- | 2 | P2₁'/m' | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | Deta |

Display representations

*[On the screen: ISODISTORT: order parameter direction]*

# ISODISTORT: order parameter direction

Space Group: 194 P6_3/mmc D6h-4, Lattice parameters: a=5.63780, b=5.63780, c=24.15830, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, Cl1 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063 , z=-0.14926, O3 12k (x,2x,z), x=-0.14584 , z=-0.04948, O4 2d (1/3,2/3,3/4)
Irrep matrices: 2011 version for all k points
Include magnetic Co4 Co5 Co6 distortions
k point: GM, k16 (0,0,0)
IR: mGM5+, mk16t11

Finish selecting the distortion mode by choosing an order parameter direction ⓘ
○P1 (a,-1.732a) 63.457 Cmcm, basis={(0,1,0),(-2,-1,0),(0,0,1)}, origin=(0,0,0), s=1, i=6, k-active= (0,0,0)
○P2 (a,0.577a) 63.462 Cm'c'm, basis={(0,1,0),(-2,-1,0),(0,0,1)}, origin=(0,0,0), s=1, i=6, k-active= (0,0,0)
○C1 (a,b) 11.50 P2_1/m, basis={(-1,0,0),(0,0,-1),(0,-1,0)}, origin=(0,0,0), s=1, i=12, k-active= (0,0,0)

OK

*Here we can see the kernel and the set of epikernels (isotopic subgroups) associated with mGM5+.*

*List of kernels and epikernels in Jana2006 (for comparison). The order parameters may differ depending on the setting of the basis.*

**List of kernels and epikernels:**

| Shubnikov space group | Axes | Origin shift | Representation |
|---|---|---|---|
| P63'/mmc' | (1,0,0\|0,1,0\|0,0,1) | (0,0,0) | mGM4- |
| Cm'c'm | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM5+ ← |
| Cmcm | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM5+ ← |
| Cmcm' | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM5- |
| Cm'c'm' | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM5- |
| Cmc'm | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM6+ |
| Cm'cm | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM6+ |
| Cmc'm' | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM6- |
| Cm'cm' | (1,0,0\|1,2,0\|0,0,1) | (0,0,0) | mGM6- |
| P21/m | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | mGM5+ ← |
| P21/m' | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | mGM5- |
| P21'/m | (0,1,0\|0,0,1\|1,0,0) | (0,0,0) | mGM6+ |

Show details

Return one step back in your Internet browser and select the representation mGM2+; OK;
[On the screen: ISODISTORT: order parameter direction]

# ISODISTORT: order parameter direction

Space Group: 194 P6_3/mmc D6h-4, Lattice parameters: a=5.63780, b=5.63780, c=24.15830, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, Cl1 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063 , z=-0.14926, O3 12k (x,2x,z), x=-0.14584 , z=-0.04948, O4 2d (1/3,2/3,3/4)
Irrep matrices: 2011 version for all k points
Include magnetic Co4 Co5 Co6 distortions
k point: GM, k16 (0,0,0)
IR: mGM2+, mk16t3

Finish selecting the distortion mode by choosing an order parameter direction (?)
◉P1 (a) 194.270 P6_3/mm'c', basis={(0,-1,0),(1,1,0),(0,0,1)}, origin=(0,0,0), s=1, i=2, k-active= (0,0,0)

OK

Select the listed ODP and press OK

[On the screen: ISODISTORT: distorsion]
Select a small starting values (0.1) for magnetic moments of Co4, Co4 and Co6;
Select "CIF file" and press OK;
Save it as a Text Document with name GM2+ into the working directory.

## ISODISTORT: distortion

Space Group: 194 P6_3/mmc D6h-4, Lattice parameters: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5 4e (0,0,z), z=0.39525, Co6 4f (1/3,2/3,z), z=-0.17818, Cl1 2c (1/3,2/3,1/4), O2 12k (x,2x,z), x=0.16063, z=-0.14926, O3 12k (x,2x,z), x=-0.14584, z=-0.04948, O4 2d (1/3,2/3,3/4)
Include magnetic Co distortions
k point: GM, k16 (0,0,0)
IR: mGM2+, mk16t3
P1 (a) 194.270 P6_3/mm'c', basis={(0,-1,0),(1,-1,0),(0,0,1)}, origin=(0,0,0), s=1, i=2, k-active= (0,0,0)
Lattice parameters of undistorted supercell: a=5.63760, b=5.63760, c=24.15760, alpha=90.00000, beta=90.00000, gamma=120.00000

○ View distortion ⑦ ○ View diffraction ⑦ ⦿ CIF file ⑦ ○ Distortion file ⑦ ○ Domains ⑦ ○ Primary order parameters ⑦ ○ Modes details ○ Complete modes details ⑦ ○
TOPAS.STR ⑦ ○ IR matrices **OK**

Enter mode and strain amplitudes: ⑦

P6_3/mmc[0,0,0]mGM2+ (a) 194.270 P6_3/mm'c', basis={(0,-1,0),(1,1,0),(0,0,1)}, origin=(0,0,0), s=1 i=2, ferromagnetic, k-active= (0,0,0)

| 0.1 | [Co4:a]A2g(a) |
| 0.1 | [Co5:e]A2(a) |
| 0.1 | [Co6:f]A2(a) |

P6_3/mmc[0,0,0]GM1+ (a) 194.264 P6_3/mmc s=1 i=1

Parameters: ⑦
"View distortion":

Atomic radius:  0.4  Angstroms

Maximum bond length:  1.91  Angstroms

Length of magnetic moment vectors:  0.5  Angstroms/magneton

Applet width:  1024  pixels

Supercell enlargement:  1  x  1  x  1

"View distortion" and "View diffraction":

Maximum displacement per mode:  1.0  Angstroms

Maximum strain per mode:  0.1

Maximum occupancy per mode:  1.0

Maximum magnetic moment per mode:  4.0  magnetons

Include strain modes in TOPAS.STR: ○yes ⦿no

☐ Use alternate (possibly nonstandard) setting in CIF file
Basis vectors of subgroup lattice relative to parent:

a' = [    ] a + [    ] b + [    ] c

b' = [    ] a + [    ] b + [    ] c

c' = [    ] a + [    ] b + [    ] c

Origin of subgroup relative to parent: [    ] a + [    ] b + [    ] c

Password for beta version: [    ]

Select "View distortion" and press OK;

⦿ View distortion ⑦  ○ View diffraction ⑦  ○ CIF file ⑦  ○ Distortion file ⑦  ○ Domains ⑦  ○ Primary order parameters ⑦  ○ Modes details
○ Complete modes details ⑦  ○ TOPAS.STR ⑦  ○ IR matrices **OK**

Make the steps related with usage of Java.
*If Java offers an update please do it, otherwise the applet may be blocked. In some cases the Java security level needs to be adjusted in Java Control Panel (and the browser restarted and the work repeated ...).*

ISODISTORT: view distortions

This applet was created in 2005 by David N. Tanner, Branton J. Campbell, and Harold T. Stokes. Other contributers include Andrew Zimmerman, Aaron P. Stewart, and Robert Watts. The 3D graphics utilize a modified version of Ken Perlin's RenderApplet.

*Using the sliders, magnetic moments of Co atoms can be changed to see mutual arrangement of magnetic moments of symmetry related atoms.*

Return back to the page ISODISTORT irreducible representation and select now mGM4+

# ISODISTORT: irreducible representation

Space Group: 194 P6_3/mmc D6h-4, Lattice parameters: a=5.63780, b=5.63780, c=24.15830, alpha
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes
Ba1 4f (1/3,2/3,z), z=-0.04041, Ba2 4f (1/3,2/3,z), z=0.36991, Ba3 2b (0,0,1/4), Co4 2a (0,0,0), Co5
12k (x,2x,z), x=0.16063 , z=-0.14926, O3 12k (x,2x,z), x=-0.14584 , z=-0.04948, O4 2d (1/3,2/3,3/4)
Irrep matrices: 2011 version for all k points
Include magnetic Co4 Co5 Co6 distortions
k point: GM, k16 (0,0,0)

Next choose an IR:   mGM4+, mk16t7   ▼  ⓘ   **OK**

Repeat the work as for GM2+ and save the CIF file as a Text Document with name GM4+ into the working directory.
Return to Jana2006

3. **Refining the model mGM2+**
   *[On the screen: Basic Jana2006 window]*
   *"File → Structure → New"; opens a file manager*
   On the right pane: Select (by the arrow button) structure name GM2+; OK
   *[On the screen: Specify type of the file to be imported]*
   Select "Structure: from CIF"
   *This opens a file manager*
   *Caution: we cannot use "Magnetic: nuclear model from CIF" because it would create the parent phase. In our case we already have the parent phase Ba5Co5 and the structure generated by ISODISTORT is one of the test magnetic structures*

On the right pane:

Uncheck "Use filter" and select the file GM2+.txt; OK;

*The imported CIF file has line separators as for UNIX and this is the reason why the file must be converted to the Windows system.*

YES to the question "Do you want to continue?".

NO to the question "Do you want to import data from file?";

*[On the screen: Basic window]*

*"File → Structure → Copy in";*

On the right pane: Select structure name Ba5Co5; OK

Copy in just m41 and m90 files (NOT m40 and m50); OK

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various" and use the button "Restrictions";

Restrict all atoms (i.e. "*") to have identical ADP parameters and but not coordinates and occupancies; OK

On the page "Various" select "Fixed commands";

Fix coordinates for all atoms (wild character *);

OK; OK; "Yes+start";

Refinement converges with Rp~3.3%, R(obs)~8.4%.

4. ***Refining the model mGM4+***

*[On the screen: Basic Jana2006 window]*

*"File → Structure → New"; opens a file manager*

On the right pane: Select structure name GM4+; OK

*[On the screen: Specify type of the file to be imported]*

Select from CIF; *opens a file manager*

On the right pane:

Uncheck "Use filter" and select the file GM4+.txt; OK;

*The imported CIF file has line separators as for UNIX and this is the reason why the file must be converted to the Windows system.*

YES to the question "Do you want to continue?".

NO to the question "Do you want to import data from file?";

*[On the screen: Basic window]*

*"File → Structure → Copy in";*

On the right pane: Select structure name Ba5Co5; OK

Copy in just m41 and m90 files; OK

Right click on the icon "Refine"; Select the "Basic" and change the "Number of cycles" to 100 and the "Damping factor" to 0.1;

Select the page "Various" and use the button "Restrictions";

Restrict all atoms to have identical ADP parameters and but not occupancies; OK

On the page "Various" select "Fixed commands";

Fix coordinates for all atoms (wild character *);

OK; OK; "Yes+start";

*Refinement converges with Rp~3.0%, R(obs)~6.0%.*

*The results are identical with those from example 12.1.*

# Example 13.1: TTB

**Solution of a tetragonal-tungsten-bronze type structure from EDT (electron diffraction tomography) data. Complete procedure from data reduction to structure refinement.**

**Revised: 04 March 2015**

**Chemical formula: $K_3Nb_{(5+x)}O_{15}$**

Electron diffraction data was measured on a transmission electron microscope Philips CM120 with a precession divice DigiStar. Accelerating voltage 120 kV.

Input data: directory dp with the set of experimental data

ttb.pts: input file for PETS – the data reduction of the beam stop

beamstop.xyz: file with the polygon defining the shape of the beam stop

ttb_start.cif_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part.

File ttb.cif_pets is the output of the data reduction.

1. *Preparing input file for PETS*

   *Make sure you correctly installed PETS and ImageJ. Check Chapter "Installation notes" (page 7) for details. File ttb.pts is the input to PETS. The file was prepared by the software used for the collection of the diffraction data, and most entries have been filled in. You have to enter two parameters: the information about the beam stop and the size of reflections.*

   Open file ttb.pts in any plain-text editor (notepad, wordpad, notepad++, vim,…)

   Open file dp/001.tif in ImageJ

   In ImageJ go to "Image → Adjust → Brightness and Contrast"

   Click the button "Auto" to adjust the constrast.

   Go to "Image → Properties" and change the values of Pixel width and Pixel height from 0.005 to 1.

   Measure the diameter of the reflections on the image.

   *There are several ways to measure the diameter of the reflections, but the simplest and sufficient way is to place the cursor to the left of the reflection, remember or write down the x-coordinate, then place the cursor to the right of the reflection, again read the x-coordinate and subtract the two coordinates. The diameter should be large enough to encompass most of the reflections, but not too large, to prevent overlaps. Do not take into account the broad, weak TDS scattering around the strongest reflections! That would give you too large diameter. In this case, value 25 is a good choice.*

   In ttb.pts, change the line "reflectionsize ??" to "reflectionsize 25"

   In ImageJ, determine the coordinates of the tip of the beamstop (white cross on the following image):
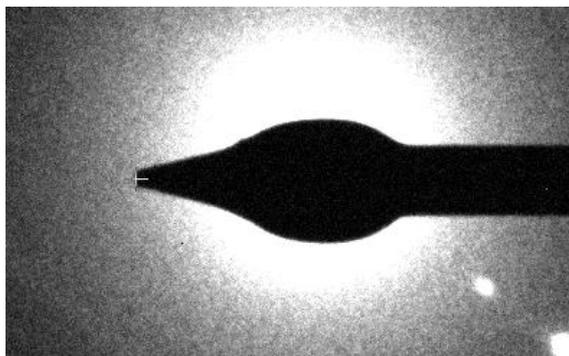
You should get coordinates very close to 913 1014.

In ttb.pts change the line "beamstop ??(yes/no)" to "beamstop yes beamstop.xyz 913 1014"

File beamstop.xyz contains the coordinates of the polygon describing the beamstop relative to a reference point. 913 and 1014 are the x- and y-coordinates of the reference point, which is in this case the tip of the beamstop. The reference point can change from one experiment to another, and must be therefore determined by the user.

Save and close ttb.pts

2. ***Run PETS and prepare files for indexation***

   Make sure ImageJ is not running. If it is, close ImageJ.

   Run PETS with the file ttb.pts

   *There are several ways of running PETS. See installation notes for detailed description. A window with initial menu of PETS opens, and ImageJ starts displaying a black image with a white circle.*

   In the window of PETS, type p[Enter]

   *The peak hunting procedure starts. ImageJ sequentially displays diffraction images with circles at points found by PETS as significant peaks. Note that PETS follows the position of the primary beam, and corrects for small shifts. Note also the significant diffuse streaks. Although they seem very intense, it is just due to the enhanced contrast of the images. Compared to the Bragg intensities, the diffuse streaks are weak and do not disturb the structure solution.*

   *At the end, the evolution of the x- and y-coordinates of the estimated primary-beam position is displayed (b&w inverted):*



   *[On screen: main menu of PETS]*

   type r[Enter]

   *As the first step after peak hunting, PETS needs to refine the azimuthal angle between the horizontal axis and the projection of the tilt axis. This angle depends on experimental parameters, and needs to be refined for each data set. ImageJ displays a cylindrical projection of the difference space of the extracted peak positions. For correct azimuthal angle, the image contains sharp peaks aligned on sinusoidal curves. This step provides a first estimate of the data quality. At the end of the refinement, you should get message:*

```
Final values of the parameters:
omega : 21.591
```
*and see this image (b&w inverted):*
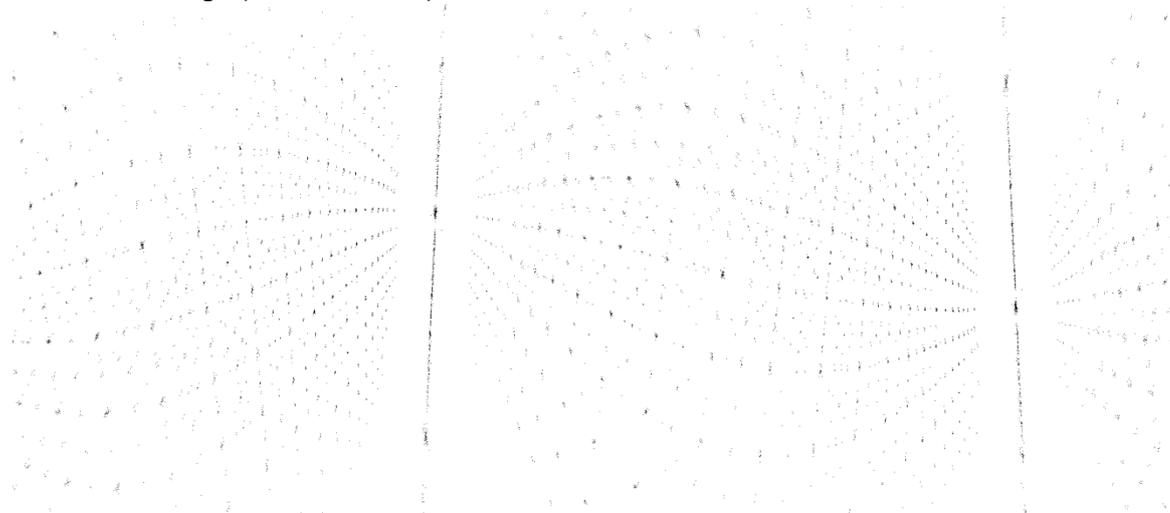


*[on screen: main menu of PETS]*

*PETS starts the analysis of the located peak positions. In the first step, distance distribution between peaks in the image plane is analyzed. A sorted plot of inter-peak distances is displayed (white curve on screen, black on the image below) with its derivative (grey curve):*



*For good quality data set, the white curve contains distinct steps, and, consequently, the grey curve has distinct peaks.*

