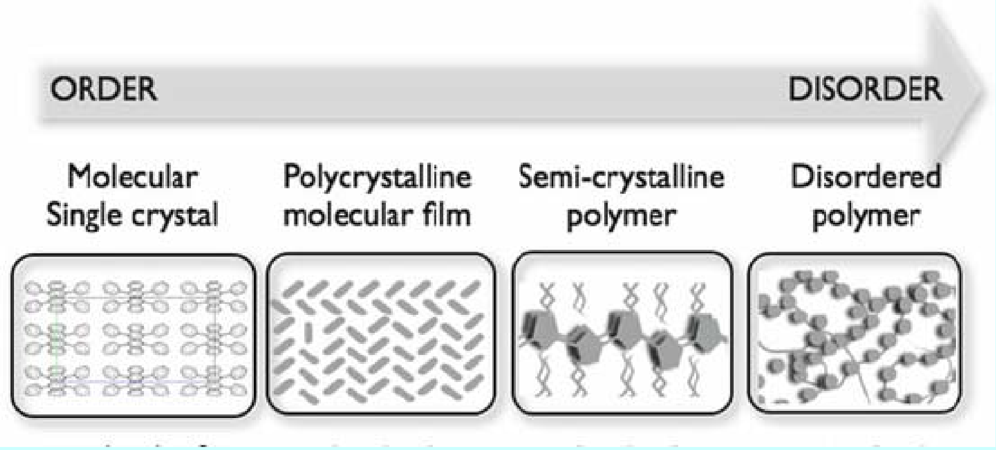
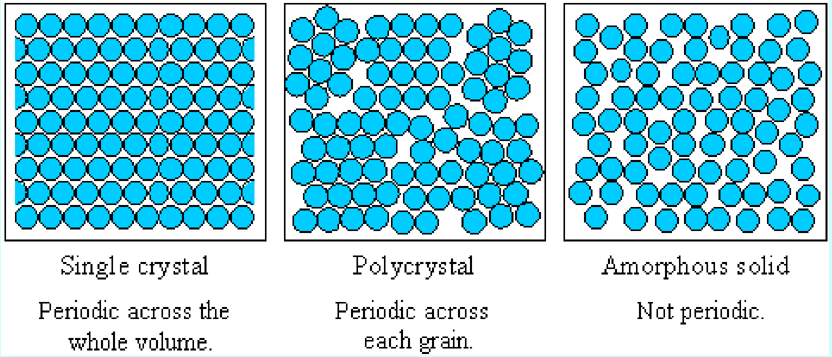
Crystalline State

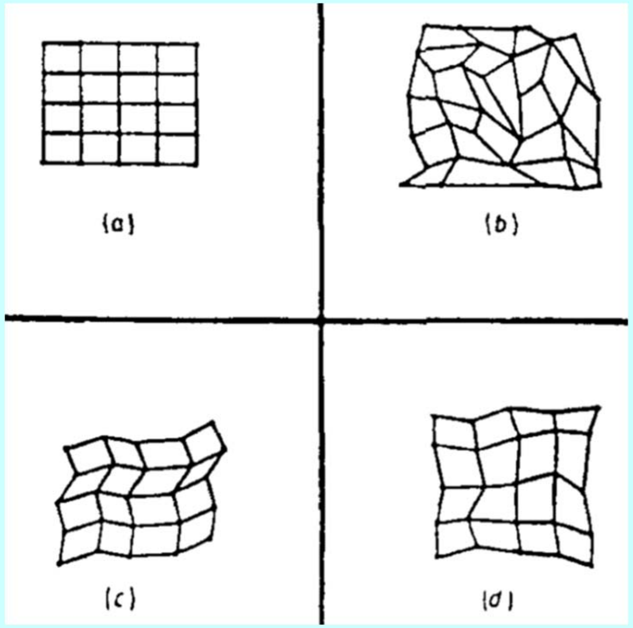
Basic Structural Chemistry

Structure Types

Degree of Crystallinity







Crystalline – 3D long range order
Single-crystalline

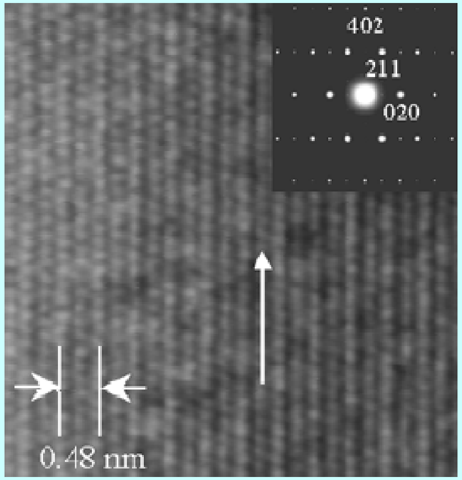
Polycrystalline - many crystallites of different sizes and orientations (random, oriented)

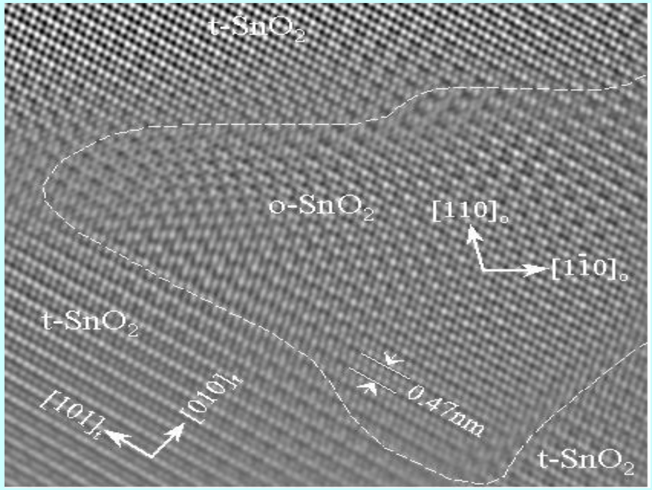
Paracrystalline - short and medium range order, distortions, lacking long range order

Amorphous – no order, random

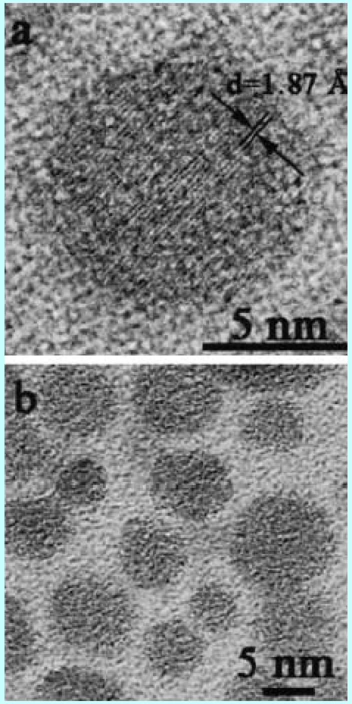
Degree of Crystallinity

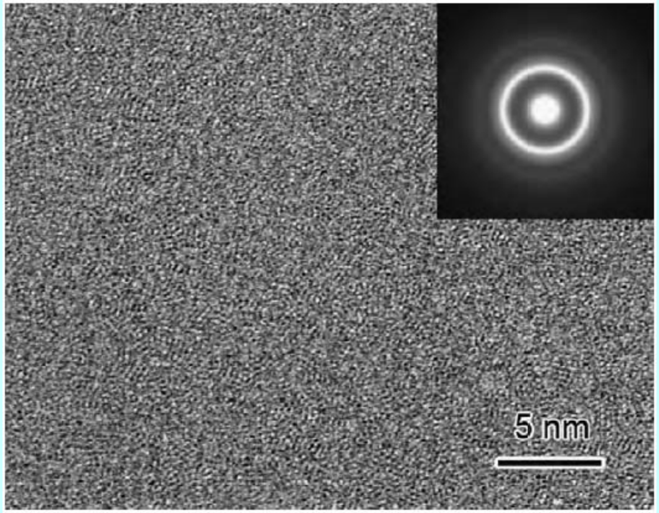
- **Single Crystalline**
- **Polycrystalline**
- **Nanocrystalline**
- **Amorphous**





Grain boundaries



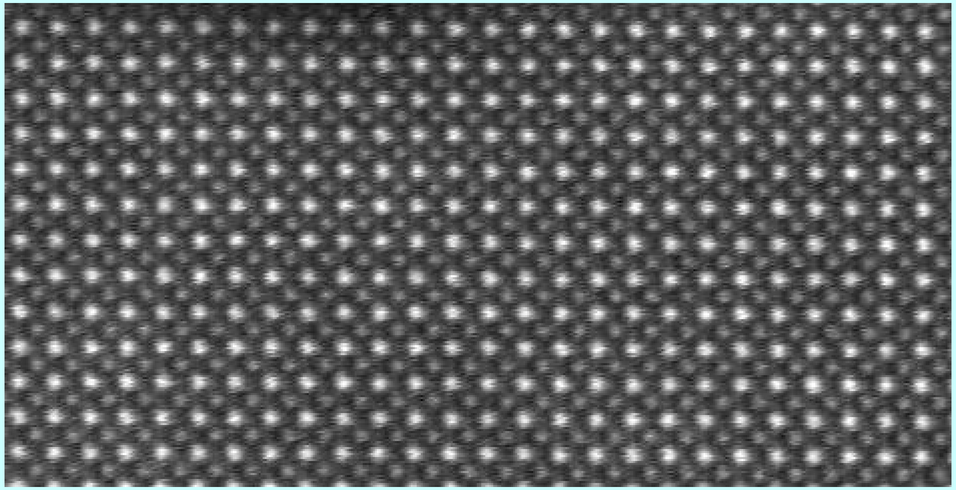


Metallic glass

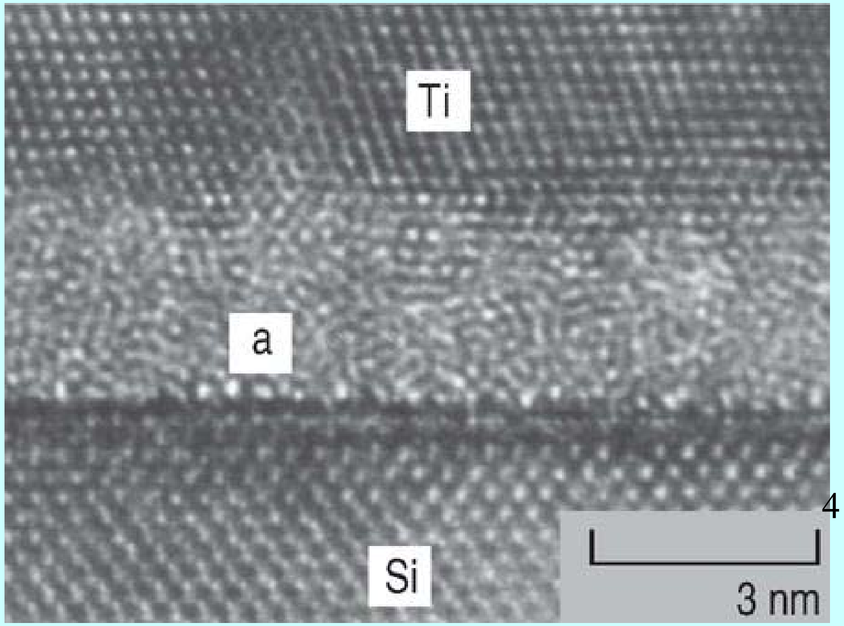
Degree of Crystallinity

A crystalline solid: HRTEM image of strontium titanate $SrTiO_3$

Brighter atoms are Sr and darker are Ti

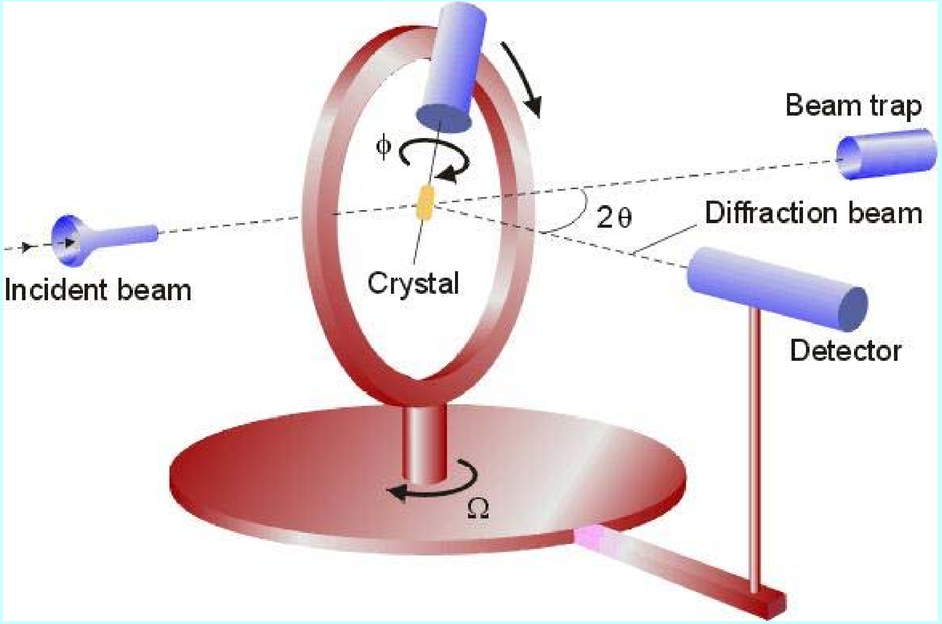


A TEM image of amorphous interlayer at the Ti/(001)Si interface in an as-deposited sample



Single-Crystal X-ray Diffraction

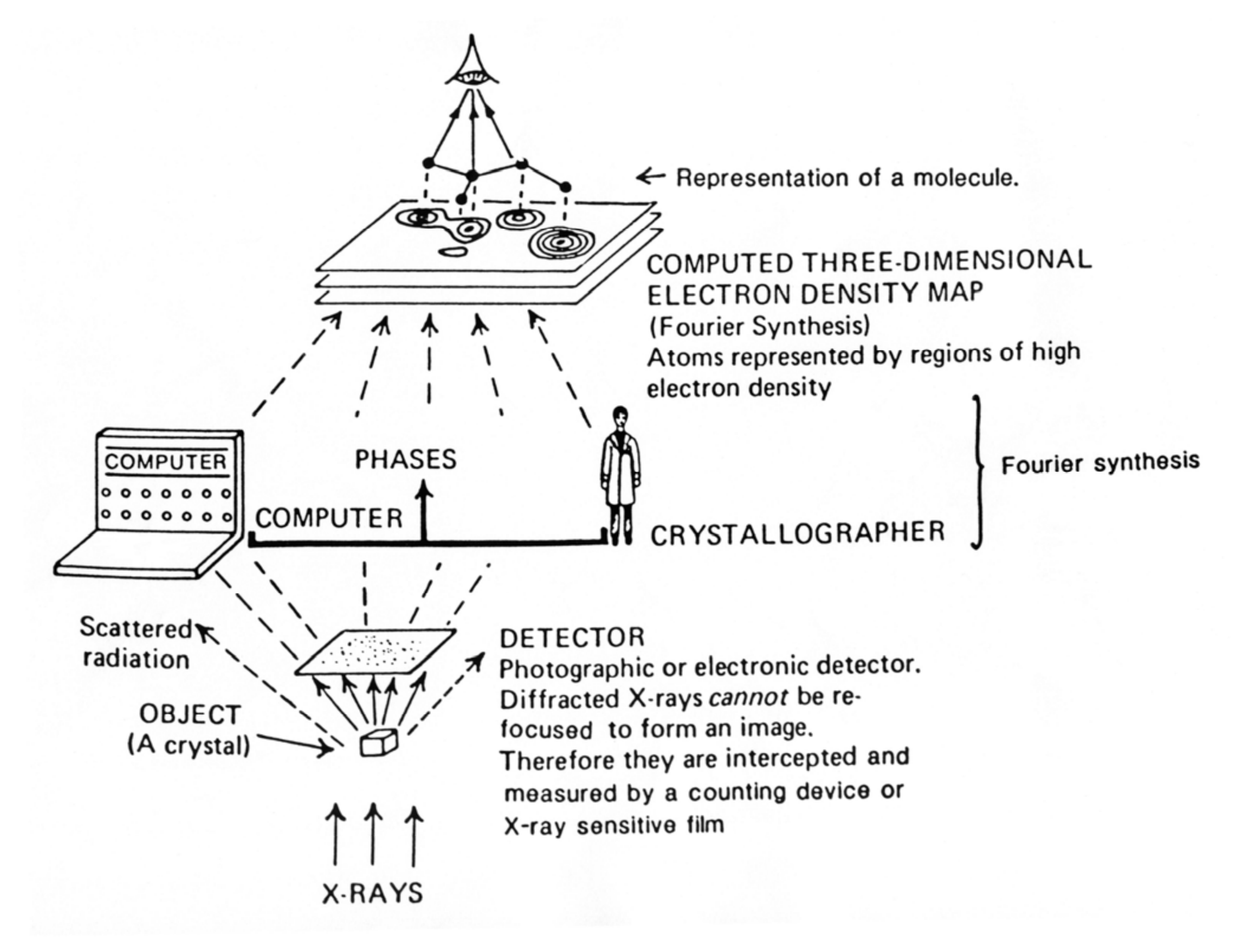
Structure Analysis



a four circle X-ray diffractometer

Single-Crystal X-ray Diffraction

Structure Analysis



Crystals

- **Crystal = a periodic arrangement of *structural motifs* = building blocks**
- **Building block is called *a basis*: an atom, a molecule, or a group of atoms or molecules**
- **A periodic arrangement must have translational symmetry such that if you move a building block by a distance:**

$$\overline{T} = n_1\overline{a} + n_2\overline{b} + n_3\overline{c}$$

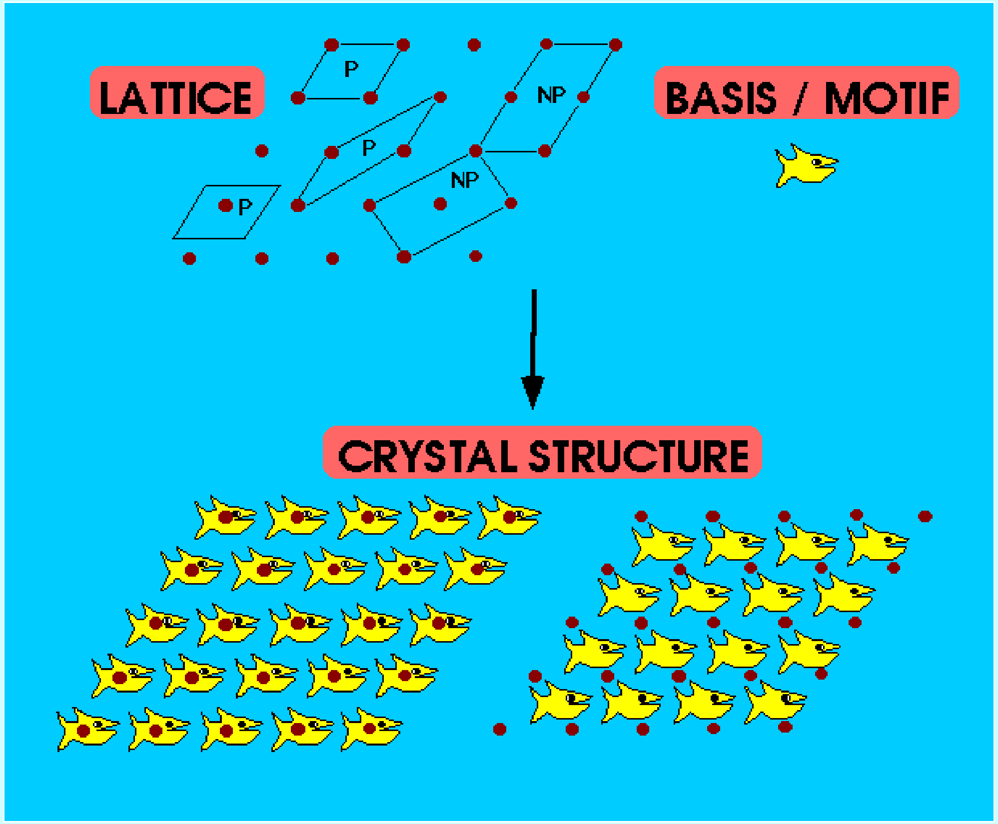
where n_1, n_2, and n_3 are integers, and $\overline{a}, \overline{b}, \overline{c}$ are vectors.

then it falls on another identical building block with the same orientation

- **If we remove the building blocks and replace them with points, then we have *a point lattice* or Bravais lattice**

Crystal Structure

Crystal Structure = Lattice + Motifs



(POINT) LATTICE
the geometrical pattern repeating periodically in space (2D or 3D) formed by points that have identical environment representing the locations of basis or motifs

MOTIF (BASIS)
the repeating unit of a pattern (an atom, a group of atoms, a molecule etc.) inside the unit cell

UNIT CELL
the smallest repetitive volume of the crystal, which when stacked together with replication reproduces the whole crystal

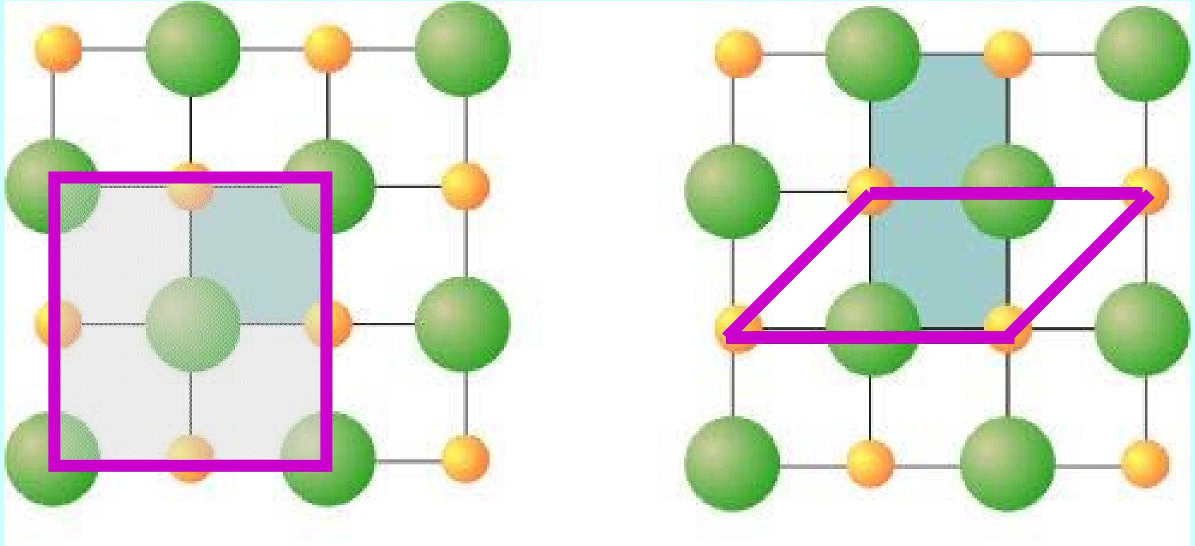
Unit Cell

An „imaginary“ parallel sided region (parallelepiped) of a structure from which the entire crystal can be constructed by purely translational displacements

Contains one unit of the translationally repeating pattern

Content of a unit cell represents its chemical composition

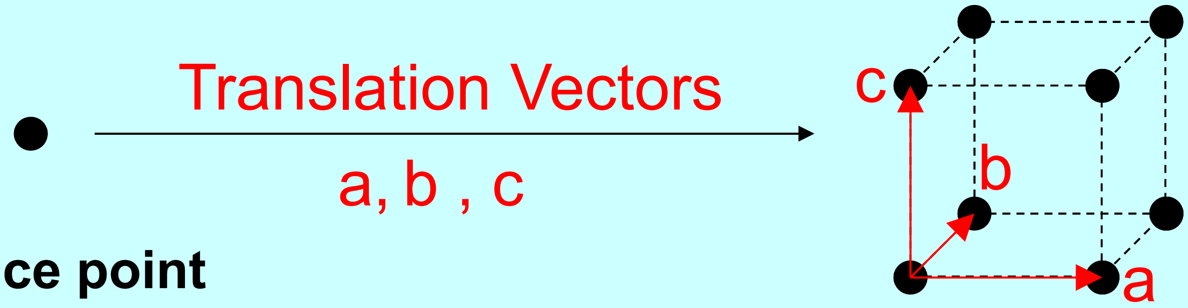
The unit cells that are commonly formed by joining neighbouring lattice points by straight lines, are called primitive unit cells



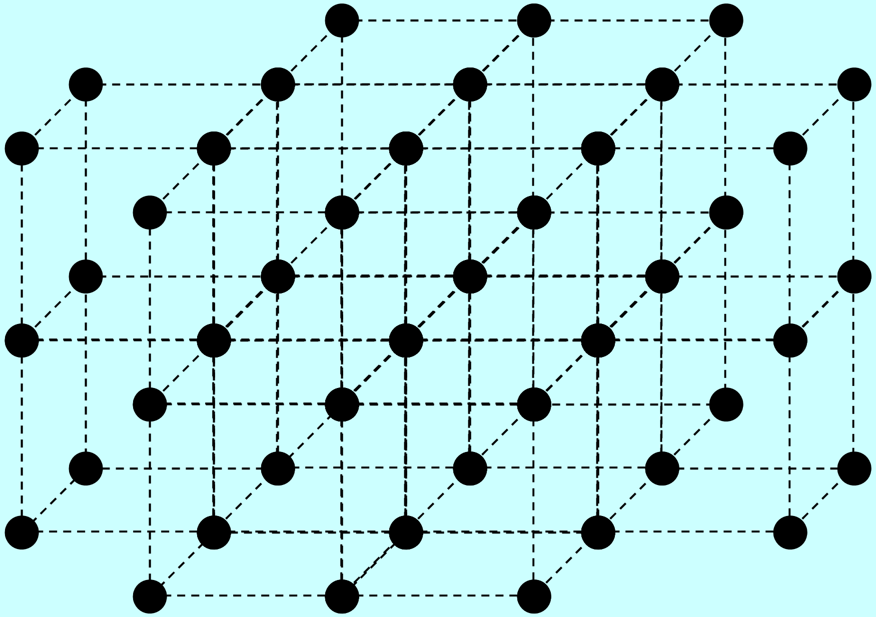
Unit cell

Primitive unit cell

Crystal = Periodic Arrays of Atoms



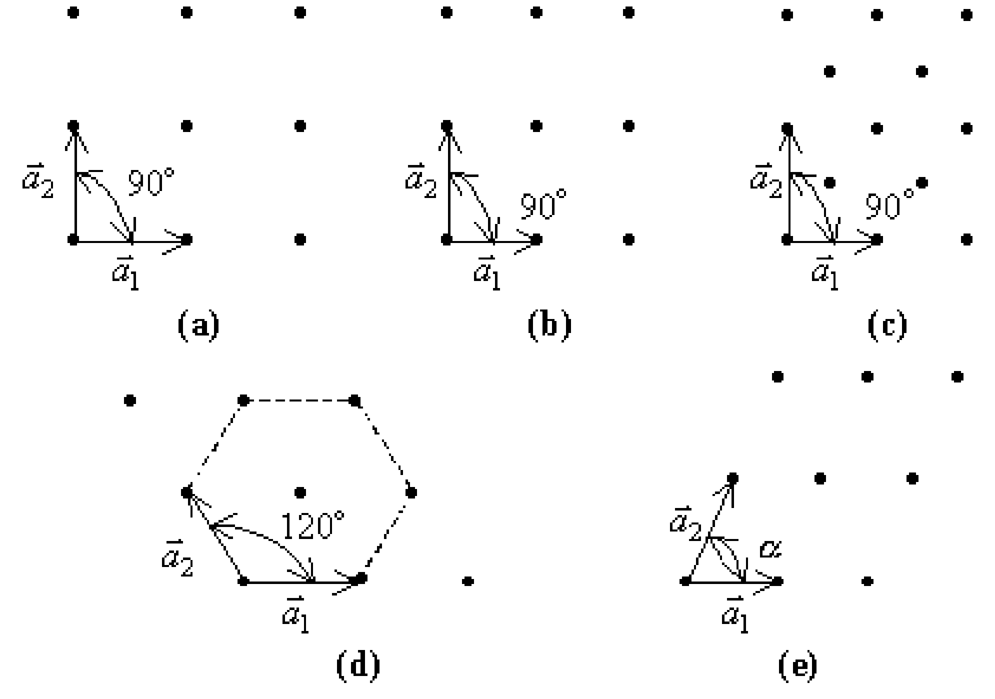
Lattice point
(Atom, molecule, group of molecules,…)

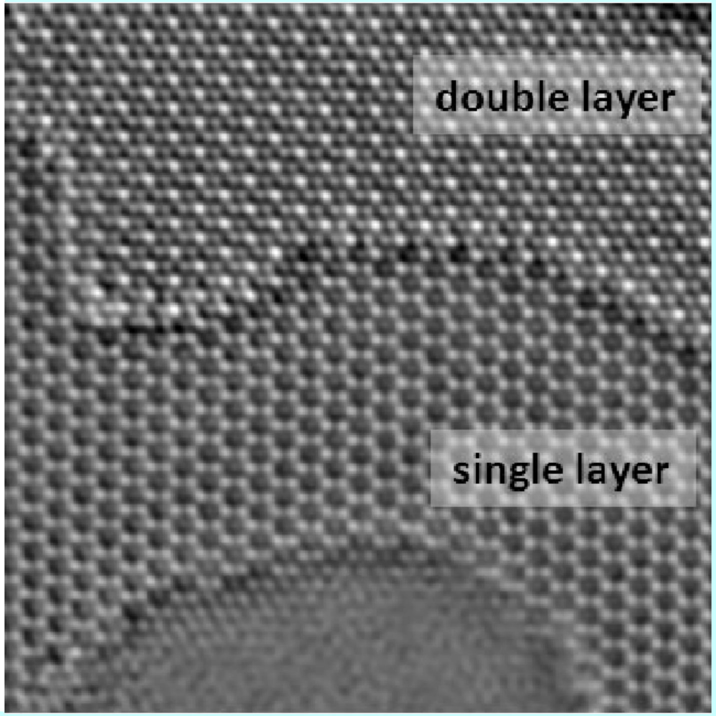


Primitive Cell:

- **Smallest building block for the crystal lattice**
- **Repetition of the primitive cell gives a crystal lattice**

Five Planar Lattices





Name		Number of Bravais lattices	Conditions
Square	a	1	$a_1 = a_2$, $\alpha = 90°$
Rectangular	b,c	2	$a_1 \neq a_2$, $\alpha = 90°$
Hexagonal	d	1	$a_1 = a_2$, $\alpha = 120°$
Oblique	e	1	$a_1 \neq a_2$, $\alpha \neq 120°$, $\alpha \neq 90°$

graphene

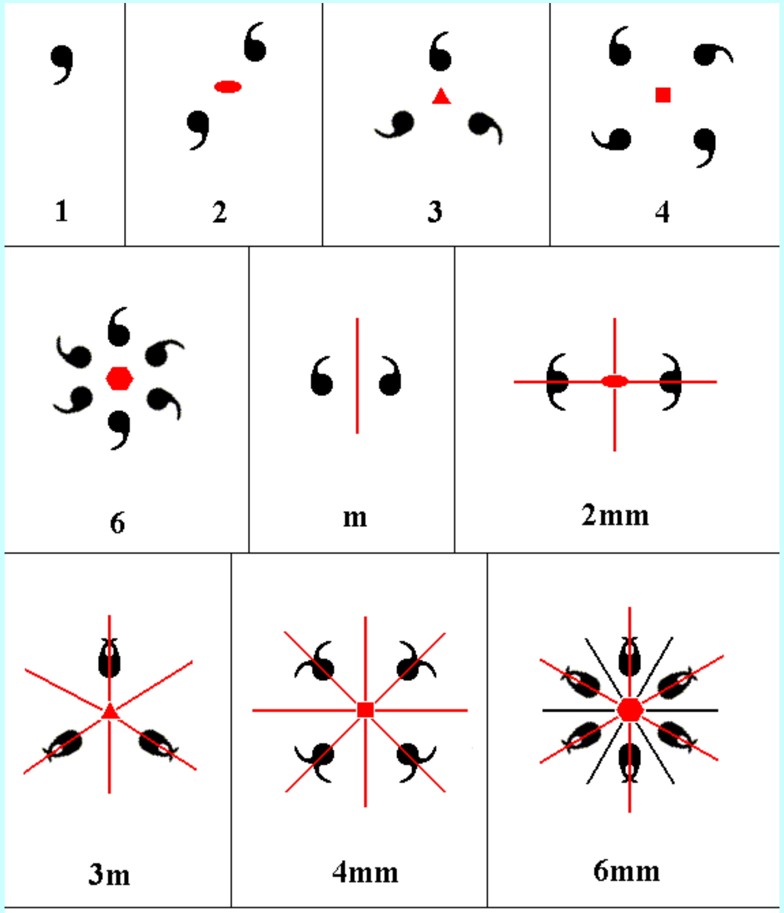
Lattice points of spherical symmetry

Ten Planar Point Groups

Symmetry
preservation of form and configuration across a point, a line, or a plane - symmetry elements

Symmetry Element
a geometric entity (line, point, plane) about which a symmetry operation takes place

Symmetry Operation
a permutation of atoms such that an object (molecule or crystal) is transformed into a state indistinguishable from the starting state



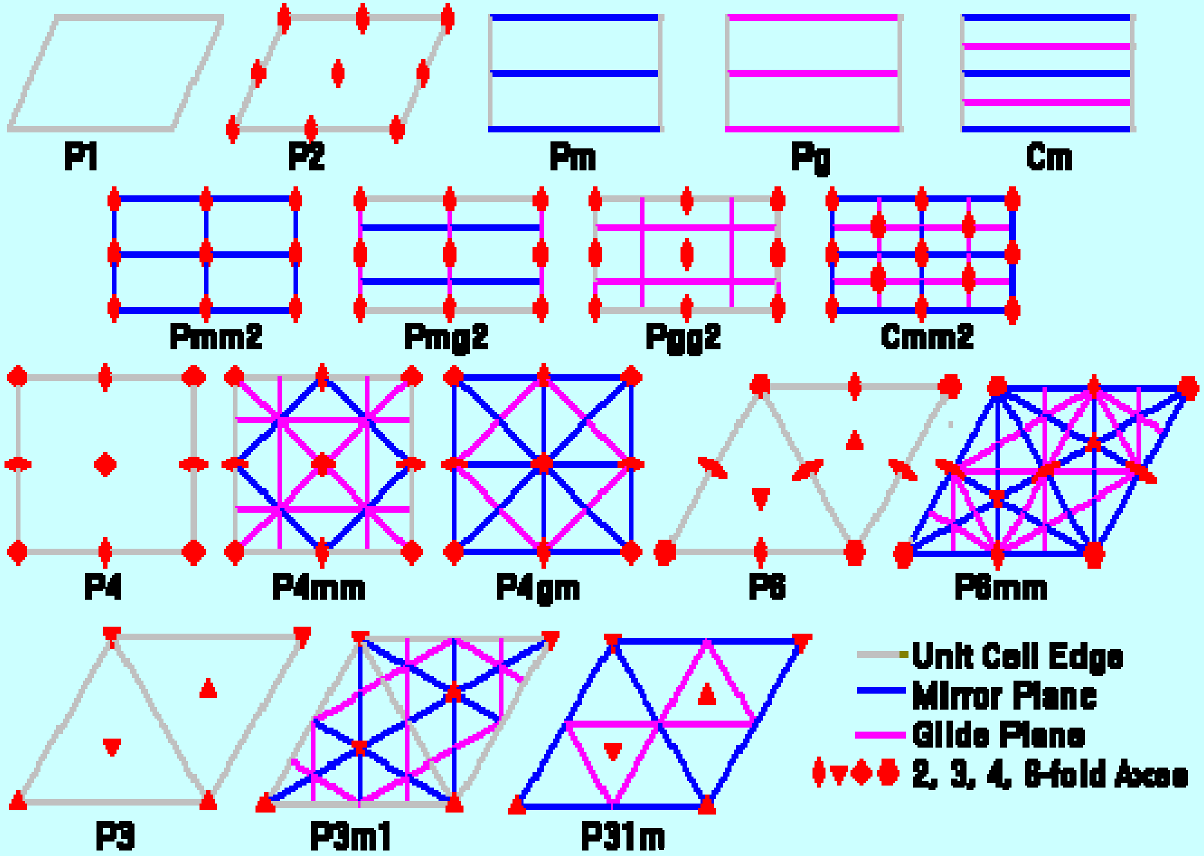
The Ten Planar Point Groups

Point Group
the collection of symmetry elements of an isolated shape, does not consider translation