Press Enter

*In the next step an autoconvolution of the diffraction pattern (difference space) is analyzed, and the groups of peaks in the autoconvolution (clusters) are replaced by the cluster centers. Again, a distance distribution is displayed, and clear-cut steps on the curve indicate a well-defined lattice.*

Press Enter

*Now the first step is finished and PETS prepared files needed for unit cell indexing. Keep the window of PETS open, you will need it later!*

3. ***Indexing with Jana2006***

Start Jana2006

*By default, Jana2006 starts with the last structure open. It may be cumbersome to change the directory every time. You may create a dummy (empty) file ttb.m40 in the example directory,*

*and use the command "Open with" from the file-manager context menu to launch Jana2006 directly in this directory.*

"Tools → Graphics → Indexing"

Locate and open file ttb.clust by double clicking it

*A 3D view of the reciprocal lattice opens. You can rotate the cloud by mouse. Use buttons* ⊕ *and* ⬚ *to switch between free rotation and rotation around z-axis. Rotate with the lattice and try to determine the crystal system and the special axes of the lattice.*

*You should come to the conclusion that the lattice is tetragonal (warning – the lattice has a few projections that look tetragonal, but are not exactly tetragonal). The following image shows the view along c\*:*
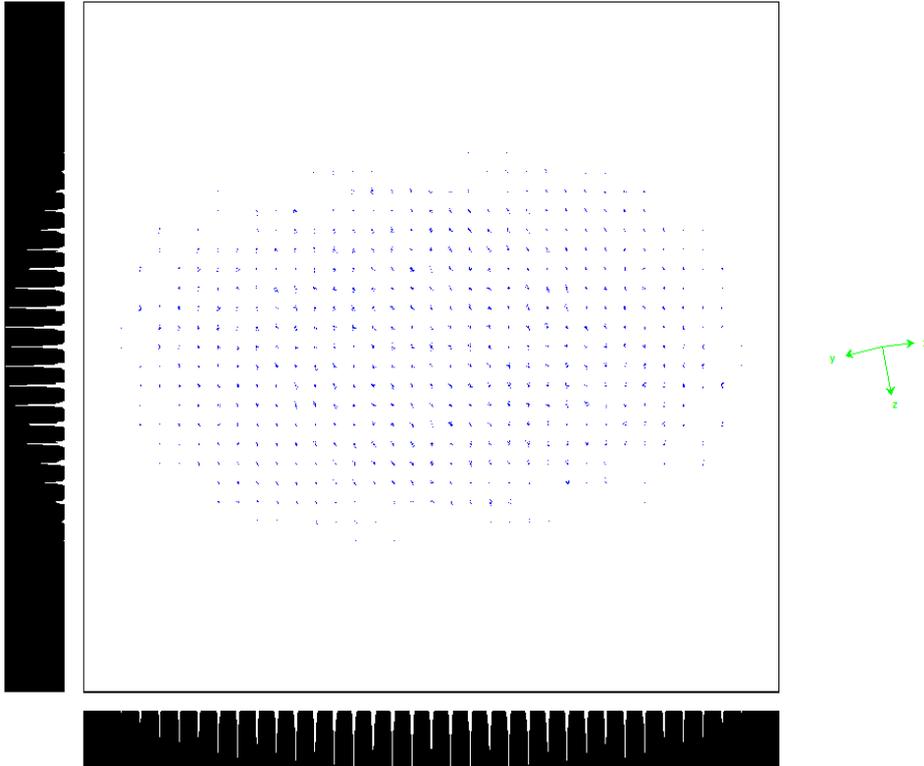


*IMPORTANT: before you continue, make sure you have the same orientation of the lattice on your computer as displayed on the picture above (check the direction of the axes on the right). If not, you may obtain slightly different results in the rest of the tutorial. While not necessarily wrong, it makes following this tutorial more difficult.*

Click the button ⇥ in the lower-left corner

Click, hold the mouse button, and drag the marker to obtain the result on this image:
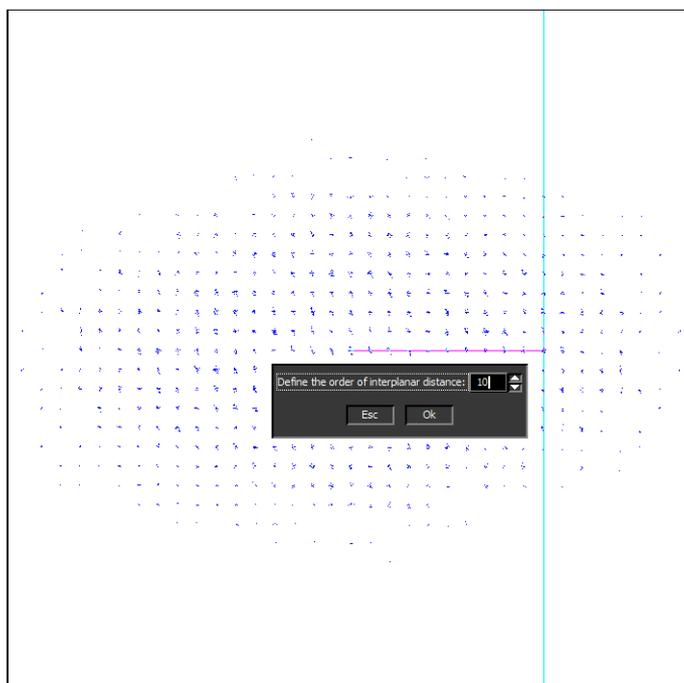
*Note that the vertical red line is on the tenth vertical row of peaks. By this action you defined the direction and length of the (direct-space) basis vector **a**. Note: if you make a mistake and need to redo this step, make sure that the radio button **a** is selected under the main window, otherwise you will modify another cell parameter.*

Repeat the action, this time drag the marker up vertically to define the vector **b**.

*Both vectors should have lengths close to 12.8 Å, and angle gamma is close to 90°.*

Click "View direction", keep default selection "a", Click OK

*The reciprocal space is now viewed along a, and b points to the right.*

In analogy to the procedure above, select the direction and length of the vector c (c points up in this view).

*When you are finished, at the bottom of the window you should see cell parameters close (within a fraction of angstrom and degree) to these values:*
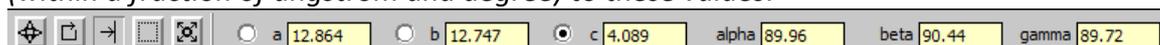


"Refine cell → Refine UB+cell"

*The orienting matrix is refined. Note that 90.3% of all peaks were indexed.*

OK; Quit

*A file ttb.smr was now produced by Jana2006. This file contains the orientation matrix and the unit cell parameters.*

Close Jana2006

4. ***Integrate the intensities with PETS***
   Return to the window of PETS.
   Type u[Enter]
   *PETS reads the orienting matrix from the smr file.*
   Type i[Enter]
   *The integration procedure starts. ImageJ displays images with circles drawn at positions predicted from the orienting matrix. A small circle inside large circle means that a peak with I>3σ(I) was found. The small circle is located on the maximum of the intensity. A diamond means that a reflection is expected on upcoming frame(s), square indicates reflection present on previous frame(s).*

*When the integration finishes, files ttb.cif_pets and ttb.hkl are created. Both can be used to import the data into Jana and to solve the structure.*

**5.** ***Create reciprocal-space sections***
In PETS, Type h[Enter]
Type y[Enter]
*You just asked PETS to scan all images and reconstruct sections through reciprocal space at planes hk0, hk1, hk2, h0l, h1l, h2l, 0kl, 1kl, 2kl. We will use these sections as an aid to determine the space group.*
When the reconstruction finishes, type q[Enter] to close PETS. You may also close ImageJ.

**6.** ***Create new structure***
*Important!* *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file ttb.cif_pets that you just created, but use the file ttb_start.cif_pets provided with the example files (Rename the file to ttb.cif_pets). Using your own cif_pets file is also possible, but your results may slightly differ from the results described in this tutorial.*
Start Jana2006
"File → Structure → New" opens a file manager
Left pane: locate the directory with input files
Right pane: double-click ttb
*Right pane detects possible Jana files and shows one jobname for each group of files*

**7.** ***Import Wizard***
Select "Known diffractometer formats"; NEXT
Select "Pets electron diffractometer"
*The file name automatically changes to ttb.cif_pets, which is a file produced by PETS containing all important information, including the list of intensities.*
NEXT
Leave all settings unchanged (note the wavelength of 120kV electrons!); NEXT
Leave all settings unchanged; NEXT
*The program reads 3777 reflections from the file*
OK
For absorption correction select "None or done before importing"; NEXT
FINISH; OK; YES to accept the data set
*You just read in the cell parameters and the intensity list. If you do not have the data in the cif_pets format, you can read them in from a general hkl file using the option "reflection file corrected for LP and absorption" at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.*

**8.** ***Symmetry Wizard***
NEXT *to close the information window and start the wizard*
*Symmetry Wizard can be started separately by "File → Reflection file → Make space group*

*test. The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances. Change the tolerances according to this screenshot:*

**Tolerances for crystal system recognition:**

Original cell parameters: 12.865 12.734 4.090 89.95 90.47 89.65

Maximal deviation for cell lengths in [A]    `0.2`

Maximal deviation for cell angles in deg    `0.5`

**Tolerances for space group recognition:**

Maximal ave(I/sig(I)) for centering    `100`

Maximal ave(I/sig(I)) for extinctions    `100`

Leave other settings default; NEXT; OK

*[On the screen: Select Laue symmetry]*

Select tetragonal Laue class 4/mmm; NEXT

*The internal R-values would be rather high for x-rays, but are normal for electron diffraction data, especially if measured in selected area mode.*

*[On the screen: Select cell centering]*

Select primitive unit cell; NEXT

*[On the screen: Select space group]*

*The window shows possible space groups.*

*The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.*

*It is difficult to select the correct space group. In particular, presence or absence of the b-glide is hard to asses, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effect. Open the file h0l.bmp and h1l.bmp, and compare the intensities of reflections with h=2n (which should be absent in the h0l plane, but present in h1l). You will see that despite a number of violations, the b-glide absences are nevertheless clearly present in the h0l plane in comparison with the h1l plane. Space group with b-glide is thus a reasonable guess. Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.*

Select P4/mbm; NEXT

Accept the space group in the standard setting; FINISH

*Symmetry is saved in file ttb.m50.*

9. ***Creating refinement reflection file***

*In this step program creates file ttb.m90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*

Proceed with the wizard, leaving all settings default

10. ***Structure Solution Wizard***

OK *to close the information window and start the wizard*

*[On the screen: window of Structure solution] Structure solution wizard can be executed separately through "Run → Solution". Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*

In "Formula" textbox type just the list of chemical elements: K Nb O

*Superflip does not need information about chemical elements but they will be required for peak assignment based on electron density map calculated by Superflip. If Jana2006 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula, you may enter it and use EDMA for peak picking (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.*

Click the checkbox next to "Use a specific random seed".

Leave other settings default; Press "Run solution"

*The specific random seed is used just to guarantee reproducibility of the results. For standard work random seed need not be defined.*

*[On the screen: window of Superflip appears with iteration running. After ten runs, open the listing of Superflip log file in "Open the listing"]*

*Superflip performed ten solution attempts, and picked the best one. Its characteristics are displayed near the bottom of the listing:*

```
Properties of the saved density:
Run Rvalue Peaks Symm. Der.SG
8   24.46  2.71  3.24  P4/mbm
```

*The space group proposed by Superflip is the same as our initial guess. The space-group selection is confirmed. Small symmetry agreement factor (column Symm.) indicated good quality of the solution. In cases of doubts or difficult problems, it is worth checking the statistics, especially the symmetry analysis, for each of the ten runs, and seeking for the most probable one.*

Press "Close" to leave the listing

Press "Accept last solution"

*The program creates file ttb.m40 with atoms of the structure model*

11. ***Verification and completion of the structure solution***

Go to "Contour → New plot → OK → Run 3D maps"

*VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Do you think it is complete?*

*You should come to the conclusion that the model is correct, all atoms were assigned correct chemical type, only one oxygen (between two atoms Nb2 is missing.*

Decrease the isosurface level to see weaker features in the density ("Properties → Isosurfaces", set isosurface level to 1)

*You can see that there is a peak between the two Nb atoms, it just was not interpreted by Jana2006 as an atom. Take-home message: it is always worth checking the density (i.e. the raw result from Superflip), because it may contain features not considered in the interpreted structure model.*

Quit VESTA (do not save the file), quit Contour.

Start "Parameters → Atoms → New → Peaks from last Fourier calculation"

*A list of maxima found in the density is displayed. In the right pane, the distances of the maximum to the nearest atoms are displayed. First eight maxima correspond to atoms interpreted by Jana2006. Max9 is a ghost peak, too close to Nb1. Max10 is at a correct distance from two Nb2 atoms – this is the oxygen atom missing in the model.*

Click "Include selected peak", type O* in the field for name; OK; Finish; Yes to include the new atom in the model

*You may now check the structure in Diamond to convince yourself that the structure is complete and chemically reasonable.*

**12.** *Initial Refinement*
*[On the screen: basic window of Jana]*
Right-click the icon of Refine.
*[On the screen: refinement options]*
Change the number of cycles to 100; OK
Choose "Yes+start"
*Refinement converges with R value about 20.0%. At this moment you may check the refinement listing with a lot of information about the refinement procedure and results.*

**13.** *Adding missing, partially occupied atom*
*[On the screen: basic window of Jana]*
Right click the icon Fourier
On the first card, select F(obs)-F(calc) – difference Fourier
Modify the setting on the second card to agree with this screenshot:
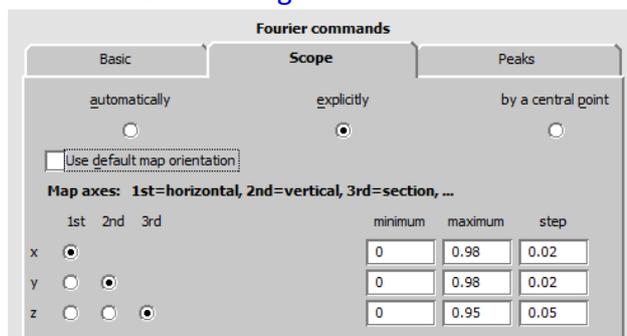


OK; Yes+Start; No; No
*Jana just calculated a difference Fourier map.*
View the map in VESTA: "Contour → New plot → OK Run → 3D maps"
*You will see that the difference map is dominated by one positive peak in the middle of an empty cage of oxygens. This position tends to be partially occupied in some TTB structures. In this case, the partial atom is Nb.*
Add the missing atom. The procedure is the same as when you added the missing oxygen atom after the solution. This time, the first maximum in the list is the correct maximum.
When defining the atom, do not forget to define the name as Nb* and type as Nb. Define "Occupancy reduction" 0.2
OK; Finish; Yes
*Now we will allow the occupancy of the niobium atom to be refined:*
Double click "Edit atoms"; double click Nb3; on card "Edit" check the check box next to the parameter "ai"; OK; OK; Yes
Double click Refine
*The model refines to R-value about 19.4%. The improvement is very small, because the occupancy of the Nb3 atom is very small, too, actually less than 10%.*
*This data set is exceptionally good. Normally, partial occupancies of atoms cannot be refined reliably from electron diffraction data. Even here the refined occupancy must be taken only as a rough indicator.*
*At this moment the structure is essentially finished. You may try to refine anisotropic displacement parameters of the heavy atoms. The R-value decreases to ~18.3%. Again, with*

*this data set such refinement is possible, and the resulting parameters are reasonable. In many other cases, anisotropic displacement parameters refine to unrealistic or even non-positive definite values.*

**The resulting structure**
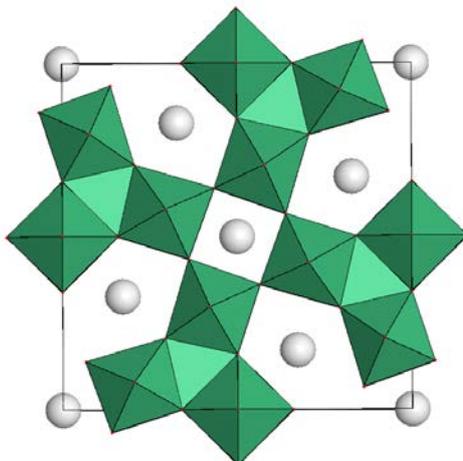
# Example 13.2: Kaňkite

**Solution of kaňkite – a hydrated Fe-bearing arsenate.**

**Revised: 3 December 2013**

**Expected chemical formula:** $Fe^{+++}AsO_4 \bullet 3.5H_2O$
Electron diffraction data measured on a transmission electron microscope Philips CM120 with precession device DigiStar. Accelerating voltage 120 kV.
Input data: directory dp with the set of experimental data,

      kankite.pts: input file for PETS – the data reduction program

      beamstop.xyz: file with the polygon defining the shape of the beam stop

      kankite_start.cif_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part. File kankite.cif_pets is the output of the data reduction.

1. **Data reduction** *using* **PETS**

   *The data processing part follows exactly the procedure described in example 13.1. Please follow that tutorial. Here only key results are provided for your control, and comments are provided for stages that require special attention.*
   *Parameters filled in the prepared file kankite.pts:*
   ```
   reflectionsize 25
   beamstop yes beamstop.xyz 927 1025
   ```
   *Refined azimuthal angle omega of the tilt axis:*
   ```
   omega : 11.752
   ```
   *Unit cell is monoclinic, C-centered. The following screenshot is the view of the reciprocal lattice along the monoclinic axis **b** (a\* horizontal, c\* vertical, pointing down):*
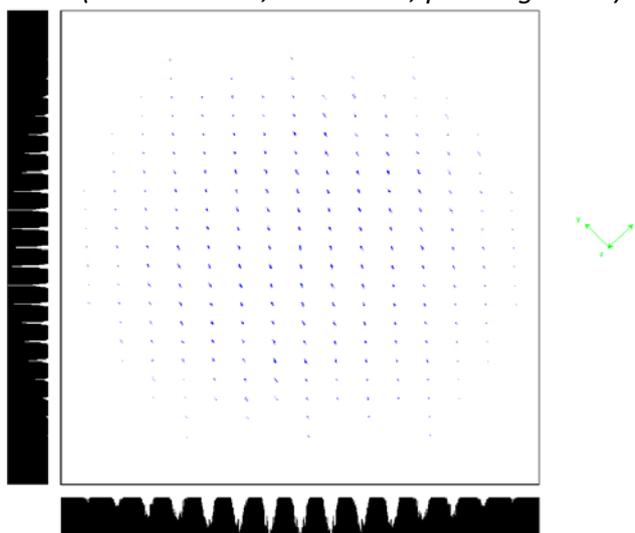


   *The direction and length of the b-axis is difficult to determine. The lattice is obscured by quite a lot of noise. This noise comes from the diffuse nature of the reflections along **b**\* and from the mosaicity of the crystal. If such noise is present, it is amplified by the data processing preceding the creation of the file .clust. In such cases it is useful to check the correctness of*

*the cell determination in the file .xyz. This file contains only the peak positions in reciprocal space, not their autoconvolution. It is thus cleaner, but much less complete.*

Click "New plot"

Locate and open the file kankite.xyz

*You will see that the plot is less complete, but the noise is less abundant.*

*Final refined cell parameters (refined against the peaks in kankite.clust):*

| a | 5.684 | b | 21.300 | c | 9.136 | alpha | 89.78 | beta | 92.75 | gamma | 89.93 |

Quit the indexing plugin to create file kankite.smr with the orienting matrix, and continue data processing in PETS by typing u[Enter] to read in the orienting matrix, and i[Enter] to integrate the intensities.

*You will note significant overlap of integration boxes (white circles) in the images displayed by ImageJ. This is, however, not a real problem, because the lattice is C-centered, and every second reflection is systematically absent.*

*PETS produced file kankite.cif_pets, which will be imported in Jana2006 in the next step.*

Type h[Enter] and y[Enter] ]to produce standard sections through reciprocal space.

*With this step the data processing in PETS is finished.*

Type q[Enter] to close PETS. You may also close ImageJ.

## 2. Create new structure

*Important!* *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file kankite.cif_pets that you just created, but use the file kankite_start.cif_pets provided with the example files (Rename the file to kankite.cif_pets). Using your own cif_pets file is possible, but your results may slightly differ from the results described in this tutorial.*

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate the directory with input files

Right pane: double-click kankite

*Right pane detects possible Jana files and shows one jobname for each group of files*

## 3. Import Wizard

Select "Known diffractometer formats"; NEXT

Select "Pets electron diffractometer"

*The file name automatically changes to kankite.cif_pets, which is a file produced by PETS containing all important information, including the list of intensities.*

NEXT

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

*The program reads 5921 reflections from the file*

OK

For absorption correction select "None or done before importing"; NEXT FINISH; OK; YES to accept the data set

*You just read in the experimental parameters, cell parameters and the intensity list.*

## 4. Symmetry Wizard

NEXT *to close the information window and start the wizard*

*Symmetry Wizard can be started separately by "File → Reflection file → Make space group test. The default settings are prepared from x-ray diffraction. For electron diffraction the tolerances should be increased. Change the tolerances according to this screenshot:*

**Tolerances for crystal system recognition:**

Original cell parameters:  5.684 21.300  9.136  89.78  92.75  89.93

Maximal deviation for cell lengths in [A]    0.2

Maximal deviation for cell angles in deg    0.5

**Tolerances for space group recognition:**

Maximal ave(I/sig(I)) for centering    100

Maximal ave(I/sig(I)) for extinctions    100

Leave other settings default; NEXT

*Jana detected a seven times larger unit cell with orthorhombic metric. This is not likely to be the correct unit cell.*

NEXT

*[On the screen: Select Laue symmetry]*

Select monoclinic Laue symmetry; NEXT

*The internal R-value of 13.21 % is very good for electron diffraction data.*

*[On the screen: Select cell centering]*

*From the table the fact that the cell is C-centered is not obvious at all. This is due to the overlap of the reflection positions during the integration. But we know the centering from the data reduction and indexing step. You may convince yourself about the correctness of the centering by inspecting the reciprocal space sections hk0, hk1 and hk2 generated by PETS.*

Select C-centering; NEXT

*[On the screen: Select space group] The window shows possible space groups. It is not obvious, if the c-glide is present or not. Out of 60 reflections forbidden by the c-glide 33 have observed intensity. Again, you should use the reciprocal-space sections to check for the c-glide. However, do not use the h0l section! Due to the short b\* axis and large mosaic spread, this section contain "ghosts" from neighboring sections, and the systematic absences are obscured. Inspection of the 0kl and 2kl section shows clearly that the reflections of the type h0l: l=2n are absent, and c-glide is thus most likely present.*

*At this point we cannot decide, which of the choices Cc or C2/c is correct. Centrosymmetric space groups are, in general, more frequent, and we will use it as a first guess.*

Select C2/c; NEXT

*Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.*

Accept the space group in the standard setting; FINISH

*Symmetry is saved in file kankite.m50.*

## 5. Creating refinement reflection file

*In this step program creates file ttb.m90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*

Proceed with the wizard, leaving all settings default

*The internal R-value decreased from 13.21% To 10.02% due to the exclusion of the systematically absent reflections.*

## 6. Structure Solution Wizard

*OK to close the information window and start the wizard*

*[On the screen: window of Structure solution]*

*Structure solution wizard can be executed separately through "Run → Solution". Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*

In "Formula" textbox type the expected formula: Fe2 As2 O15

In "Formula units" textbox type 4

*This value gives a reasonable value of density: 3.01 g/cm3*

Click the checkbox next to "Use a specific random seed" and leave the value 111.

*The specific random seed is used just to guarantee reproducibility of the results. For standard work, random seed need not be defined.*

Click the radio button "EDMA – take as it is"

*EDMA is an external program for interpretation of electron densities. It can take the chemical formula and interpret the density using this formula.*

Leave other settings default; OK

*[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]*

*Superflip performed ten solution attempts. Check the space groups derived by Superflip from each of the attempts. The most frequently proposed space group is Cc (eight of ten attempts). Inversion center and two-fold axis have much worse symmetry agreement factors. It is likely that the correct space group is Cc and not C2/c.*

Press CLOSE to leave the listing

Press "Discard the result"

Back in the structure solution window, change the space group to Cc and recreate the refinement reflection file

OK

*[On the screen: Superflip runs again, this time creating output in Cc. EDMA is used to interpret the density]*

"Accept the result"

*The result is a file kankite.m40 with atoms of the structure model.*

7. **Verification and completion of the structure solution**

   Go to "Contour → New plot → OK → Run 3D maps"

   *VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Try to recognize the structural motifs. The main expected motifs are $AsO_4$ tetrahedra and $FeO_6$ octahedra. The analysis will be simpler if you display the bonds between atoms:*

   Go to Edit → Bonds, and set up the options according to this screenshot:
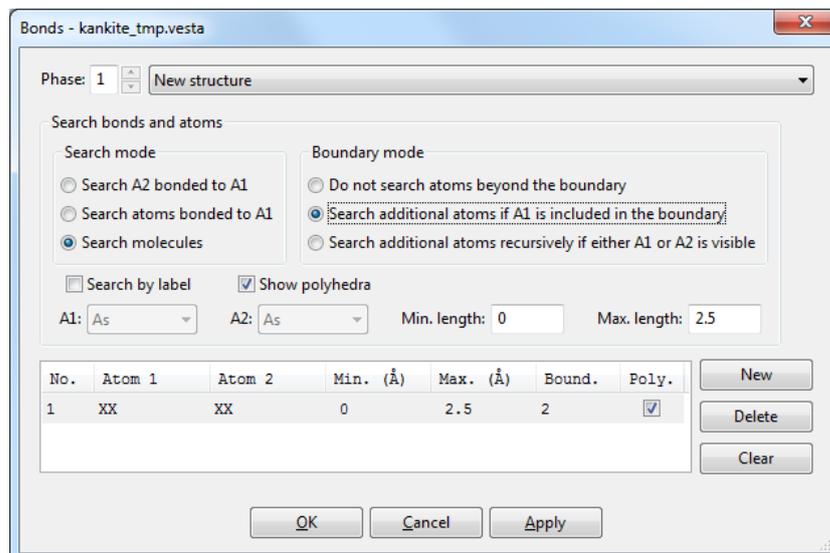
*It is also useful to show only positive isosurfaces (Properties > Isosurfaces). Viewing the structure solution in VESTA has the advantage that you can directly check, if the raw density was correctly interpreted. In this case, atom As1 should be Fe, and Fe1 should be As. You may inspect the model also in Diamond. You should come to the conclusion that the model is almost complete. Two oxygen atoms are missing (around Fe2) and five oxygen atoms in the list (O10, O11, O12, O14 and O15) are ghost peaks.*

**8. Delete ghost atoms and change atomic types**
Double click icon Edit atoms
Select atoms O10, O11, O12, O14 and O15 (Click while holding Ctrl)
"Action → Delete atoms → Yes to all"
Select atom As1
"Action → Edit/Define atoms → Type → Fe"
Repeat the assignment process to atom Fe1 (type As)
OK
"Select all → Action → Rename selected atoms to "atom_type"+number"
 OK; Yes

**9. Structure refinement**
*[On the screen: basic window of Jana]*
Right-click the icon of Refine.
*[On the screen: refinement options]*
Set Number of cycles to 100; OK Choose "Yes+start"
*Refinement converges to an R value about 19%*

**10. Adding the missing atom[On the screen: basic window of Jana]**
Right click the icon Fourier
On the first card, select F(obs)-F(calc) – difference Fourier
Modify the setting on the second card to agree with this screenshot:
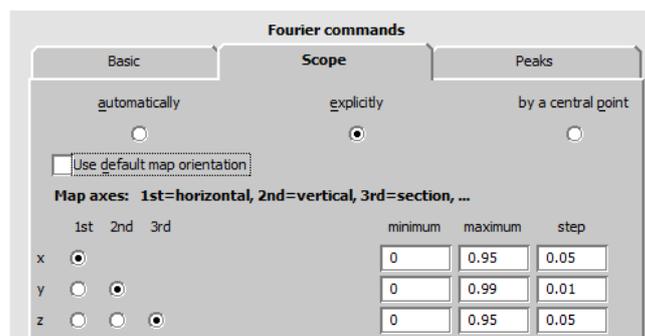
OK; Yes+Start; No; No

*Jana just calculated a difference Fourier map.*

View the map in VESTA: "Contour → New plot → OK → Run 3D maps"

*You will see that the difference map is dominated by two positive peaks around the atom Fe2. These maxima correspond to the two missing atoms.*

Close VESTA and return to the main window of Jana2006

"Parameters → Atoms → New → Peaks from last Fourier calculation"

*A list of maxima found in the density is displayed. In the right pane, the distances of the maximum to the nearest atoms are displayed. The first two maxima correspond to the missing oxygen – they have the right distance to Fe2.*

Select Max1, click "Include selected peak", type O* in the field for name; OK;

Select Max2, click "Include selected peak", type O* in the field for name; OK;

Finish; Yes to include the new atoms in the model

Double click the icon Refine to refine the completed model.

*The structure refines to 15.89%. At this moment the refinement is finished. It is possible to refine anisotropic ADP parameter of the atoms. The R-value drops to 11.63%, but the ADPs are unrealistic – they have an extremely large component along **b**. This effect comes from the data quality – reflections with high k-index are systematically weakened.*

## 11. Identification of OH and H2O groups

*The data quality is by far not good enough to see directly the hydrogen atoms. However, we can estimate the positions of OH and $H_2O$ groups by the coordination and bond-valence sums of the oxygen atoms.*

Right-click icon Dist

Click button "Define coefficients for bond valences"

Define pair of atoms Fe, O; Click "From file → Fe3+ O2- (fourth in the list) → OK → Add"

Repeat for pair As – O, select the entry As5+ O2- from the list → OK → Add

OK;

*[On screen: main dialog window of the Dist module]*

Uncheck checkbox "dmax derived from atomic radii and typical distances"

OK; Yes+start; Yes to open the listing

*At the end of the listing you will find the following table of bond-valence sums:*

```
Bond valence for : Fe1 2.48(6)
Bond valence for : As1 4.32(12)
Bond valence for : As2 5.46(19)
Bond valence for : Fe2 2.33(6)
Bond valence for : O1 1.42(8)
Bond valence for : O2 1.86(8)
Bond valence for : O3 1.53(7)
```

```
Bond valence for : O4 1.46(4)
Bond valence for : O5 2.08(15)
Bond valence for : O6 0.99(5)
Bond valence for : O7 0.35(3)
Bond valence for : O8 0.90(5)
Bond valence for : O9 0.40(2)
Bond valence for : O10 1.53(5)
Bond valence for : O11 0.326(18)
Bond valence for : O12 1.75(8)
```

*You can see three types of oxygen atoms. Most of oxygens have bond-valence sums above 1.4, two around 0.9 (O6 and O8) and three very low – below 0.5 (O7, O9, O11). O6 and O8 correspond to OH groups, and O7, O9, O11 are water molecules coordinating Fe atoms. This is a view of the structure with OH and H2O groups labeled:*
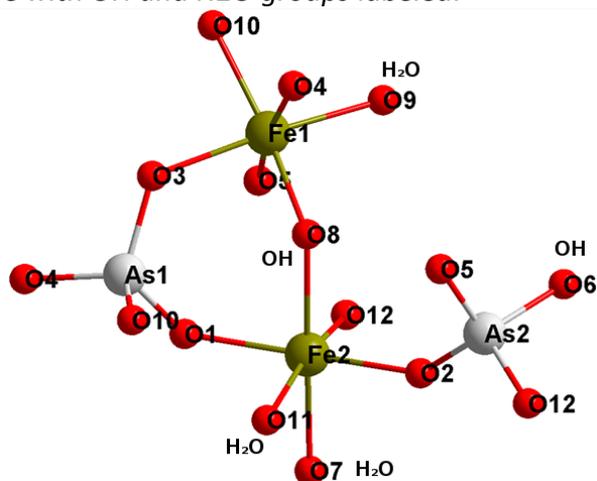


*Thus, the published formula is not correct. The correct formula is*
*$Fe_2(OH)(AsO_4)(AsO_3OH).3H_2O$ or $Fe_2As_2O_7(OH)_2.3H_2O$*

# Example 13.3: Orthopyroxene

**Refinement of atomic occupancies from electron diffraction data using dynamical diffraction theory**

**Revised: October 2015**

## Background information:

Orthopyroxene (opx) is a rockforming mineral – iron-magnesium silicate $(Fe,Mg)_2Si_2O_6$, P$bca$, a=18.268, b= 8.868, c=5.202. It contains two symmetry-independent octahedral sites with Mg and Fe. The distribution of Mg and Fe in these two sites depends on the crystallization conditions, and it can therefore be used to infer information about the formation of the rock.

Orthopyroxene often forms only microcrystalline aggregates or intergrowths with other minerals. It is thus desirable to determine the occupancies of Fe and Mg on the two sites from individual micro- or nano-crystals of opx.

Electron diffraction data were measured on FEI Tecnai $G^2$ 20 operated at 200 kV with precession device DigiStar.

Input data: opx_001.tif: the experimental diffraction pattern, zone axis [001] of orthopyroxene.

> opx_001.pts: input file for PETS with experimental information
> opx_xray.cif: cif file with the model of the opx structure refined against x-ray data set.
> opx_001_dyn_start.cif_pets: result of data processing with PETS. This file is provided so that this example can be solved without the data processing part.

1. ***Data reduction using PETS***

   *File opx_001.pts contains instructions for PETS. Open the file and check the instructions. Compared to tomographic data, the input is much simpler in this case – the tilt-axis azimuth need not be defined, and the orientation angles can be set to 0.*

   *Note the line "background 32768". The tif file was obtained by conversion of a dm3 file (Digital Micrograph format). By default, the zero level of such file is at $2^{15}=32768$. The byword background 32768 corrects for this shifted zero level.*

   Start PETS with the file opx_001.pts
   Type p[Enter]
   *PETS will extract peaks from the image and save them in file opx_001.cor. Check the image shown by ImageJ. The central part is shown here:*
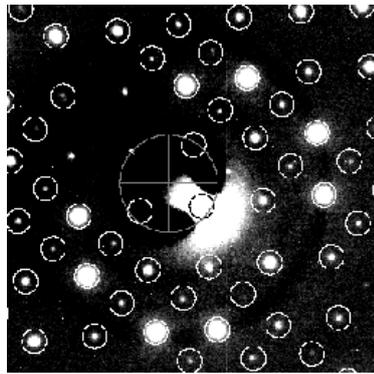
*The encircled black cross shows the predicted position of the primary beam. Obviously, the automatic location of the center failed. We have to provide the center explicitly.*

Type q[Enter] to quit PETS.

Open the file opx_001.tif in ImageJ

Go to "Image → Properties" and change the values of Pixel width and Pixel height from 0.005 to 1.

Read the coordinates of the direct beam.

*The coordinates are close to 1990 1393*

Close ImageJ

Open file opx_001.pts in a plain-text editor (e.g. Notepad) and modify the line "center AUTO" to "center 1990 1393"

Save and close opx_001.pts.