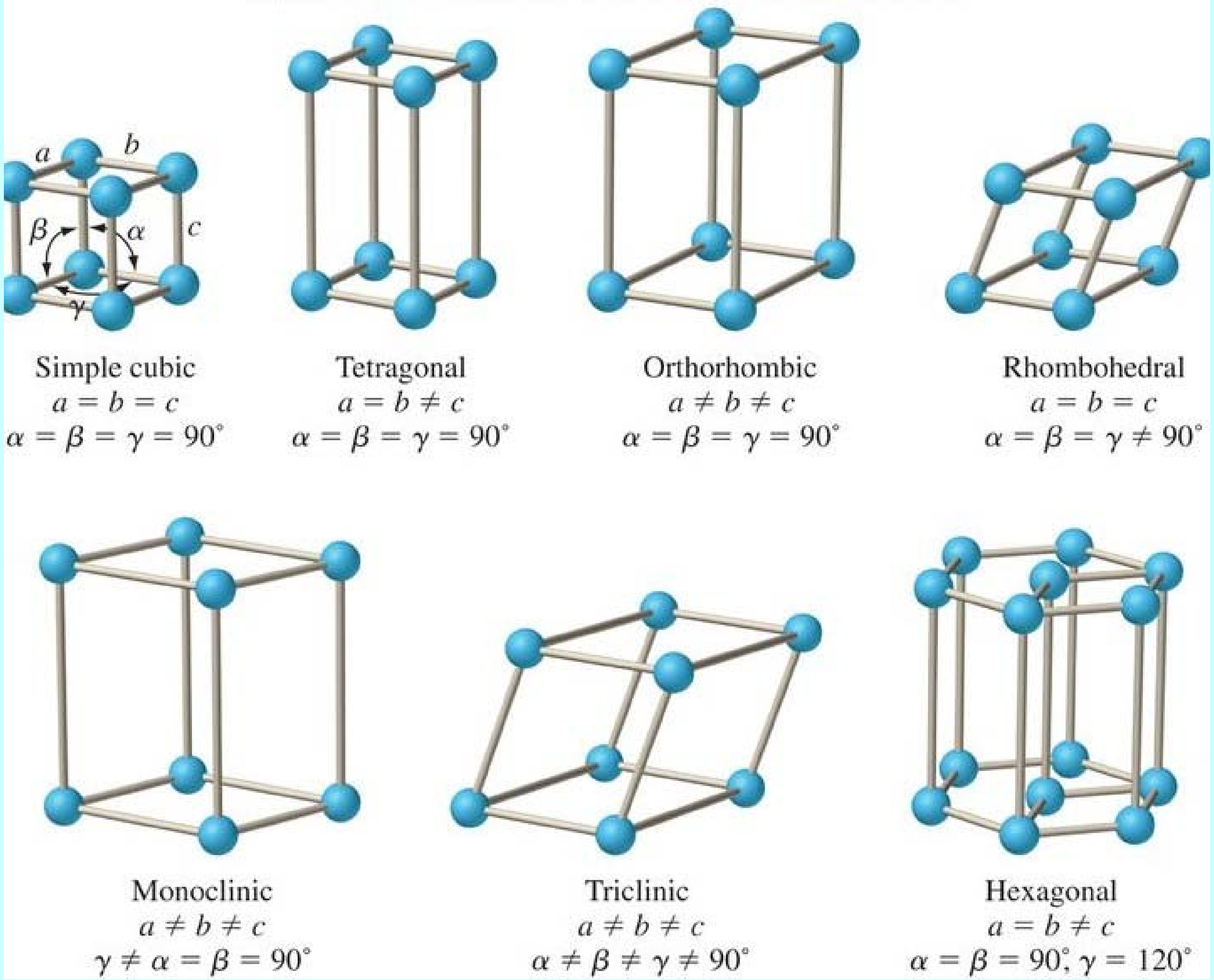
Lattice points occupied by motifs of nonspherical symmetry

17 Plane Space Groups - Wallpaper

A space group = a complete set of all symmetry elements and translations



Seven Crystal Systems in 3D



Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$

Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$

Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90^\circ$

Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

Hexagonal
$a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

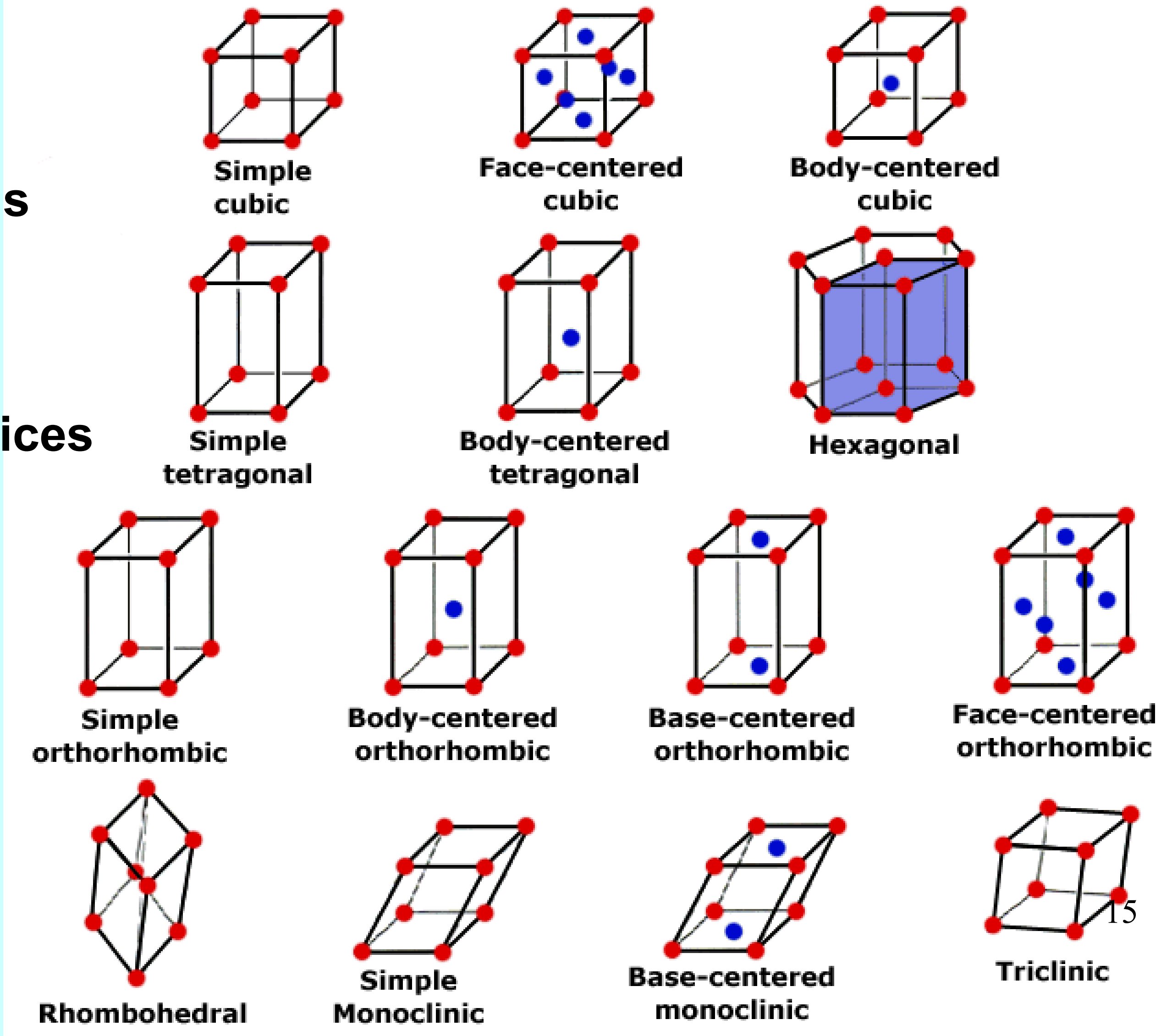
Lattice points of spherical symmetry

Fourteen Bravais Lattices in 3D

7 Crystal Systems

+ Centering

= 14 Bravais Lattices



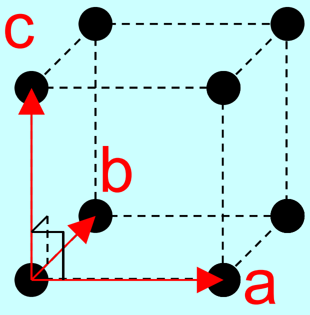
Centering

Simple Cubic (SC)

$a = b = c$

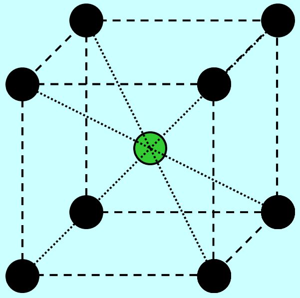
$a \perp b \perp c$

Conventional Cell = Primitive Cell

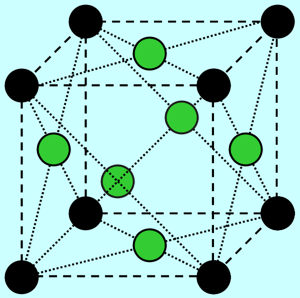


Add one atom at the center of the cube

Add one atom at the center of each face



Body-Centered Cubic (BCC)

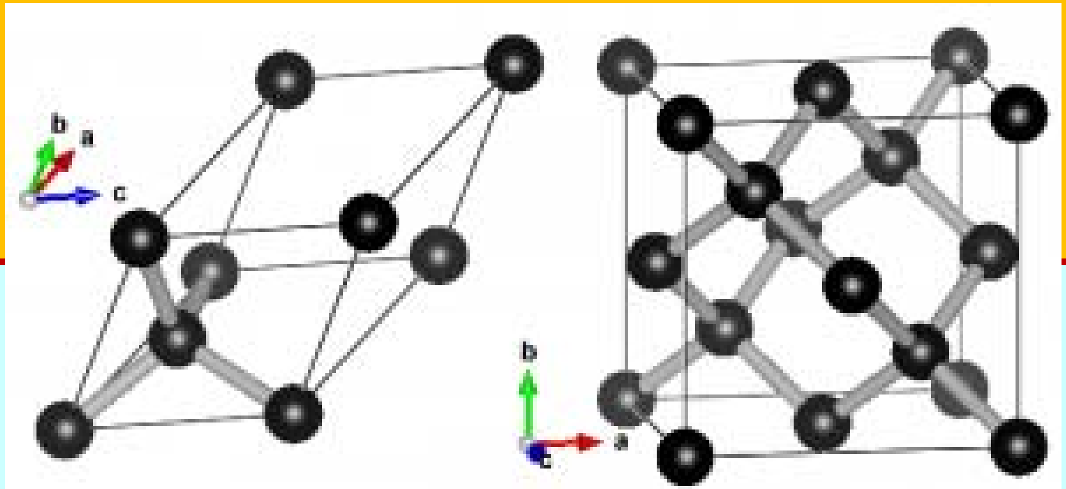


Face-Centered Cubic (FCC)

Conventional Unit Cell ≠ Primitive Cell

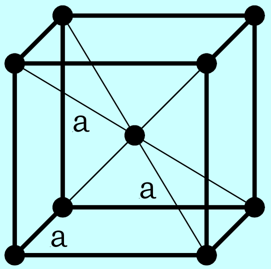
3D Lattices and Space Groups

	Bravais Lattice (Lattice point = Basis of Spherical Symmetry)	Crystal Structure (Structural motif = Basis of Arbitrary Symmetry)
Number of point groups:	7 (7 crystal systems)	32 (32 crystallographic point groups)
Number of space groups:	14 (14 Bravais lattices)	230 (230 space groups)



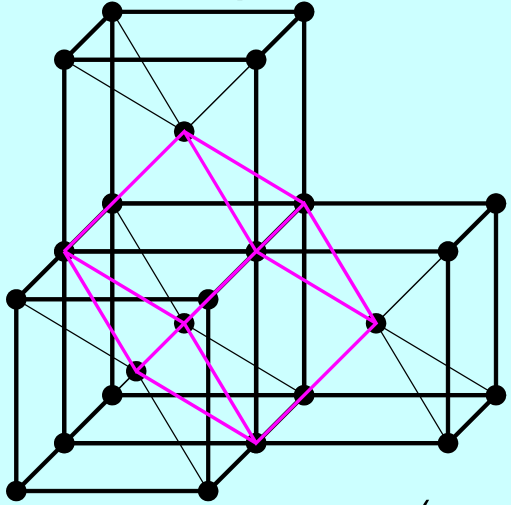
Primitive Cell

- The **smallest** cell that can be translated throughout space to completely recreate the entire lattice
- Volume of space translated through all the vectors in a lattice that just fills all of space without overlapping or leaving voids
- Contains just **one Bravais lattice point (Z = 1)**
- There is not one unique primitive cell, many (∞) possible shapes
- The primitive cell for the simple cubic lattice is equal to the simple cubic unit cell (they are identical)



Body-Centered
Cubic (I)

Unit Cell



(magenta)

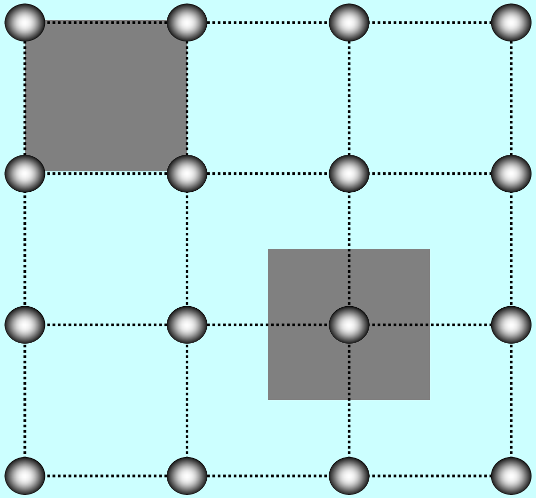
Primitive Cell

Primitive Cell

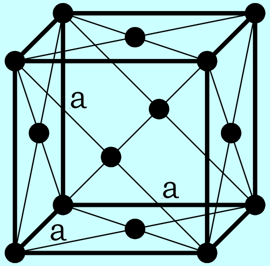
A primitive cell of the lattice may be constructed in 2 ways:

The primitive cell may have the lattice point confined at its CENTER = the WIGNER-SEITZ cell

The primitive cell may be formed by constructing lines BETWEEN lattice points, the lattice points lie at the VERTICES of the cell

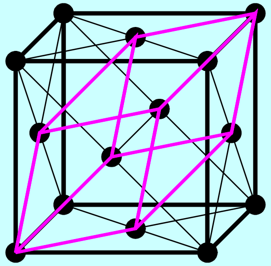


Nonprimitive Unit Cell vs. Primitive Cell

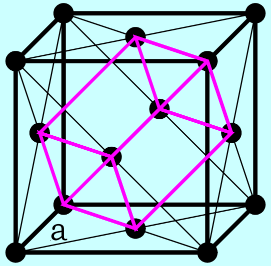


Face-Centered
Cubic (F)

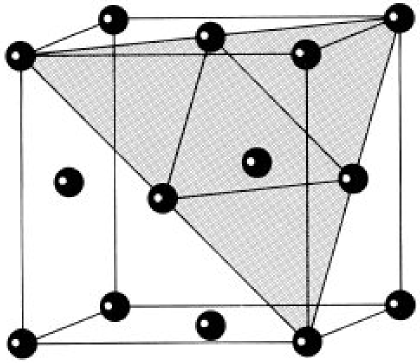
Unit Cell



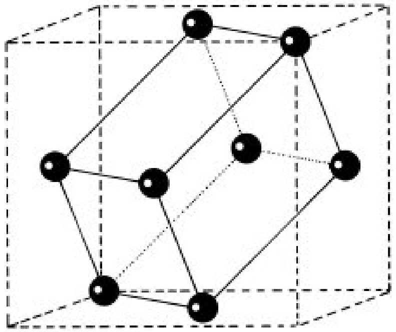
Primitive Cell



Rotated 90°



(*a*) Conventional non-primitive cubic unit cell showing a close-packed (1 1 1) plane



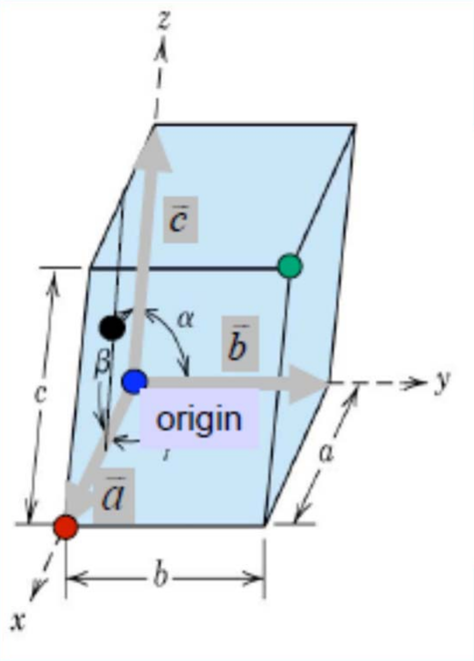
(*b*) Primitive rhombohedral unit cell

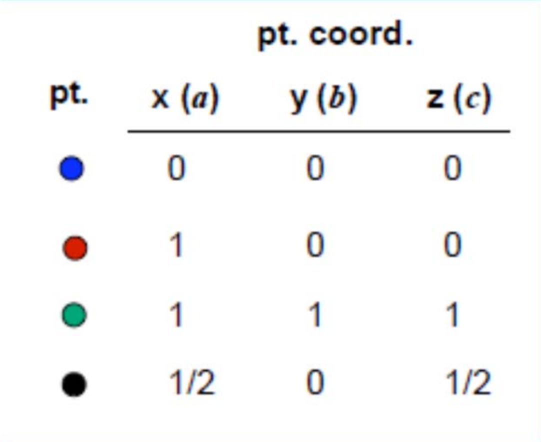
The primitive cell is smaller or equal in size to the unit cell
The unit cells possesses the highest symmetry present in the lattice (for example Cubic)

Index System for Points

1) **Coordinates within a unit cell**

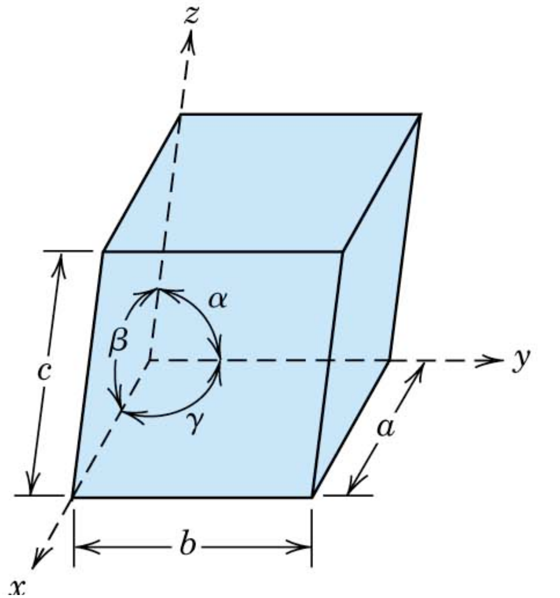
2) **Express the coordinates u, v, w as fractions of unit cell vectors (lattice parameters) a, b, and c: (h, k, l)**
3) **Do not clear fractions**
4) **Entire lattice can be referenced by one unit cell**



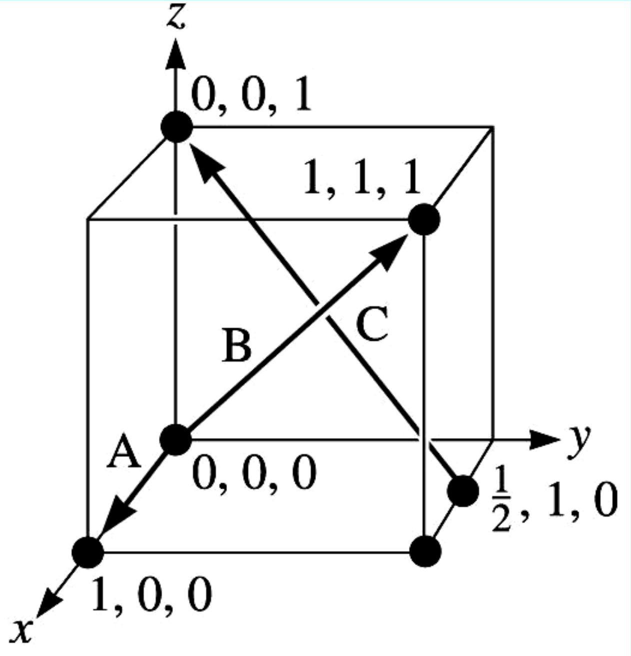


	pt. coord.		
pt.	x (*a*)	y (*b*)	z (*c*)
🔵	0	0	0
🔴	1	0	0
🟢	1	1	1
⚫	1/2	0	1/2

Central point coordinates?



Index System for Directions
(Miller Indices)



A = [100]
B = [111]
C = [1¯2¯2]

1) Determine coordinates of two points in direction of interest (simplified – origin):

u1 v1 w1 and u2 v2 w2

2) Subtract coordinates of the second point from those of the first point:

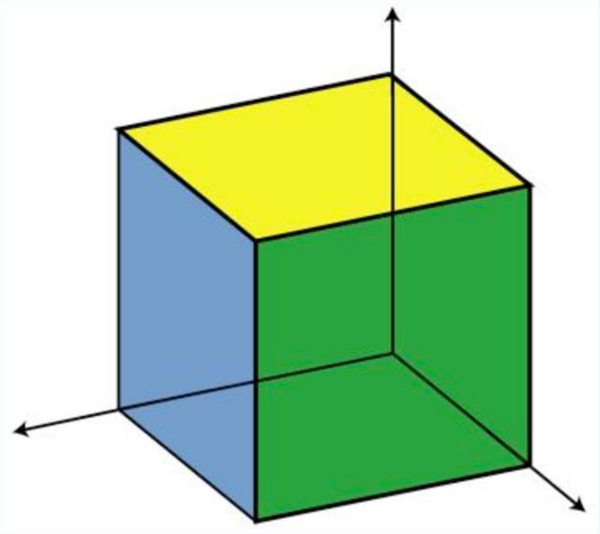
u’ = u1 - u2,   v’ = v1 - v2,   w’ = w1 - w2

3) Clear fractions from the differences to give indices in lowest integer values

4) Write indices in [ ] brackets - [uvw]

5) Negative = a bar over the integer

Index System for Directions (Miller Indices)



In the cubic system directions having the same indices regardless of order or sign are equivalent

For cubic crystals, the directions are all equivalent by symmetry:

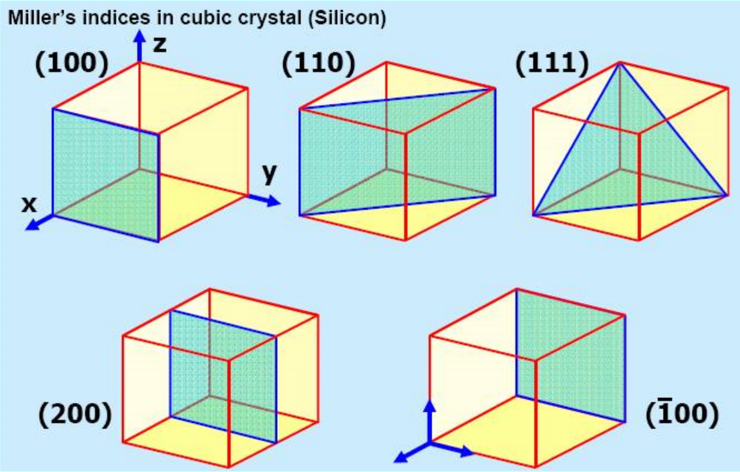
$[1\ 0\ 0]$, $[\bar{1}\ 0\ 0]$, $[0\ 1\ 0]$, $[0\ \bar{1}\ 0]$, $[0\ 0\ 1]$, $[0\ 0\ \bar{1}]$

Families of crystallographic directions
e.g. <1 0 0>

Angled brackets denote a family of crystallographic directions

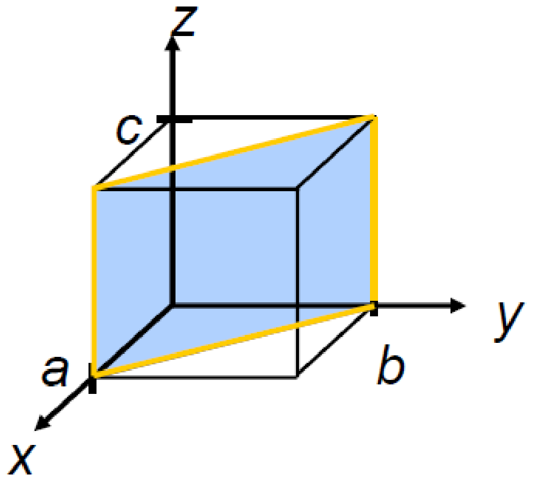
Index System for Crystal Planes (Miller Indices)

1. If the plane passes through the origin, select an equivalent plane or move the origin
2. Find the intercepts on the axes in terms of the lattice constants a, b, c. The axes may be those of a primitive or nonprimitive unit cell
3. Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers
4. (1/∞ = 0)
5. The result enclosed in parenthesis (*hkl)*, is called the index of the plane

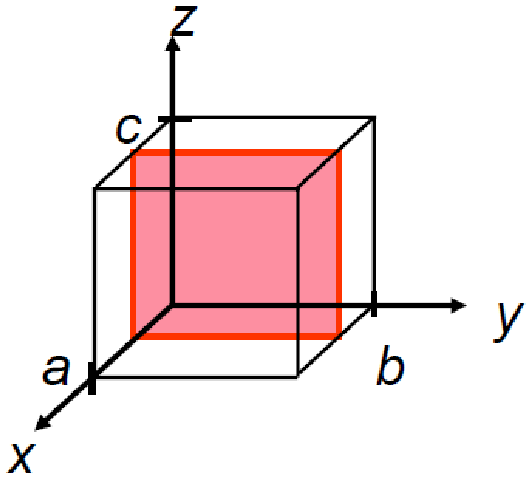


Index System for Crystal Planes (Miller Indices)

Example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		



Example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		

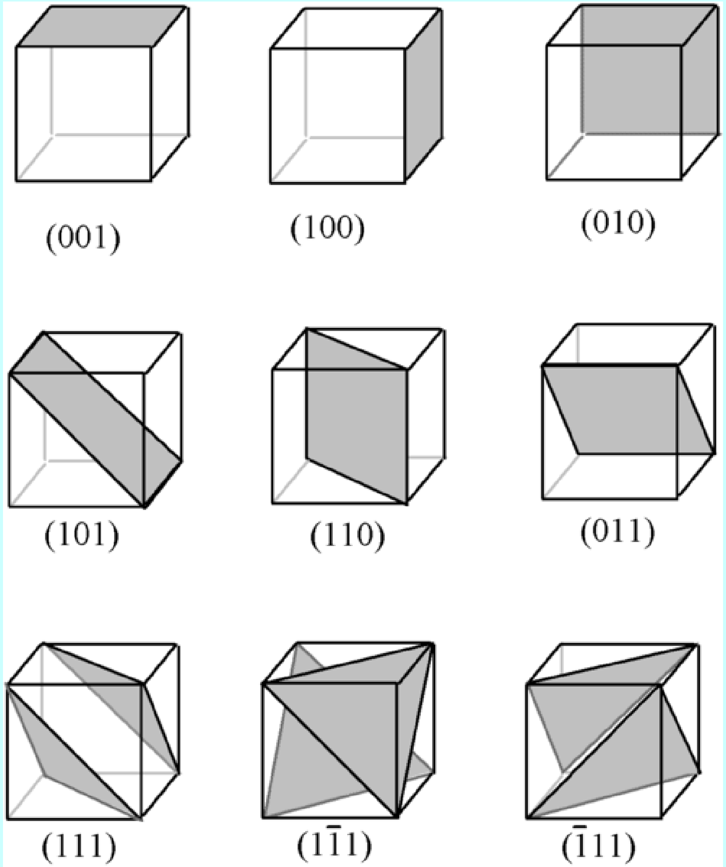


Index System for Crystal Planes
(Miller Indices)

Cubic system - planes having the same indices regardless of order or sign are equivalent - braces {hkl}

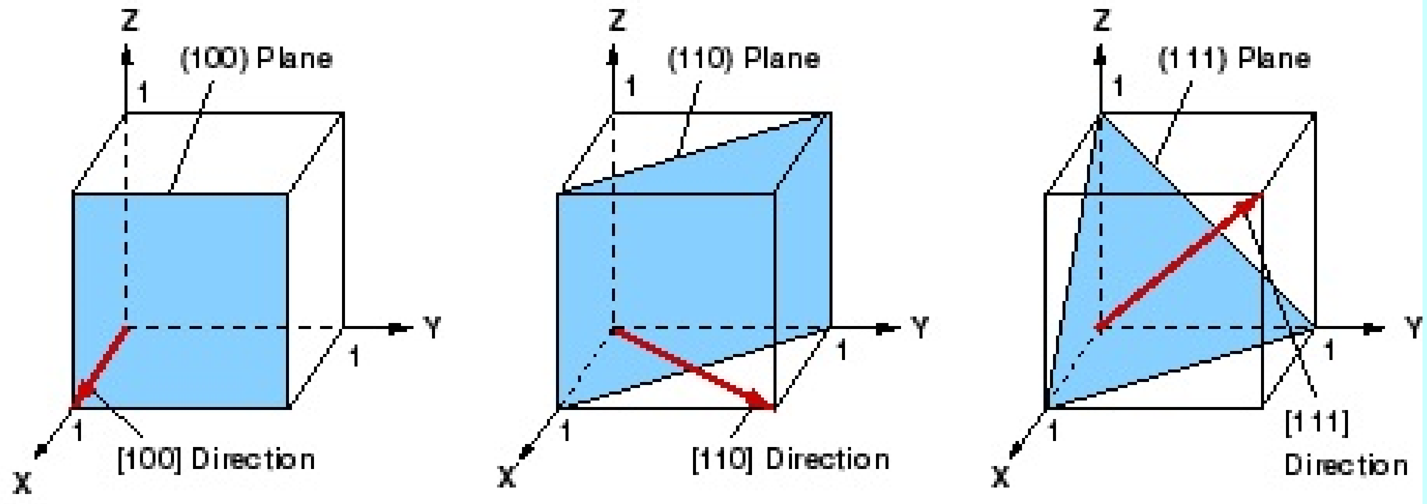
(111), (11¯1), (111¯) ….
belong to {111} family

(100), (1¯00), (010), and (001) …..
belong to {100} family

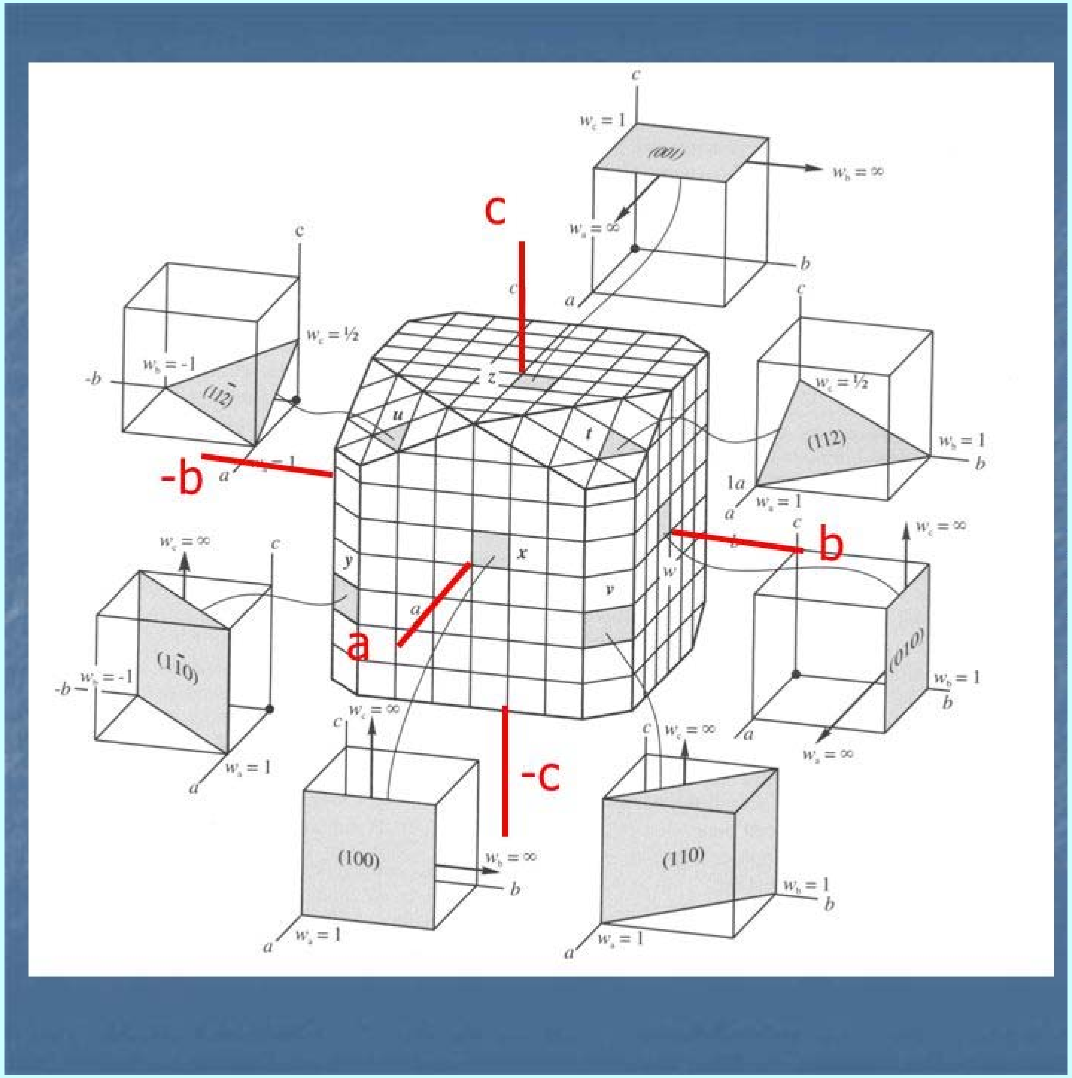


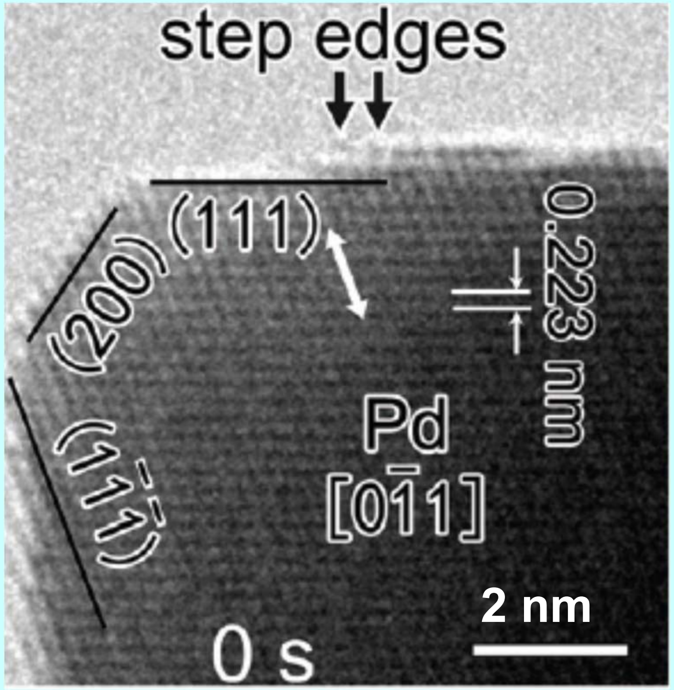
Index System for Crystal Planes
(Miller Indices)

The Miller indices (hkl) is the same vector as the normal to the plane [hkl]



Index System for Crystal Planes
(Miller Indices)

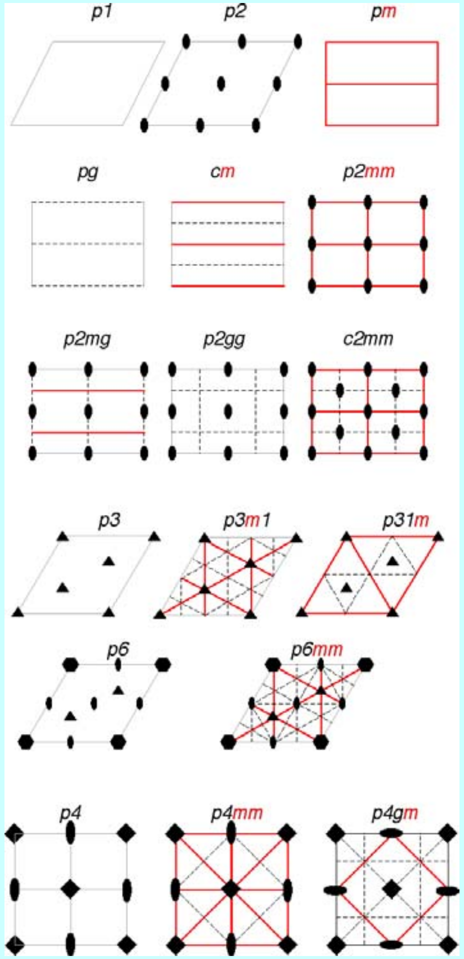




Atomic planes influence
- **Optical properties**
- **Reactivity**
- **Surface tension**
- **Dislocations**

Quasiperiodic Crystals

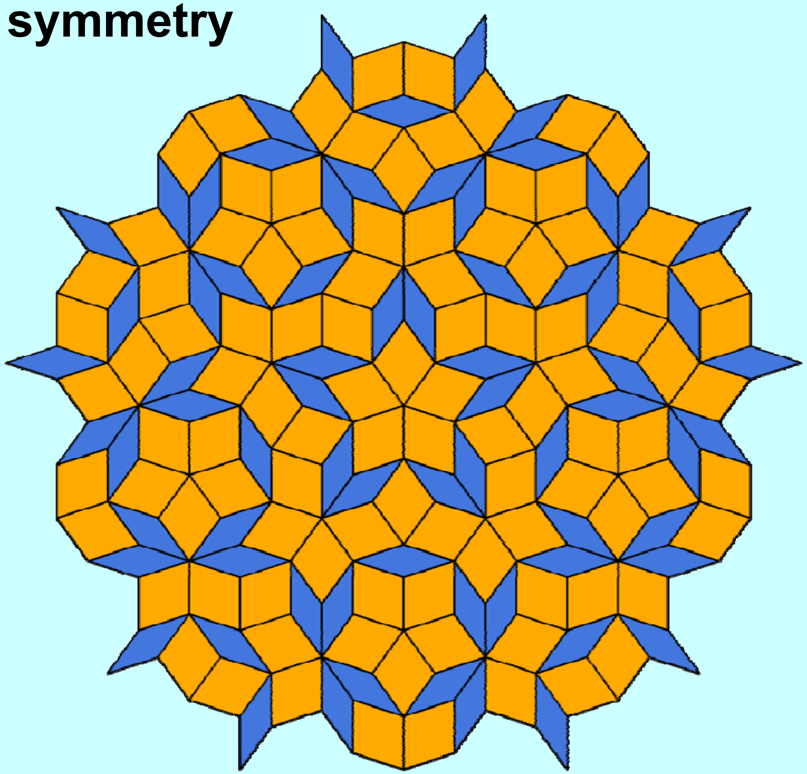
Quasiperiodic crystal = a structure that is ordered but not periodic continuously fills all available space, but it lacks translational symmetry



Penrose - a plane filled in a nonperiodic fashion using two different types of tiles

Five-fold symmetry

Only 2, 3, 4, 6-fold symmetry allowed to fill 2D plane completely



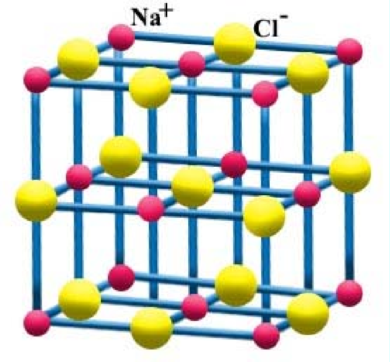
Crystals and Crystal Bonding

- **metallic** (Cu, Fe, Au, Ba, alloys)

  metallic bonding, electron delocalization

- **ionic** (NaCl, CsCl, CaF_2, ...)

  ionic bonds, cations and anions, electrostatic interactions, ions pack into extremely regular crystalline structures, in an arrangement that minimizes the lattice energy (maximizing attractions and minimizing repulsions). The lattice energy is the summation of the interaction of all sites with all other sites.