Start PETS again with the updated file opx_001.pts

Type p[Enter]

*This time the center is located properly.*

*We will not use the peak-processing functions of PETS, because the amount of data is not sufficient. We will use directly the file opx_001.cor produced by PETS after the peak hunting.*

Start Jana2006

Go to "Tools → Graphics → Indexing"

Locate the example directory and select file opx_001.cor; OK

*You will see a plot of located peaks. The peaks form only a 2D layer. We have to use a 2D indexing option of the indexing plugin to index the layer.*

Click the button "2d section ON"

*Jana2006 finds the best plane through the peaks, and fixes the view on this plane.*

Click on the "indexing" button ⃞ in the lower left corner.

*Now if you drag the mouse with left button pressed, you will move an arrow on the screen. By this arrow, you should locate a reflection, of which you know the indices. This is a little tricky, because the plane [001] contains systematically absent reflections (due to the a-glide), and, in addition, a pseudo n-glide. You should locate the vector **a** according to the following screenshot. Note that reflection 12 0 0 was selected:*
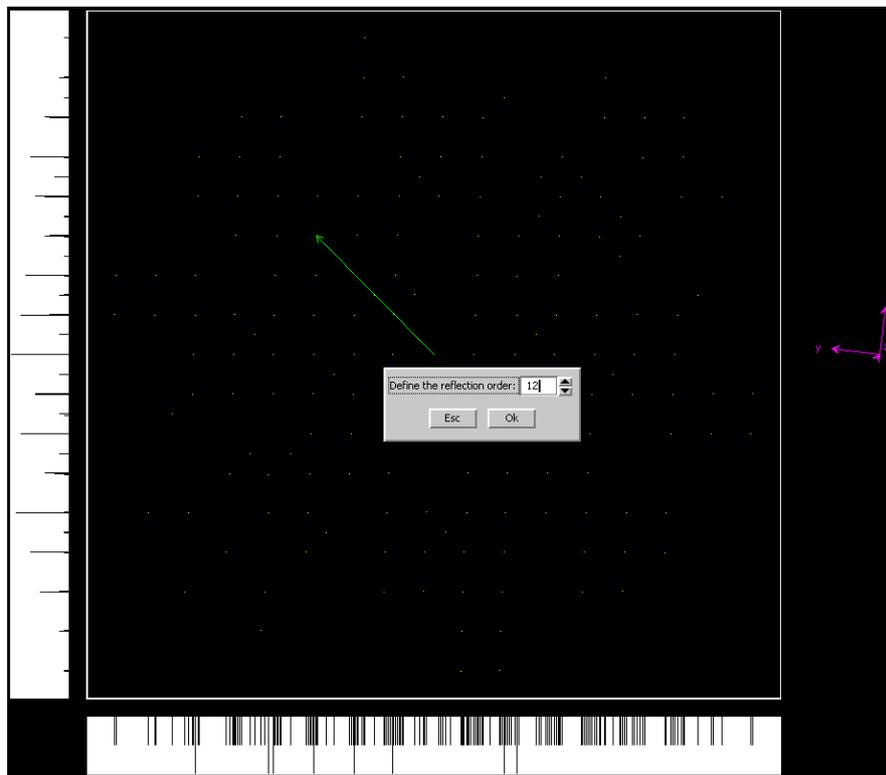
*Similarly, vector **b** is located as follows (reflection 0 6 0 selected, hence order 6):*
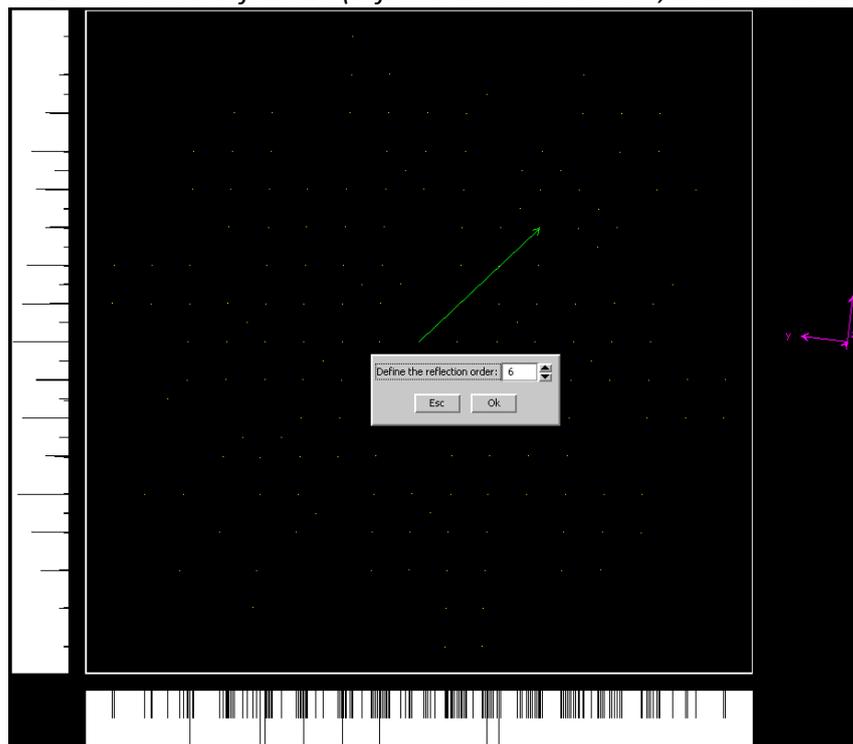


*If you get lost, open the original diffraction pattern in ImageJ and compare the distribution of reflections with the peak positions in Jana2006.*

*Once the two vectors are defined, the selected 2D cell can be refined:*

"Refine cell → Refine UB+cell"

*You should obtain a result very close to the following 2D cell:*

OK to quit the refinement dialog

*This cell must be converted to a 3D cell to produce an orientation matrix:*

Click "2d section OFF"

*A dialog for the 2D to 3D transformation appears*

Type the cell parameters: 18.268 8.868 5.202 90 90 90

In the line labeled "(h,k,l) for 2d axial direction #1" type 1 0 0

In the line labeled "(h,k,l) for 2d axial direction #2" type 0 1 0

Click "Calculate"

*You should obtain the following result:*



OK; Quit

*Now you have an orientation matrix that you can read back to PETS, and extract intensities.*

*[On screen: window with PETS, main menu]*

Type u[Enter]

*PETS read in the orientation matrix calculated by Jana2006.*

Type d[Enter]

*D stands for "integration for **d**ynamical refinement". PETS extracts all intensities up to d\*=1.4, and produces file opx_001_dyn.cif_pets.*

2. **Import structure in jana2006**
3. *Important!* *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file opx_001_dyn.cif_pets that you just created, but use the file opx_001_dyn_start.cif_pets provided with the example files. Before continuing, make a copy of the file and name it opx_001_dyn.cif_pets. Using your own cif_pets file is also possible, but your results may slightly differ from the results described in this tutorial.*
4. *Now we will import the file opx_001_dyn.cif_pets in Jana2006.*

Start Jana2006

"File → Structure → New"

In the left pane, locate the example directory

In the right pane, double click the label opx_001_dyn
Select "Single crystal: known diffractometer format"; NEXT
Select "Pets – electron diffractometer"; NEXT; NEXT; NEXT; OK; NEXT; FINISH; OK; Yes
*You have just imported the data from cif_pets using default options. At this point Jana offers symmetry determination wizard, but we will escape the standard procedure, which is not useful for us.*
Cancel; Cancel to cancel the symmetry wizard and the production of reflection file.
*Now we have to import the structure model from the provided CIF file:*
"File → Import model from → CIF"
Locate file opx_001.cif and double click it
OK to accept the new model
Cancel to avoid production of the refinement reflection file
*If we accepted to produce the refinement reflection file at this stage, it would be prepared for kinematical refinement. We will use dynamical refinement.*

5. ***Setting up dynamical refinement***
*[On screen: Main windows of Jana2006]*
"Parameters → Electron diffraction"
*You should see this dialog:*



*This dialog contains experimental information relevant for the dynamical refinement, and information about the zone axis (or several zone axes, if there are more zone axes imported). Most options are now blank, because the reflection file for dynamical refinement has not yet been prepared.*
Check the box next to "Use dynamic approach"
OK to create refinement reflection file
Follow the wizard and accept default choices
*[On screen: Electron diffraction dialog]*
*Now we have to find initial values for the sample thickness, scale factor and orientation. As a first quick check, we will calculate only the thickness curve, using fixed orientation. This*

*calculation is much faster that the optimization of orientation, and it provides first estimated of the data quality.*

Click "except of scale optimize also: Thickness → Run optimization"

*Jana2006 generates reflections and calls Dyngo.exe. Dyngo.exe calculates the reflection intensities using dynamical diffraction theory.*

*[On screen: Electron diffraction dialog]*

*Next to the indication of the zone number you see the best R-value: R(all)=8.1174%. This is a very promising value and indicates that already now the fit of the model to the data is quite good.*

Click "Show thickness plots"

*You should obtain the following plot:*



R-factor/Thickess for zone #1
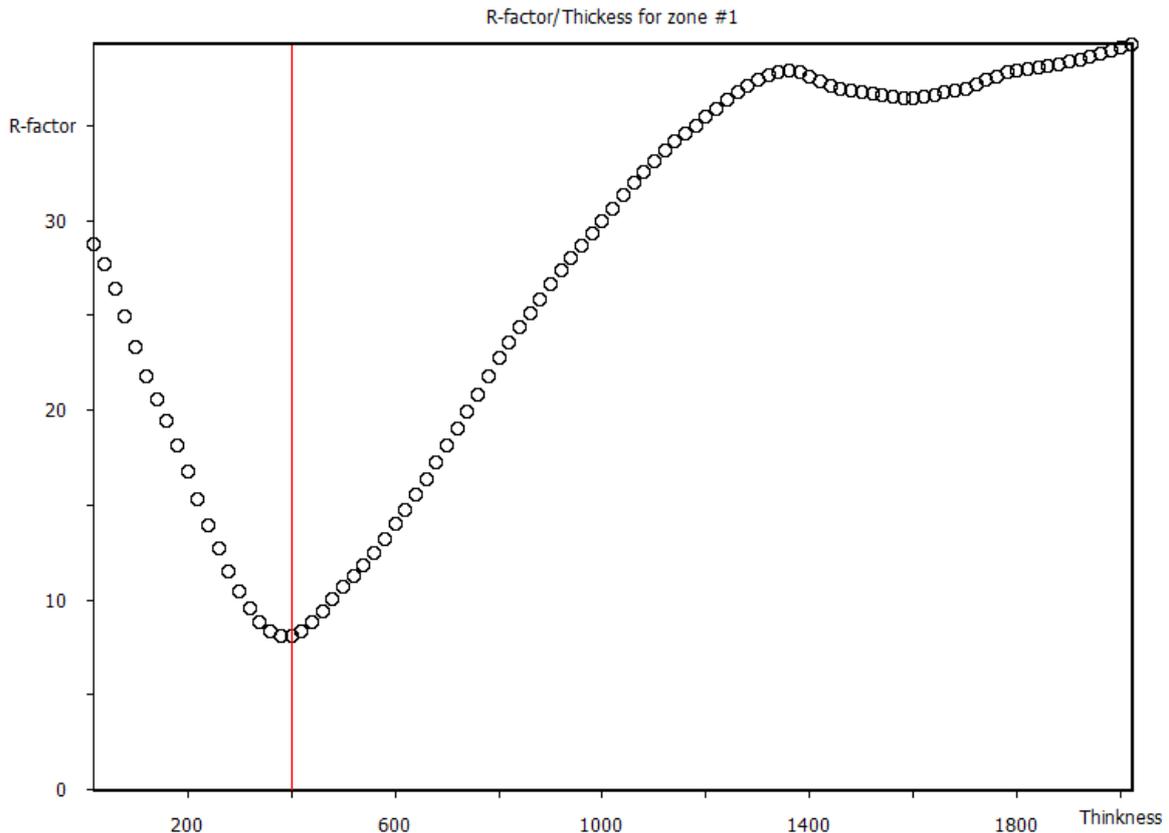
*This plot shows a clearly defined minimum at the thickness 400 Å. This together with the low R-value shows that the starting point for the refinement is reasonable.*

Quit the display of the thickness plot

Click "except of scale optimize also: orientation → Run optimization"

*The orientation of the experimental pattern is never perfect. Dyngo finds the parameters of the misalignment of the zone axis from the perfect orientation predicted by the orientation matrix. This calculation requires repeated evaluations of reflection intensities and may take some time. You may follow the progress of the simplex algorithm in the window of Dyngo. After the optimization, the zone axis parameters look like this:*

| EDScale | 2680.311 | ✓ | EDThick | 400 | ✓ |
| EDPhi | 180 | | EDTheta | 0.15 | |

*The R-value decreased only slightly to 7.9963%. Value 0.15 of EDtheta means that the diffraction pattern was recorded at an angle of 0.15 degrees away from the perfect*

*orientation. EDPhi is the azimuth of the tilt axis. Given the large precession angle, this value is within the precision of the method, and means that the pattern was essentially perfectly oriented.*

Quit the Electron diffraction dialog and confirm changes in the m42 file.

6. ***Dynamical least-squares refinement***
   *We will first refine only the scale and thickness.*
   "Right-click Refine → Various → Fixed commands"
   In the line labeled "Atoms/parameters" type * (star)
   Click the arrow next to "Add"
   *You have fixed all structure parameters of all atoms. An exception is the atomic occupancy, which is not fixed by this command, but we did not explicitly allow its refinement either, and therefore the occupancies will remain, for the moment, fixed, too.*
   OK; OK; Yes+Start
   *Refinement converges smoothly to an R-value of 7.28%.*
   *Now we will allow the refinement of occupancies.*
   "Right-click Refine → Various → Restrictions"
   In the line labeled Atoms/molecules type "Fe1 Mg1"
   Click radio button next to "Occupancies: keep overall sum"
   Click the arrow next to "Add"
   Repeat the action for the pair "Fe2 Mg2"
   OK; OK; Yes to save the changes, but do not start the refinement
   *We have now restricted the occupancies of the two atoms to sum to 1. Only one occupancy for each pair will be refined.*
   *Now we have to allow the refinement of occupancies of Fe1 and Fe2:*
   Double click the icon "Edit atoms"
   Double click atom Fe1
   On the card "Edit" check the box next to the parameter "ai"; OK
   Repeat for atom Fe2
   OK to close the Edit atoms dialog
   Double click Refine to start refinement
   *Refinement converges smoothly. R-value decreases only very little to 7.25%.*
   *Refined occupancies are o(Fe1)=0.050(11), o(Fe2)=0.52(11). The occupancies refined from the same sample with x-ray data are o(Fe1)=0.035(3), o(Fe2)=0.552(3). In general, the refinement against electron diffraction data is in a good agreement with the refinement against bulk material using x-rays.*
   *If you wish, you may convince yourself that even from more distant starting values of the occupancies the refinement will converge to the same values. You may, however, need to use smaller damping factor (right-click Refine → Damping factor) to avoid oscillation or locking in a false minimum, if you start from too distant values.*

7. ***Kinematical least-squares refinement***
   *We will perform a kinematical refinement for comparison.*
   *[On screen: main window of Jana2006]*
   "File → Structure → Save as"
   Type "opx_001_kin" in the window under the right pane; OK; Yes
   *We saved the structure under another name to preserve the dynamical refinement.*

"Parameters → Electron diffraction"

Uncheck the box next to "Use dynamic approach"; Yes to save changes

Accept the proposal to recreate the refinement file and follow the instructions. Leave all settings default.

Double click "Refine" to start refinement

*With a few clicks we switched from dynamical to kinematical refinement. The refinement R-value is 31.03%, and the refined occupancies are o(Fe1)=0.280(87) and o(Fe2)=0.435(90).*

# Example 13.4: Silicon

**Complete procedure from structure solution to dynamical structure refinement from three zone-axis patterns.**

**Revised 11 December 2013**

Input data: si_ZAPs.cif_pets: a cif_pets file containing the orientation matrix, positional angles and intensity information from three zone-axis patterns collected on the same sample – a wedge-shaped silicon single crystal. The file was obtained from raw diffraction patterns using the procedure analogical to example 13.1.

1. ***Import data to Jana2006***
   Start Jana2006
   "File → Structure → New"
   In the left pane, locate the example directory
   In the right pane, double click green label si_ZAPs
   Select "Single crystal: known diffractometer format"; NEXT
   Select "Pets – electron diffractometer"; NEXT; NEXT; NEXT; OK; NEXT; FINISH; OK; Yes
   *You have just imported the data from cif_pets using default options.*
   *As a next step Jana starts the symmetry determination wizard. The data set we have is not really complete, but we may nevertheless attempt to proceed with the wizard:*
   Next to start the wizard
   On the next screen, set up the tolerances according to this screenshot:
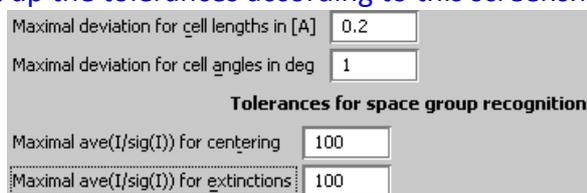
   | Maximal deviation for cell lengths in [A] | 0.2 |
   |---|---|
   | Maximal deviation for cell angles in deg | 1 |
   | **Tolerances for space group recognition:** | |
   | Maximal ave(I/sig(I)) for centering | 100 |
   | Maximal ave(I/sig(I)) for extinctions | 100 |

   Next; OK;
   *You now look at a table of $R_{int}$ values for various Laue classes. The cubic Laue classes have acceptable $R_{int}$ values, and there is little doubt the structure is indeed cubic.*
   Select Laue class m-3m; Next
   *The data were already integrated assuming F-centering, therefore there are zero reflections matching the F-centering absences in the data set.*
   Select centering F; Next
   *On the next screen a list of possible space groups is presented. For the space group Fd-3m, 7 out of 24 forbidden reflections have $I>3\sigma(I)$. However, looking at the details (click the button "Details") you will find that these reflections are in fact only two - 0 0 2 and 0 0 6. The d-glide is thus likely to be present. Indeed, the space group of silicon is Fd-3m.*
   Select "Fd-3m"; Next; Finish
   *In the next step we prepare a "standard" reflection file suitable for structure solution.*
   Next; OK; OK
   *[On screen: the window with three radio buttons for the choice of the handling of scales]*
   *Jana treats can data from each zone axis on a separate scale. For the structure solution and kinematical refinement, we will, however, assume that the data are on the same scale. The number of common reflections is insufficient to determine a reliable common scale.*

Select "Ignore scale flags"; Next; Next; OK; Finish

2. ***Structure solution and kinematical refinement***

*[On screen: Information window explaining that the next step is structure solution]*
OK to open the structure solution dialog
Type Si in the dialog box for formula; change the number of formula units to 8
Leave all settings default
OK to start solution by Superflip
*Superflip runs and produces a structure solution.*
When Superflip exits, accept the solution
Plot structure in Diamond to make sure it has been correctly solved
Right-click Refine; change number of cycles to 100; OK; Yes+start
*Jana2006 refines the structure using kinematical calculation of diffracted intensities. The structure refines to the following values (note that there are only 13 symmetry independent reflections!):*

```
R factors : [13=13+0/2],   Damping factor:  1.0000
GOF(obs)= 45.83   GOF(all)= 45.83
R(obs)= 23.25    wR(obs)= 41.88    R(all)= 23.25    wR(all)= 41.88
Last wR(all): 49.75 46.57 44.61 43.45 42.29 41.98 41.90 41.88
Maximum change/s.u. :   0.0304 for scale1
```

Open the refinement listing (Edit → View of Refine) and check the statistics.
*The displacement parameter of silicon refines to -0.0106.*

3. ***Origin shift***

*The default origin of the space group Fd-3m is at the point -43m, which does not contain inversion center. For the dynamical refinement it is desirable to have the origin in the inversion center, if possible. We will now shift the origin of the unit cell to the inversion center:*
*[On screen: Main window of Jana2006]*
"Tools → Transformations → Origin shift"
Type "1/8" in all three fields; OK

4. ***Initiation of dynamical refinement***

*[On screen: Main window of Jana2006]*
*The displacement parameter of silicon did not refine to physically meaningful value. Before initiating the dynamical refinement it is good to reset it to a more correct value. It is not strictly necessary in this example, but it is generally a good practice.*
Double click the icon Edit atoms
Double click Si1
On the card Edit, change Uiso to 0.005
OK; OK; Yes
*[On screen: Main window of Jana2006]*
"Parameters → Electron diffraction"

*You will see the following dialog:*



*Default excitation error is too small for the current data – it must be increased:*

Change Maximal excitation error to 0.03

Check the box next to "Use dynamic approach"

OK to create refinement reflection file

Follow the wizard and accept default choices

*[On screen: Electron diffraction dialog]*

*Now we have to find initial values for the sample thickness, scale factors and orientations of all three zones. As a first quick check, if the data quality is acceptable, we will calculate only the thickness curve, using fixed orientation. This calculation is much faster that the optimization of orientation, and it provides a first estimate of the data quality.*

Click "Optimize thickness and scale"

*Jana2006 generates reflections and calls Dyngo.exe for each zone separately. Dyngo.exe calculates the reflection intensities using dynamical diffraction theory. Wait until Dyngo.exe terminates.*

*[On screen: Electron diffraction dialog]*

Click "Show thickness plots"

*Go through the thickness plots. You should see three curves with more-or-less well defined minima between 500 and 1000 Å. The best R-values are around 15%. This is a good start, but it is still not satisfactory. It is necessary to optimize the orientations:*

Quit the display of the thickness plot

Click "optimize thickness, scale and orientation"

*This option optimizes all three parameters simultaneously, using a simplex algorithm. This calculation requires repeated evaluations of reflection intensities and is thus much longer that just the thickness optimization. Wait unil all three runs of Dyngo finish.*

*[On screen: Electron diffraction dialog]*

*Check the refined tilt angles. EDtheta is the azimuth of the tilt, EDphi is the amplitude. You will see that the refined misorientations range between 0.13 and 0.39 degrees – very reasonable values.*

Click "Optimize thickness and scale"

*Repeat the thickness orientation to view the updated thickness curves. When viewing the thickness curves again, you will see much better defined minima.*
*However, for zone 3 you will find the following curve:*
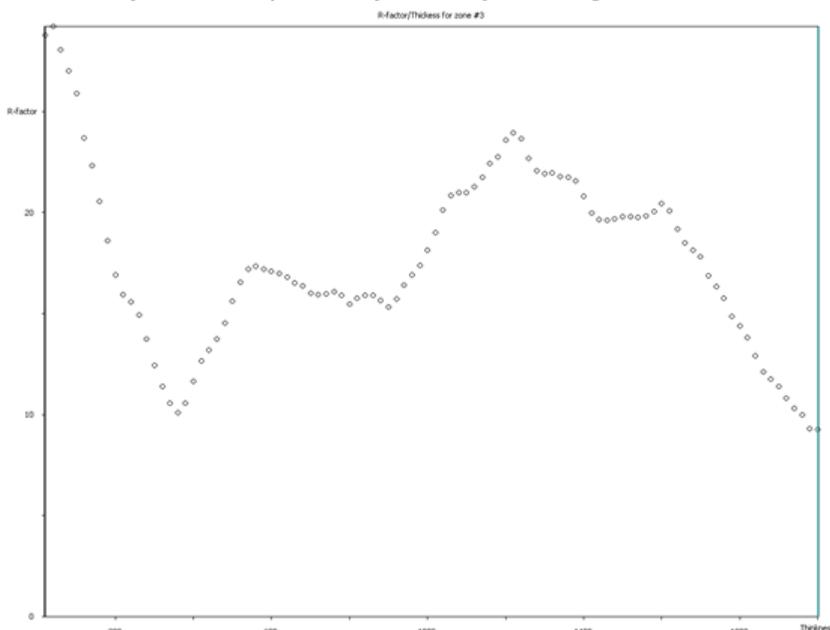


*There is a clear and reasonable minimum at t=350 Å, but the lowest R-value is found for the thickness of 2000 Å. It is necessary to manually reset the thickness to 350 Å before the refinement.*

Quit; Locate zone 3 and set the thickness according to the following screenshot:



*The data are now checked and ready for least-squares refinement.*
OK; Yes to exit the Electron diffraction dialog

5. **Structure refinement**
   *[On screen: Main window of Jana2006]*
   *The dynamical refinement tends to be unstable with default damping factor, it is thus better to decrease it:*
   Right click "Refine"
   Set damping factor to 0.2
   OK; Yes+Start
   *The dynamical refinement starts. You may follow the progress in the window of Jana2006. You may also interrupt the refinement or change the parameters the same way as for the standard refinement.*

   *The refinement converges after 21 cycles to R(obs)=6.8%. (Compare with 23% obtained with kinematical refinement).*

*Uiso(Si1) refines to -0.0010(19). This is a much better value than the result of kinematical refinement, but it is, of course, not satisfactory. A detailed investigation shows that even if only one zone-axis at a time is used for the refinement, Uiso(Si1) remains slightly negative. It is thus probably a problem related to the experiment. Unfortunately, the sample used for the data collection was damaged, and we could not remeasure the data. Previous measurements on the same samples yielded correct Uiso around 0.005, but these measurements were single-zone only, and they are thus not so well suited for demonstration of the complete procedure.*

*By repeating the optimization of orientation and rerefining the structure, the R-value can be decreased even more to 5.0%. However, Uiso(Si1) remains negative.*

# Example 13.5: Ni2Si

**Solution of nickel silicide Ni2Si by PEDT (precession electron diffraction tomography) data. Complete procedure from data reduction to structure refinement using the dynamical approach.**

<span style="color:red">**Revised: October 2015**</span>

## Chemical formula: Ni2Si

Electron diffraction data was measured on a transmission electron microscope Philips CM120 with a precession divice DigiStar. Accelerating voltage of 120 kV.

Input data:

> directory dp-150 with the set of experimental data (reflection images)
>
> directory img with the set of experimental images from the crystal tilt
>
> Ni2Si.pts: input file for PETS
>
> Ni2Si_start.cif_pets: result of the data processing. This file is provided so that this example can be solved without the data processing part, and to warrant reproducibility of the solution and refinement part. File Ni2Si.cif_pets will be the output of the data reduction.
>
> Ni2Si_start_dyn.cif_pets: result of the data processing for dynamical refinement. This file is provided so that the dynamical approach can be used without the processing part, and to warrant the reproducibility of the refinement.

1. *Preparing input file for PETS*

   *Make sure you correctly installed PETS and ImageJ. Check Chapter "Installation notes" (page 7) for details. File Ni2Si.pts is the input to PETS. The file was prepared by the software used for the collection of the diffraction data, and most entries have been filled in. You have to enter two parameters: the information about beam stop and the size of reflections.*

   <span style="color:blue">Open file Ni2Si.pts in any plain-text editor (notepad, wordpad, notepad++, vim,…)</span>

   <span style="color:blue">Open file dp-150/001.tif in ImageJ</span>

   <span style="color:blue">In ImageJ go to "Image → Adjust → Brightness and Contrast"</span>

   <span style="color:blue">Click the button "Auto" to adjust the contrast</span>

   <span style="color:blue">Go to "Image → Properties" and change the values of Pixel width and Pixel height from 0.005 to 1</span>

   <span style="color:blue">Measure the diameter of the reflections on the image</span>

   *There are several ways to measure the diameter of the reflections, but the simplest and sufficient way is to place the cursor to the left of the reflection, remember or write down the x-coordinate, then place the cursor to the right of the reflection, again read the x-coordinate and subtract the two coordinates. The diameter should be large enough to encompass most of the reflections, but not too large, to prevent overlaps. Do not take into account the broad, weak TDS scattering around the strongest reflections! That would give you a too large diameter. In this case, value 25 is a good choice.*

   <span style="color:blue">In Ni2Si.pts, change the line "reflectionsize ??" to "reflectionsize 25"</span>

   <span style="color:blue">This measurement was performed without beamstop (microdiffraction). In Ni2Si.pts change the line "beamstop ??(yes/no)" to "beamstop no"</span>

2. ***Run PETS and prepare files for indexing***
Make sure ImageJ is not running. If it is, close ImageJ.
Run PETS with the file Ni2Si.pts

*There are several ways of running PETS. See installation notes for detailed description. A window with initial menu of PETS opens, and ImageJ starts displaying a black image with a white circle.*

In the window of PETS, type p[Enter]

*The peak hunting procedure starts. ImageJ sequentially displays diffraction images with circles at points found by PETS as significant peaks. Note that PETS follows the position of the primary beam, and corrects for small shifts. Note also the significant diffuse streaks. Although they seem very intense, it is just due to the enhanced contrast of the images. Compared to the Bragg intensities, the diffuse streaks are weak and do not disturb the structure solution.*

*At the end, the evolution of the x- and y-coordinates of the estimated primary-beam position is displayed (b&w inverted):*



*[On screen: main menu of PETS]*

type r[Enter]

*The next step after peak hunting is the refinement of the azimuthal angle between the horizontal axis (x axis of the micrograph) and the projection of the tilt axis. This angle depends on experimental setup, and needs to be refined for each data set. ImageJ displays a cylindrical projection of the difference space of the extracted peak positions. A correct azimuthal angle refinement results in the image containing sharp peaks aligned on sinusoidal curves. This step provides a first estimation of data quality. At the end of the refinement the omega angle should be close to 13°.*

*On the screen:*

```
Final values of the parameters:
omega : 13.165
```

*and see this image (b&w inverted):*
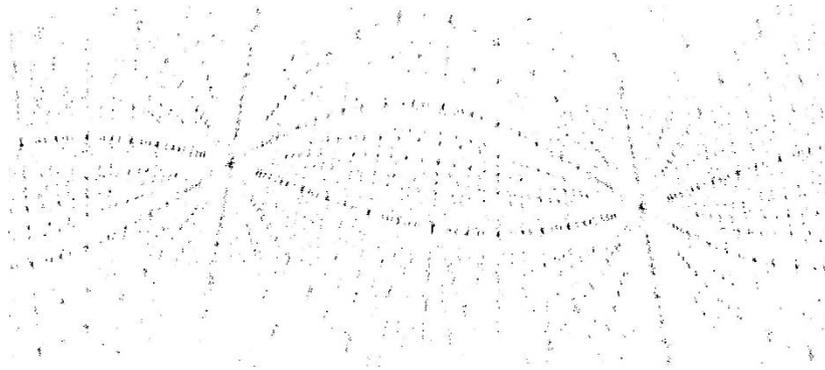
*[on screen: main menu of PETS]*

type a[Enter]

*PETS starts the analysis of the peak positions obtained in the peak hunting procedure. In the first step, distance distribution between peaks in the image plane is analyzed. A sorted plot of inter-peak distances is displayed (white curve on screen, black on the image below) with its derivative (grey curve):*



*For good quality data set, the white curve contains distinct steps, and, consequently, the grey curve has distinct peaks.*

Press Enter

*In the next step an autoconvolution of the diffraction pattern (difference space) is analyzed, and the groups of peaks in the autoconvolution (clusters) are replaced by the cluster centers. Again, a distance distribution is displayed, and clear-cut steps on the curve indicate a well-defined lattice.*

Press Enter

*Now the first step is finished and PETS prepared the files needed for unit cell indexing. Keep the window of PETS open, you will need it later!*

3. ***Indexing with Jana2006***

Start Jana2006

*By default, Jana2006 starts with the last structure open. It may be cumbersome to change the directory every time. You may create a dummy (empty) file Ni2Si.m40 in the example directory, and use the command "Open with" from the file-manager context menu to launch Jana2006 directly in this directory.*

"Tools → Graphics → Indexing"

Locate and open file Ni2Si.clust by double clicking it

*A 3D view of the reciprocal lattice opens. You can rotate the cloud by mouse. Use buttons*
⊕ *and* ▣ *to switch between free rotation and rotation around z-axis. Rotate with the lattice and try to determine the crystal system and the special axes of the lattice.*

*You should come to the conclusion that the lattice is orthorhombic. The following image shows the view along **c***:*
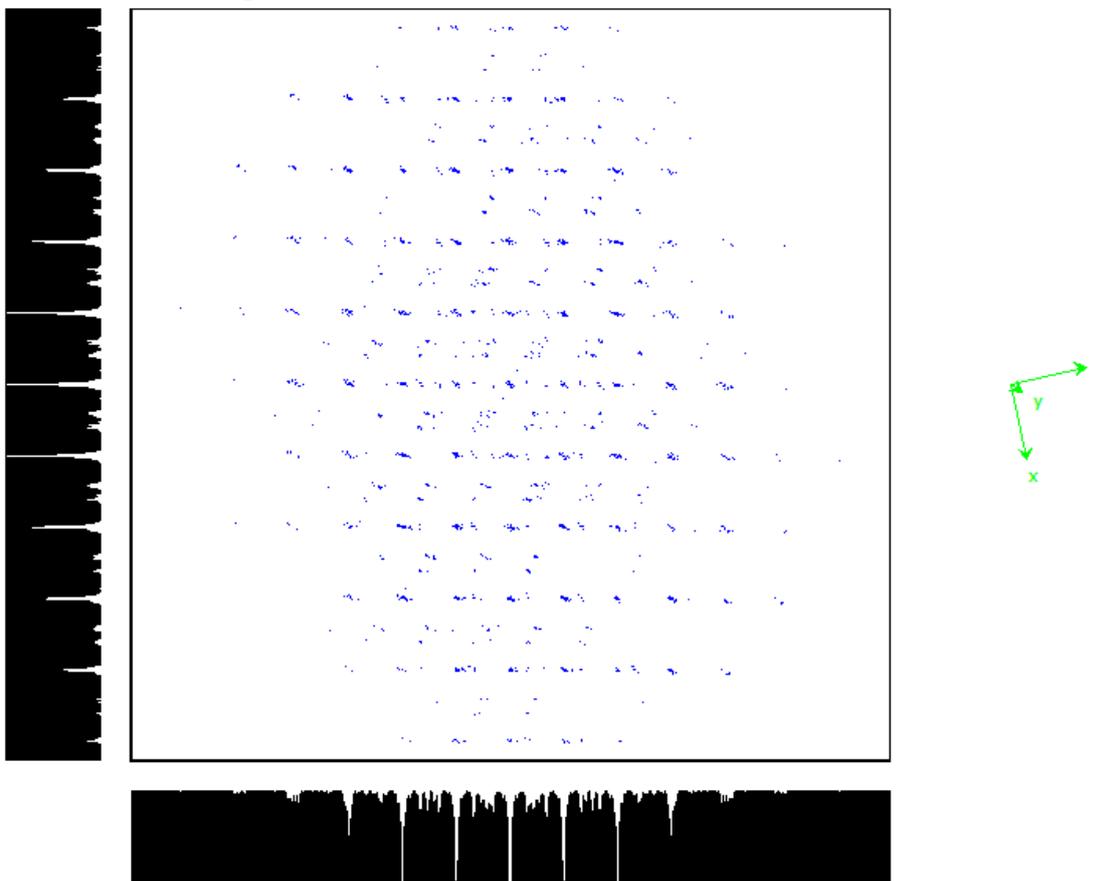


IMPORTANT: *before you continue, make sure you have the same orientation of the lattice on your computer as displayed on the picture above (check the direction of the axes on the right). If not, you may obtain slightly different results in the rest of the tutorial. While not necessarily wrong, it makes following this tutorial more difficult.*

Click the button ⇥ in the lower-left corner and choose the radio button for **a** vector setting (right to the ⇥ button ).