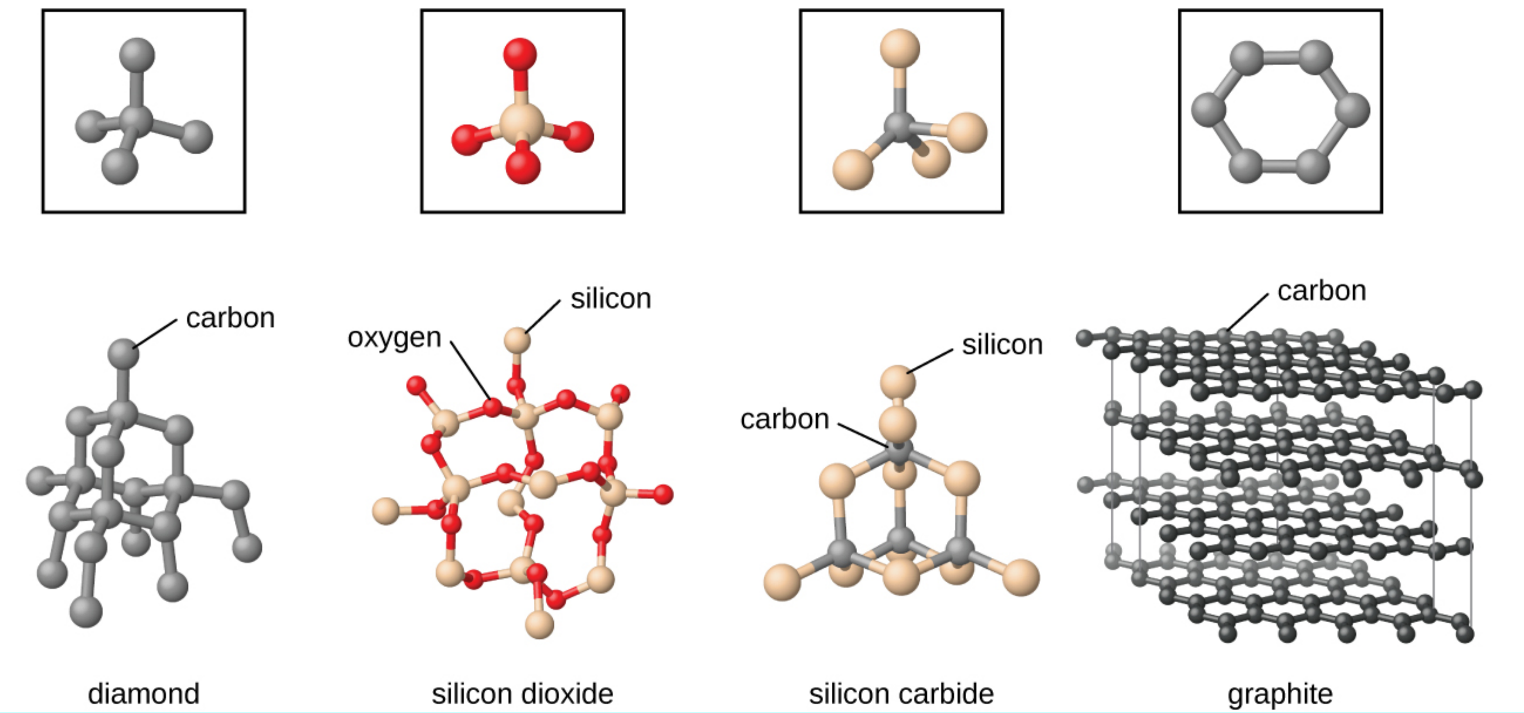
- **covalent network solid** (diamond, graphite, SiO_2, AlN,...)

  atoms, covalent bonding, a chemical compound (or element) in which the atoms are bonded by covalent bonds in a continuous network extending throughout the material, there are no individual molecules, the entire crystal or amorphous solid may be considered a macromolecule

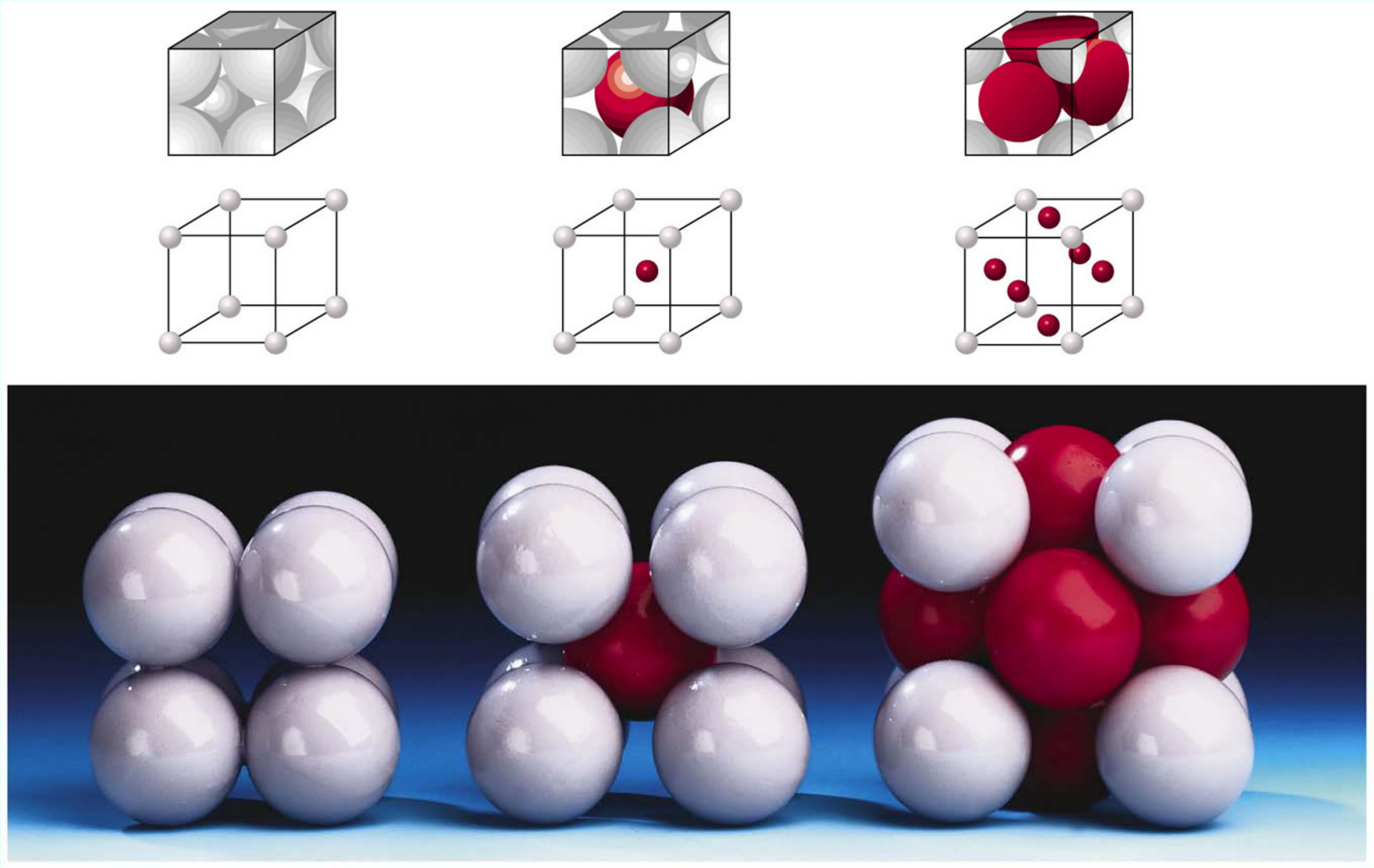
- **molecular** (Ar, C_{60}, HF, H_2O, organics, proteins)

  molecules, van der Waals and hydrogen bonding

Covalent Network Solids

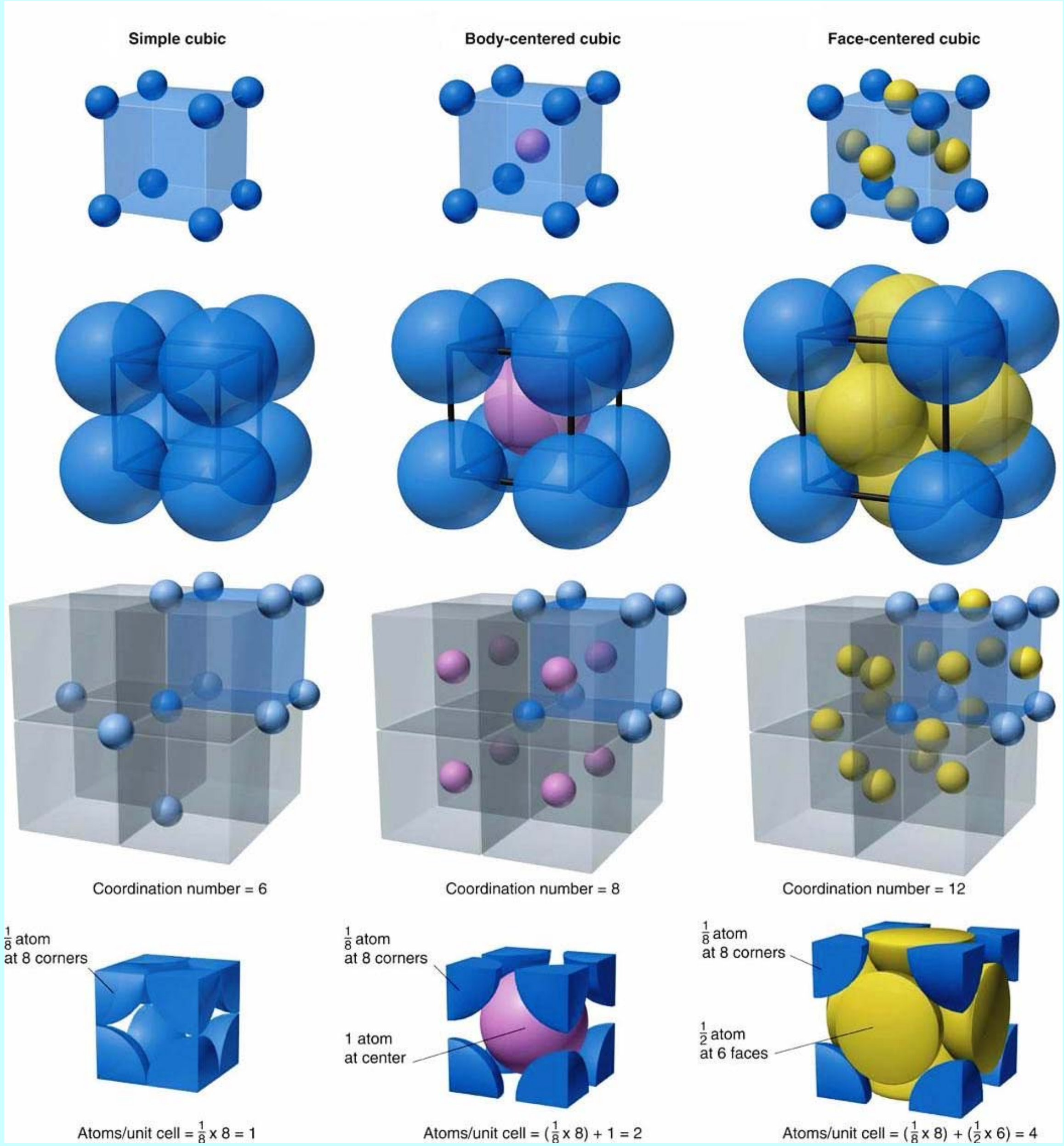


Three Cubic Cells



SC or Primitive (P) **BCC (I)** **FCC (F)**

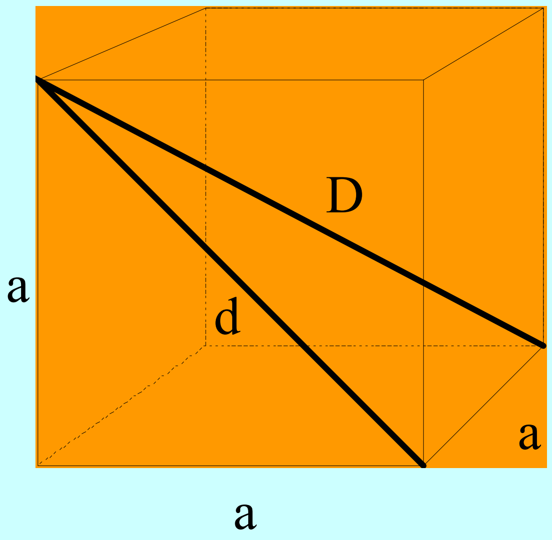
SC or Primitive (P) **BCC (I)** **FCC (F)**



Coordination number

Z = number of lattice points per unit cell

Cube



a = edge

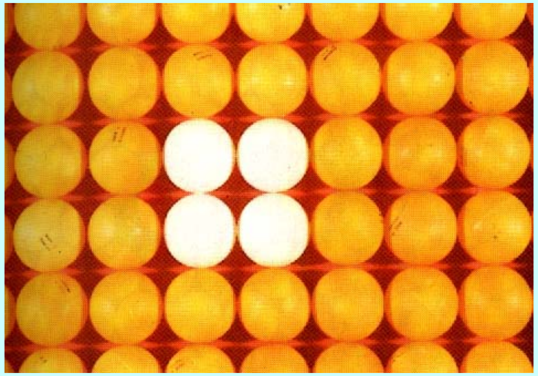
d = face diagonl
$(d^2 = a^2 + a^2 = 2a^2)$

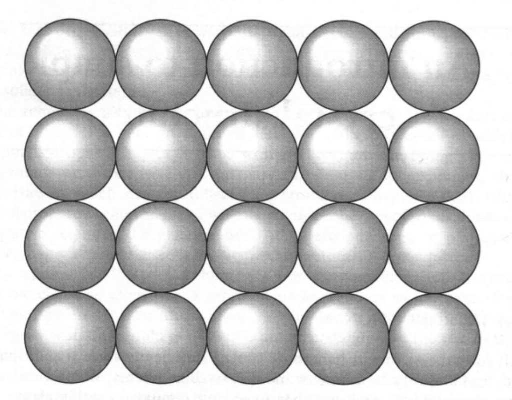
D = body diagonal
$(D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2)$