Click, hold the mouse button, and drag the marker to obtain the result on this image:
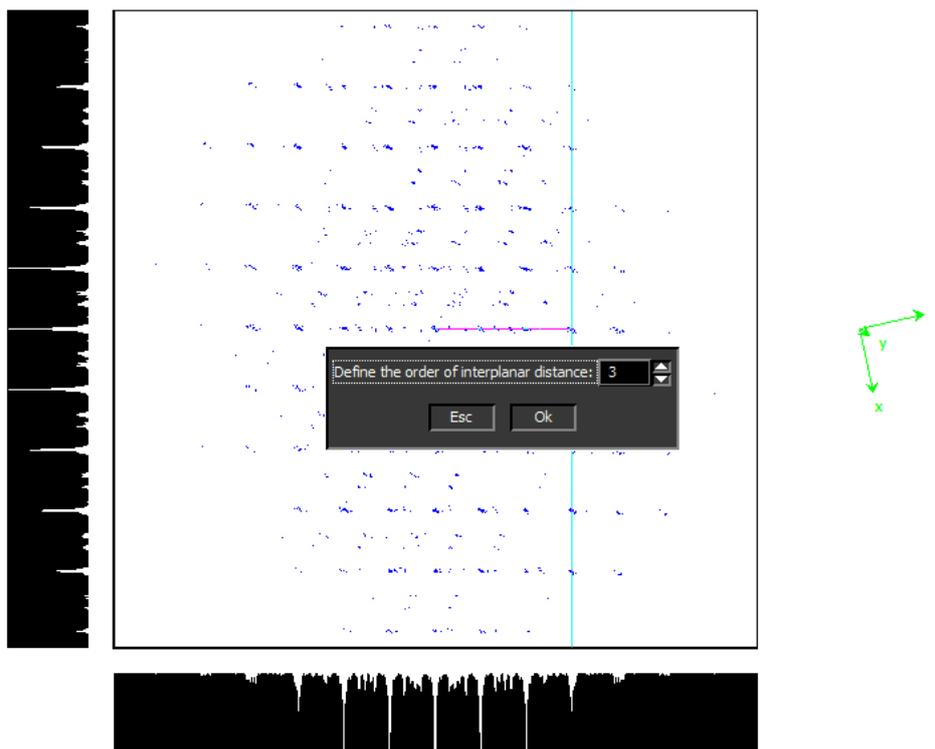
Set the order of the interplanar distance to 3.

*Note that the vertical red line is on the third vertical row of peaks. By this action you defined the direction and length of the (direct-space) basis vector **a**. Note: if you make a mistake and need to redo this step, make sure that the radio button **a** is selected bellow the main window, otherwise you will modify another cell parameter.*

Repeat the action, this time drag the marker up vertically to define the vector **b**.

*Vector **a** should have length close to 5.00 Å, vector **b** should have length close 3.73 Å, angles alpha and beta should be close to 90°.*

Click "View direction", select "a", Click OK

*The reciprocal space is now viewed along **a**, and **c** points up.*

In analogy to the procedure above, select the direction and length of the vector **c**.

*When you are finished, at the bottom of the window you should see cell parameters close (within a fraction of angstrom and degree) to these values:*



"Refine cell → Refine UB+cell"

*The orientation matrix is refined. Note that 44.9% of all peaks were indexed.*

OK; Quit

*The file Ni2Si.smr was now produced by Jana2006. This file contains the orientation matrix and the unit cell parameters.*

Close Jana2006

4. ***Integrate the intensities with PETS***

   Return to the window of PETS.

   Type u[Enter]

   *PETS reads the orienting matrix from the Ni2Si.smr file.*

   Type i[Enter]

*The integration procedure starts. ImageJ displays images with circles drawn at positions predicted from the orienting matrix. A small circle inside large circle means that a peak with I>3σ(I) was found. The small circle is located on the maximum of the intensity. A diamond means that a reflection is expected on upcoming frame(s), square indicates reflection present on previous frame(s).*

*When the integration finishes, files Ni2Si.cif_pets and Ni2Si.hkl are created. Both can be used to import the data into Jana and to solve the structure.*

5. ***Create reciprocal-space sections***
   In PETS, Type h[Enter]
   Type y[Enter]
   *You just asked PETS to scan all images and reconstruct sections through reciprocal space at planes hk0, hk1, hk2, h0l, h1l, h2l, 0kl, 1kl, 2kl. We will use these sections as an aid to determine the space group.*
   When the reconstruction finishes, type q[Enter] to close PETS. You may also close ImageJ.

6. ***Create new structure***
   *Important!* *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the file Ni2Si.cif_pets that you just created, but use the file Ni2Si_start.cif_pets provided with the example files (Rename the file to Ni2Si.cif_pets). Using your own cif_pets file is also possible, but your results may slightly differ from the results described in this tutorial.*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click Ni2Si
   *Right panel detects possible Jana files and shows one jobname for each group of files*

7. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Pets electron diffractometer"
   *The file name automatically changes to Ni2Si.cif_pets, which is a file produced by PETS containing all important information, including the list of intensities.*
   NEXT
   Leave all settings unchanged (note the wavelength of 120kV electrons!); NEXT
   Leave all settings unchanged; NEXT
   *The program reads 614 reflections from the file*
   OK
   For absorption correction select "None or done before importing"; NEXT
   FINISH; OK; YES to accept the data set
   *You just read in the cell parameters and the intensity list. If you do not have the data in the cif_pets format, you can read them in from a general hkl file using the option "reflection file corrected for LP and absorption" at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.*

8. ***Symmetry Wizard***

NEXT *to close the information window and start the symmetry wizard.*
*Symmetry Wizard can be started separately by "File → Reflection file → Make space group Test". The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances. Change the tolerances according to this screenshot:*

| Tolerances for crystal system recognition: | |
|---|---|
| Original cell parameters: 5.050 3.759 7.111 89.97 89.93 90.40 | |
| Maximal deviation for cell lengths in [A] | 0.2 |
| Maximal deviation for cell angles in deg | 0.5 |
| **Tolerances for space group recognition:** | |
| Maximal ave(I/sig(I)) for centering | 100 |
| Maximal ave(I/sig(I)) for extinctions | 100 |
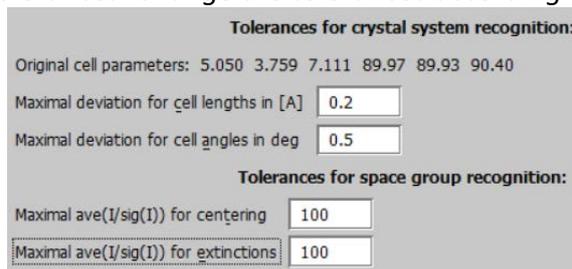
Leave other settings default; NEXT; OK
*[On the screen: Select Laue symmetry]*
Select orthorhombic Laue class mmm; NEXT
*The internal R-values would be rather high for x-rays, but are low for electron diffraction data.*
*[On the screen: Select cell centering]*
Select primitive unit cell; NEXT
*[On the screen: Select space group]*
*The window shows possible space groups.*
*The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.*
*It is difficult to select the correct space group. In particular, presence or absence of the glide is hard to asses, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effect. In this case the missing wedge leaves almost no information in* hk0 *reciprocal-space section. Open images 0kl and 1kl and check the intensities with k+l=2n+1 (which should be absent in the 0kl plane, but present in 1kl). You will see that despite some violations and the missing information in the center of the image, the n-glide absences are nevertheless clearly present in the 0kl plane in comparison with the 1kl plane. Space group with n-glide is thus a reasonable guess.*
*Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.*

Select Pnma; NEXT
Accept the space group in the standard setting; FINISH
*Symmetry is saved in file Ni2Si.m50.*

9. ***Creating refinement reflection file***
    *In this step program creates file Ni2Si.m90 containing the data set merged by symmetry and with discarded forbidden reflections. .m90 will be used for refinement.*
    Proceed with the wizard, leaving all settings default

10. ***Structure Solution Wizard***
    OK *to close the information window and start the solution wizard*
    *[On the screen: window of Structure solution] Structure solution wizard can be executed separately through "Run → Solution". Jana2006 does not contain solution procedures, it*

*calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*

In "Formula" textbox type just the list of chemical elements: Ni Si
*Superflip does not need information about chemical elements but they will be required for peak assignment based on electron density map calculated by Superflip. If Jana2006 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula, you may enter it and use EDMA for peak picking (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.*
Click the checkbox next to "Use a specific random seed" and enter the value 111.
Leave other settings default; "Run solution".
*The specific random seed is used just to guarantee reproducibility of the results. For standard work random seed need not be defined.*
*[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]*
*Superflip performed ten solution attempts, and picked the best one. Its characteristics are displayed near the bottom of the listing:*

```
Properties of the saved density:
  Run Rvalue Peaks Symm. Der.SG
  10   51.46  2.23  1.37  Pnma
```

*The space group proposed by Superflip is the same as our initial guess. The space-group selection is confirmed. Small symmetry agreement factor (column Symm.) indicated good quality of the solution. In cases of doubts or difficult problems, it is worth checking the statistics, especially the symmetry analysis, for each of the ten runs, and seeking for the most probable one.*
Press "Close" to leave the listing
Press "Accept last solution"
*The program creates file Ni2Si.m40 with atoms of the structure model*

11. ***Verification of the structure solution***
    Go to "Contour → New plot → OK → Run 3D maps"
    *VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Do you think it is complete?*
    *You should come to the conclusion that the model is correct, correct elements were assigned to all maxima.*
    Quit VESTA (do not save the file), quit Contour.

*You may now check the structure in Diamond to convince yourself that the structure is complete and chemically reasonable.*

12. **Initial Refinement**

*[On the screen: basic window of Jana]*

Right-click the icon of Refine.

*[On the screen: refinement options]*

Change the number of cycles to 100; OK

Choose "Yes+start"

*Refinement converges with R value about 11.07%. At this moment you may check the refinement listing with a lot of information about the refinement procedure and results. As you can see, the refinement is already very good for electron diffraction. R values are low, all the ADPs were positive definite. Refinement of anisotropic atomic displacements would decrease the residue value (R=8.79%), but the ratio reflections per parameter is already low.*

**The resulting structure**
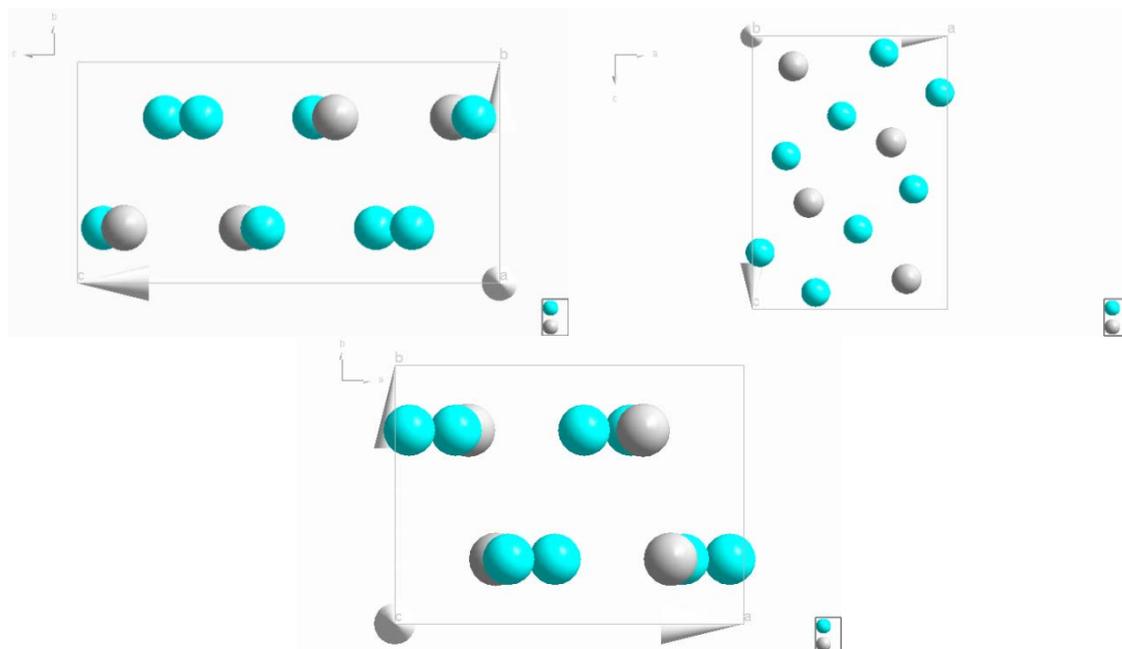


13. **Preparation of reflection file for the dynamical refinement**

Open Ni2Si.pts again. Type "o" to read the peak table, "u" to read the orientation matrix and "d" to integrate the intensities for the dynamical refinement.

*The integration for the dynamical refinement considers each diffraction image separately. The result is a list with the hkl indices, the measured intensity with the respective sigma and the number of the frame in which the intensity is present. PETS creates the file Ni2Si_dyn.cif_pets with all these information, which will be used in Jana2006. Note that the same hkl reflection might be present in several frames, with different intensity due to the multiple scattering relative to different crystal orientation and thickness at this condition.*

Quit PETS and go back to Jana2006. "Structure→Save as" and save a new structure Ni2Si_dyn for the dynamical refinement. Continue with the new structure.
*This will be the structure with the dynamical refinement*

"File→Reflection file→Import/modify the reflection file→Reimport"
*Again, if you want to be sure that you can exactly reproduce the following part of the tutorial, use the file Ni2Si_start_dyn.cif_pets provided with the example files. Rename this file to Ni2Si_dyn.cif_pets.*
Select the Ni2Si_dyn.cif_pets as the new reflection file. NEXT, NEXT, NEXT.
Now, Jana reads 4825 reflections from all the frames.
OK, NEXT, Finish, OK, Yes, Cancel.
*It is not necessary to average the intensities, because the intensities will be used independently for each frame during the dynamical refinement.*

14. ***Starting the dynamical refinement***
*[On the screen: basic window of Jana]*
"Parameters", "Electron diffraction".
*[On the screen: Parameters for electron diffraction data]*
Enable "Use dynamic approach". OK, NEXT, OK, OK, OK, Finish.
*Notice that now, 1673 reflections are symmetrically independent from the 4825 reflections read. From these, 12 were rejected because they violate the systematic extinctions. You can see these information in the file .rre. In this same file you can see the completeness of the data (63% for theta full (0.76 °).*
*[On the screen: Parameters for electron diffraction data]*
*The default values for the selection of the intensities are: g(max)=2, maximal excitation error Sg(matrix)=0.01, maximal excitation error Sg(refine)=0.1 and Rsg=0.4.*

15. ***Optimization of thickness***
Enable "Except of scale optimize also: Thickness", "Run optimizations".
*[On the screen: Intensity calculation for optimizing of thickness].*
*Dyngo calculates wR-factor for the thickness varying from 0 to 2000 Å.*
"Show thickness plots". Check the variation of the thickness of the crystal for the frames. Quit.
*Most frames have well defined wR-fator minima for one thickness. However, some frames either have poorly defined minimum or the minimum is defined for very different thickness. For example frames 13, 18, 22 and 44 have a plateau for thickness between 0 and 400 Å. Frame 36 have minimum at very high thickness (around 1500 Å). Check the problematic frames. You will notice that for most frames there is no problem with the reflection image, in this case, and for some of them 1 or 2 reflections are stronger the all the rest. Notice also that the maximum R-factor is 17.64% for the last frame. You can check the wR(all) going through the zones in the main window of "parameters for electron diffraction data" or while seeing the graphs. The different thickness is not a problem now, but if the frame would have some problem (the crystal mostly moved from the beam, for example) it could be removed from the refinement.*

16. ***Defining all the zones with the same thickness***
"Define zones of equal thickness". "Select all", OK.

*The crystal is a nanowire and the thickness is mostly constant along the sample. However, the thickness changes according to the tilt of the sample, because the nanowire lies roughly perpendicular to the tilting axis of the sample holder. Then, it is possible to define the same thickness for all the frames but still refine the variations of the thickness according to the tilting of the sample.*

*There are two ways of defining the same thickness of the crystal for all the frames. You can either estimate a reasonable thickness, based on the plots of wR versus thickness, and type it for all frames, or run 0 cycle of refinement and average the thickness. It will be used the first option here. From the plots the minima are well defined mostly for EDThick under 200 Å. Also based on the image of the crystal (it can be measured using imageJ) 150 (15 nm) for EDThick is a reasonable value.*

"Select zones for editing→ Select all → OK" and type 150 for "EDThick". OK, Yes.

Right-click on icon "Refine", change the number of cycles to 100 and the damping factor to 0.3 in order to avoid instability of the refinement.