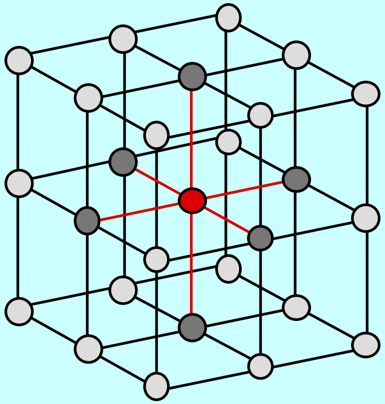
$$d = \sqrt{2} \cdot \mathrm{a}$$

$$D = \sqrt{3} \cdot \mathrm{a}$$

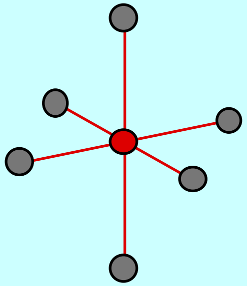
Simple Cubic SC = Polonium

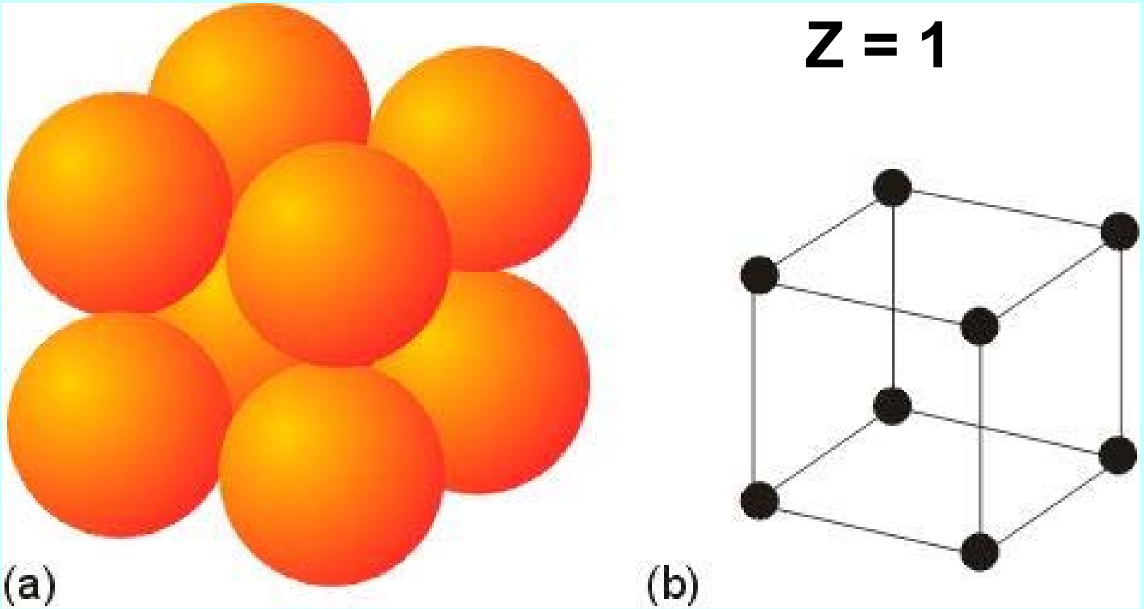




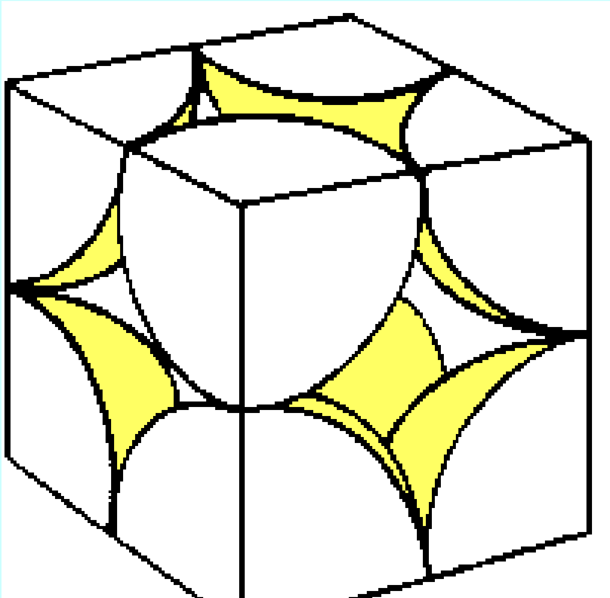


CN 6



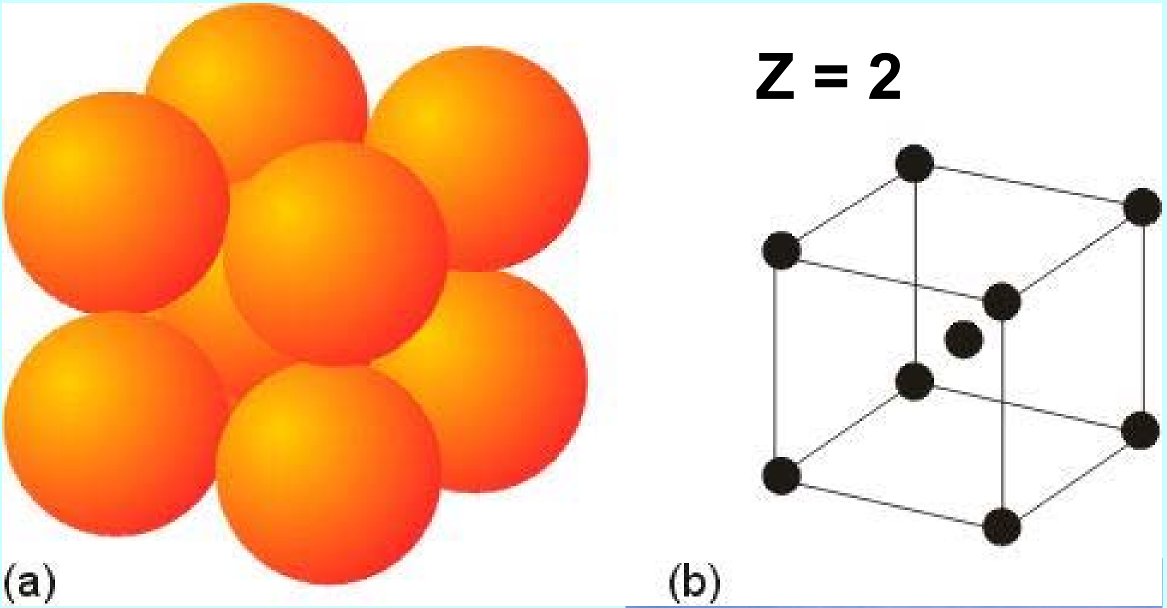


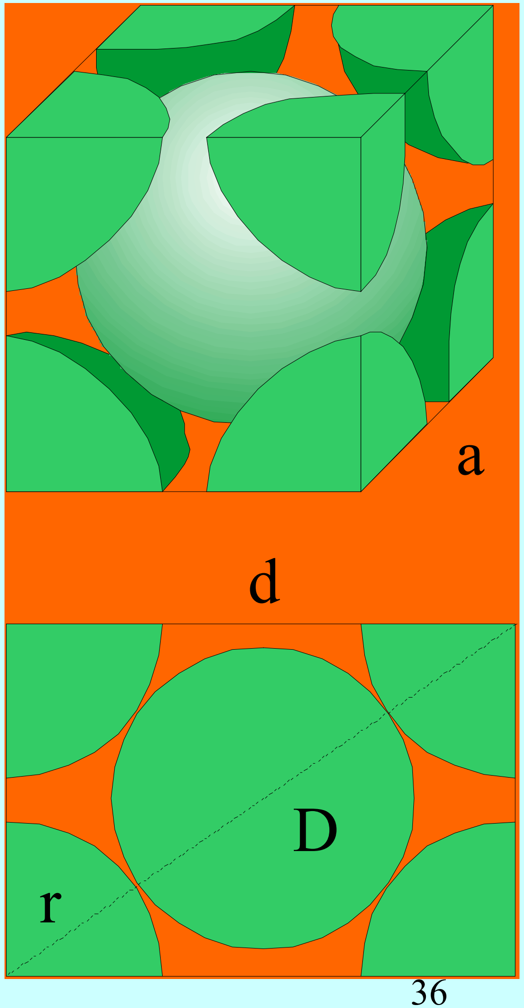
Z = 1



Space filling 52%

BCC = W, Tungsten





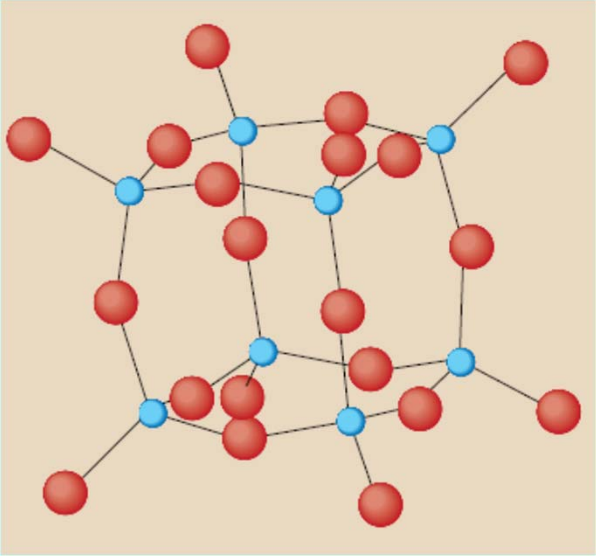
Space filling 68%

CN 8

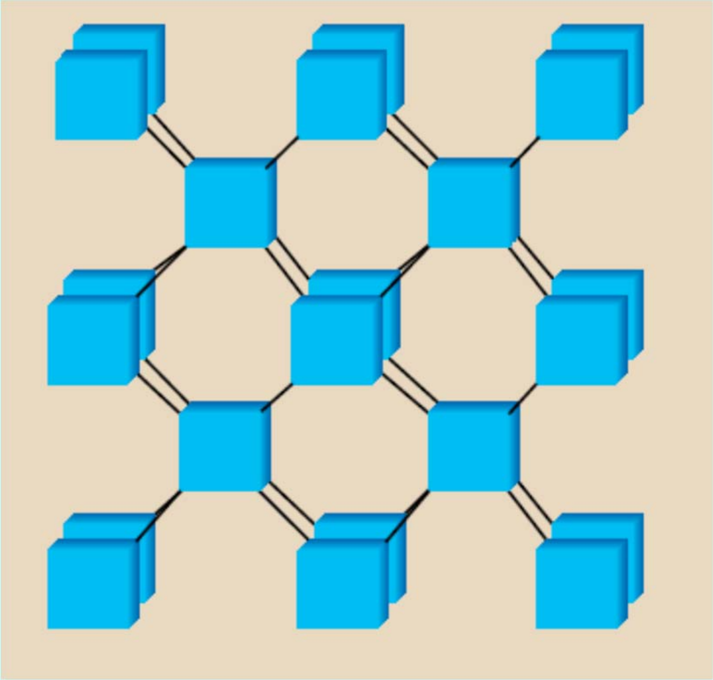
α-Fe, Cr, V, Li-Cs, Ba

BCC

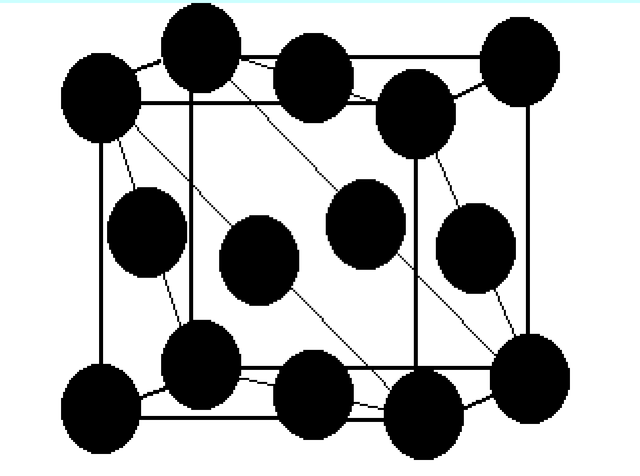
Octasilicate = motif

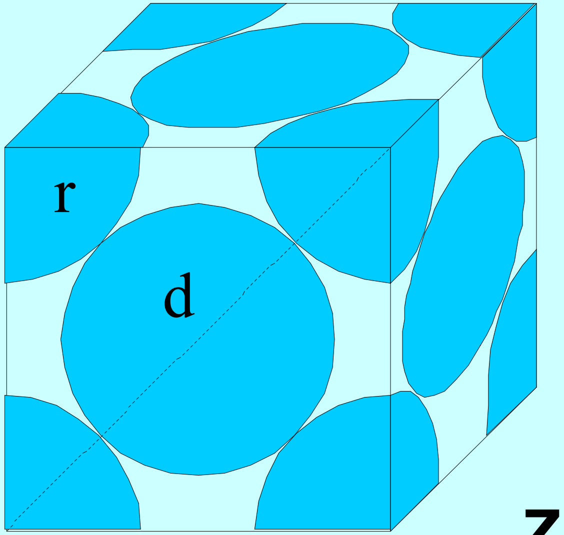


Zeolite

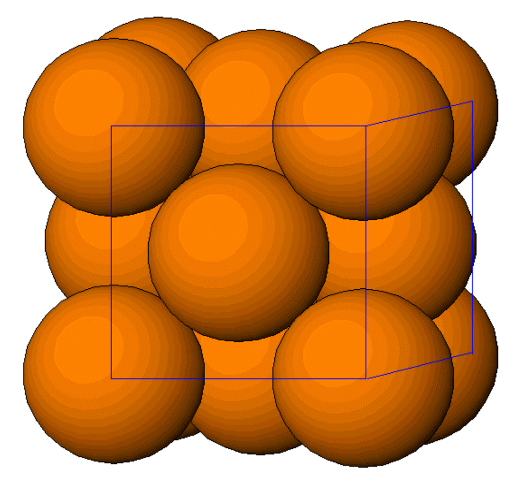


FCC = Copper, Cu = CCP





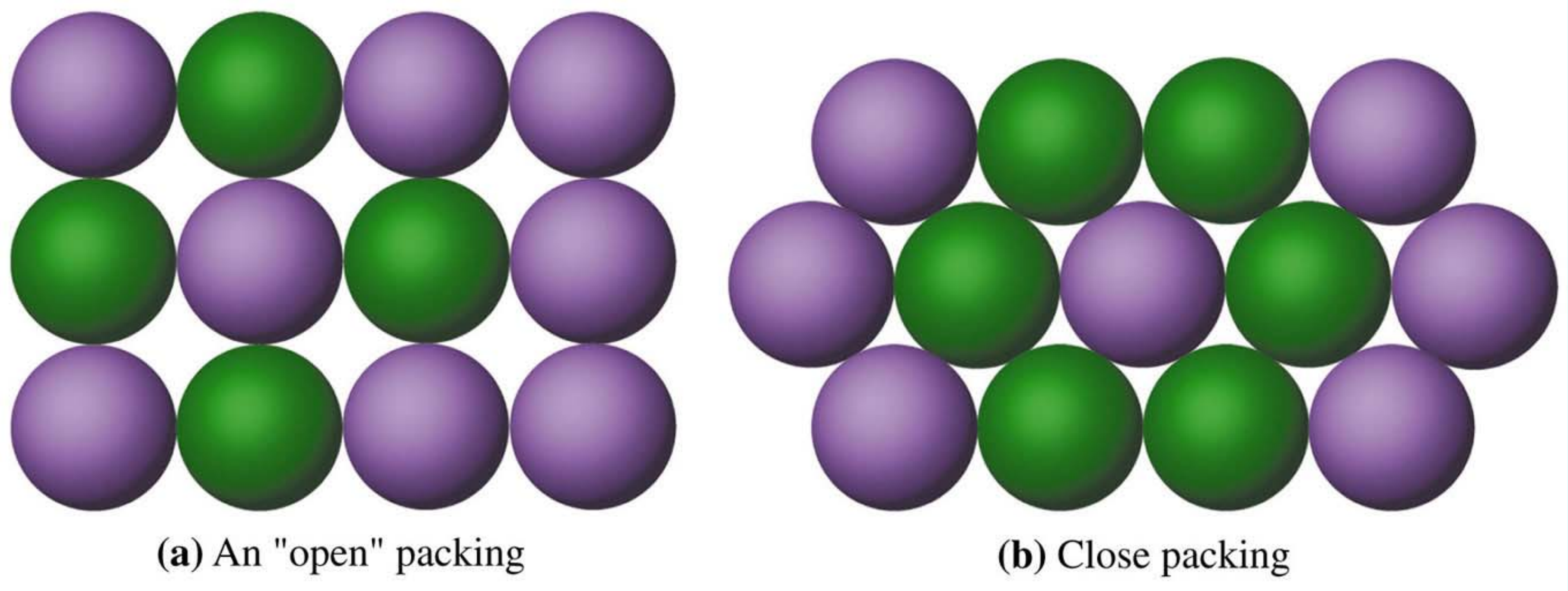
Z = 4



Space filling 74%

CN 12

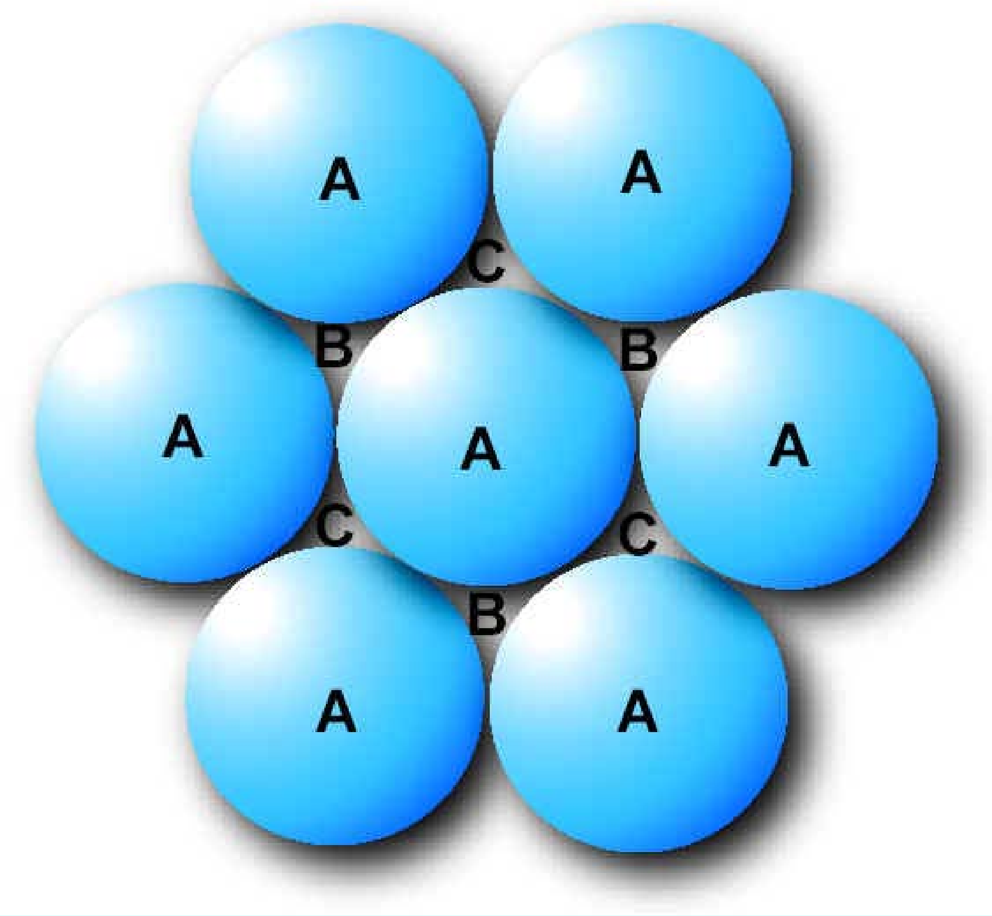
Close Packing in Plane 2D

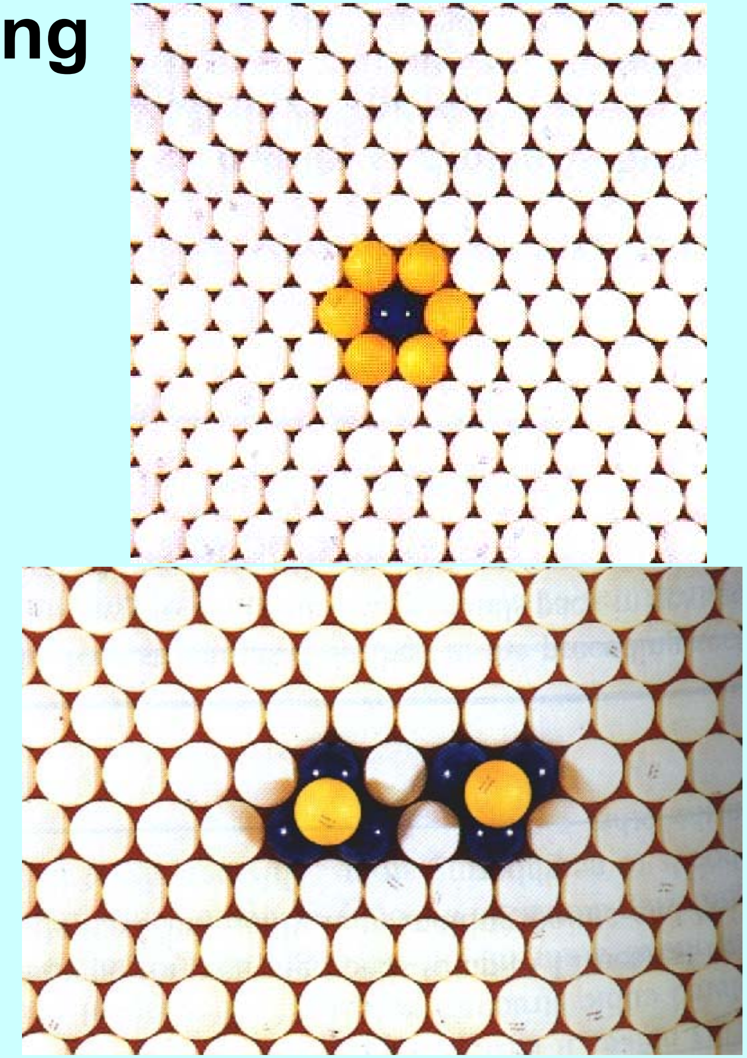


(a) An "open" packing

(b) Close packing

Close Packing



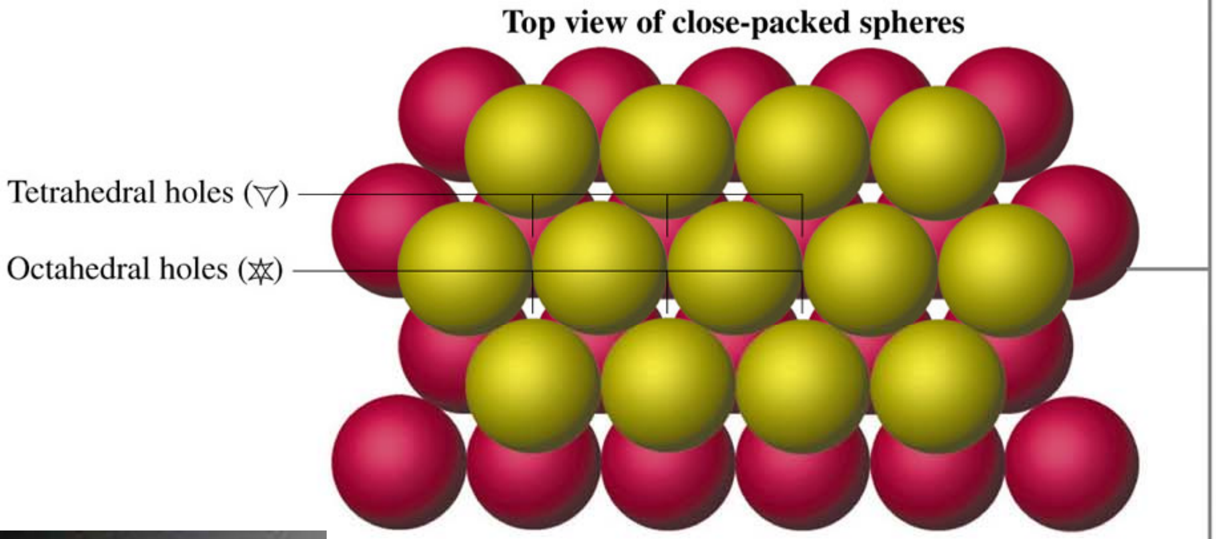


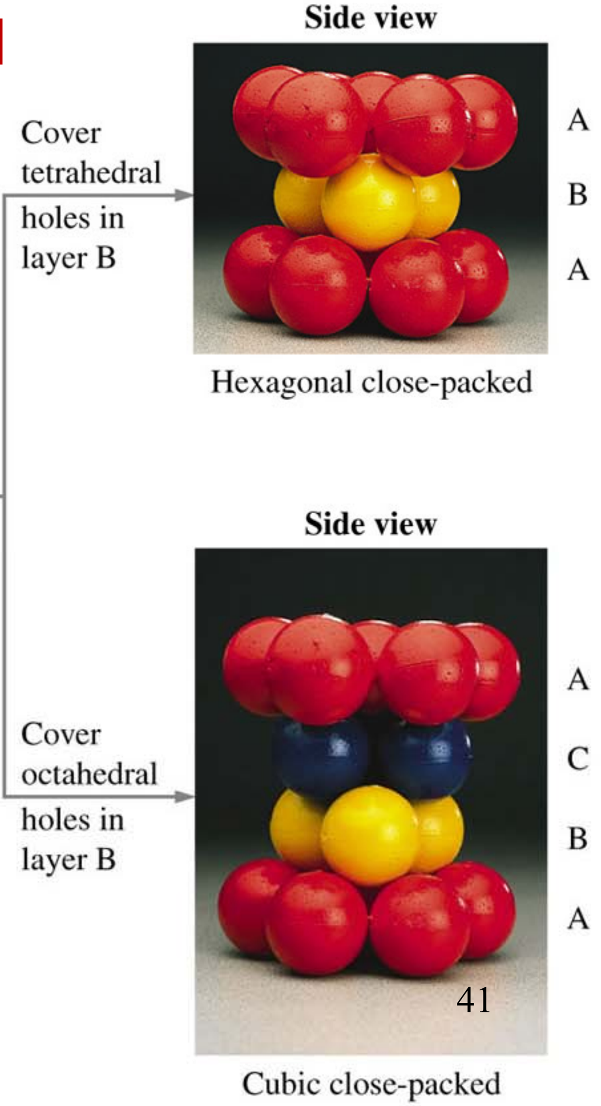
The second layer - B and C holes cannot be occupied at the same time

Close Packing in Space 3D

The third layer decides:

Hexagonal
HCP



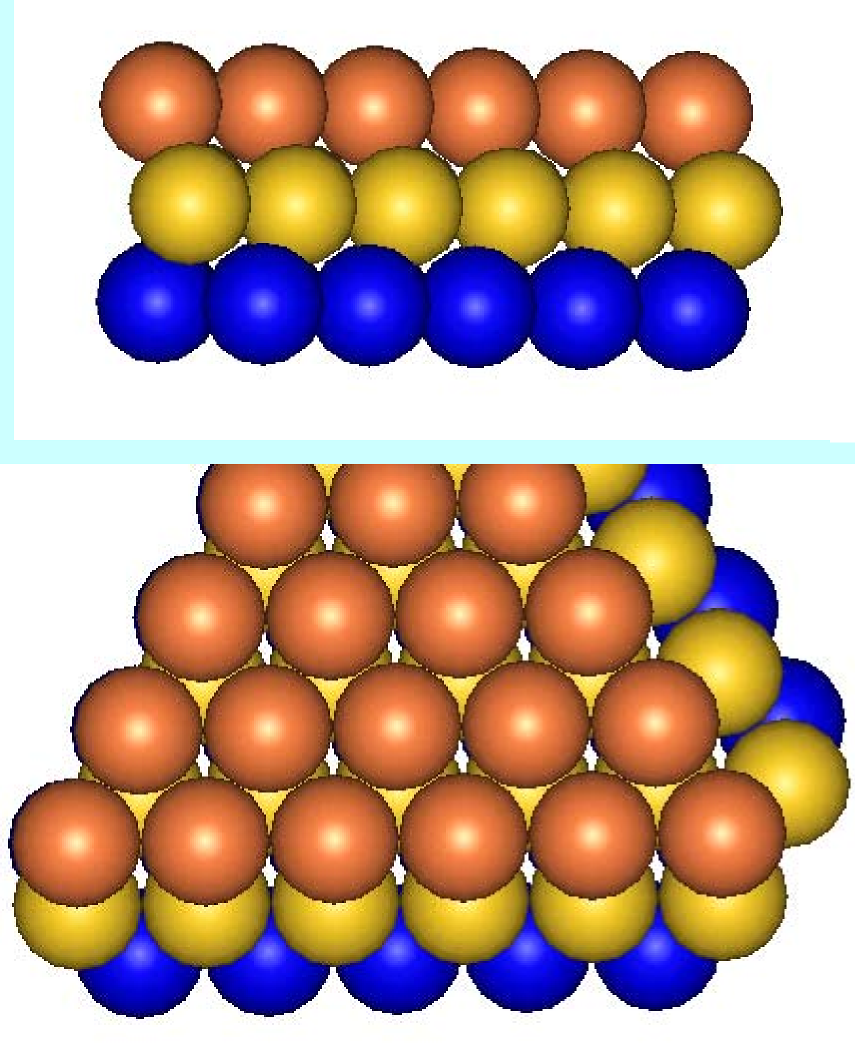


Hexagonal close-packed

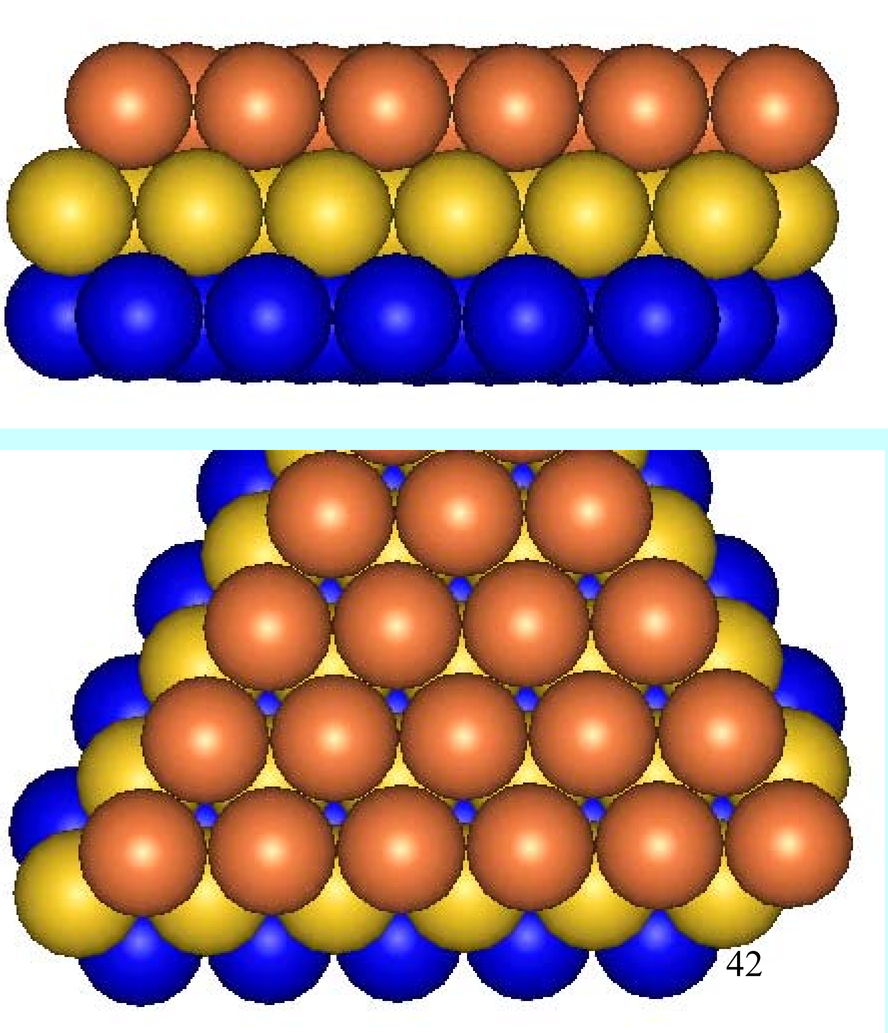
Cubic close-packed

Cubic
CCP

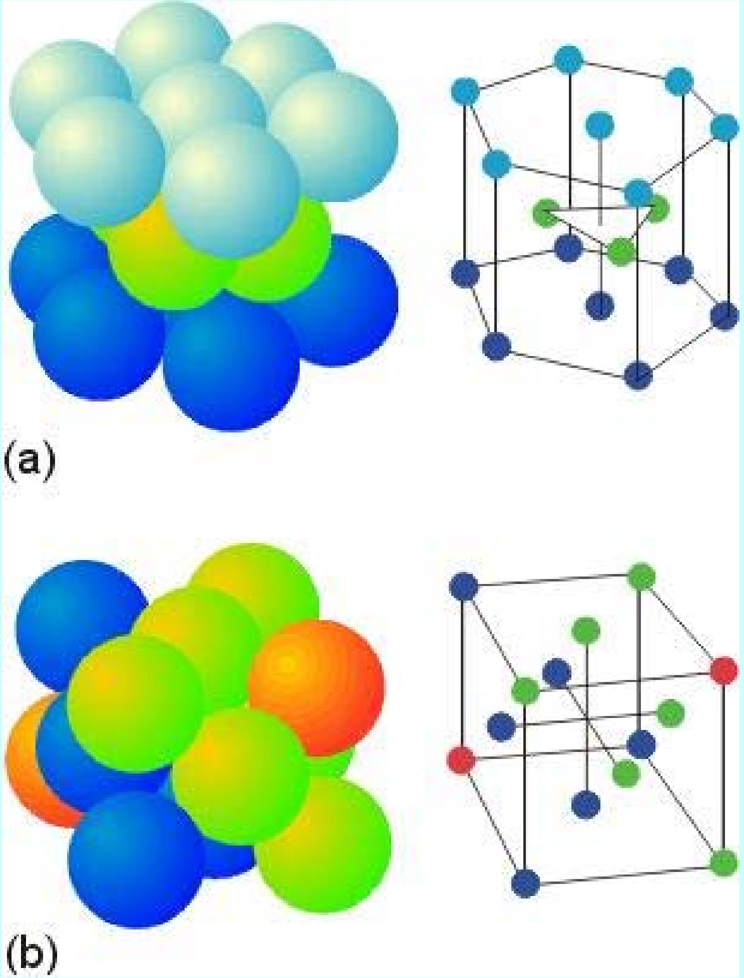
Hexagonal
HCP

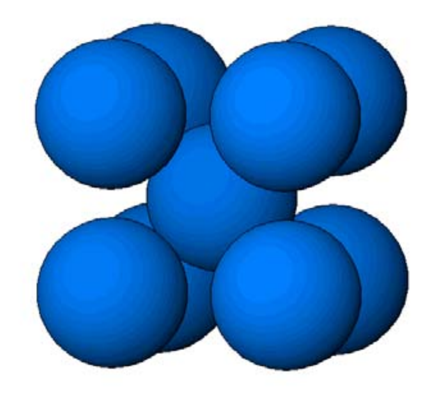


Cubic
CCP

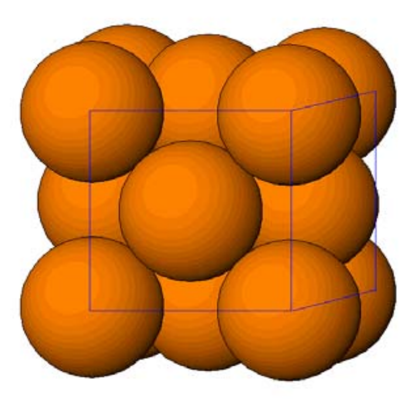


Mg, Be, Zn, Ni, Li, Os, Sc, Ti, Co, Y, Ru, solid He





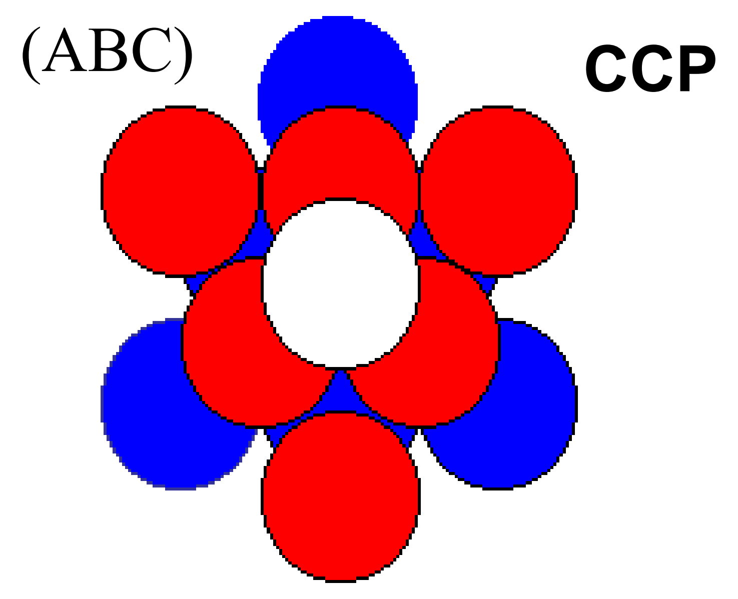
Hexagonal
HCP

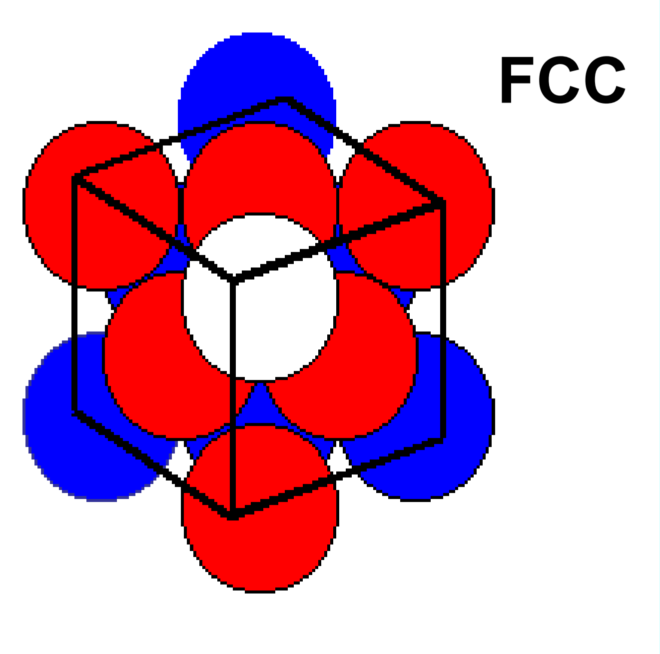


Cubic
CCP
= FCC

Cu, γ-Fe (austenite), Ca, Sr, Ag, Au, Ni, Rh, solid Ne-Xe, F_2, C_{60}, opal (300 nm)

CCP = FCC

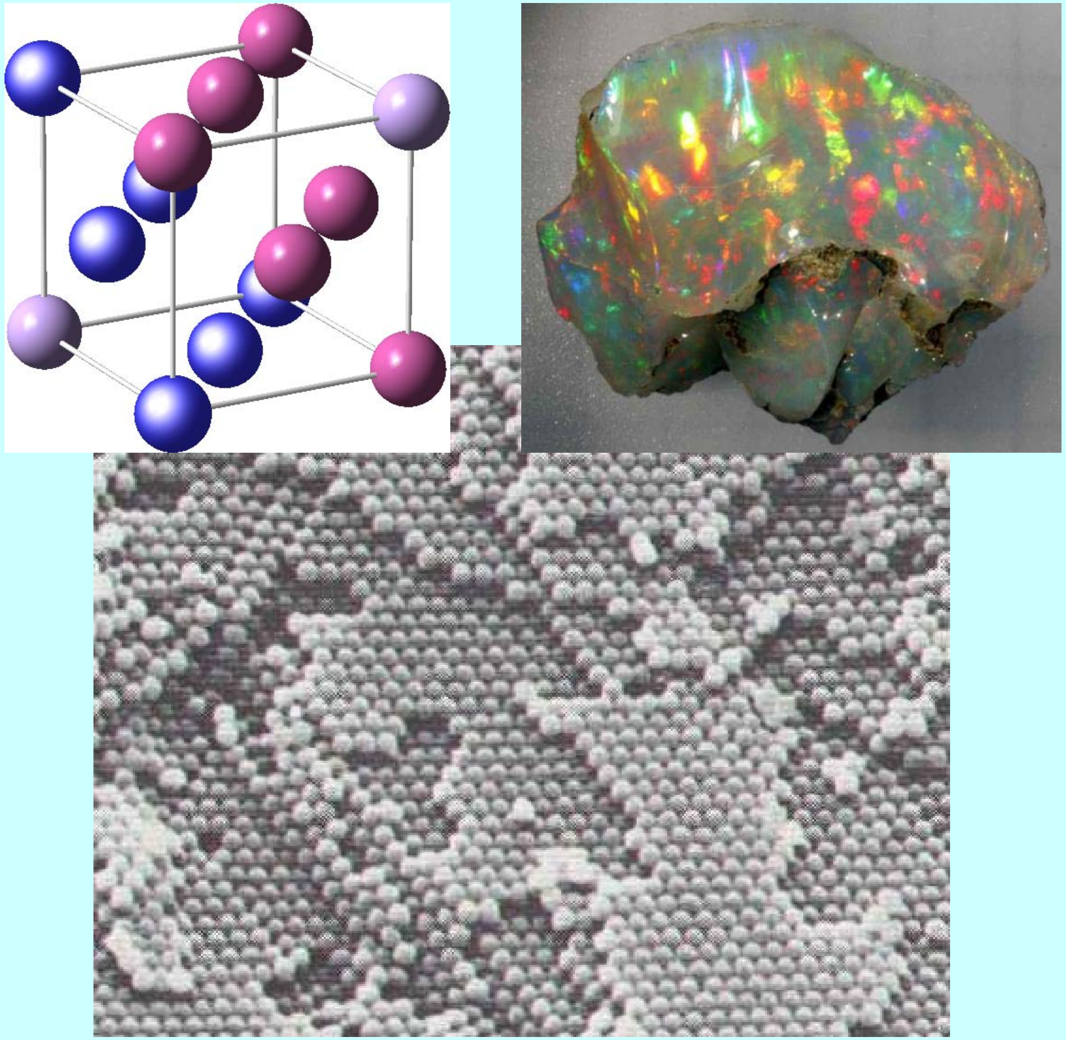




Close packed layers of CCP are oriented perpendicularly to the body diagonal of the cubic cell of FCC

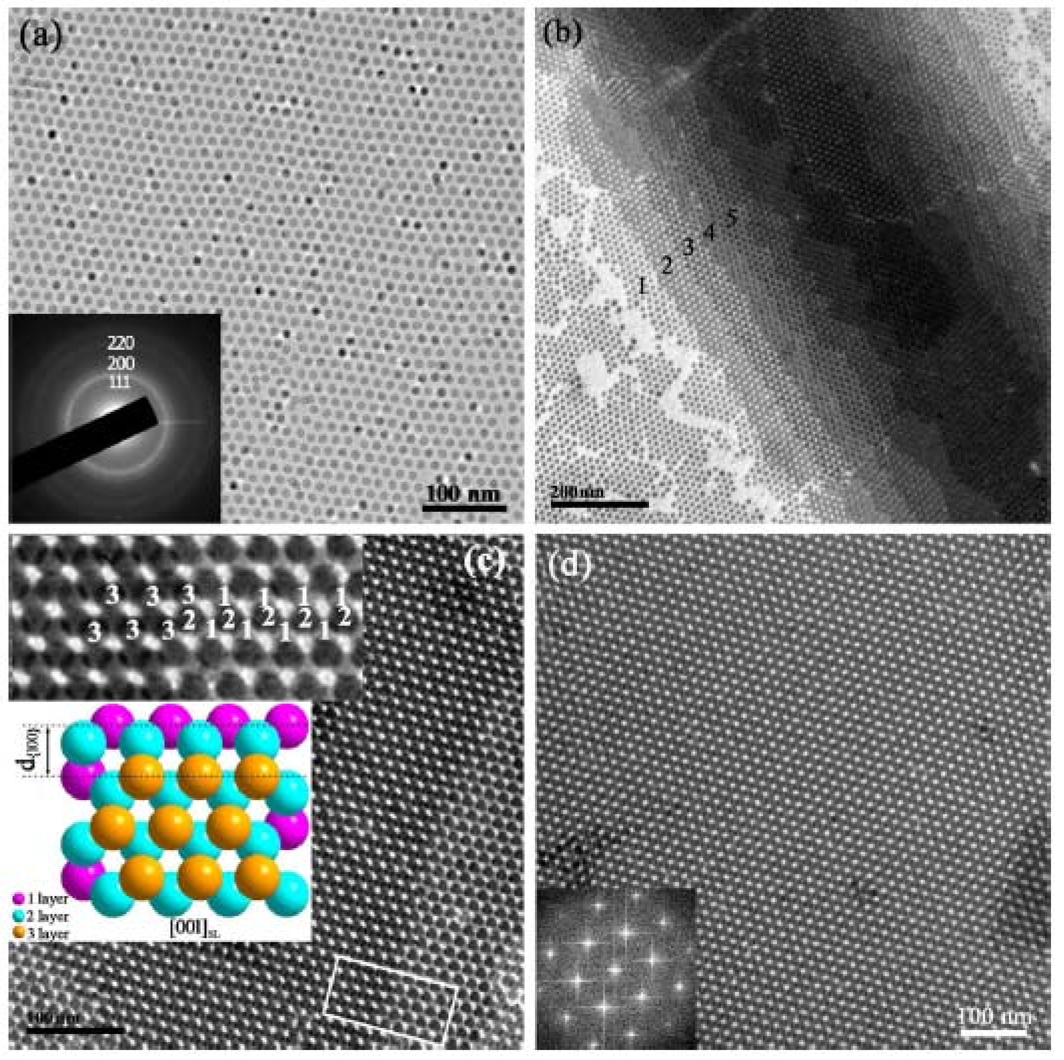
Structures with Larger Motifs

C_{60} - FCC = CCP



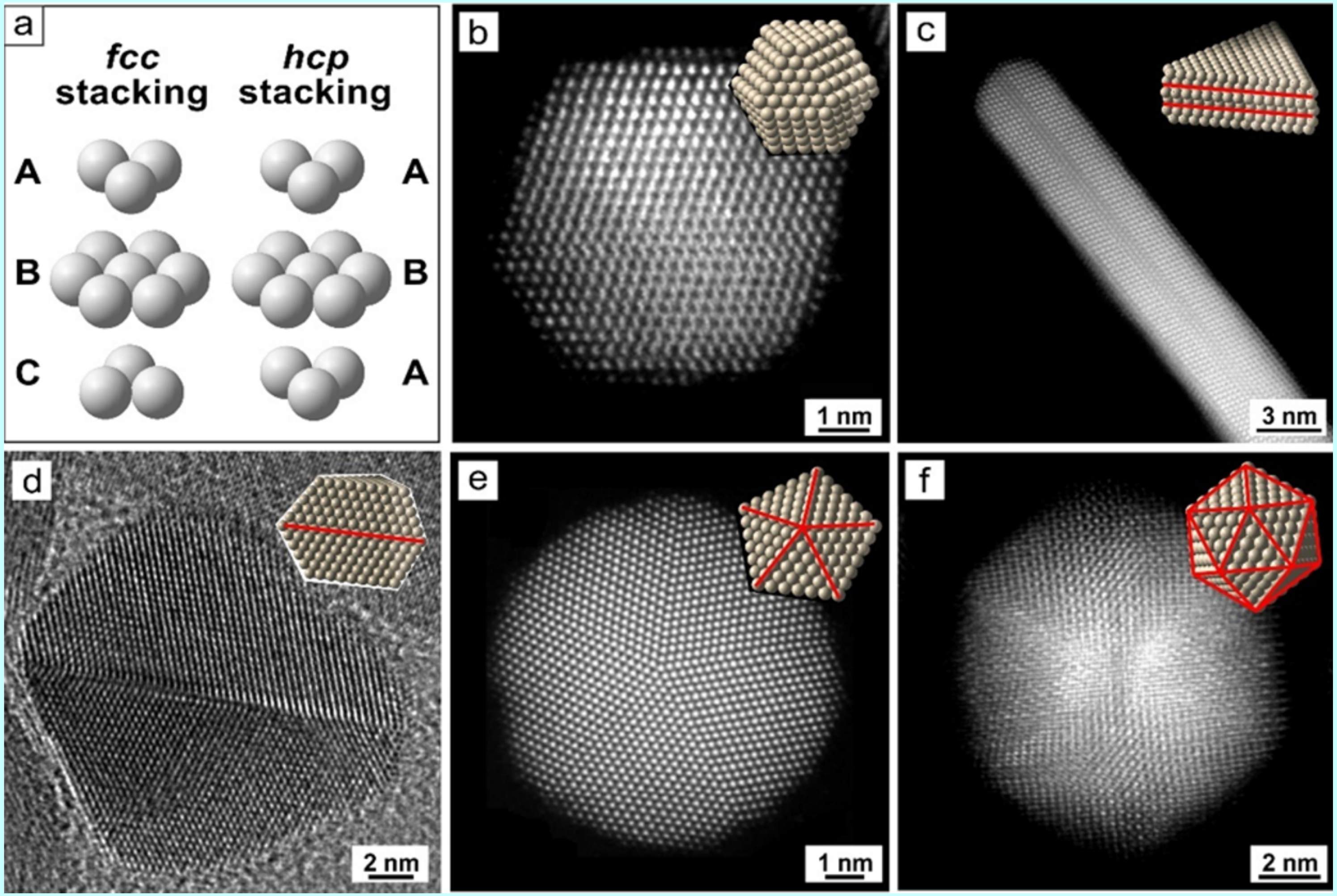
SEM - Opal – 300 nm SiO_2 FCC = CCP

Structures with Larger Motifs



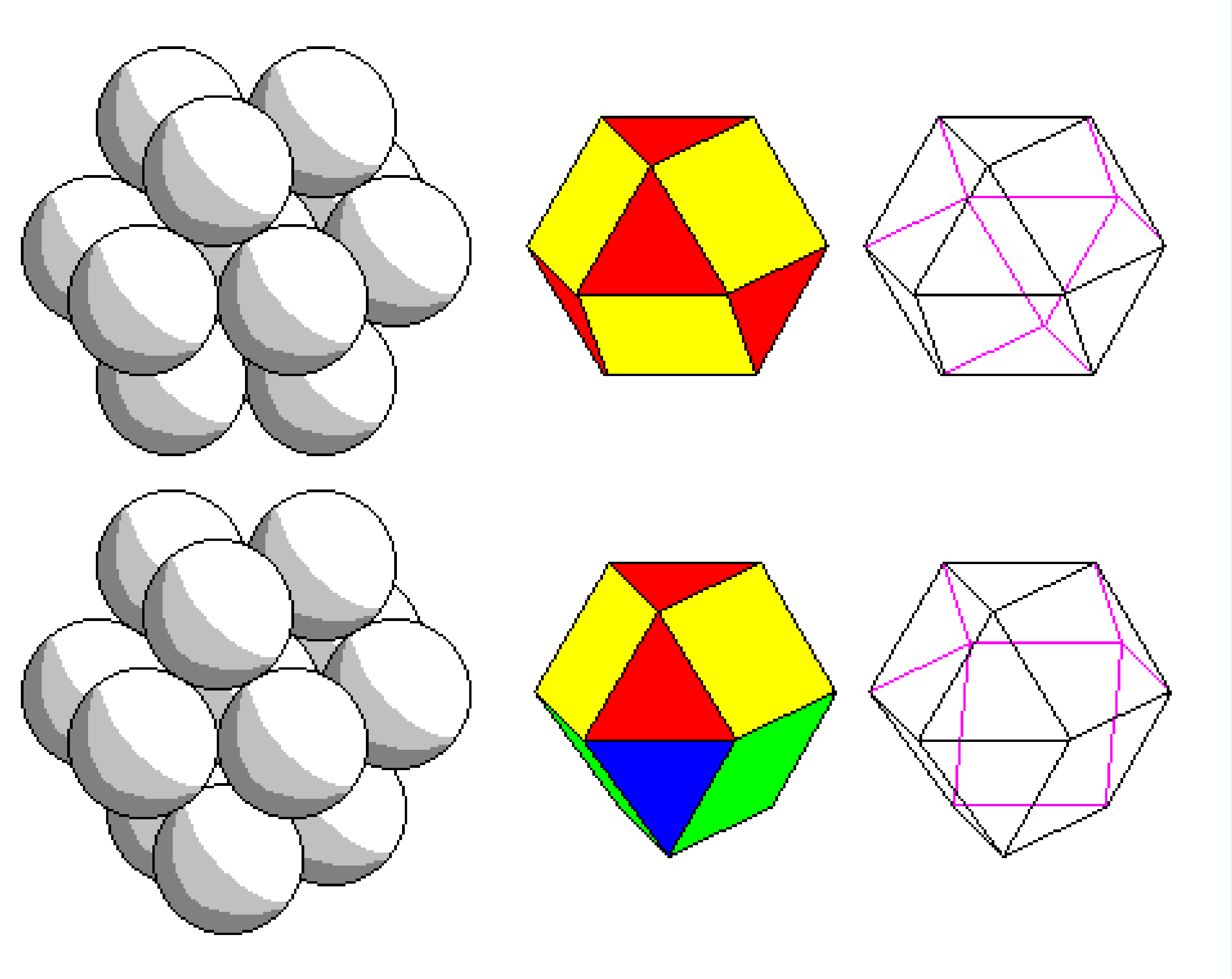
TEM images of superlattices composed of 11.3 nm Ni nanoparticles

Structures with Larger Motifs



Coordination Polyhedrons

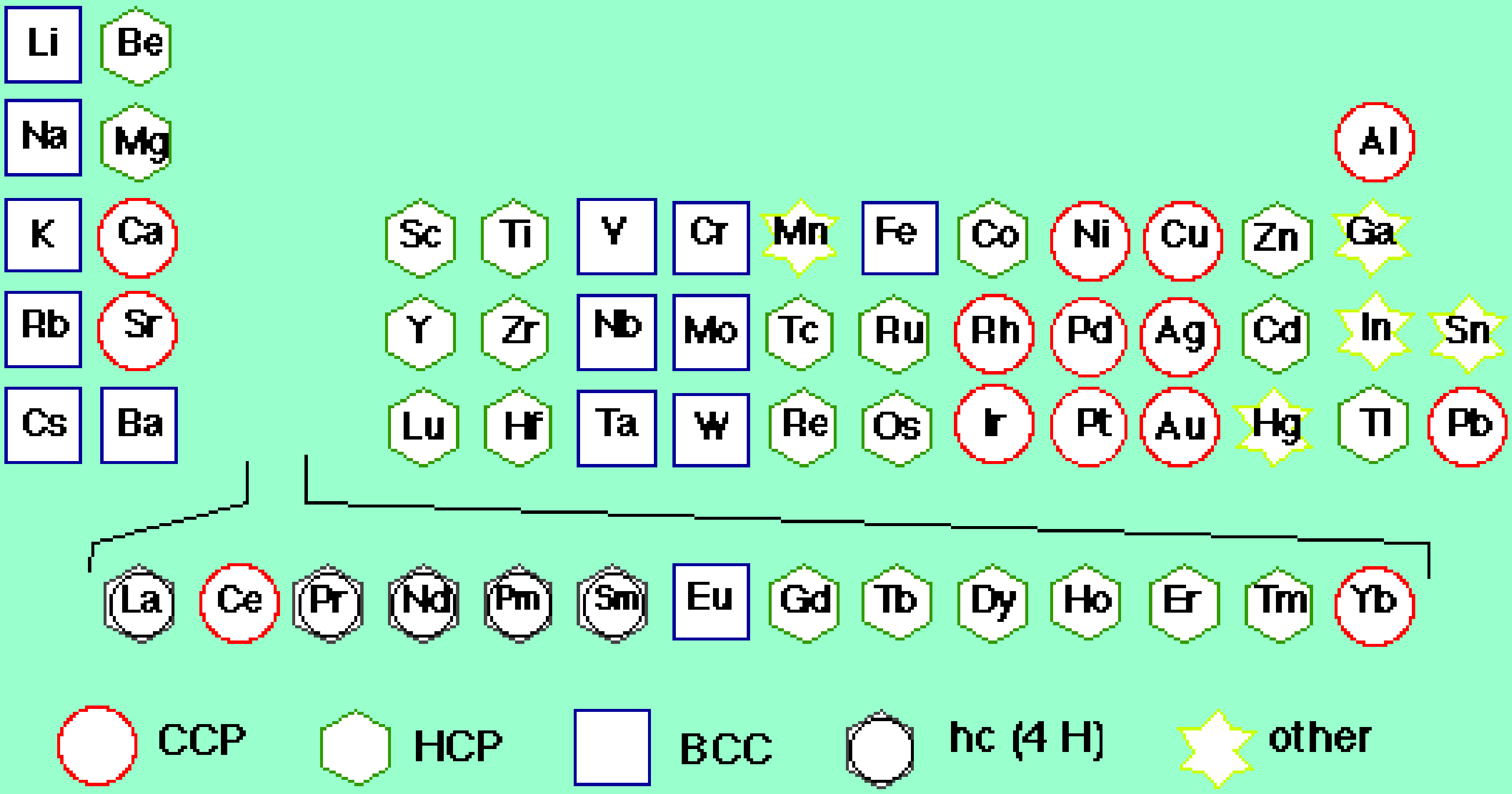
Which is HCP and which is CCP?