*The refinement runs 23 cycles, each cycle takes less than 2 minutes (depending on your computer). You can see the details of the refinement in the file Ni2Si.ref (Edit/View→ View of Refine). The refinement converges with R=7.79%. However, the ratio reflections per parameter refined is around 5 (454/84) and it is advisable to increase it. It can be done by changing RSg (selecting more reflections for the refinement).*

*Another important thing to check is the number of observed reflections per zone. Also in the Ni2Si.ref file, you can see "R-factors for individual zones", where it is shown the list of zones with the respective R-factors and number of reflections.*

17. ***Optimization of orientation***

Save a new structure "File→save as→Ni2Si_dyn_ori", OK, Yes.
"Parameter→electron diffraction", change the "Limit on RSg" to 0.75
Enable "Run optimizations except of scale optimize also: Orientation", "Run optimization".

*[On the screen: Intensity calculation for optimizing of orientation].*

*Check the EDTheta for the frames. As said before, the orientation of the crystal during the measurement plays an important role in the dynamical scatterings. Typically, a deviation of 0.5° is already considered high. The frames with high misorientation are: 8, 24, 32, 41, 60, 61, 62 and 73. If you check these frames, most have few reflections (because the unit cell is small), the reflections are mostly weak (the nanowire is very thin) and some frames have 1 or 2 peaks visibly stronger than the rest. These stronger reflections dominate the optimization and hamper the correct estimative of orientation. Frames with EDTheta larger than 0.5° will be removed from the refinement.*

"Select zones for refinement"
*Disable the frames 8, 24, 32, 41, 60, 61, 62 and 73 (Ctrl + left mouse button).*

OK, OK, Yes. Double click on "Refine".
*The refinement converges with R=7.11% after 13 cycles. Since there are more reflections, it is possible to refine the anisotropic displacement parameters.*

18. ***Refinement of anisotropic atomic displacement parameters***

Save the structure as Ni2Si_dyn_ori_aniso, "Edit atoms→select all→double click in one of the atoms→ADP parameter(s): harmonic", OK, OK, Yes
*[On the screen: Mains window of Jana2006].*
Double-click on icon "Refine".

*Now the refinement converges with R= 6.52% after 15 cycles. If you check the ellipsoid model, you will see that Si is elongated along **a***, which was the noisiest direction when defining the unit cell.*

**Final structure model:**
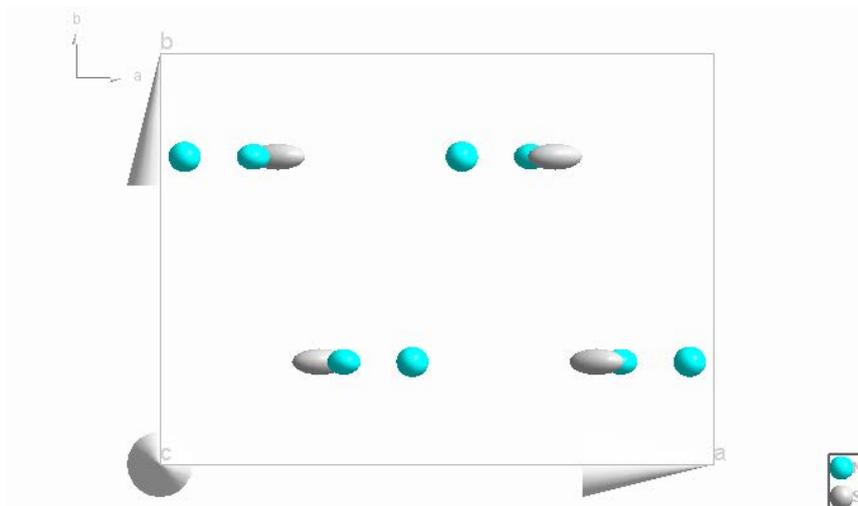
# Example 13.6: Orthopyroxene from EDT

**A complete procedure from structure solution to dynamical structure refinement from electron diffraction tomography data.**

**Revised: 13 October 2015**

Warning: this is a complex and time-consuming example. The computations in the last stages may take up to several hours.

Input data: directory dp with the set of experimental data,
opx.pts: input file for PETS – the data reduction program
opx_start.cif_pets and opx_dyn_start.cif_pets: results of the data processing. These files are provided so that this example can be solved without the data processing part, and to warrant reproducibility of the second part. Files opx.cif_pets and opx_dyn_start.cif_pets is the output of the data reduction.

1. *Data reduction using PETS*
   *The data processing part follows exactly the procedure described in example 13.1. Please follow that tutorial. Here only key results are provided for your control, and comments are provided for stages that require special attention. Be aware that the peak search and integration take a long time, because the original images are rather large.*
   *Parameters filled in the prepared file opx.pts:*
```
reflectionsize 30
beamstop no
```

   *Refined azimuthal angle omega of the tilt axis:*
```
omega  :   57.922
```

   *Unit cell is orthorhombic, primitive. The following screenshot is the view of the reciprocal lattice along the axis **c** (a\* horizontal, b\* vertical):*

*Final refined cell parameters (refined against the peaks in opx.clust):*

| a | 18.463 | b | 8.881 | c | 5.239 | alpha | 90.03 | beta | 89.98 | gamma | 90.94 |

Quit the indexing plugin to create file opx.smr with the orienting matrix, and continue data processing in PETS by typing u[Enter] to read in the orienting matrix, and i[Enter] to integrate the intensities.

*PETS produced file opx.cif_pets, which contains intensities suitable for structure solution and kinematical refinement. We have to produce another intensity set for dynamical refinement:*

In PETS type d[Enter]

*PETS will make another integration, this time producing file opx_dyn.cif_pets.*

Type h[Enter] and y[Enter] ]to produce a standard set of sections through reciprocal space.

*The sections will be useful for confirming the space group.*

*With this step the data processing in PETS is finished.*

Type q[Enter] to close PETS. You may also close ImageJ.

## 2. Create new structure

*Important!* *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can exactly reproduce the following part of the tutorial, do not use the files opx.cif_pets and opx_dyn.cif_pets that you just created, but use the files opx_start.cif_pets and opx_dyn_start.cif_pets provided with the example files (Rename the files to opx.cif_pets and opx_dyn.cif_pets). Using your own cif_pets files is possible, but your results may slightly differ from the results described in this tutorial.*

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate the directory with input files

Right pane: double-click opx

### 3. Import Wizard

Select "Known diffractometer formats"; NEXT
Select "Pets electron diffractometer"
*The file name automatically changes to opx.cif_pets, which is a file produced by PETS containing all important information, including the list of intensities.*
NEXT
Leave all settings unchanged; NEXT
Leave all settings unchanged; NEXT
*The program reads 5232 reflections from the file*
OK
For absorption correction select "None or done before importing"; NEXT
FINISH; OK; YES to accept the data set
*You just read in the experimental parameters, cell parameters and the intensity list.*

### 4. Symmetry Wizard

NEXT *to close the information window and start the wizard*
*Symmetry Wizard can be started separately by "File → Reflection file → Make space group test.*
*The default settings are prepared from x-ray diffraction. For electron diffraction the tolerances should be increased so that Jana properly detect that the cell is orthorhombic. Change the tolerances according to this screenshot:*

| Tolerances for crystal system recognition: | |
| --- | --- |
| Original cell parameters: 18.525 8.906 5.259 90.04 90.00 89.06 | |
| Maximal deviation for cell lengths in [A] | 0.2 |
| Maximal deviation for cell angles in deg | 1 |
| **Tolerances for space group recognition:** | |
| Maximal ave(I/sig(I)) for centering | 100 |
| Maximal ave(I/sig(I)) for extinctions | 100 |

Leave other settings default; NEXT; OK
 *[On the screen: Select Laue symmetry]*
Select orthorhombic Laue symmetry; NEXT
*The internal R-value of 23.68% is quite acceptable for EDT data.*
*[On the screen: Select cell centering]*
*The numbers in the table indicate that the only acceptable lattice type is primitive. In general it is a good practice to check the centering in the reciprocal-space reconstructions.*
Select centering P; NEXT
*[On the screen: Select space group]*
*The window shows possible space groups. It can be quite tricky to determine the correct space group form EDT data, as the systematic absences can be violated in electron diffraction. You should use the reconstructions of the reciprocal-space layers to check, if you can see some systematic absences. From the inspection of the section* hk0.pgm (open the file in ImageJ) *the presence of the a-glide is quite obvious. The b-glide and c-glide conditions in the files* 0kl.pgm *and* h0l.pgm *are violated by a couple of weak reflections, but still their presence is very likely.* Pbca *is therefore a good first guess.*

Select *Pbca*; NEXT
*Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use Superflip, which will make additional check for the most probable space group.*
Accept the space group in the standard setting; FINISH
*Symmetry is saved in file opx.m50.*

5. **Creating refinement reflection file**
*In this step the program creates file opx.m90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.*
Proceed with the wizard, leaving all settings default.

6. **Structure Solution Wizard**
OK *to close the information window and start the wizard*
*[On the screen: window of Structure solution]*
*Structure solution wizard can be executed separately through "Run → Solution".*
*Jana2006 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2006.*
In "Formula" textbox type the expected formula: Fe Mg Si2 O6
In "Formula units" textbox type 8
Click the checkbox next to "Use a specific random seed" and leave the value 111.
*The specific random seed is used just to guarantee reproducibility of the results. For standard work, random seed need not be defined.*
Click the radio button "EDMA – fixed composition"
*EDMA is an external program for interpretation of electron densities. It can take the chemical formula and interpret the density using this formula.*
Leave other settings default; OK
*[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed]*
*Superflip performed ten solution attempts. Check the space groups derived by Superflip from each of the attempts. In eight out of ten cases the proposed space group is Pbca. It is thus likely (though not guaranteed!) that Pbca is indeed the correct space group.*
Press CLOSE to leave the listing but stay in the dialog "Structure solution
*The result is a file opx.m40 with atoms of the structure model.*

7. **Verification of the structure solution**
Click "Draw 3D map"
*VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure. Try to recognize the structural motifs. The main expected motifs are SiO$_4$ tetrahedra and (FeMg)O$_6$ octahedra. The analysis will be simpler if you display the atomic bonds:*
Go to Edit → Bonds, and set up the options according to this screenshot:
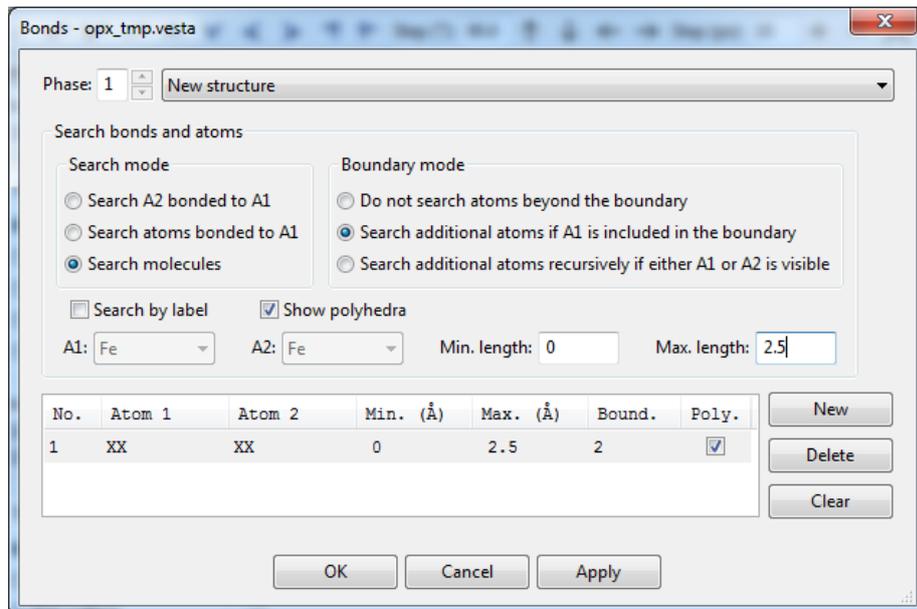
*Viewing the structure solution in VESTA has the advantage that you can directly check, if the raw density was correctly interpreted. In this case, the solution is very good and all atoms are properly located. The only problem is that some cations have been assigned a wrong atomic type. By inspecting the structure you should come to the conclusion that the following two atoms need to be changed:*
*Mg1 -> Si*
*Si2 -> Mg or Fe – we will choose Mg for the moment*
Quit VESTA (do not save changes)
Click "Accept last solution"

**8. *Change the atomic types***
Double click icon Edit atoms
Double click atom Si1
Change its name to Mg2
Change its atomic type to Mg
OK
Repeat the procedure for the atom Mg1 and rename it to Si2
Close the dialog for editing atoms and confirm changes

**9. *Structure refinement***
*[On the screen: basic window of Jana]*
Double click the icon Refine.
*Refinement converges smoothly to an R value about 25%.*

*The octahedral positions are not exclusively occupied by iron or magnesium, but by both elements. We have to refine the mixed occupancy in these sites.*
*[On the screen: basic window of Jana]*
Double click icon Edit atoms
Right-click atom Fe1 → Split atomic position
Set up the dialog according to the following screen shot:
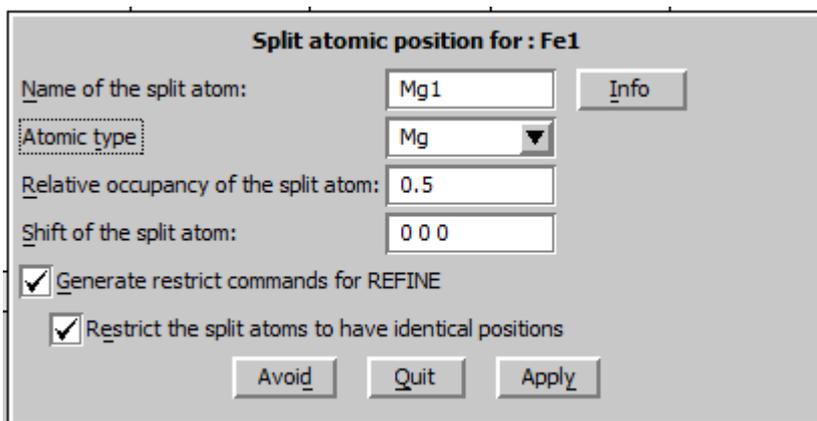
Apply
Repeat the procedure with Mg2 to generate atom Fe2 at the same position.

*The procedure generated a pair of atoms with restricted ADP parameters and coordinates and with a restricted sum of occupancies. The only small problem (although rather esthetic than real) is that in one pair the Fe atom is the "Master" and Mg the "slave", while for the other pair it is vice versa. We will modify the restrictions to be both the same.*
*[On the screen: basic window of Jana]*
Right-click Refine → Various → Restrictions
Load the restriction on atoms Mg2 and Fe2
Exchange the order of atoms in the restriction (type Fe 2 Mg2 in the line "Atoms/molecules), so that Fe is the "master" atom. Rewrite the restriction. When finished, the dialog should look like this:
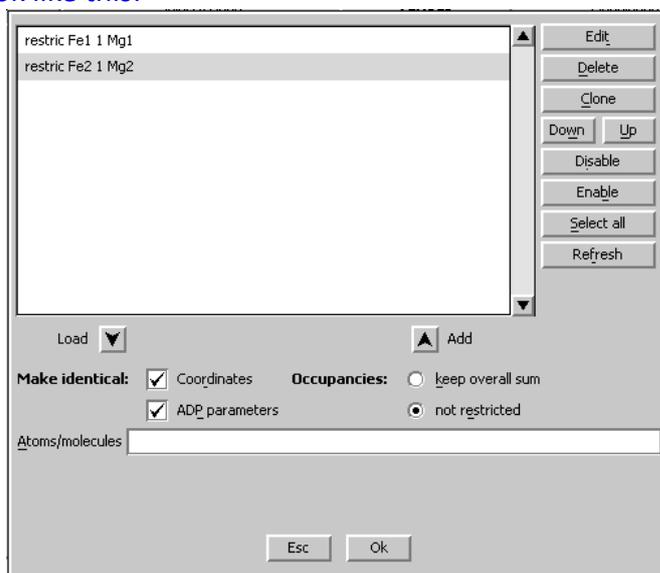


OK; OK; Yes (do not start refinement yet!)
*Now we have restricted the atomic pairs, but the occupancies are still fixed and would not be refined. We have to allow their refinement explicitly:*
Double click the icon "Edit atoms"
Double click atom Fe1
On the card "Edit" check the box next to the parameter "ai"; OK
Repeat for atom Fe2
OK to close the Edit atoms dialog

<span style="color:blue">Double click Refine to start refinement</span>

*Refinement converges to R-value of 24.25%. The refined atomic occupancies are:*
*Fe1: 0.44(5)*
*Fe2: 0.44(5)*
*Note that the equal occupancies and their e.s.d. is a pure coincidence and not a result of some restriction or symmetry.*

## 10. Set up dynamical refinement

*At this moment there is very little we can do with the kinematical refinement. We have a satisfactory refinement, the structure makes sense, the occupancies have been refined, but their accuracy cannot be estimated from the kinematical refinement. Furthermore, some ADPs are negative. We will now proceed to the structure refinement using dynamical diffraction theory.*

<span style="color:blue">File → Structure → Save as</span>
<span style="color:blue">Save the structure as opx_dyn</span>
<span style="color:blue">Answer Yes to the question if you want to continue with the new structure</span>
<span style="color:blue">File → Reflection file → Import/modify the reflection file</span>
<span style="color:blue">Reimport; Browse for the file opx_dyn.cif_pets; NEXT; NEXT; NEXT; OK; NEXT; Finish; OK; Yes</span>

*You have just replaced the previous reflection data with new data set suitable for dynamical refinement.*

<span style="color:blue">Cancel to avoid the production of refinement reflection file</span>