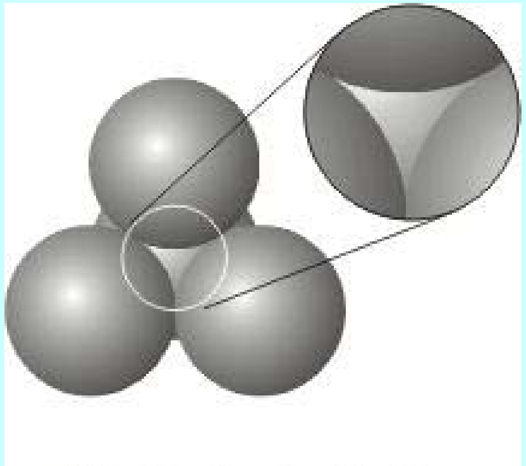
Space Filling

a = lattice parameter	Atom Radius, r	Number of Atoms (lattice points), Z	Space filling
SC	a/2	1	52%
BCC	√3a/4	2	68%
FCC	√2a/4	4	74%
Diamond	√3a/8	8	34%

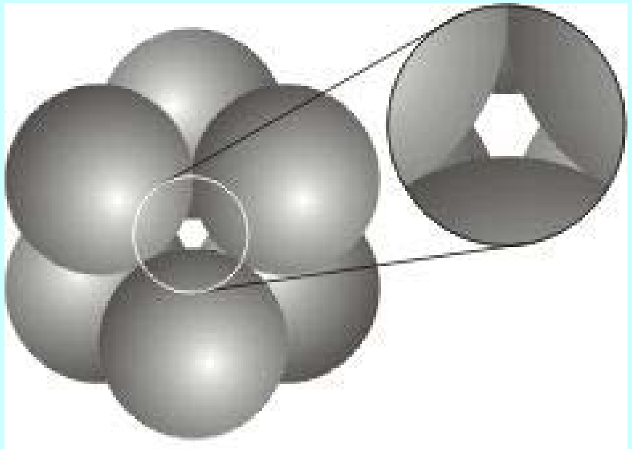
Periodic Table of Metal Structures



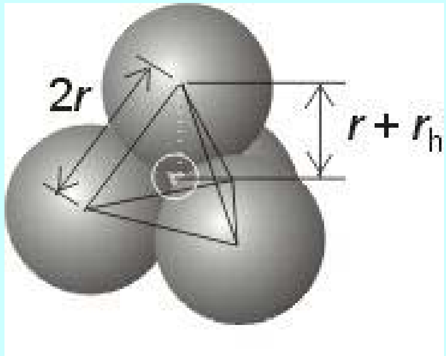
Two Types of Voids (Holes) in Close-Packed Structures (CCP and HCP)

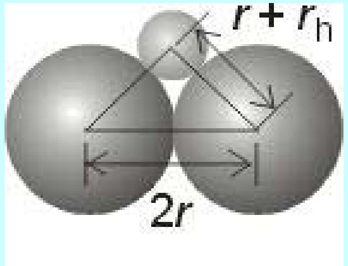


5 Tetrahedral hole

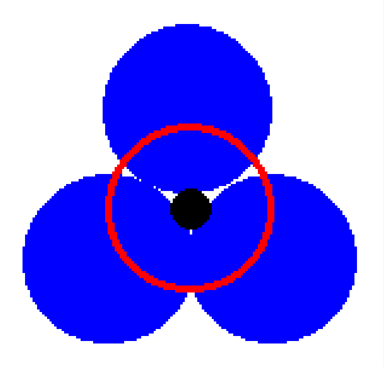


2 Octahedral hole

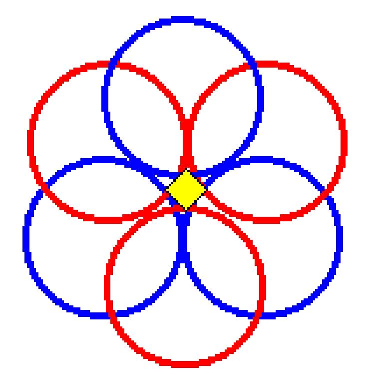




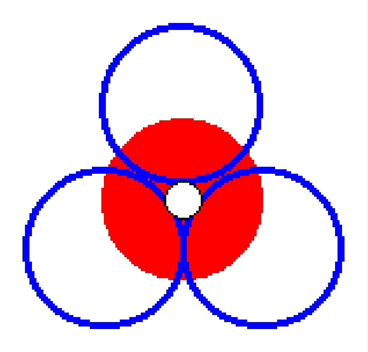
3



Tetrahedral Holes T+



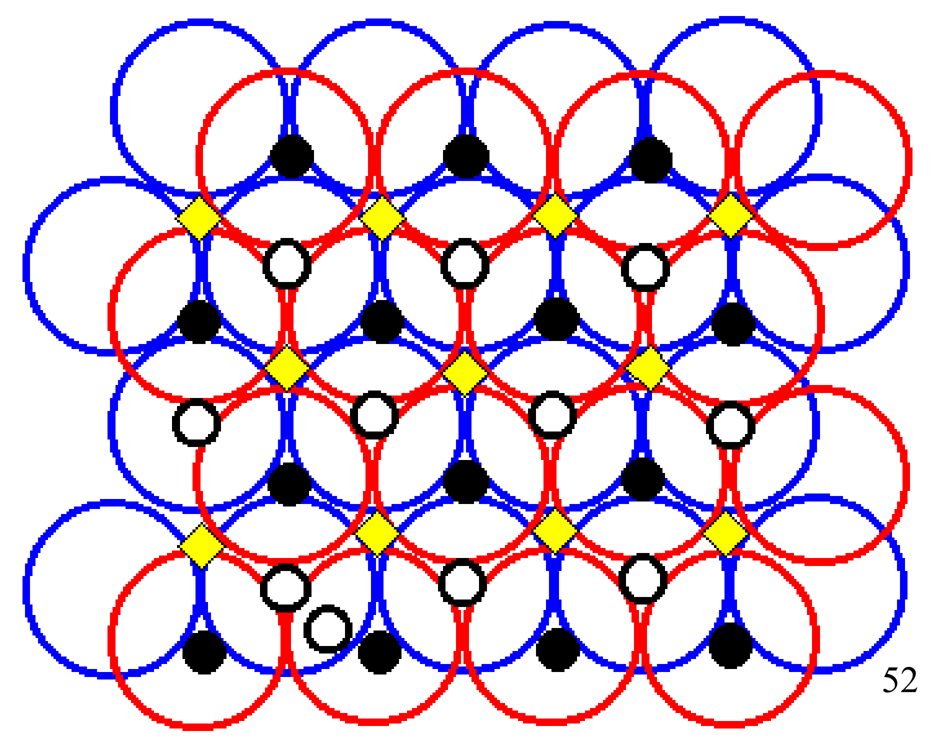
Octahedral Holes



Tetrahedral Holes T-

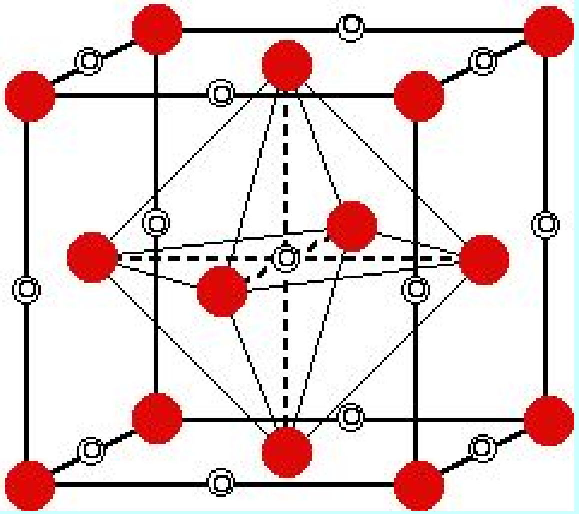
N cp atoms in a lattice cell

N Octahedral Holes
2N Tetrahedral Holes



Two Types of Voids (Holes)

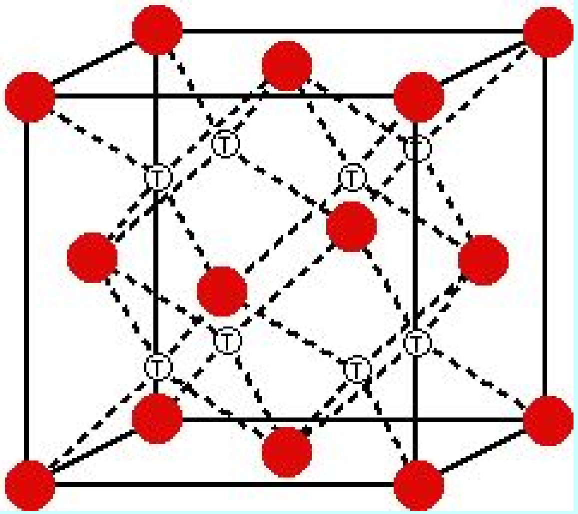
Octahedral Holes (O)



Z = 4
number of atoms in the CCP cell (N)

O = 4 number of octahedral holes (N)

Tetrahedral Holes (T)



Z = 4
number of atoms in the CCP cell (N)

T = 8 number of tetrahedral holes (2N)

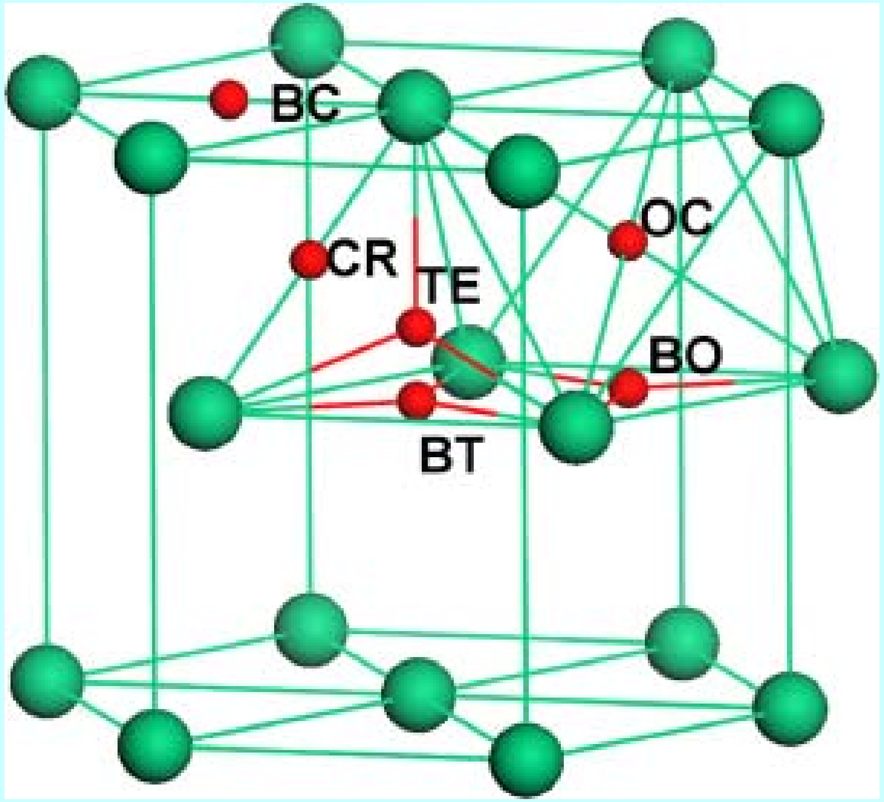
Two Types of Voids (Holes)

HCP

N hcp atoms in a lattice cell

N Octahedral Holes (OC)

2N Tetrahedral Holes (TE)



Characteristic Structures of Solids

= Structure Types

Rock salt NaCl: LiCl, KBr, AgCl, MgO, TiO, FeO, SnAs, UC, TiN, ...

Fluorite CaF_2: $BaCl_2$, K_2O, PbO_2 ...

Lithium bismutide Li_3Bi: Fe_3Al, M_3C_{60}

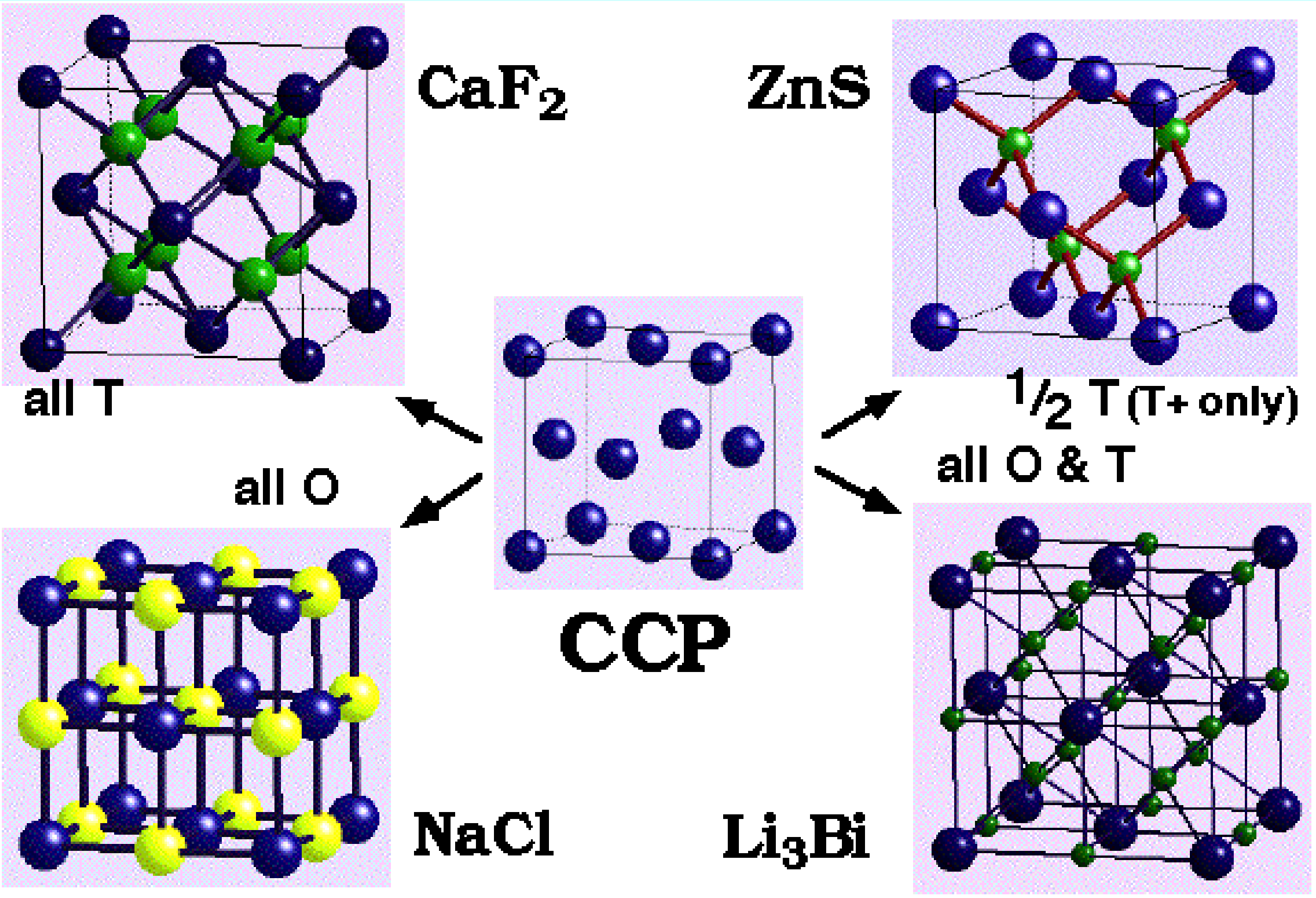
Sphalerite (zinc blende) ZnS: CuCl, HgS, GaAs ...

Nickel arsenide NiAs: FeS, PtSn, CoS ...

Wurtzite ZnS: ZnO, MnS, SiC

ICSD
3555 NaCl
3438 MgAl2O4
2628 GdFeO3

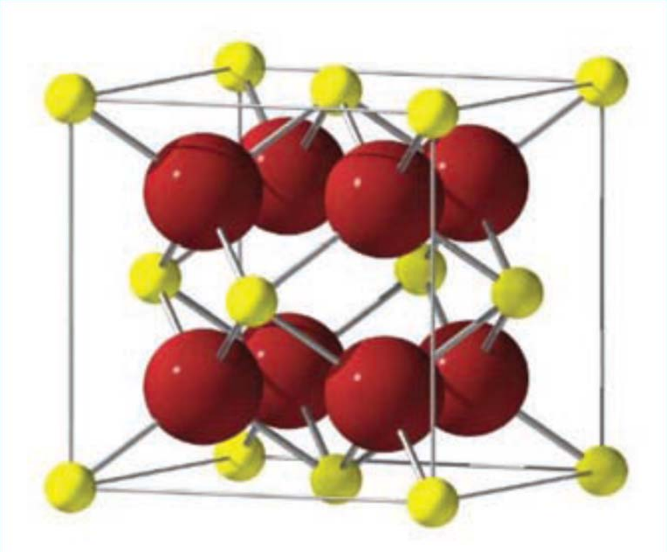
Structure Types Derived from CCP = FCC



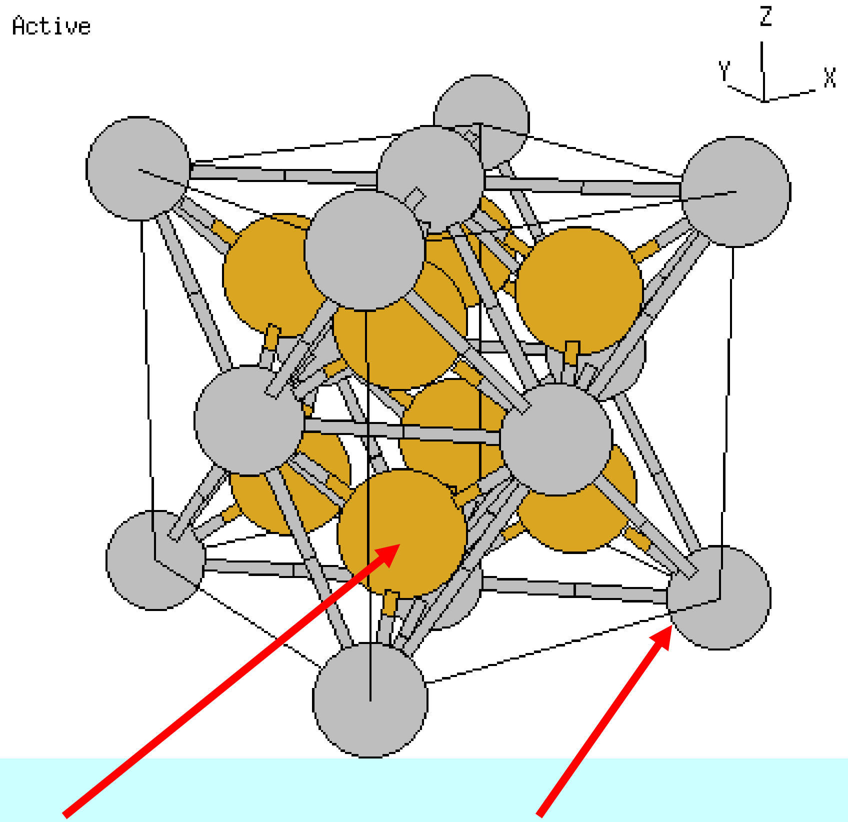
Fluorite CaF_2 and Antifluorite Li_2O

Fluorite structure = a face-centered cubic array (FCC) of cations = cubic close packing (CCP) of cations with all tetrahedral holes filled by anions = a simple cubic (SC) array of anions

Antifluorite structure = a face-centred cubic (FCC) array of anions = cubic close packing (CCP) of anions, with cations in all of the tetrahedral holes (the reverse of the fluorite structure)

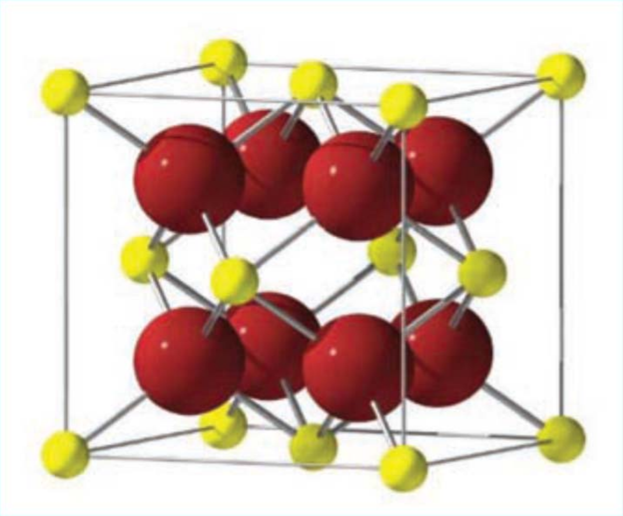


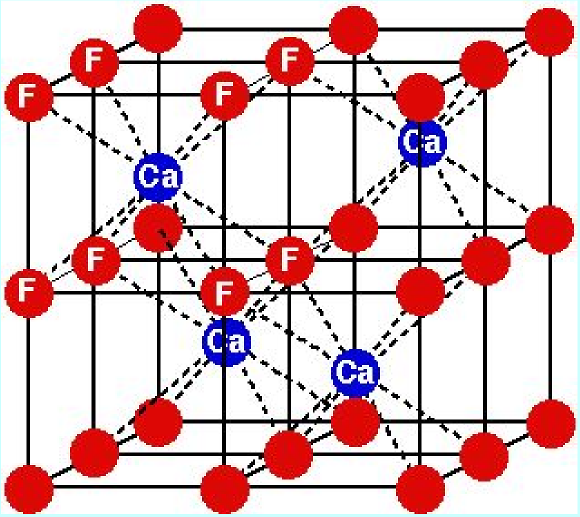
Fluorite CaF_2 and Antifluorite Li_2O



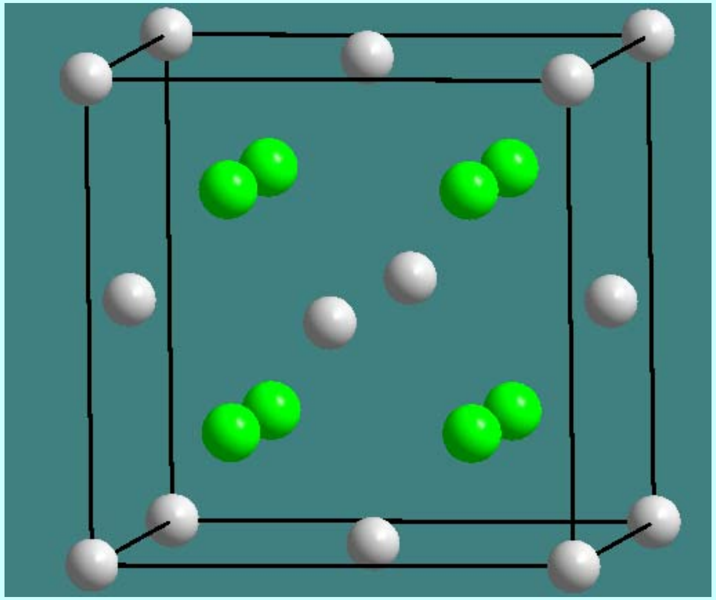
F / Li

Ca / O





Fluorite CaF_2 and Antifluorite Li_2O



Oxides: Na_2O, K_2O, UO_2, ZrO_2, ThO_2

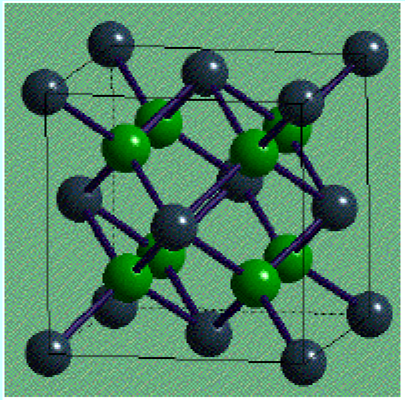
alkali metal sulfides, selenides and tellurides

$K_2[PtCl_6]$, $(NH_4)_2[PtCl_6]$, $Cs_2[SiF_6]$, $[Fe(NH_3)_6][TaF_6]_2$

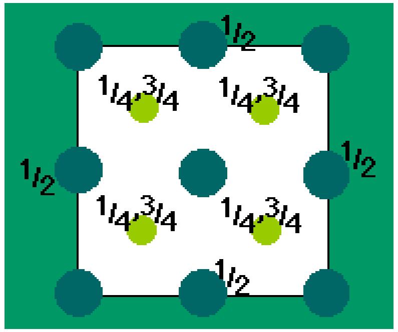
CaF_2, SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, CdF_2, HgF_2, EuF_2, β-PbF_2, PbO_2

Li_2O, Li_2S, Li_2Se, Li_2Te, Na_2O, Na_2S, Na_2Se, Na_2Te, K_2O, K_2S

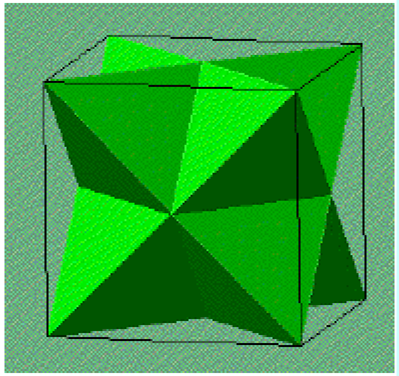
Fluorite CaF_2 and Antifluorite Li_2O



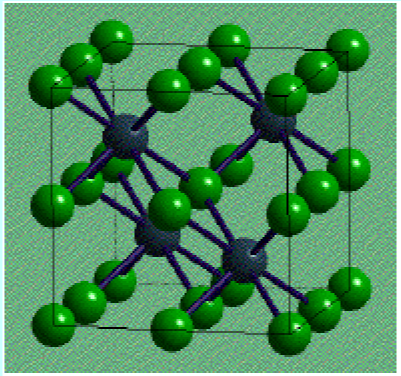
Fluorite A-cell



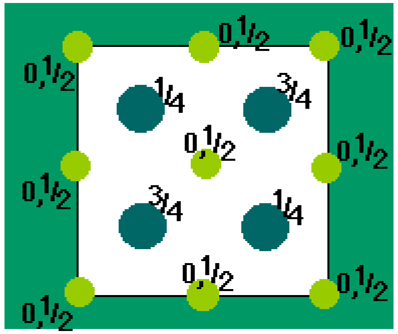
Plan view



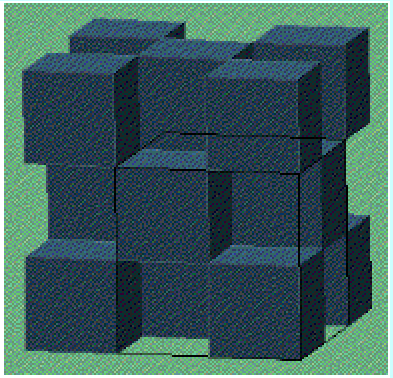
FCa_4 Tetrahedra



Fluorite B-cell



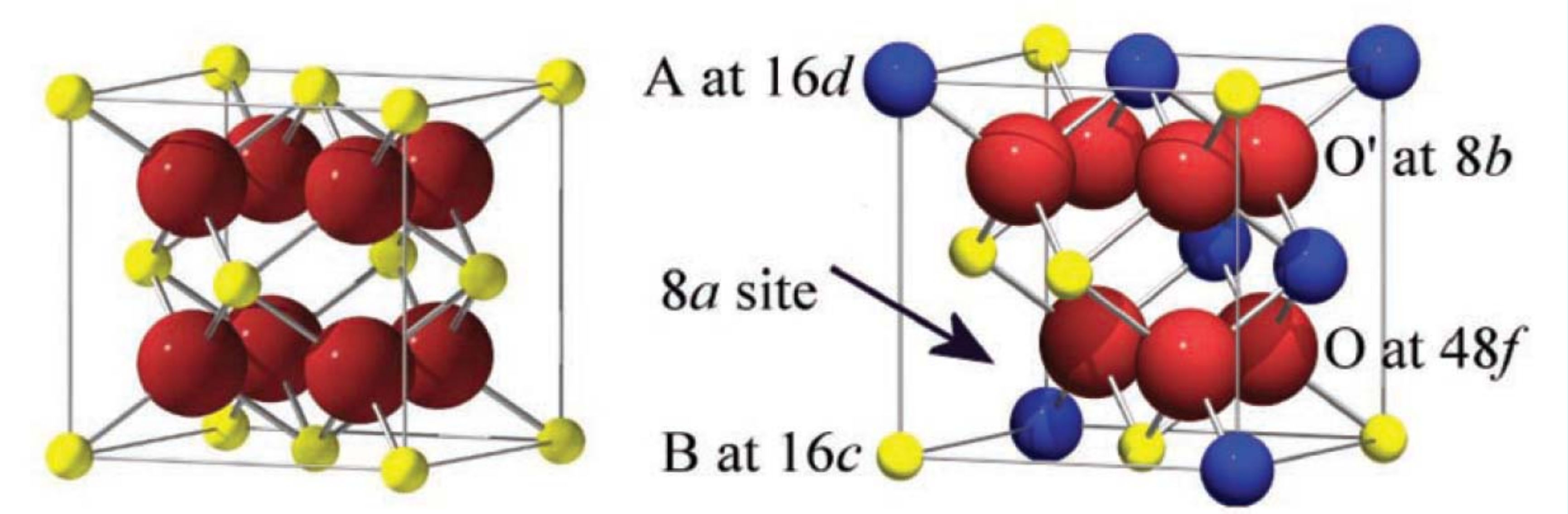
Plan view



CaF_8 Cubes

Pyrochlores = Disordered Fluorite

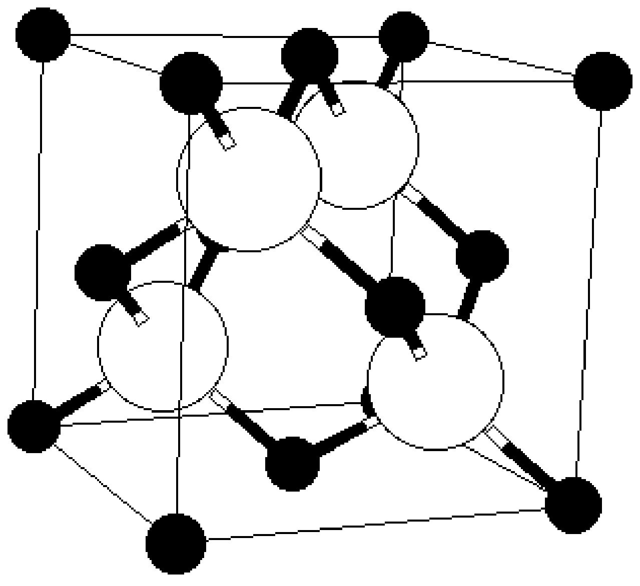
CaF_2 (Ca_4F_8) **Pyrochlore $A_2B_2O_7$**

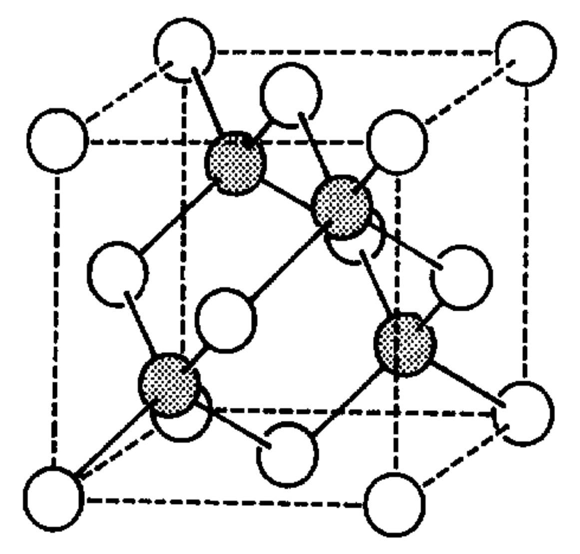


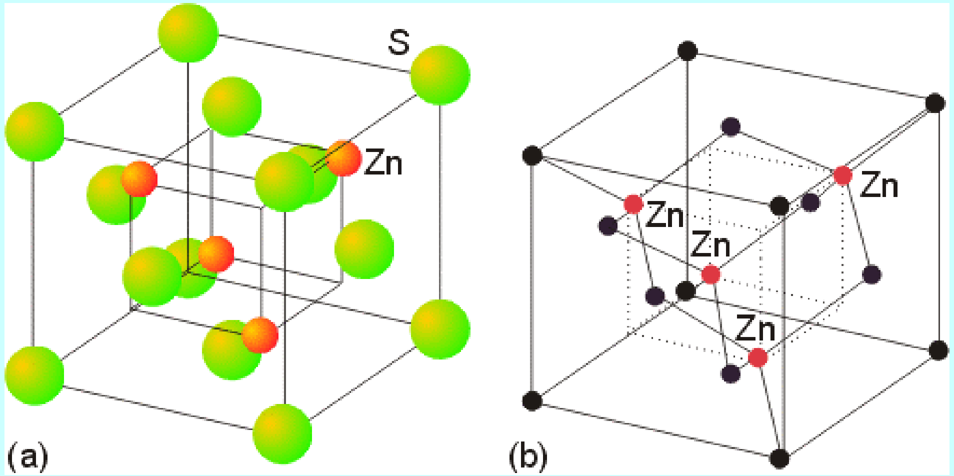
$(Na,Ca)_2Nb_2O_6(OH,F)$

$Y_2Ti_2O_7$, $La_2Zr_2O_7$

Sphalerite (zincblende, ZnS)

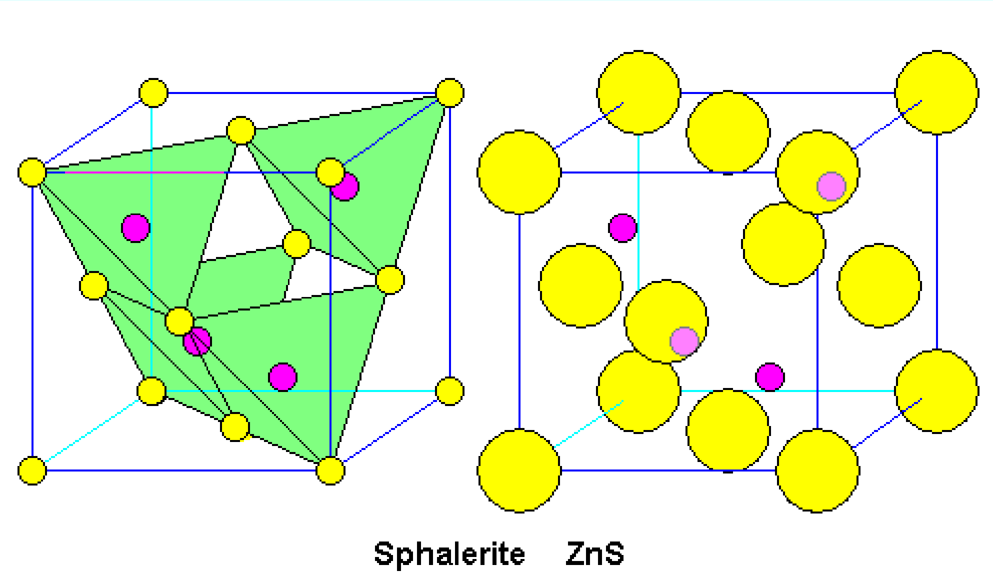






Cubic close packing of anions with 1/2 tetrahedral holes filled by cations

Sphalerite (zincblende, ZnS)



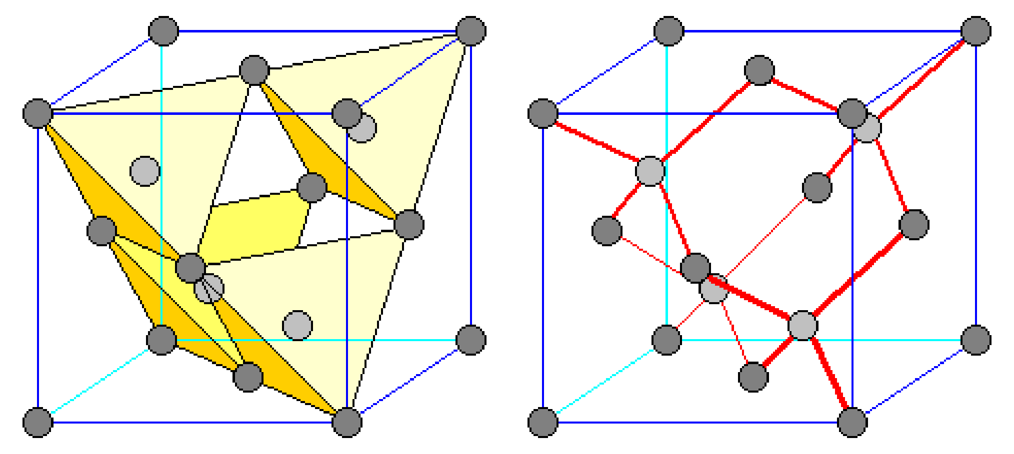
13-15 compounds: BP, BAs, AlP, AlAs, GaAs, GaP, GaSb, AlSb, InP, InAs, InSb

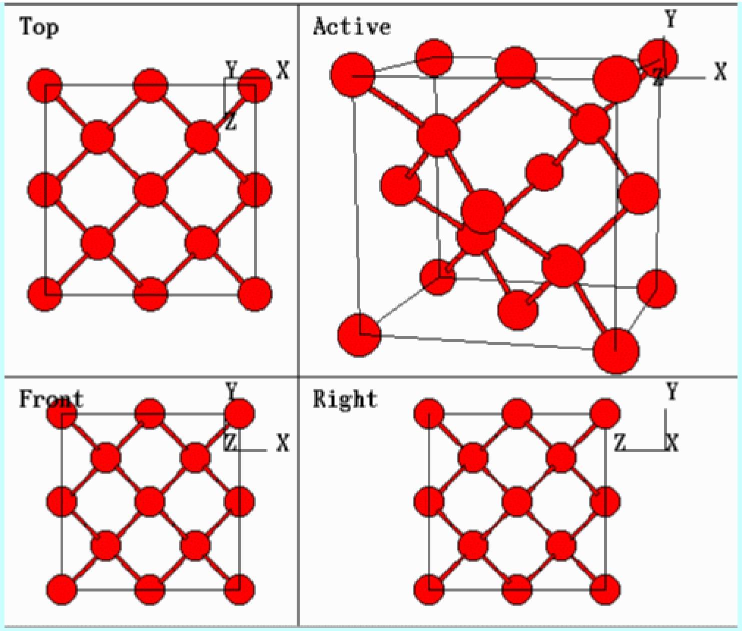
12-16 compounds: BeS, BeSe, BeTe, b-MnS (red), β-MnSe, β-CdS, CdSe, CdTe, HgS, HgSe, HgTe, ZnSe, ZnTe

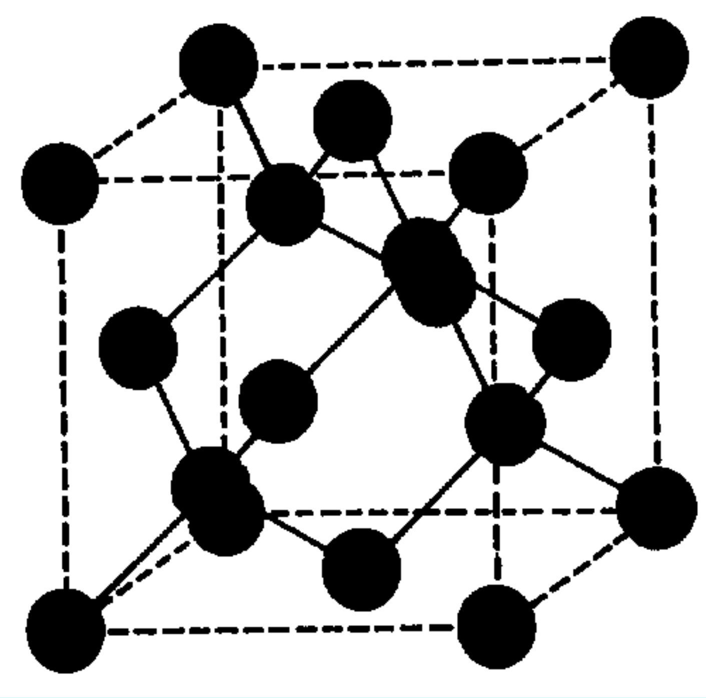
Halogenides: AgI, CuF, CuCl, CuBr, CuI, NH_4F

Borides: PB, AsB
Carbides: β-SiC
Nitrides: BN

Cubic Diamond







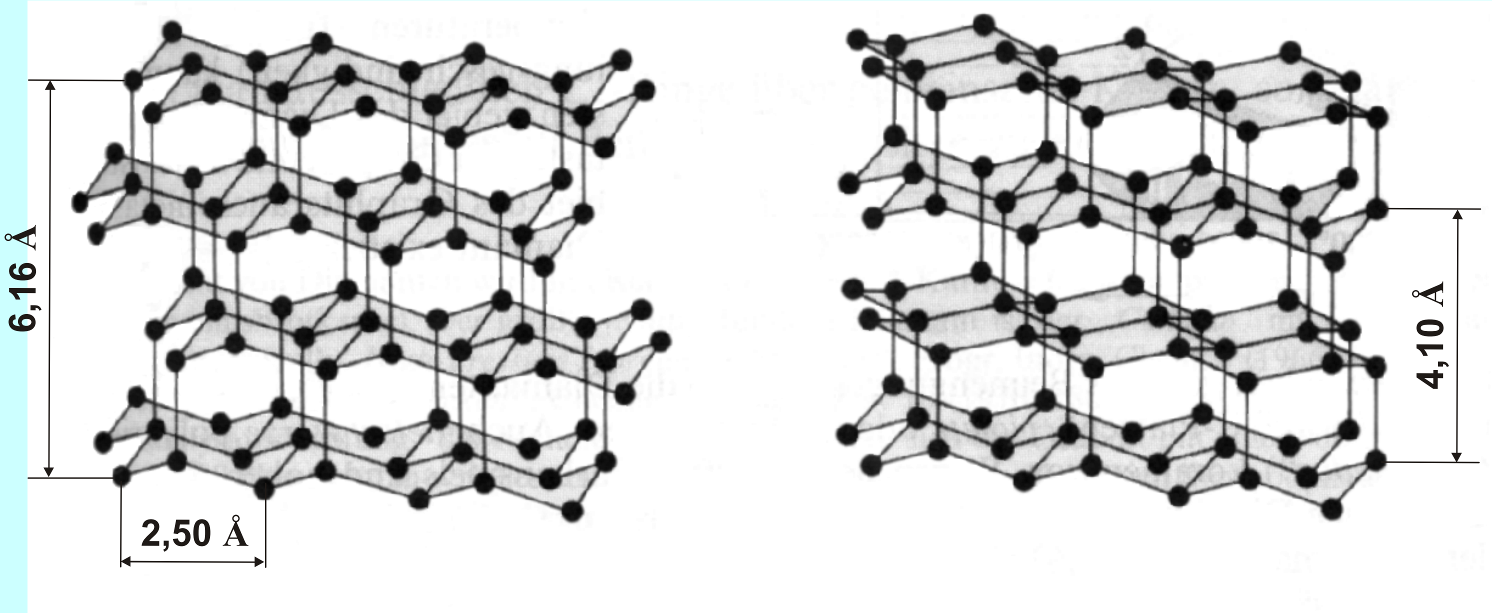
Diamond

Sphalerite

Cubic = chairs only

Wurzite

Hexagonal = chairs + boats



SiO_2 cristobalite

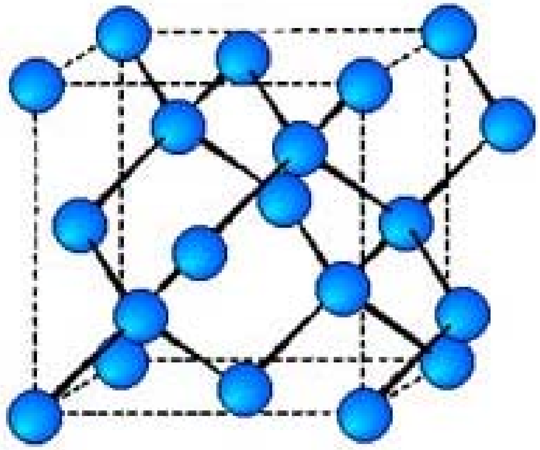
Replace C-C with Si-O-Si

Lonsdaleite
SiO_2 tridymite

Ice-hexagonal
Replace C-C with O-H····O

Diamond Structure

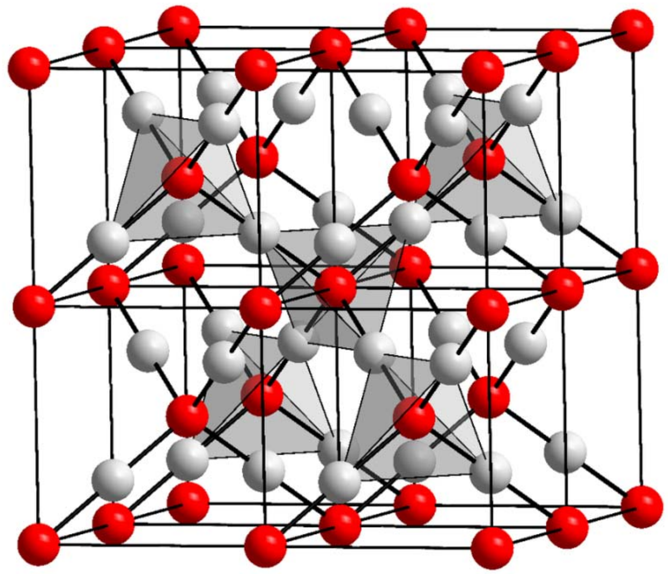
Elements of Group 14: C, Si, Ge, grey-Sn

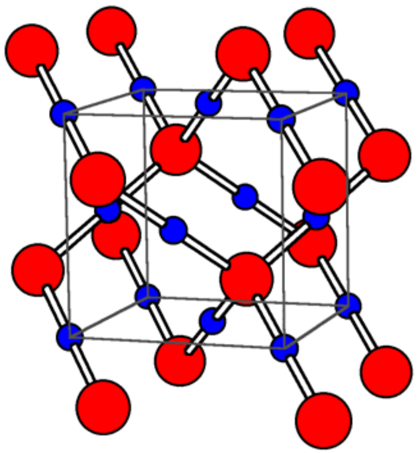


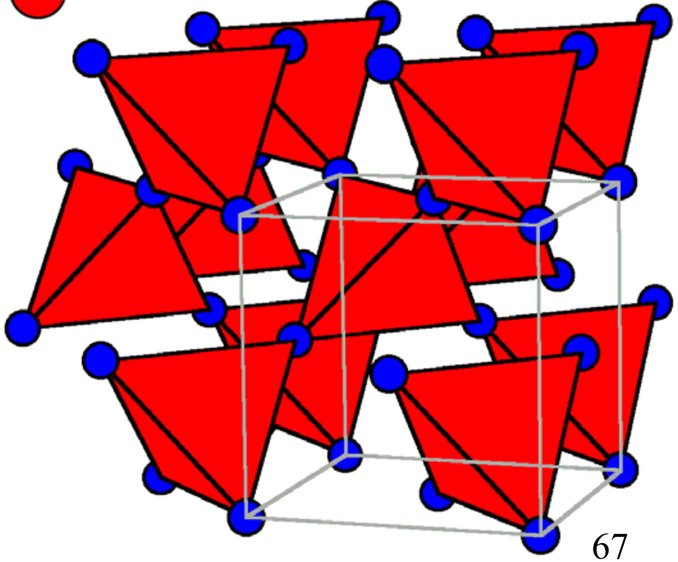
	a (Å)	d (g.cm^{-3})
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
a-Sn	6.489	7.285

- Add 4 atoms to FCC/CCP to ½ of tetrahedral holes
- Tetrahedral bond arrangement of all atoms
- Each atom has 4 nearest neighbors and 12 next nearest neighbors

Cuprite Cu_2O - Cubic Diamond Lattices



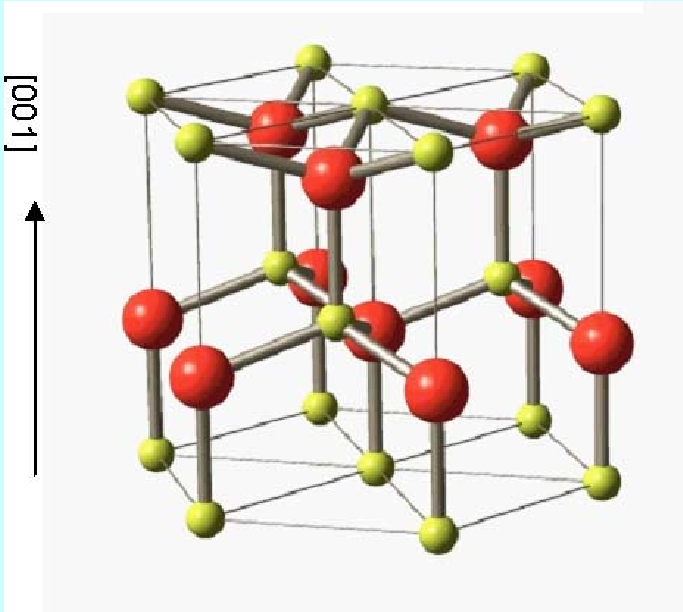




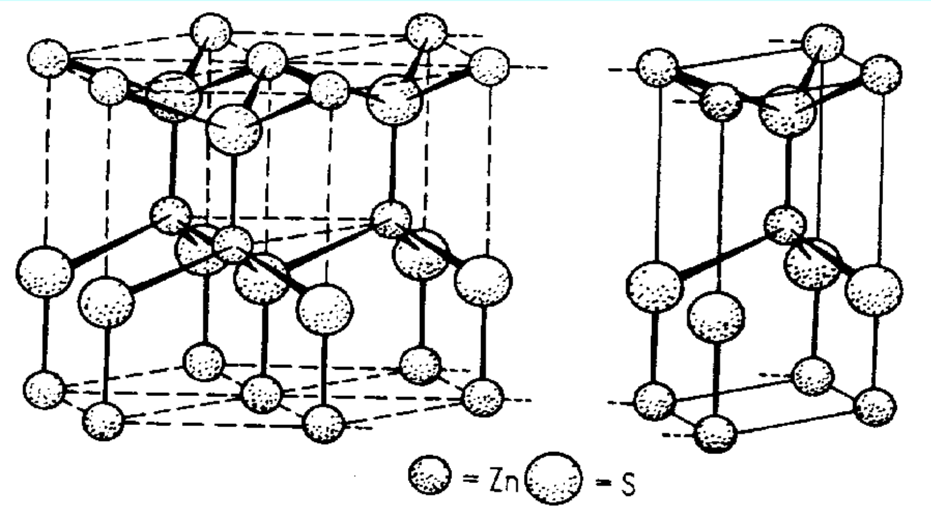
Two interpenetrating diamond lattices

Replace C-C with O-Cu-O

Wurzite, ZnS

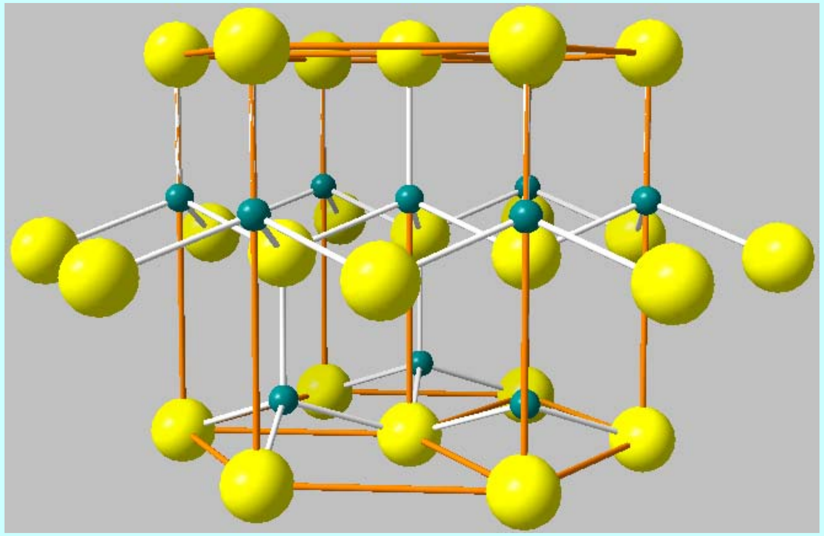


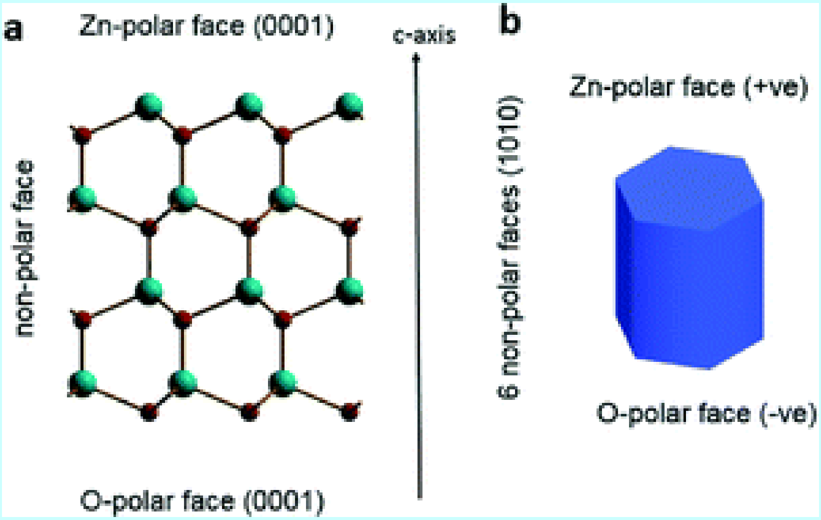
Hexagonal close packing of anions with 1/2 tetrahedral holes filled by cations

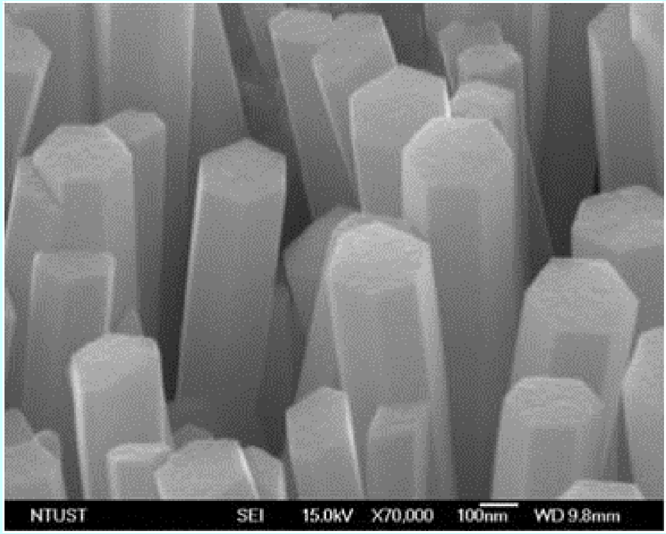


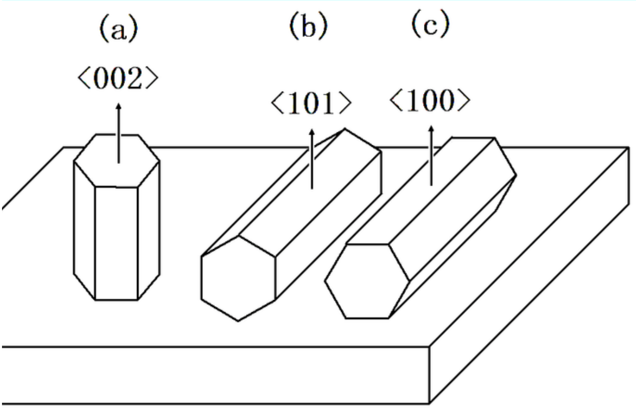
ZnO, ZnS, ZnSe, ZnTe, BeO, CdS, CdSe, MnS, AgI, AlN, GaN Lonsdaleite

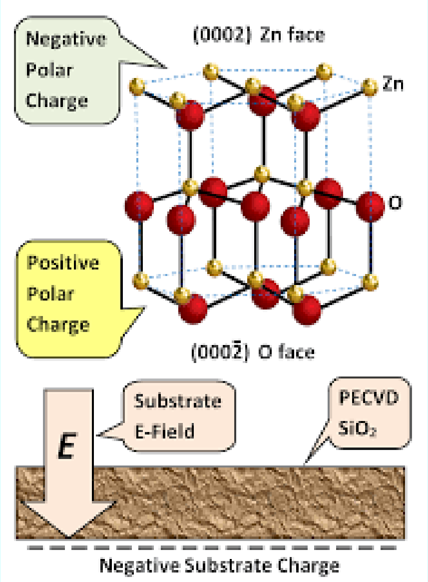
Zincite, ZnO




a
Zn-polar face (0001)
c-axis
non-polar face
O-polar face (0001)
b
6 non-polar faces (1010)
Zn-polar face (+ve)
O-polar face (-ve)

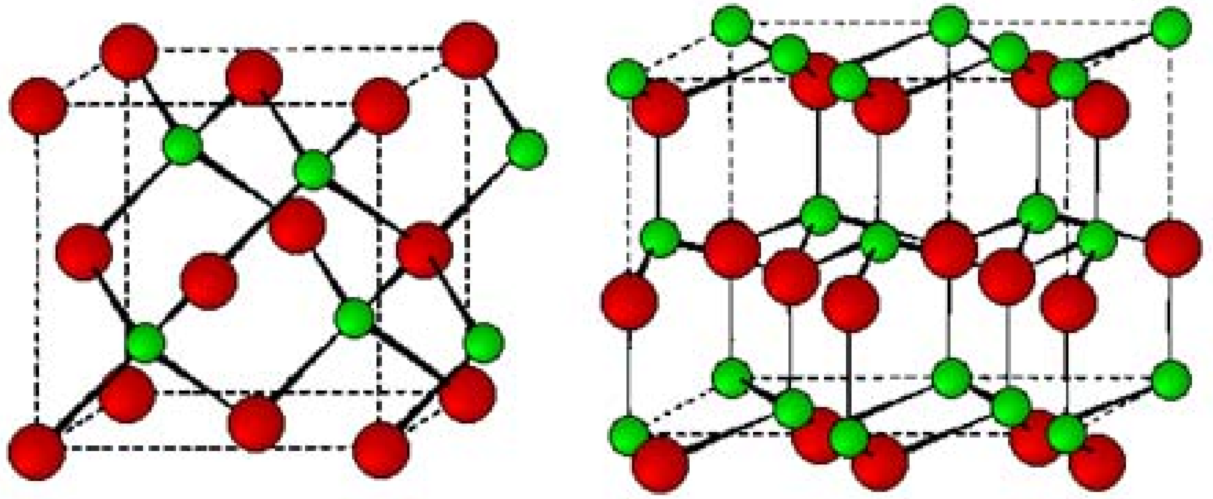

NTUST
SEI
15.0kV
X70,000
100nm
WD 9.8mm


(a)
(b)
(c)
⟨002⟩
⟨101⟩
⟨100⟩


Negative Polar Charge
(0002) Zn face
Zn
O
Positive Polar Charge
(000$\bar{2}$) O face
Substrate E-Field
E
PECVD SiO₂
Negative Substrate Charge

Semiconductors of 13-15 and 12-16 type

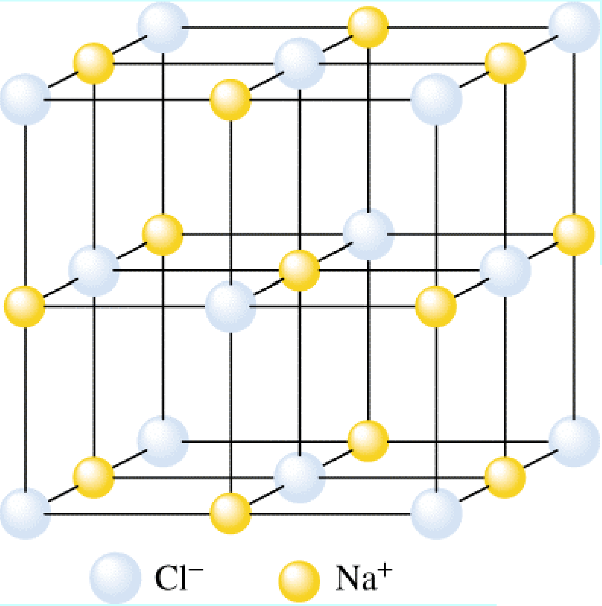
Structure of III-V and II-VI
Compound Semiconductors

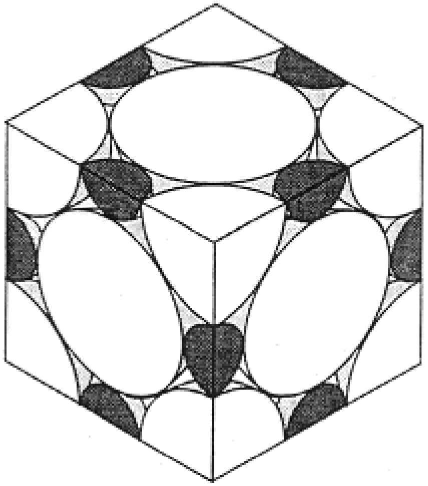


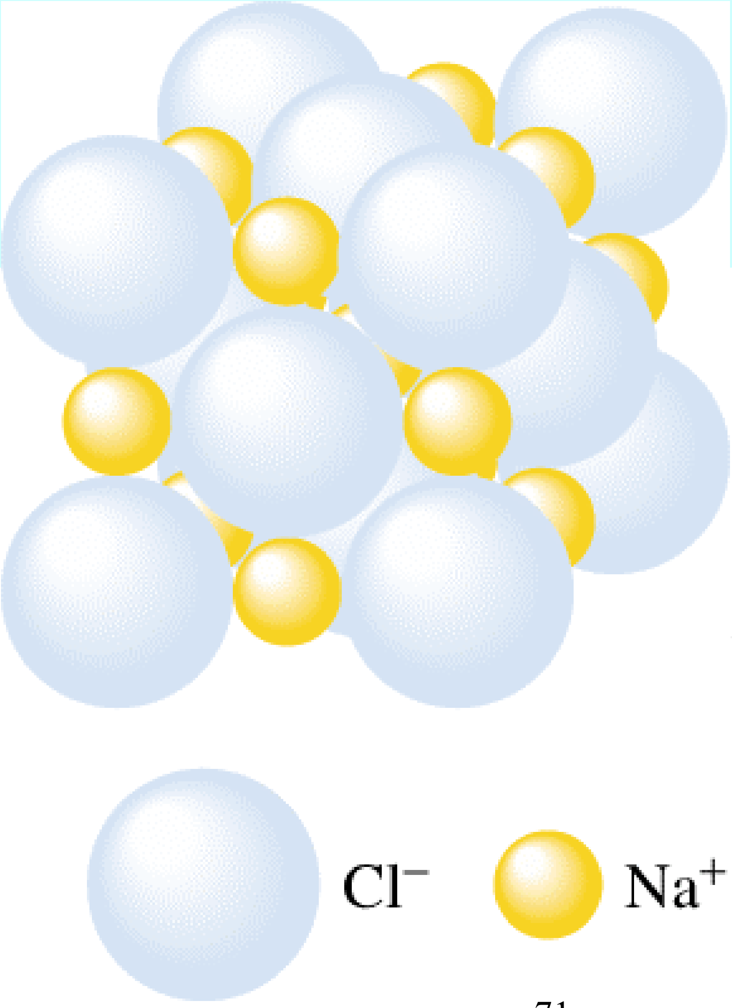
Zinc blende

Wurtzite

Rock Salt, NaCl

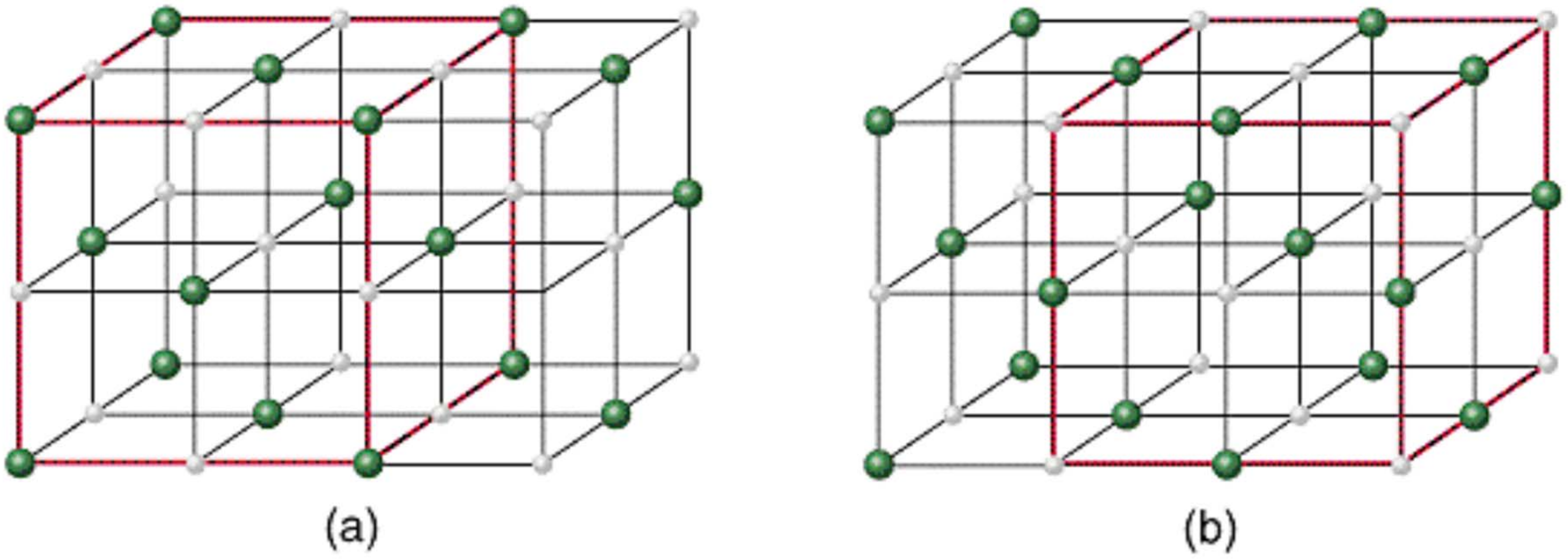






Cubic close packing of anions with all octahedral holes filled by cations

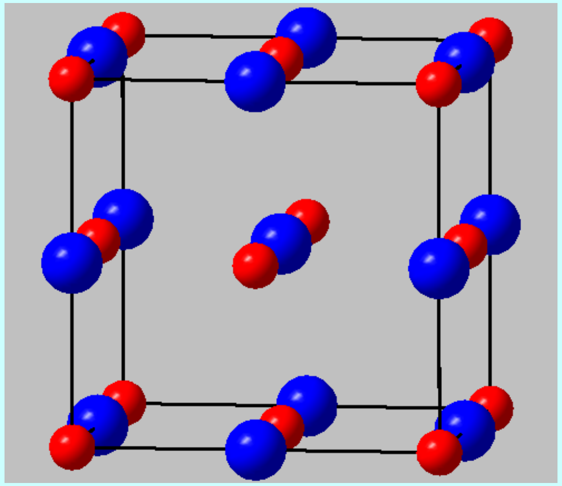
Rock Salt, NaCl

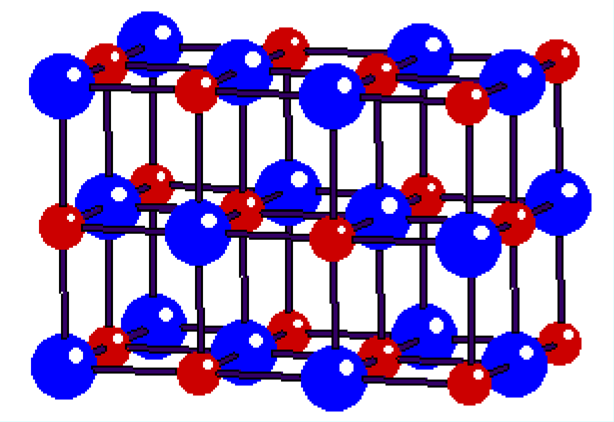


Anion and cation sublattices = same FCC/CCP

Rock salt (NaCl) = Anti-rock salt (ClNa)

Rock Salt Structures (NaCl)





Hydrides: LiH, NaH, KH,
NH_4BH_4 – H_2 storage material Pd(H)

Borides: ZrB, HfB

Carbides: TiC, ZrC, VC, UC

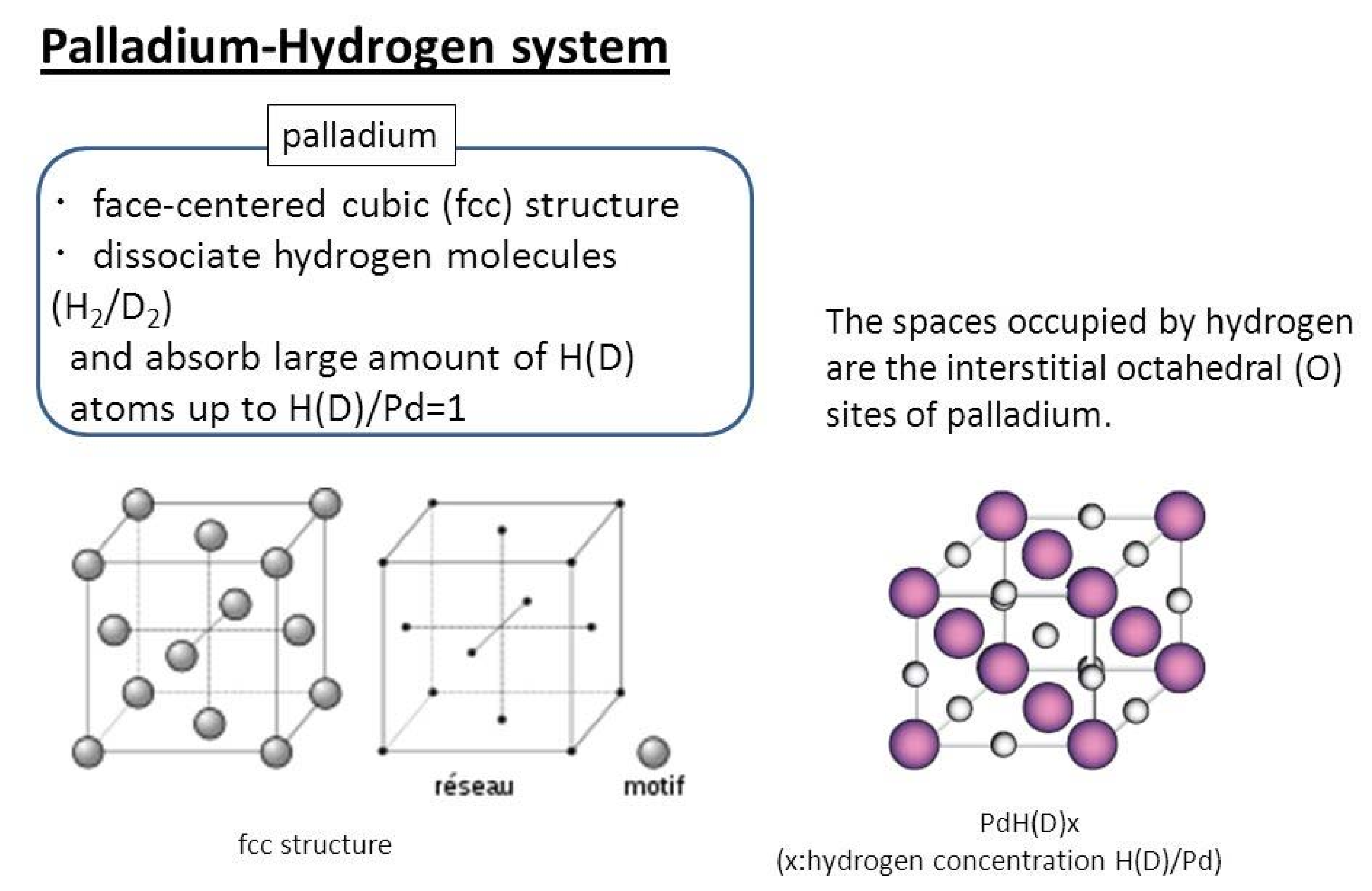
Nitrides: ScN, TiN, UN, CrN, VN, ZrN

Oxides: MgO, CaO, SrO, BaO, TiO, VO, MnO, FeO, CoO, NiO
Chalcogenides: MgS, CaS, SrS, BaS, a-MnS, MgSe, CaSe, SrSe, BaSe, CaTe

Halides: LiF, LiCl, LiBr, LiI, NaF, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, AgCl, AgF, AgBr

Intermetallics: SnAs
Other
FeS_2 (pyrite), CaC_2, NaO_2

Rock Salt Structures (NaCl)



Palladium-Hydrogen system

palladium

- face-centered cubic (fcc) structure
- dissociate hydrogen molecules (H_2/D_2) and absorb large amount of H(D) atoms up to H(D)/Pd=1

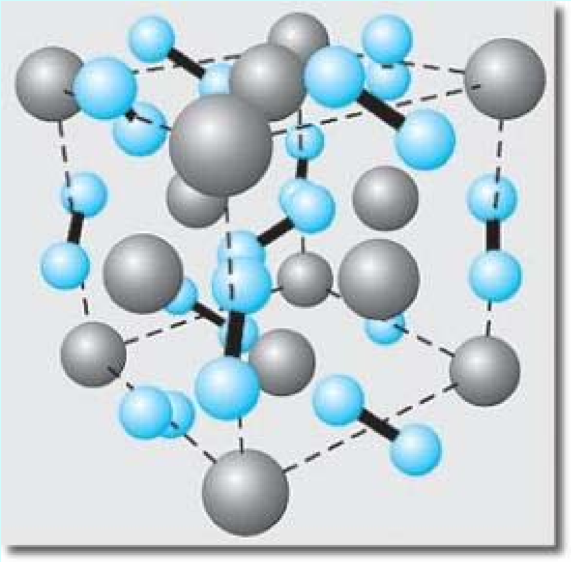
The spaces occupied by hydrogen are the interstitial octahedral (O) sites of palladium.