*If we continued, we would have produced a symmetry-averaged file for kinematical refinement. For dynamical refinement the intensities on each frame must be kept separate. We will now enable the dynamical refinement option:*

<span style="color:blue">Go to "Parameters → Electron diffraction"</span>
<span style="color:blue">Check the checkbox "Use dynamical approach"</span>
<span style="color:blue">Proceed with creation of the reflection file, leave all settings default.</span>

*At this point we are ready to start dynamical calculations. Because the calculations are very time consuming, we will not, in this example, use all 90 zones, but only nine selected zones.*

<span style="color:blue">Click "Select zones for refinement"; In the line below the table, set the following:</span>

| From the zone # | 10 | select each | 10 | th zone |
|---|---|---|---|---|

<span style="color:blue">Click the button</span> `select each` <span style="color:blue">; OK</span>

*Only zones 10, 20, 30, 40, 50, 60, 70, 80 and 90 are now selected for refinement.*

*The data collection was performed on one crystal and there is also no reason to expect that the thickness varies for each zone. We will therefore restrict the thickness to the sam value for all zones:*

<span style="color:blue">Click "Define zones of equal thicknesses; Select all; OK</span>

*Dyngo – the external executable that performs the heavy calculations – can run in a parallel mode. In the field "Number of threads" you can decide, how many parallel threads Dyngo may use. For the fastest performance set this number to the number of cores of your processor.* <span style="color:red">Important!</span> *Most Intel processors indicate twice as many threads available than*

*they have cores due to the hyper-threading technology. Do not set the number of threads to the number of threads available on your processor, but to the number of ture distinct cores!*

*As a first step we have to check, if our model fits the data sufficiently well to start the refinement. For that, we will run thickness optimization. This procedure is relatively fast, and for each selected zone it calculates an R-value as a function of thickness. For good data set and reasonable starting model, this curve should have a minimum at a meaningful thickness, and all curves should indicate approximately the same thickness.*

Check the checkbox next to "Thickness" and click [Run optimalizations]
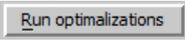
*Jana calls Dyngo for each zone. When the calculation is finished, each selected zone has next to the zone number in the dialog the best R-value, e.g.:*

Zone#: 80     R(all)= 13.3208%

*All zones' R-values are lower than 20%, some of them even lower than 10%. This is a pretty good start.*

Click "Show thickness plots"

*Now you can view the curves R-value vs. thickness for all zones. In most cases the curve has a well-defined minimum, only in zones 30 and 70 the minimum is at the lowest thickness. The best thickness varies in a relatively broad interval, but the minima are broad, and our structure model is far from perfect at this stage, so this is not surprising.*

Quit the viewer of the thickness curves

*We want the thickess to be the same for all zones in the refinement. Now the thicknesses are all different and we should reset them to a common most appropriate value. The best practice seems to be a visual estimation of the "typical" thickness in the thickness plots. In this case 500 angstroms seems to be a good guess. Do not worry about the inaccuracy of such guess – the thickness is a very robust parameter and it will refine to the correct value even from a quite distant start.*

Click "Select zones for editing"; "Select all"; OK

Double click the yellow field EDThick and type "500" in the field

*This procedure reset the thickness of all zones to 500 angstroms.*

*We have to recalculate the scale factors for each zone, because the scale changes with changing thickness:*

Click the button [Run optimalizations] without any other checkbox checked (neither thickness nor Orientation)

When the calculation finishes,click OK to close the electron diffraction dialog.

*You can now start the structure refinement.*

*[On the screen: basic window of Jana]*

Double click the icon Refine

*After the first cycle the refinement R-value Robs is 13.13%. After 5 cycles the refinement should converge to an R-value of 8.29%.*

*In the next step we will optimize the orientation of each zone. Due to the inaccuracy of goniometer positioning and orientation matrix, the positional angles of each diffraction pattern are not exactly correct, and a correction should be found.*

Go to "Parameters → Electron diffraction"

Check the checkbox next to "Orientation"

Click the button **Run optimizations**
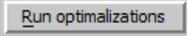
*An optimization procedure starts that finds the best zone-axis orientation for each pattern. Wait until the calculation finishes. Now you can now run a few more cycles of structure refinement.*

Click OK to close the form "Electron diffraction"

Double click the icon Refine

*The refinement converges after 10 cycles to an R-value of 5.10%. Inspection of the structure model shows that the occupancies of Fe1 and Fe2 refined to 0.33(3) and 0.06(2), respectively. This is still relatively far from the values from x-ray refinement, which are 0.432(3) and 0.157(3). However, there are only 188 observed reflections in this limited dataset for the refinement of 52 parameters. The data to parameter ratio is thus poor. If all 90 zones are included in the refinement and the whole procedure is repeated with them, the final result is:*

*Robs=5.89%*

*occ(Fe1)=0.389(7)*

*occ(Fe2)=0.148(7)*

# Example 20.1: CeAsSe

**Merohedric twin with extinction imported from SHELX to Jana2006.**

## Chemical formula: CeAsSe

**Reference:** Structure provided by Max Planck Institute for Chemical Physics of Solids
Input files: CeAsSe.hkl, CeAsSe.ins

1. *Creating new jobname*
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click CeAsCe

2. *Importing structure from SHELX*
   *[On the screen: Specify type of the file to be imported]*
   Select "Structure – from SHELX"; Next
   In File manager double-click CeAsSe.ins
   *The program reads the structure, detects the presence of CeAsSe.hkl and starts import of reflections*
   Go through the usual steps of the Import Wizard
   Rint = 4.69%

3. *Checking the twinning of the imported structure*
   Start EditM50
   The twinning check box must be selected
   Press "Matrices"
   The twinning matrix should be 0 1 0 | -1 0 0 | 0 0 1
   Leave EditM50
   Start "Parameters → Twin fractions"
   The parameter "twwol2" must be 0.46346
   Activate refinement of "twvol2"
   Save the changes and leave to the basic window

4. *Refinement*
   Run refinement
   It converges with R=3.2%
   Open refinement listing, GoTo Statistics
   Higher R value for the strongest reflections indicates that extinction correction is needed
   Close the refinement listing
   Start "Parameters → Extinction"
   Activate Isotropic extinction with Gaussian model
   Save changes and leave to the basic window
   Repeat refinement
   In converges with R=2.75%. The reason extinction has not been imported from the ins file is that SHELX and Jana use different parameters for extinction correction

# Example 20.2: HfPdGe

**Six-fold twin with reflections in HKLF5 format, imported from SHELX to Jana2006.**

## Chemical formula: HfPdGe

**Reference:** Structure provided by Max Planck Institute for Chemical Physics of Solids
Input files: HfPdGe.hkl, HfPdGe.ins

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click HfPdGe

2. ***Importing structure from SHELX***
   *[On the screen: Specify type of the file to be imported]*
   Select "Structure – from SHELX"; Next
   In File manager double-click HfPdGe.ins
   *The program reads the structure, detects the presence of HfPdGe.hkl, automatically recognizes HKLF5 format and starts import of reflections*
   Go through the usual steps of the Import Wizard
   Rint = ----

3. ***Checking the twinning of the imported structure***
   Start EditM50
   The twinning check box must be selected, number of twin domains should be six
   Press "Matrices"
   The twinning matrices are all unit matrices because for HKLF5 data they have just a formal meaning
   Leave EditM50
   Start Parameters → Twin fractions
   The parameters "twwol2", …. "twvol6" must contain the numbers from the BASF commans of the ins file.
   Activate refinement of all twin volume fractions
   Save the changes and leave to the basic window

4. ***Refinement***
   Run refinement
   It converges with R=4.1% for 60 parameters. There were very large changes of the twin fractions during the refinement because probably the order of twin fractions in SHELX and Jana differs.
   Open refinement listing, GoTo Statistics
   There is no indication of extinction and at the bottom of the listing no warnings.

# References

**List of references related to methods used in Jana2006, including external programs for charge flipping and electron diffraction.**

**Revised: 10 May 2015**

Petricek, V., Coppens, P. and Becker, P. (1985). Acta Cryst. A41, 478-483
*Structure-analysis of displacively modulated molecular-crystals*

Petricek, V. and Coppens, P. (1988). Acta Cryst A44, 235-239
*Structure-analysis of modulated molecular-crystals .3. Scattering formalism and symmetry considerations - extension to higher-dimensional space-groups*

Petricek. V. (1989). Act aCryst. 45, 109-111
*The possible translational parts of (3+d) superspace symmetry operations*

Petricek, V., Maly, K., Coppens, P., Bu, X., Cisarova, I. and Frost-Jensen, A. (1991). Acta Cryst. A47, 210-216
*The description and analysis of composite crystals*

Petricek, V., van der Lee, A. and Evain. M. (1995). Acta Cryst. A51, 529-535
*On the use of crenel functions for occupationally modulated structures*

Palatinus. L. (2007). Acta Cryst. A60, 127-237
*Ab initio determination of incommensurately modulated structures by charge flipping in superspace*

Palatinus, L. and Chapuis, G. (2007). J. Appl. Cryst., 41, 786–790
*SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions*

Baerlocher, C., McCusker, L. B., Palatinus, L. (2007). Z. Kristallogr. 222, 47-53
*Charge flipping combined with histogram matching to solve complex crystal structures from powder diffraction data*

Leineweber, A. and Petříček, V. (2007). J. Appl. Cryst. 40, 1027-1034
*Microstrain-like diffraction-line broadening as exhibited by incommensurate phases in powder diffraction patterns*

Petříček, V., Fuksa, J. and Dušek, M. (2010). Acta Cryst., A66, 649–655
*Magnetic space and superspace groups, representation analysis: competing or friendly concepts?*

Palatinus, L., Fleischer, F. Pattison, P., Weber. T. and Steurer, W. (2011). Acta Cryst. A67, 9-20.
*Ab initio reconstruction of difference densities by charge flipping*

Perez-Mato, J.M., Ribeiro, J.L., Petříček, V. and Aroyo, M.I. (2012). J.Phys.: Condens. Matter, 24, 163201
*Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases*

Palatinus, L., Jacob, D., Cuvillier, P., Klementová, M., Sinkler, W. and Marks, L.D. (2013). Acta Cryst, A69, 171-188
*Structure refinement from precession electron diffraction data*

Palatinus L. (2013). Acta Cryst. B69, 1-16.
*The charge-flipping algorithm in crystallography*

Petříček, V., Dušek, M. and Palatinus, L. (2014). Z. Kristallogr., 229, 345–352
*Jana2006: general features*

Palatinus, L., Petříček, V. and Correa, C.A. (2015). Acta Cryst., A71, 235-244
*Structure refinement using precession electron diffraction tomography and dynamical diffraction: theory and implementation*

Palatinus, L. (2015). Acta Cryst. B71, 125-126
*Taking a closer look for a broader view: combining powder diffraction with electron crystallography for a better understanding of modulated structures*

# Appendix 1.1: File format PRF

**PRF file is used for powder refinement. It contains Bragg positions and profile points.**

Format of PRF is sometimes requested by users to obtain data points of powder profiles for different purposes. For work with powders in Jana2006, knowledge of the PRF format is not needed.

**Revised: 10 May 2015**

As Jana2006 allows refinement against more data sets, PRF file may consist of several data blocks:

Block1 begin

........................

........................

Block1 end

Block2 begin

........................

........................

Block2 end

In the case that there is just one data block, the labels are omitted.

Each block consists of three parts: header, Bragg positions and profile points:

```
  2    0    0    2    3    3
  1   -1    2   3.    1   10.9743    0.0237    0.0380    0.547364E+01
  1    0   -2   3.    1   10.9743    0.0237    0.0380    0.547364E+01
  1   -1   -4   3.    1   13.7339    0.0236    0.0414    0.698639E+01
  1    0    4   3.    1   13.7339    0.0236    0.0414    0.698639E+01
  0    0   -6   1.    1   14.2831    0.0236    0.0421    0.130568E+01
  0    0    6   1.    1   14.2831    0.0236    0.0421    0.130568E+01
  2   -1    0   6.    1   17.1683    0.0235    0.0456    0.668545E+01
  2   -1   -3   6.    1   18.6097    0.0235    0.0474    0.768642E+01
  2   -2    4   3.    1   22.0509    0.0234    0.0517    0.238082E+01
  2    0   -4   3.    1   22.0509    0.0234    0.0517    0.238082E+01
  2   -1    6   6.    1   22.4023    0.0234    0.0522    0.573109E+00
  2   -1   -6   6.    1   22.4023    0.0234    0.0522    0.573109E+00
  1    0    1   8.    2   25.3002    0.0232    0.0598    0.194769E+02
..................................
..................................
 999
  6.000000    0.209300E+04    0.249015E+04    0.457493E+02   6.023784    0   0.000000E+00   0.000000E+00   0.249015E+04
  6.016766    0.209500E+04    0.247949E+04    0.457712E+02   6.040549    0   0.000000E+00   0.000000E+00   0.247949E+04
  6.033532    0.217100E+04    0.246891E+04    0.465940E+02   6.057315    0   0.000000E+00   0.000000E+00   0.246891E+04
  6.050298    0.206100E+04    0.245839E+04    0.453982E+02   6.074081    0   0.000000E+00   0.000000E+00   0.245839E+04
  6.067064    0.204200E+04    0.244793E+04    0.451885E+02   6.090847    0   0.000000E+00   0.000000E+00   0.244793E+04
  6.083830    0.217300E+04    0.243755E+04    0.466154E+02   6.107612    0   0.000000E+00   0.000000E+00   0.243755E+04
  6.100596    0.210500E+04    0.242723E+04    0.458803E+02   6.124378    0   0.000000E+00   0.000000E+00   0.242723E+04
...............
...............
 10.593884    0.102600E+04    0.986969E+03    0.320312E+02  10.617599    1   0.000000E+00   0.000000E+00   0.986969E+03
 10.610650    0.108400E+04    0.101817E+04    0.329242E+02  10.634364    1   0.340796E+02   0.000000E+00   0.984355E+03
 10.627417    0.991000E+03    0.101999E+04    0.314802E+02  10.651131    1   0.385393E+02   0.000000E+00   0.981752E+03
 10.644182    0.105600E+04    0.102260E+04    0.324962E+02  10.667895    1   0.437751E+02   0.000000E+00   0.979160E+03
 10.660948    0.104400E+04    0.102623E+04    0.323110E+02  10.684661    1   0.500343E+02   0.000000E+00   0.976579E+03
...............
...............
 24.710857    0.361000E+03    0.316545E+03    0.190000E+02  24.734123    1   0.000000E+00   0.000000E+00   0.316545E+03
 24.727623    0.347000E+03    0.316369E+03    0.186279E+02  24.750887    1   0.000000E+00   0.000000E+00   0.316369E+03
 24.744389    0.341000E+03    0.353730E+03    0.184662E+02  24.767653    1   0.000000E+00   0.378276E+02   0.316194E+03
 24.761154    0.353000E+03    0.356299E+03    0.187883E+02  24.784416    1   0.000000E+00   0.405929E+02   0.316019E+03
 24.777920    0.385000E+03    0.359047E+03    0.196214E+02  24.801182    1   0.000000E+00   0.435381E+02   0.315845E+03
 24.878517    0.375000E+03    0.383491E+03    0.193649E+02  24.901773    1   0.000000E+00   0.692188E+02   0.314806E+03
...............
...............
 999.
```

**Header**

| kType | 2 | for Jana2006 |
|---|---|---|
| KADoublet | 0 | data for data measured with wave length |
| | 1 | for Kα$_1$ and Kα$_2$ |
| DataType | 0 | X-ray/neutron CW data |
| | 1 | TOF data as a function of time |
| | 2 | TOF data in d values |
| | 3 | energy dispersive data |
| NPhases | | number of phases |
| (NDim(i),i=1,NPhases) | | number of indices used for each phases |

**Bragg positions**

| h,k,l,... | n diffraction indices, where n = max(NDim(1), …, NDim(NPhases)). For phases having the dimension smaller than n the indices are completed by zeros. |
|---|---|
| Multiplicity | multiplicity of the reflection following from the symmetry |
| KPhase | defines the phase the reflection belongs to |
| *The following four items are repeated twice if KADoublet=1. The first block corresponds to Kα$_1$* | |
| TwoTheta/Time /d/energy | angular position/time (or for TOF d value/energy) of the peak as calculated from cell parameters and modulation vectors |
| Shift | the angular shift of the peak position due to a zero shift, sycos and sysin parameters (it need not be constant for all reflections). The actual of reflections with respected to the profile should be calculated as: [TwoTheta/Time/d/energy] -Shift |
| FWHM | in the same units are previous values |
| Icalc(h,k,l) | intensity as calculated from Rietveld (corrected for multiplicity and preference orientation) or as extracted from the profile by le Bail fit. |
| *The list of Bragg peaks ends with the integer 999 at the position of the h index.* | |

**Profile points**

| TwoTheta/Time/d/energy | diffraction angle/time for TOF/d value/energy of the profile point |
|---|---|
| Iobs | observed intensity |
| Icalc | calculated intensity |
| sig(Iobs) | standard uncertainty of Iobs |
| TwoTheta-corr/Time-corr/ d-corr/energy-corr | diffraction angle/time for TOF/d value/energy of the profile point corrected for zero shift, sysin and sycos |
| Icalc | calculated intensity |
| Skip flag | 0        if the profile point was used in the refinement |
| | 1        if the profile point belongs to one of excluded region |
| Icalc(1) | calculated intensity of the first phase |
| | . . . . |
| Icalc(NPhases) | calculated intensity of the first phase |
| Ib | background intensity |
| *The list of peak points ends with the real number "999.".* | |