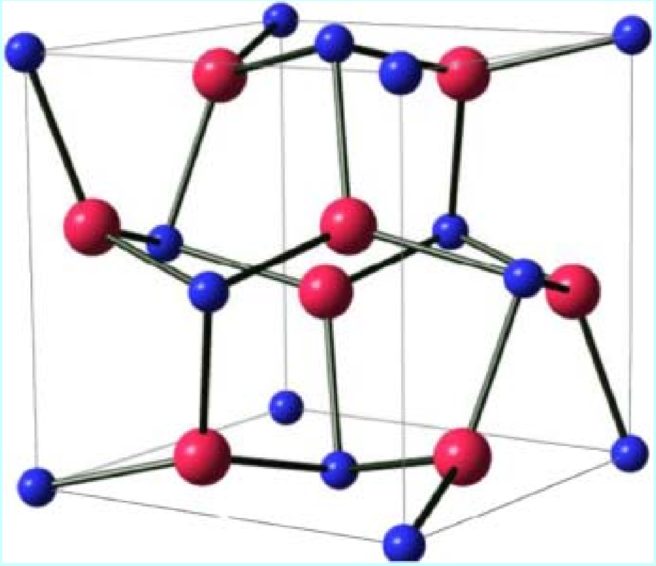
fcc structure

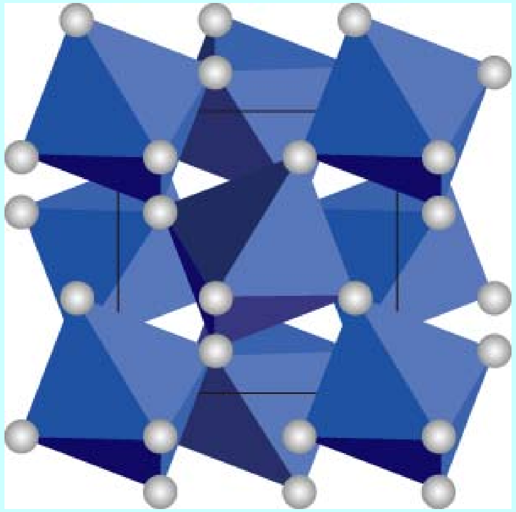
PdH(D)x
(x:hydrogen concentration H(D)/Pd)

Rock Salt Structures (NaCl)

FeS_2 (pyrite), CaC_2, NaO_2

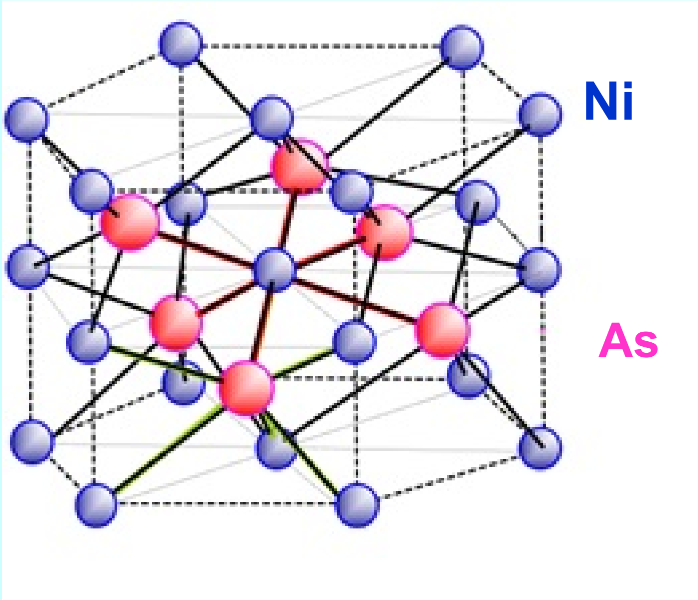






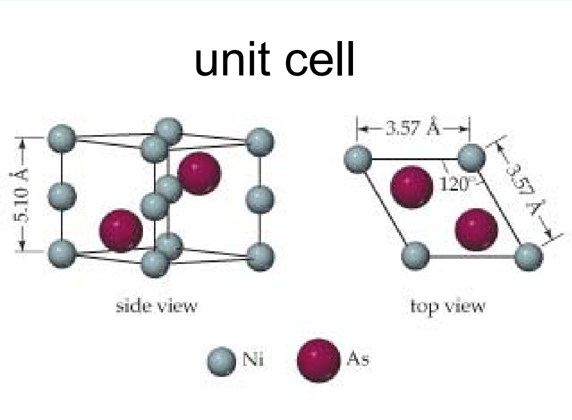
SiO_2 pyrite - high pressure polymorph, in Uranus and Neptune core

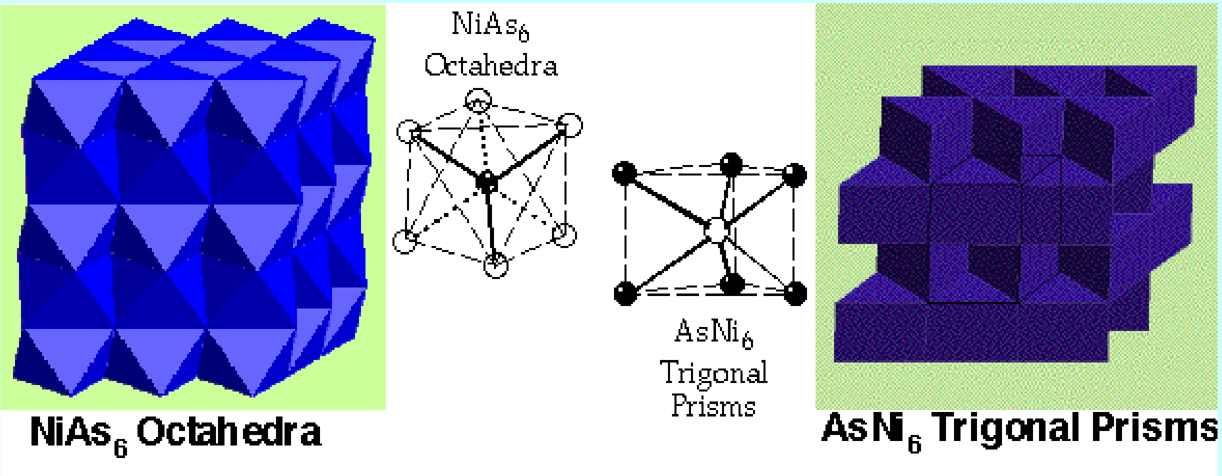
Nickel Arsenide, NiAs



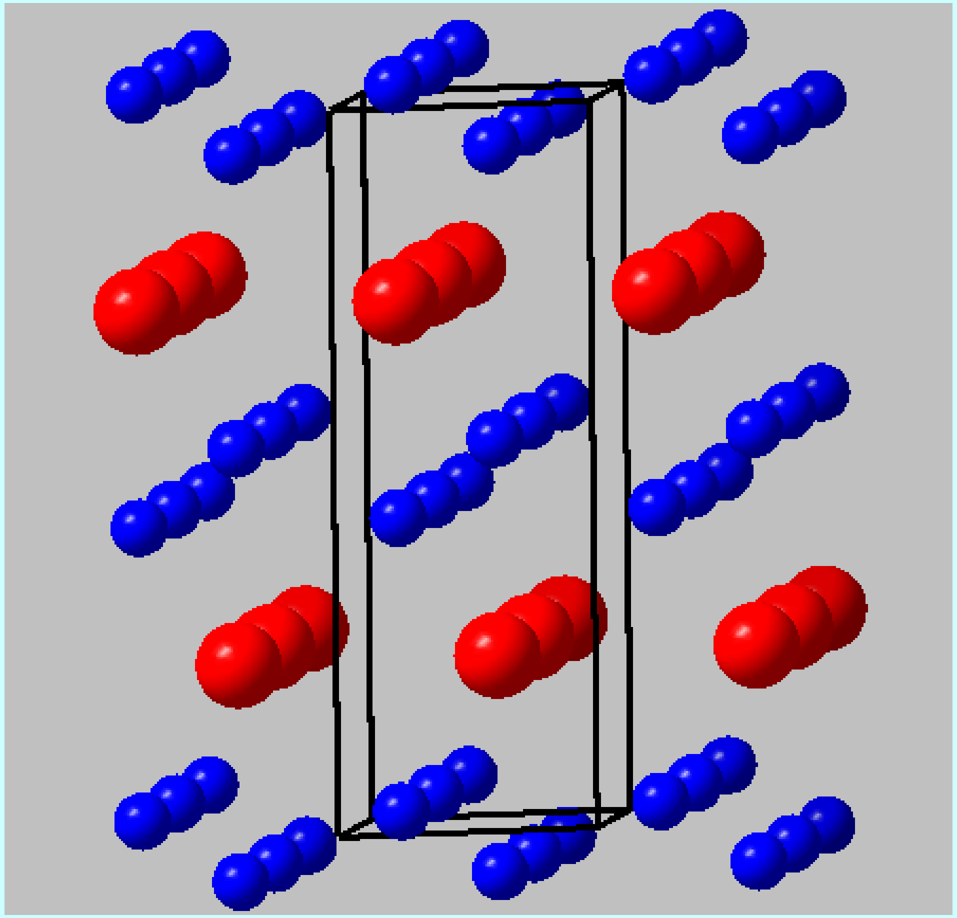
Hexagonal close packing of anions (As) with all octahedral holes filled by cations (Ni)

NiS, NiAs, NiSb, NiSe, NiSn, NiTe,
FeS, FeSe, FeTe, FeSb, PtSn, CoS,
CoSe, CoTe, CoSb, CrSe, CrTe,
CoSb,
PtB (anti-NiAs structure)



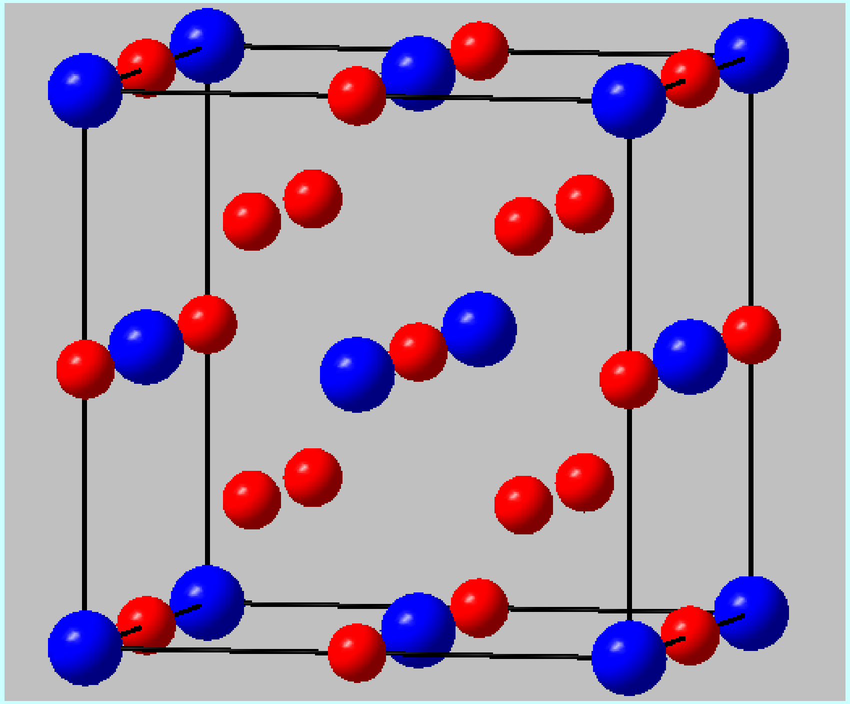


ReB_2 - type

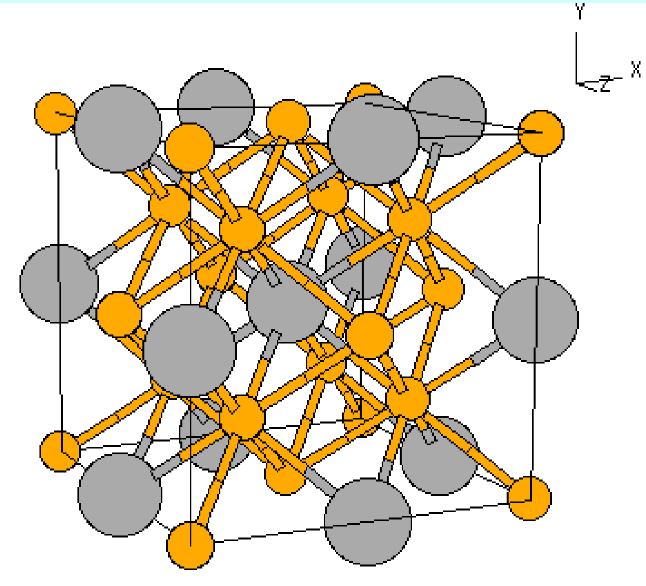


Hexagonal close packing of anions with all tetrahedral holes filled by cations

Li_3Bi (anti BiF_3)



Cubic close packing of anions with all tetrahedral and octahedral holes filled by cations

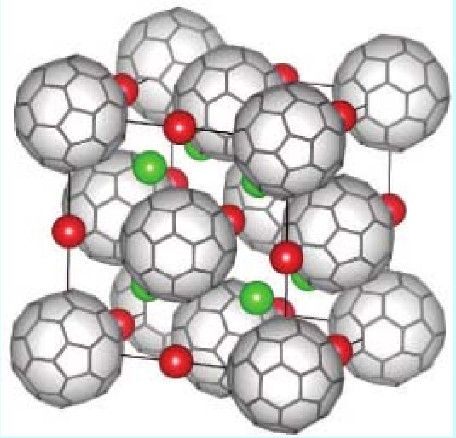


Fe_3Al

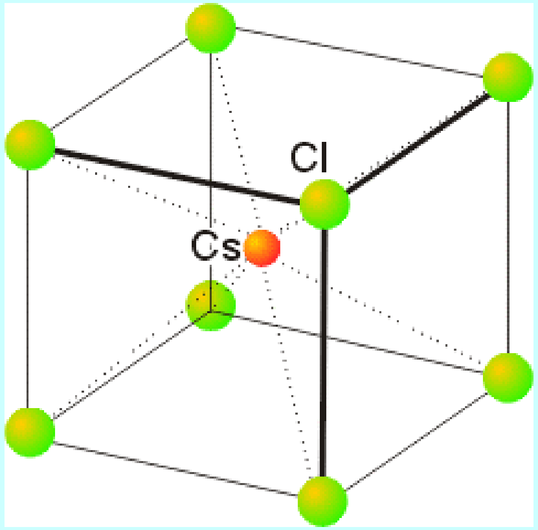
$[Cr(NH_3)_6]Cl_3$

$K_3[Fe(CN)_6]$

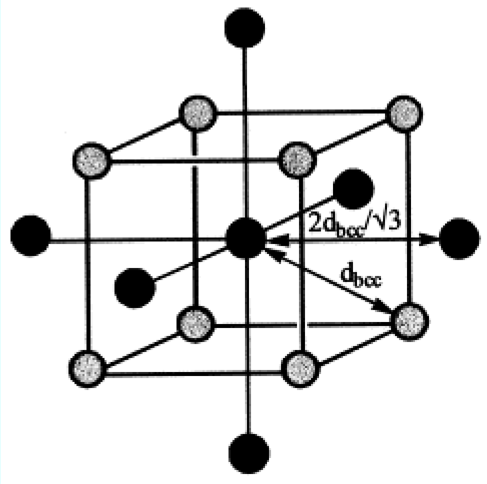
M_3C_{60}

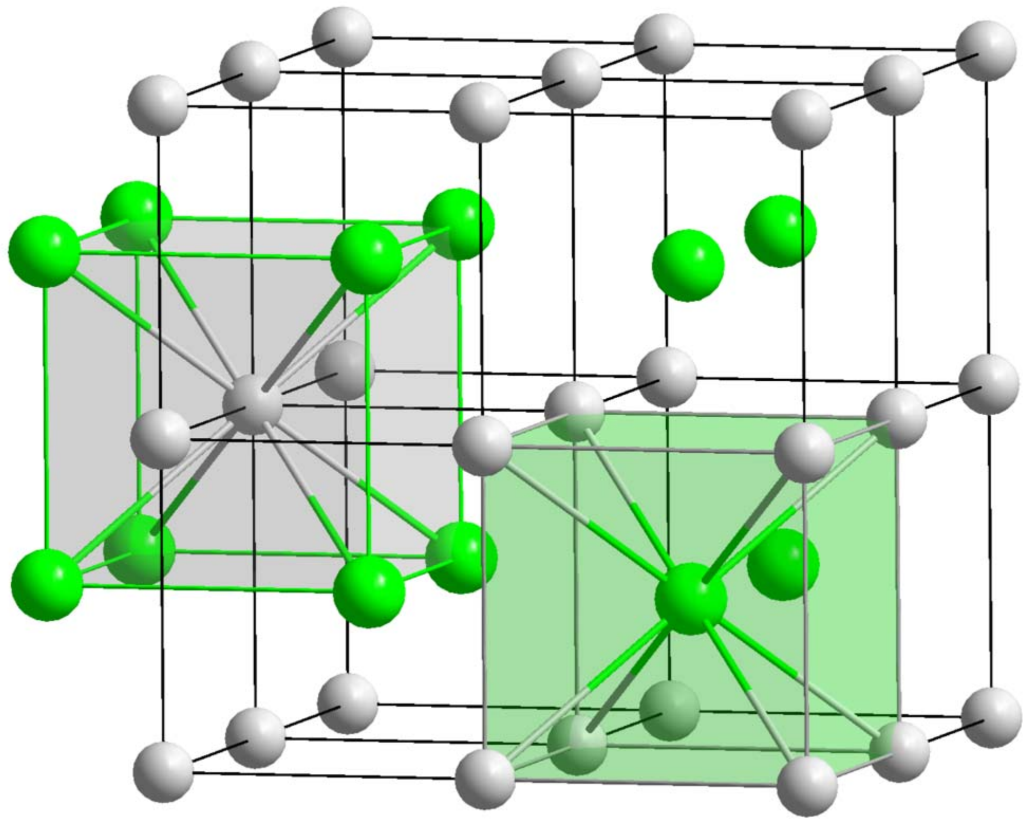


CsCl



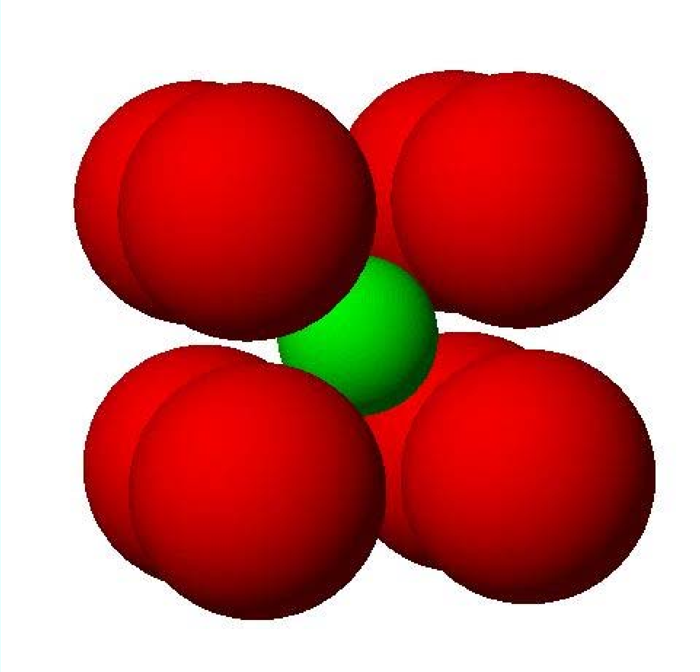
Primitive cubic packing of anions with all cubic holes filled by cations



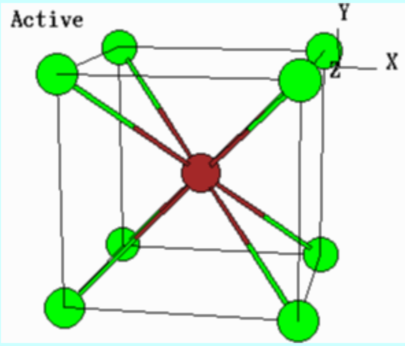


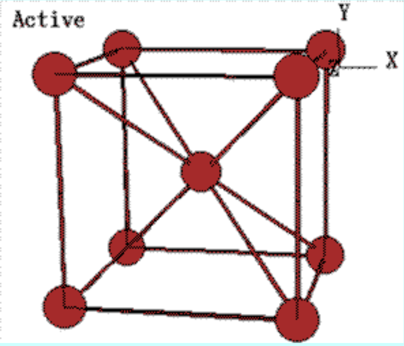
Primitive cubic packing of $CsCl_8$ cubes sharing all faces

CsCl



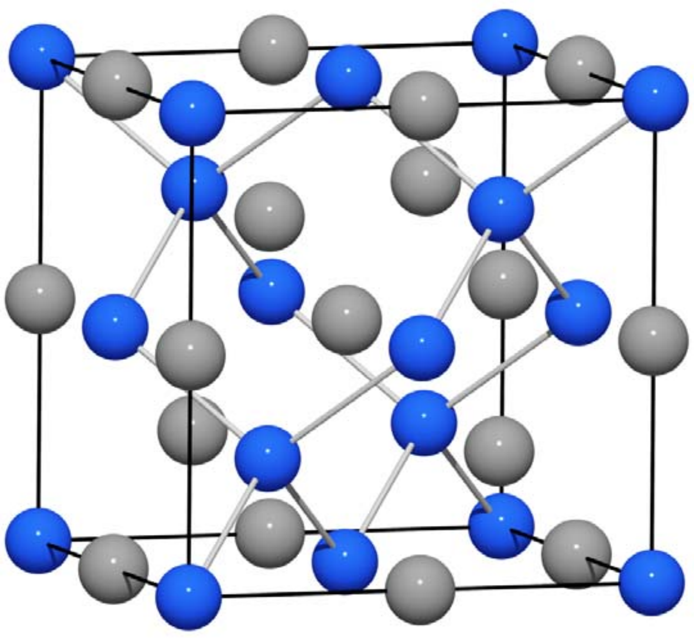
CsCl is not BCC

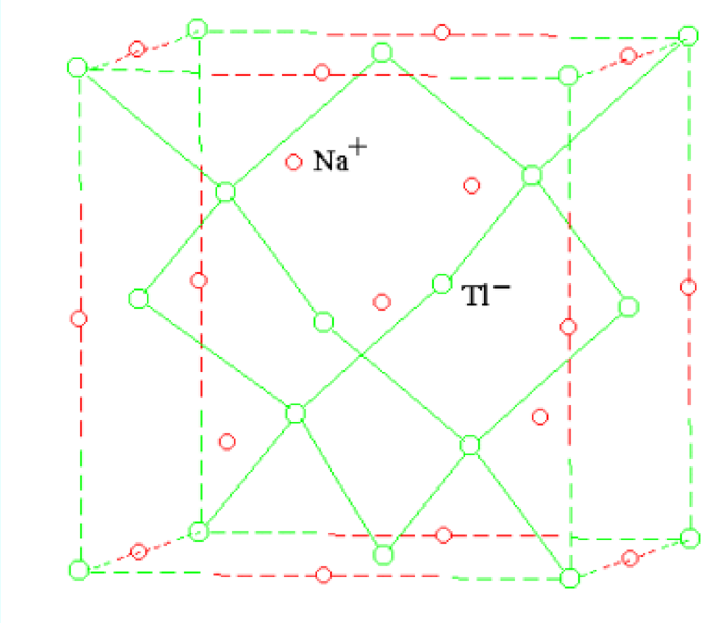




CsBr, CsI, CsCN, NH_4Cl, NH_4Br, TlCl, TlBr, TlI, CuZn, CuPd, LiHg

NaTl

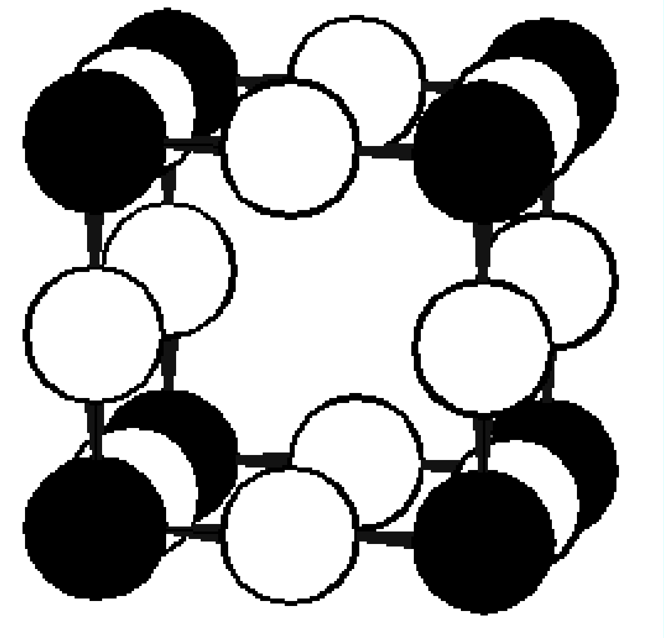


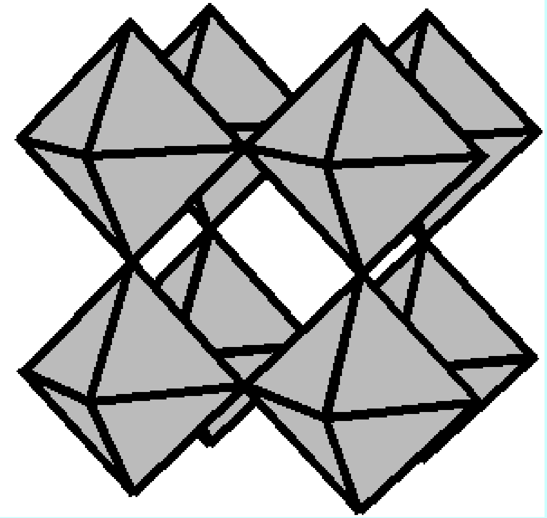


Both sublattices form independent diamond structures.
The atoms sit on the sites of a bcc lattice with a_{bcc} = ½ a

Niggli – 230 space groups – restrictions on arrangement of atoms:
There are only 4 possible AB cubic structures:
NaCl, ZnS-sphalerite, CsCl, and NaTl

ReO_3





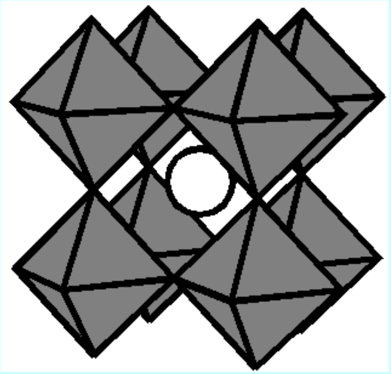
What type of unit cell?
sc, bcc, fcc

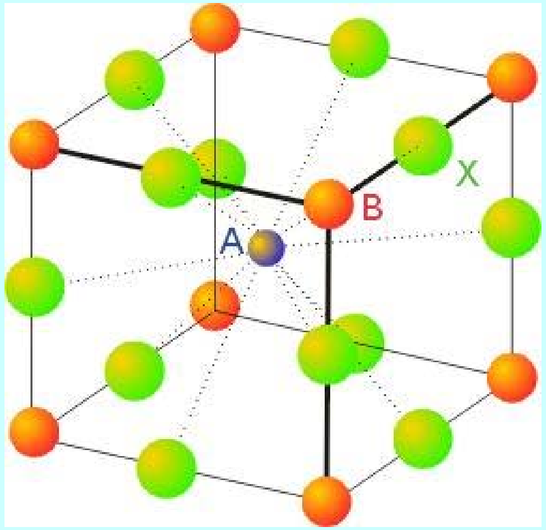
SC of ReO_6 octahedra

NaCl structure with 3/4 of cations removed and 1/4 of anions removed

Cubic-WO_3, UO_3, MoF_3, NbF_3, TaF_3, AlF_3, Cu_3N

Perovskite Structure $CaTiO_3$





1839 G. Rose named mineral after

C. A. Perovski

TiO_6 – octahedra

CaO_{12} – cuboctahedra

(Ca^{2+} and O^{2-} form a cubic close packing)

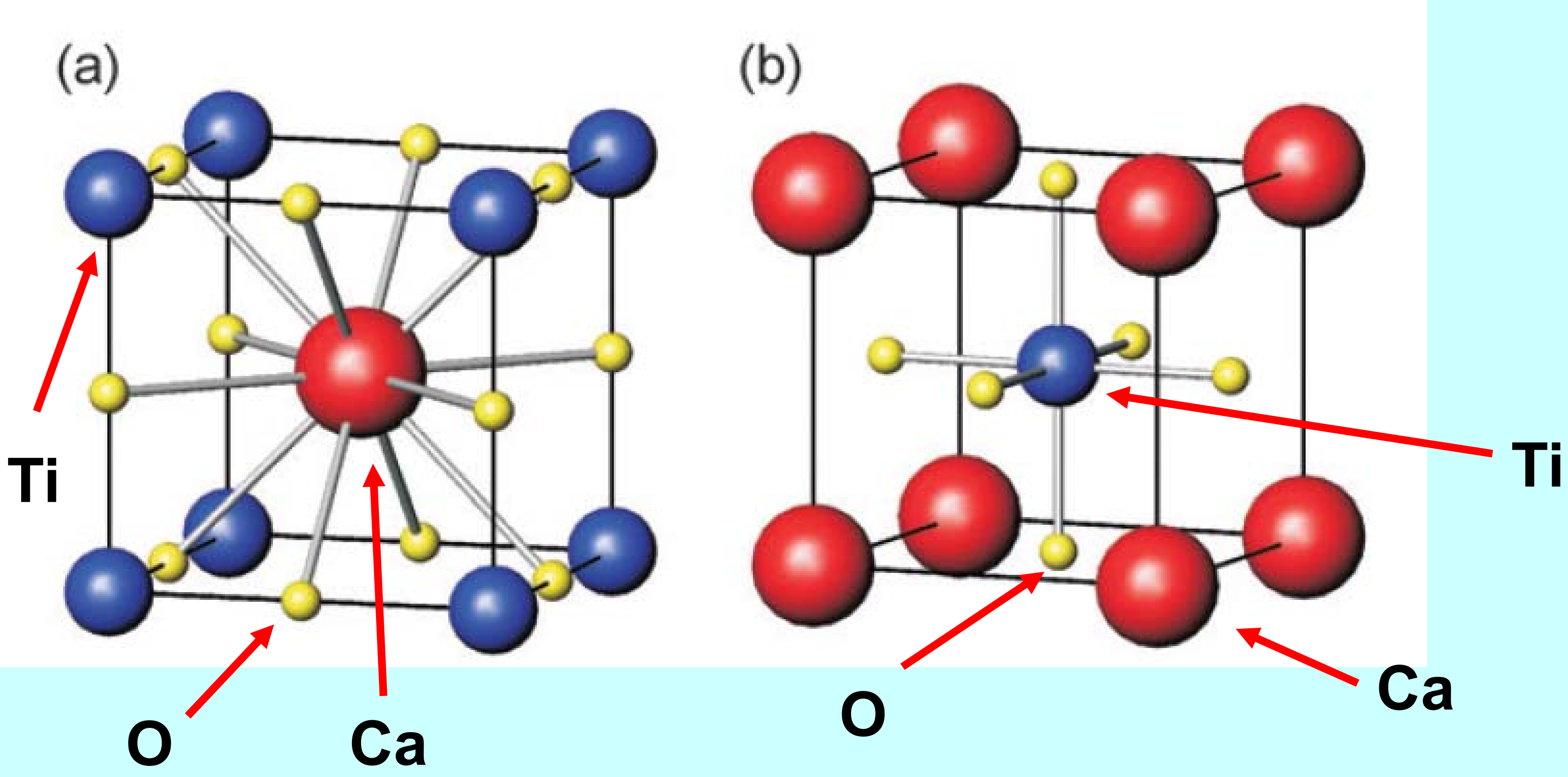
preferred structure of piezoelectric, ferroelectric and superconducting materials

$$t = \frac{r_{A\text{-}X}}{\sqrt{2}\, r_{B\text{-}X}} = \frac{r_A + r_X}{\sqrt{2}\,(r_B + r_X)}$$

Goldschmidt’s tolerance factor

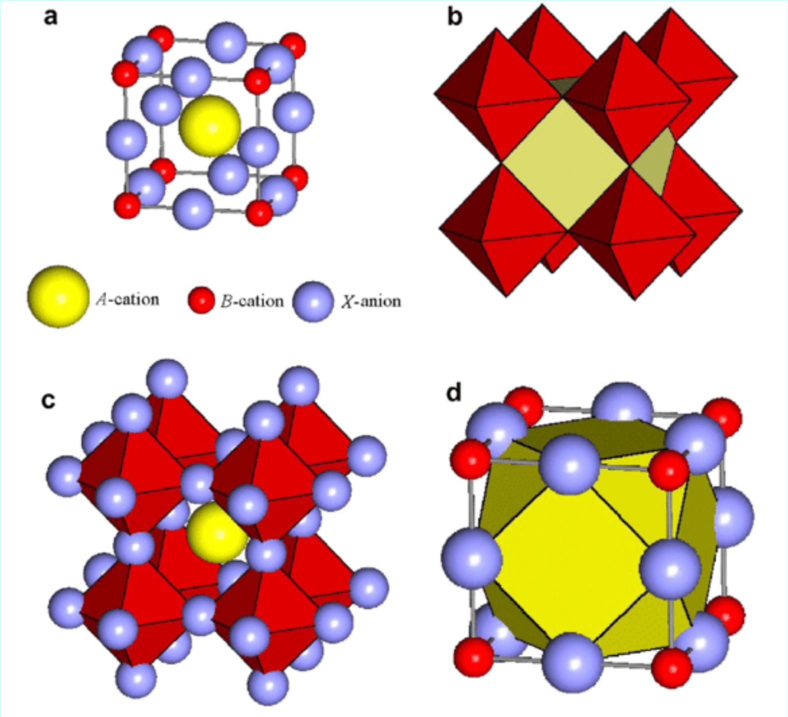
Perovskite, $CaTiO_3$

Two equvivalent views of the unit cell of perovskite



Cubic close packing of Ca and O
with 1/4 octahedral holes filled by Ti cations

Perovskite, ABX_3



$MgSiO_3$, $CaSiO_3$

$KNbO_3$, $KTaO_3$, KIO_3,
$NaNbO_3$, $NaWO_3$,
$LaCoO_3$, $LaCrO_3$,
$LaFeO_3$, $LaGaO_3$, $LaVO_3$,
$SrTiO_3$, $SrZrO_3$, $SrFeO_3$

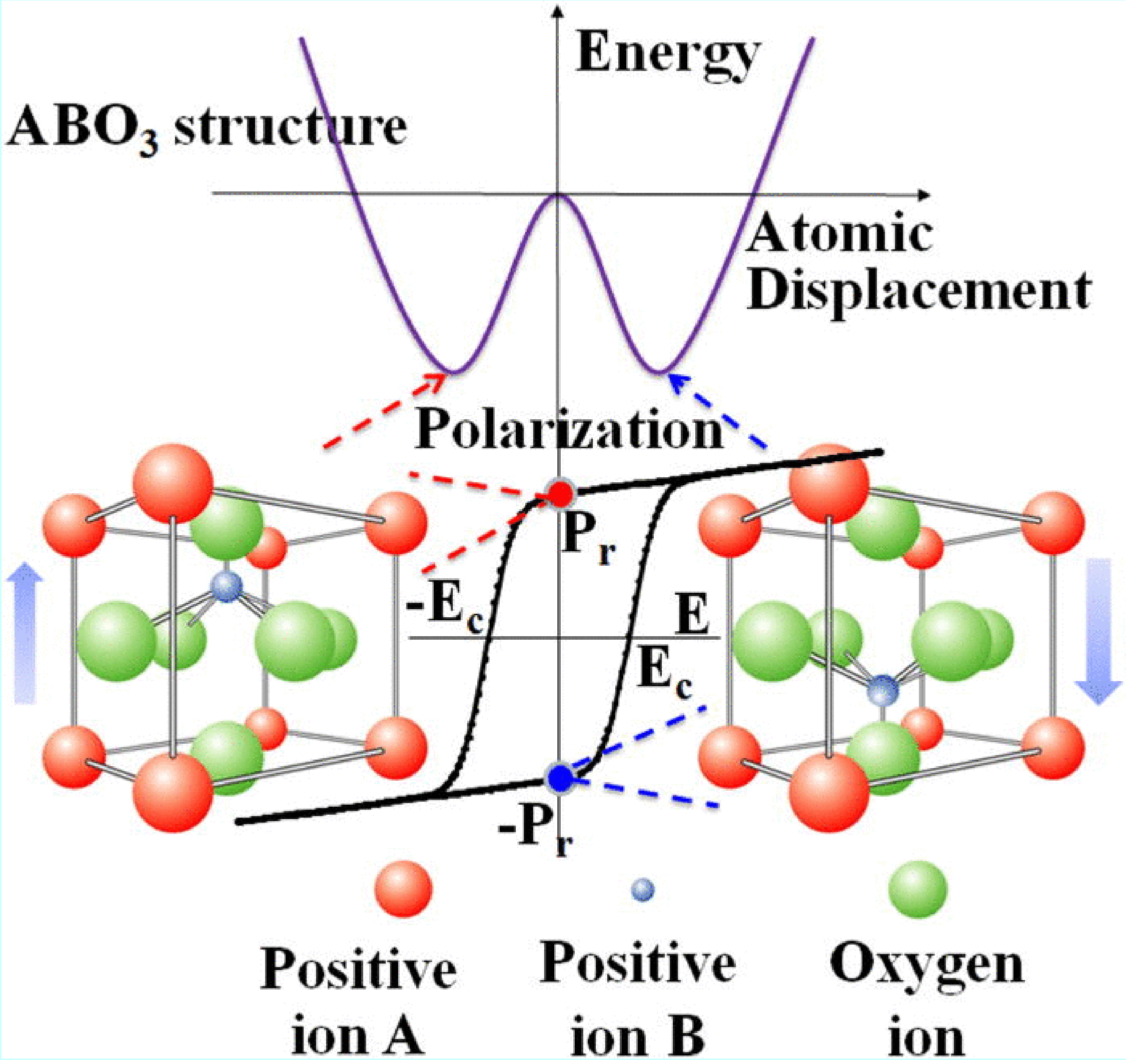
$ThTaN_3$, $BaTaO_2N$

Goldschmidt's tolerance factor

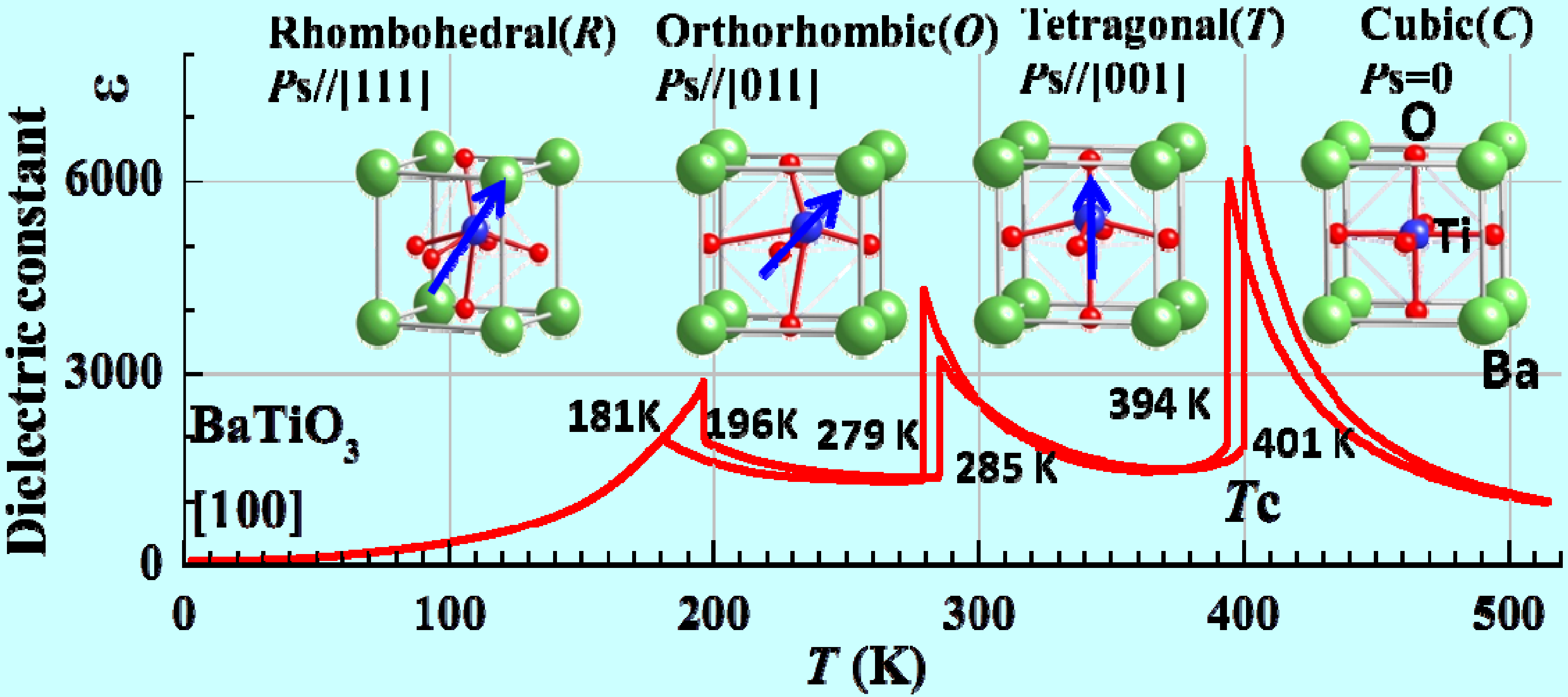
$$t = \frac{r_{A\text{-}X}}{\sqrt{2}\, r_{B\text{-}X}} = \frac{r_A + r_X}{\sqrt{2}\left(r_B + r_X\right)}$$

$0.8 < t < 0.9$ orthorhombic/monoclinic
$0.9 < t < 0.97$ cubic
$0.97 < t < 1.02$ tetragonal

Perovskite - Ferroelectric $BaTiO_3$

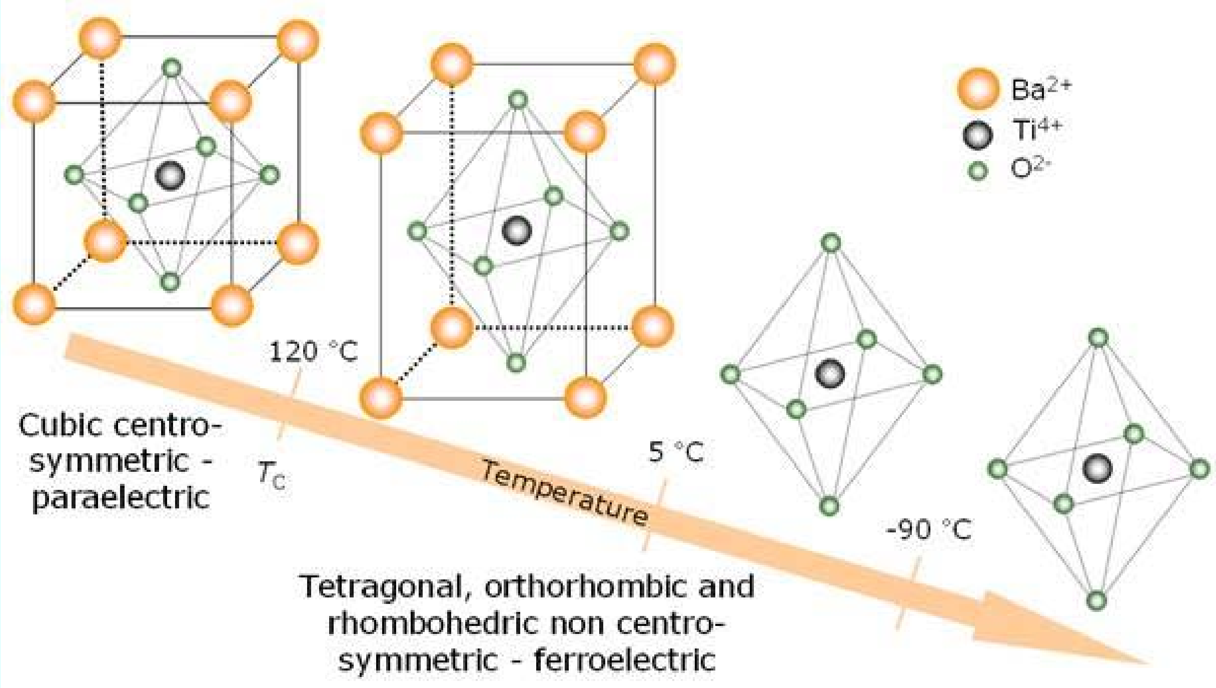


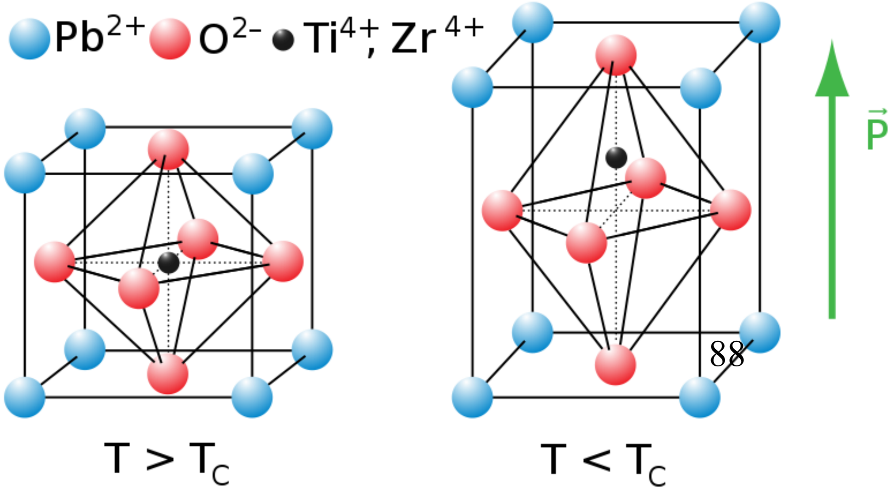
Perovskite, $BaTiO_3$



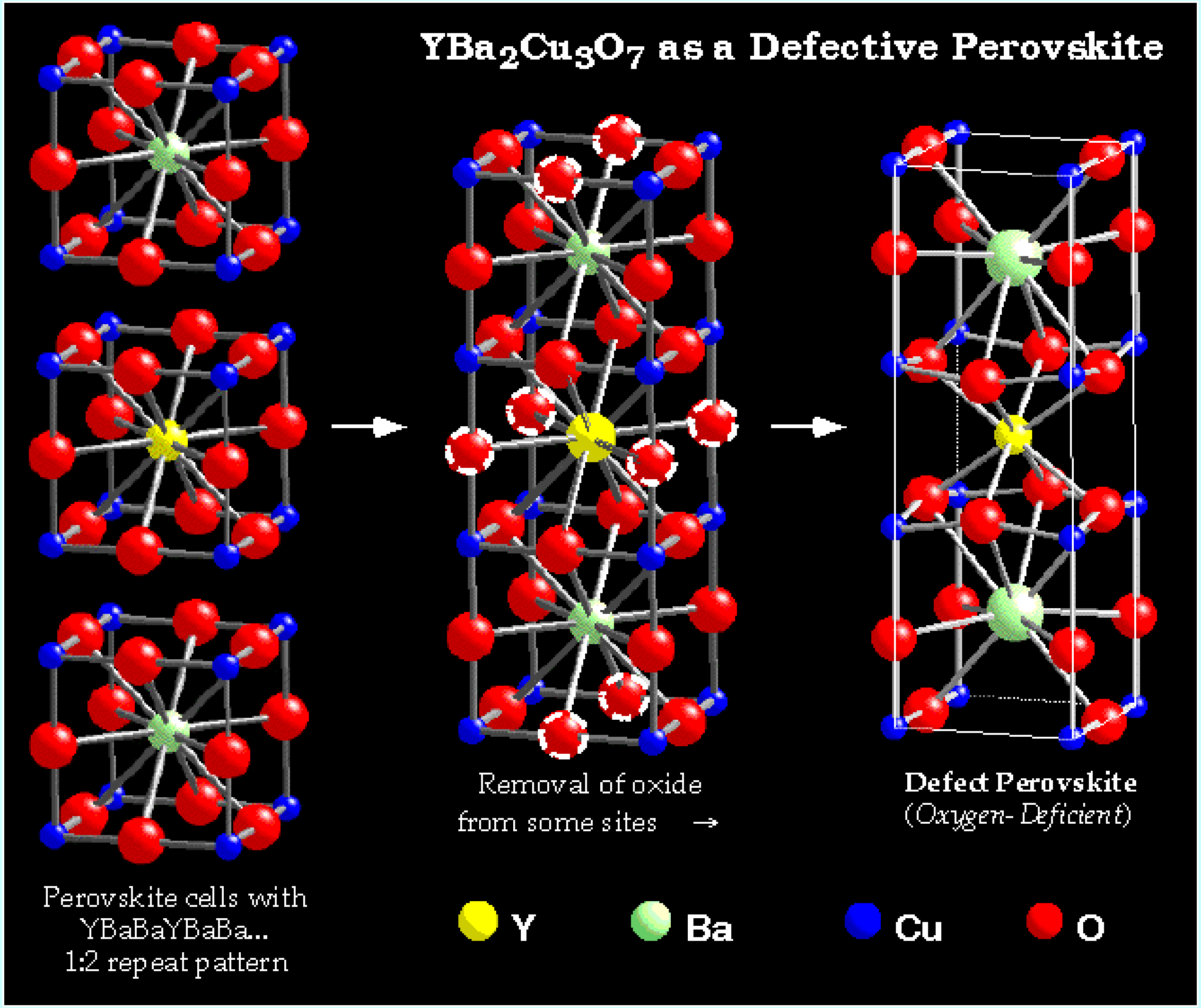
T_c = critical temperature

Perovskite - Ferroelectric $BaTiO_3$

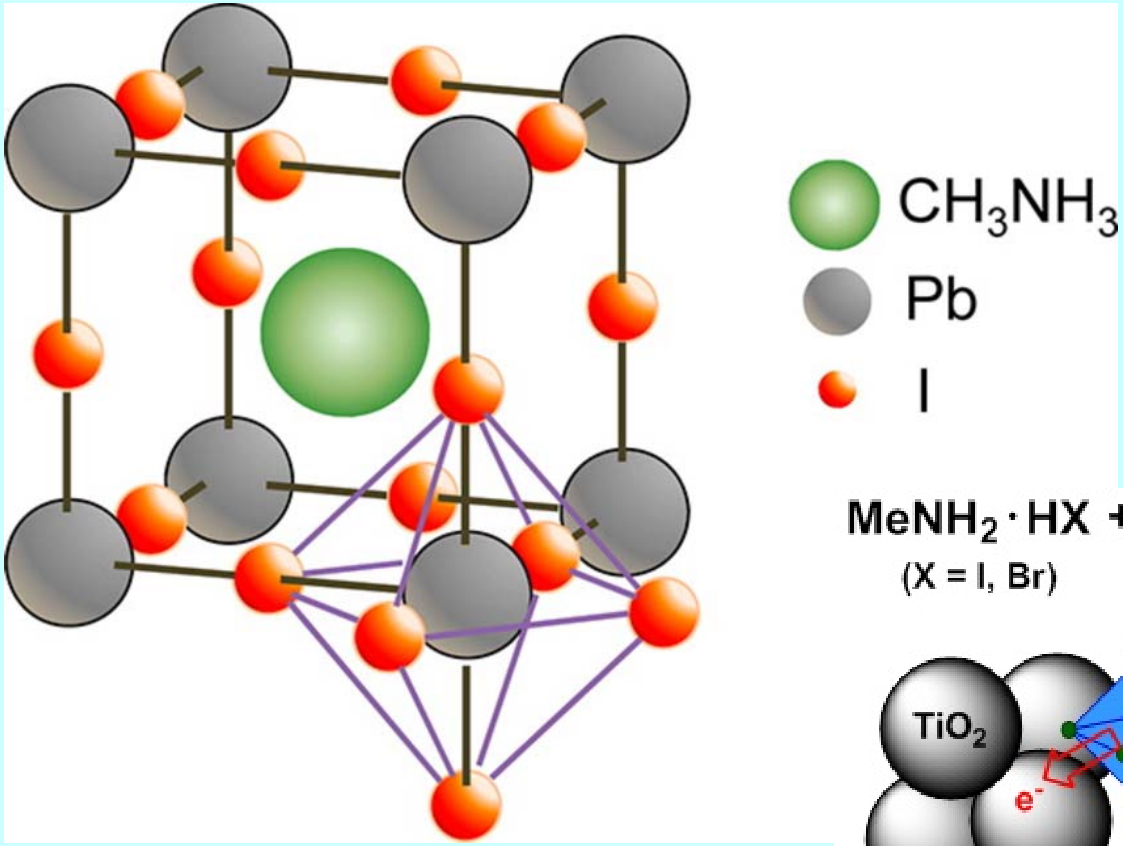


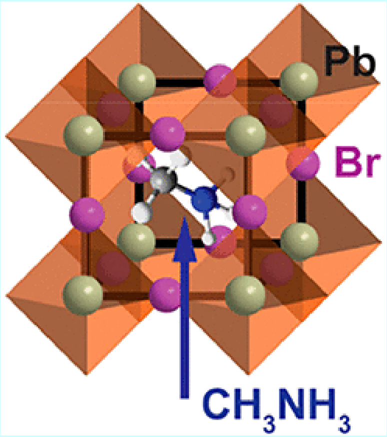


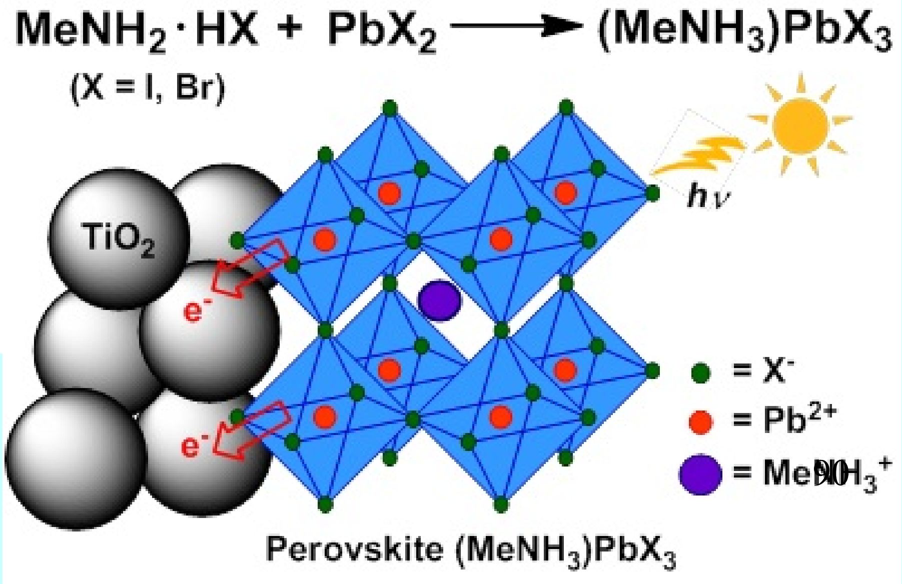
Perovskite Structure of YBCO



Perovskite Structure of $CH_3NH_3PbI_3$



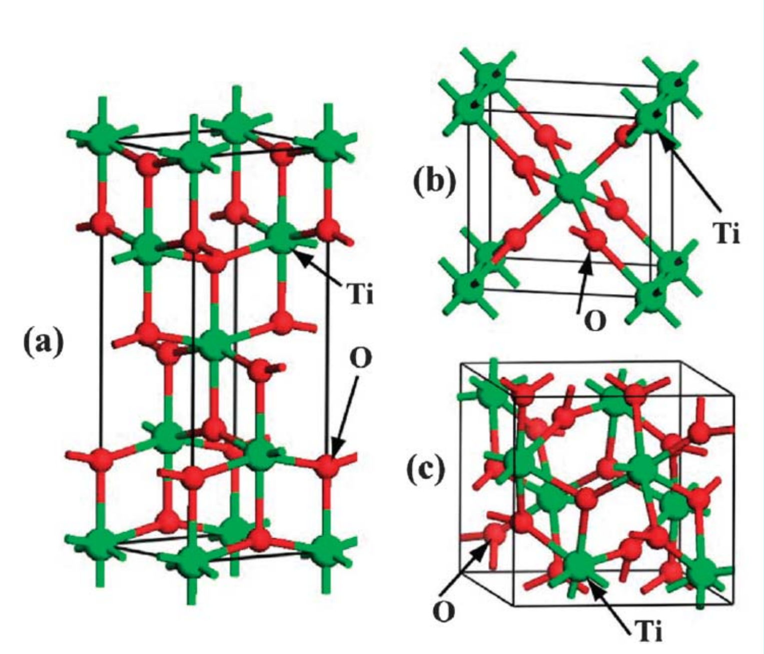


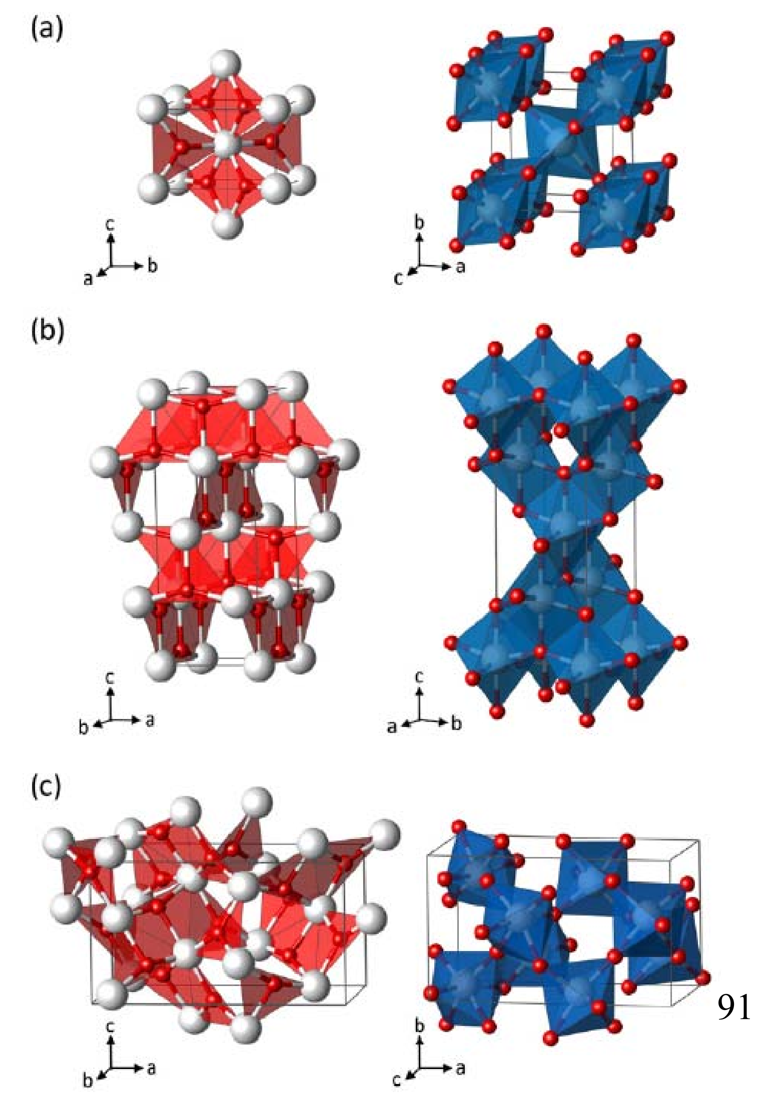

$$MeNH_2 \cdot HX + PbX_2 \longrightarrow (MeNH_3)PbX_3$$

(X = I, Br)

Perovskite $(MeNH_3)PbX_3$

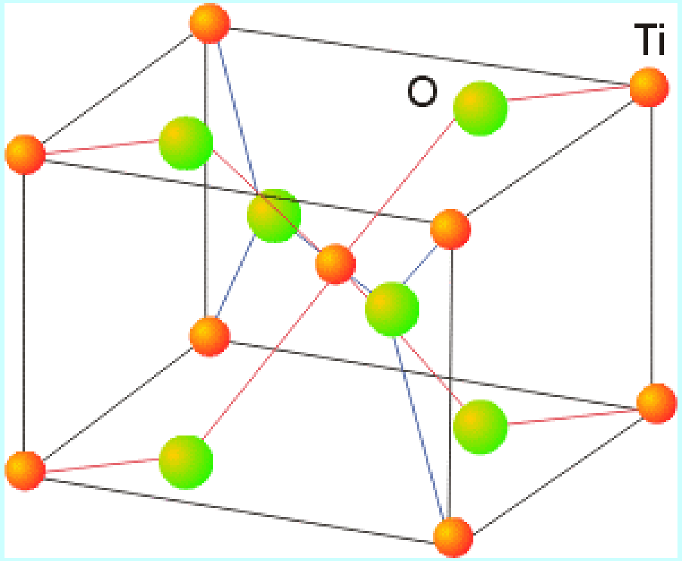
Three Polymorphs of TiO_2

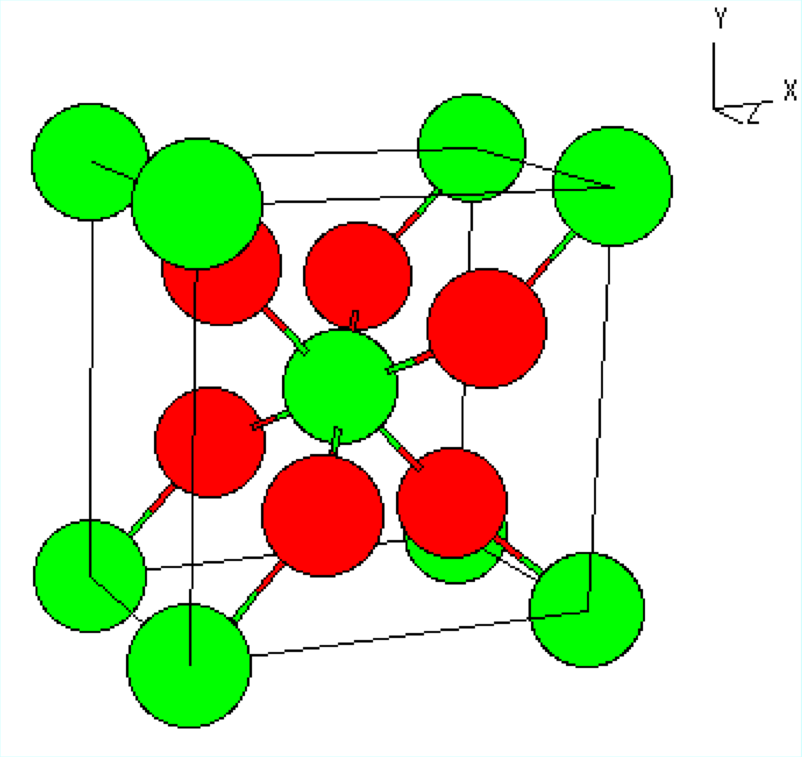




anatase (a), rutile (b) and brookite (c)

Rutile, TiO_2



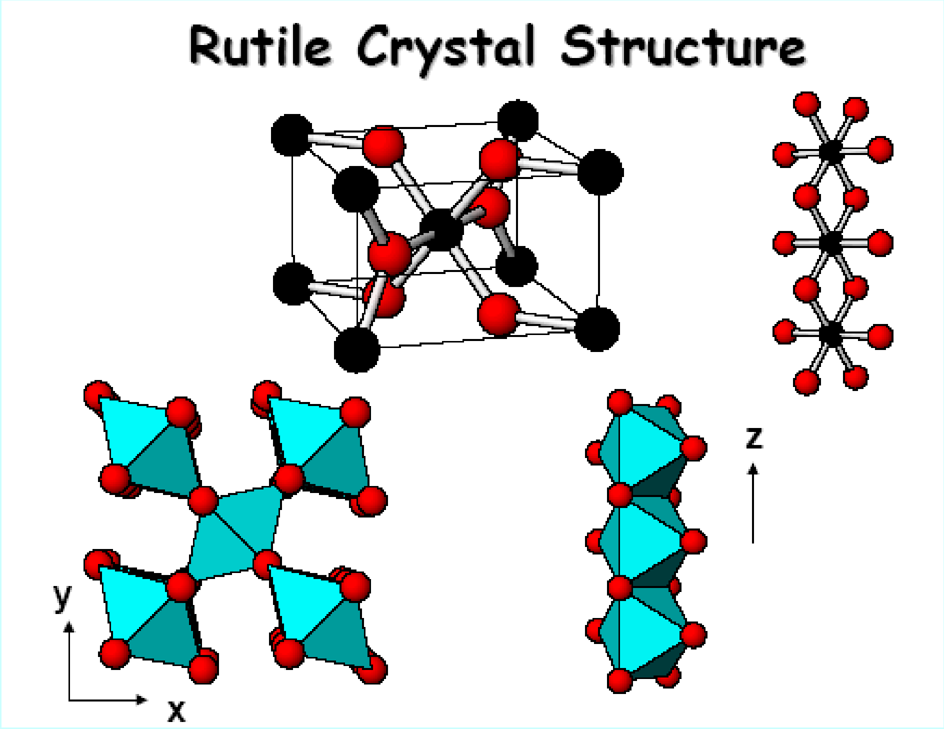


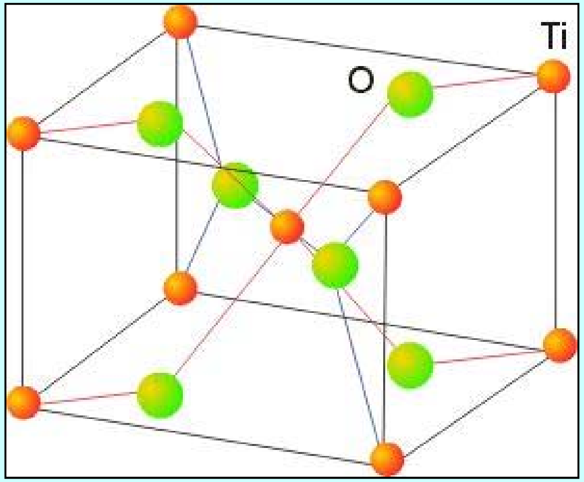
CN – stoichiometry Rule
A_xB_y

CN(A) / CN(B) = y / x

Distorted hexagonal close packing of anions with 1/2 octahedral holes filled by cations (giving a tetragonal lattice)

Rutile, TiO_2

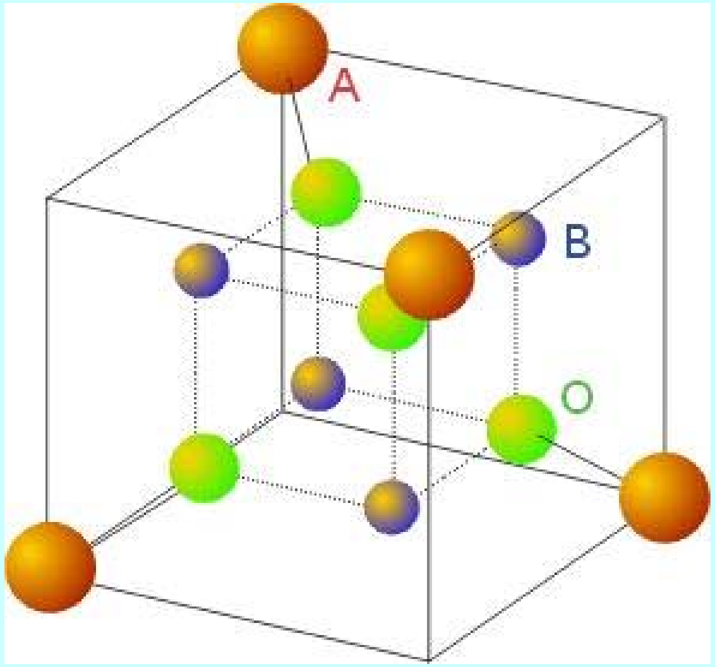




TiO_6 – octahedra
OTi_3 – trigonal planar
(alternative to CaF_2 for highly charged smaller cations)

GeO_2, CrO_2, IrO_2, MoO_2, WO_2, NbO_2, β-MnO_2, OsO_2, VO_2 (>340 K), RuO_2, CoF_2, FeF_2, MgF_2, MnF_2

The Spinel Structure: $MgAl_2O_4$



FCC array of O^{2-} ions, A^{2+} occupies 1/8 of the tetrahedral and B^{3+} 1/2 of the octahedral holes

→ normal spinel:

AB_2O_4

→ inverse spinel:

$B[AB]O_4$

$Fe_3O_4 = Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$

→ basis structure for several magnetic materials

Magnetite (Fe_3O_4) and Maghemite (γ-Fe_2O_3)

Cubic inverse spinel

O^{2-} atoms are arranged in close-packed FCC lattice

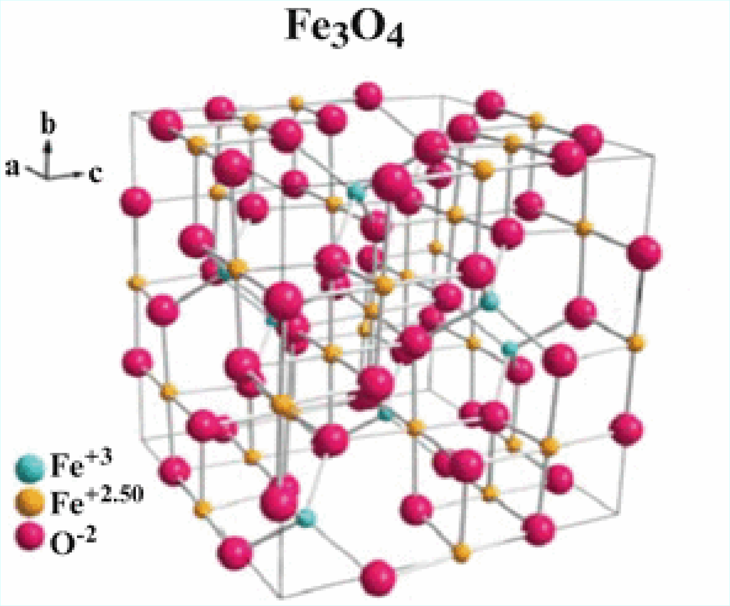
Fe^{2+} occupy ½ of OCT sites

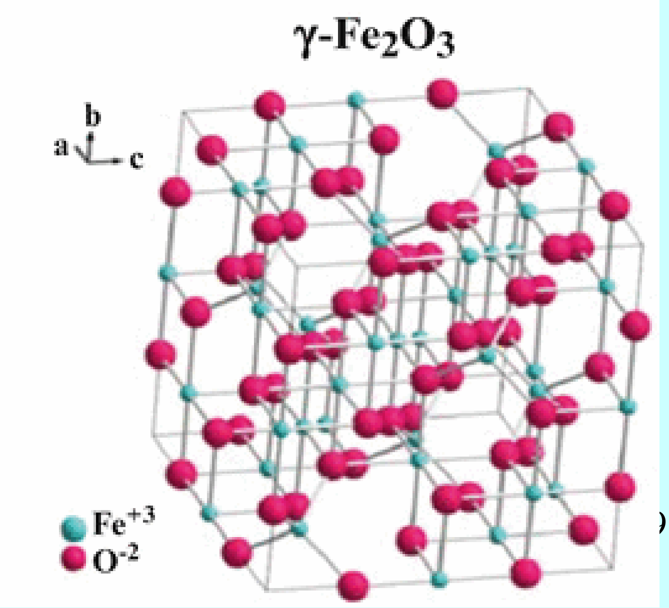
Fe^{3+} are split evenly across the remaining OCT and TET sites

Fully oxidized form of magnetite

Inverse spinel with cation deficiency

One of every six octahedral sites in magnetite is vacant
Stoichiometry $\mathrm{Fe}^{tet}(\mathrm{Fe}_{5/3}\square_{1/3})^{oct}\mathrm{O}_4$





Spinels, AB_2X_4

AB_2X_4 Spinel normal: Cubic close packing of anions with 1/2 octahedral holes filled by B cations and 1/8 tetrahedral holes by A cations

$MgAl_2O_4$, $CoAl_2O_4$, $MgTi_2O_4$, Fe_2GeO_4, $NiAl_2O_4$, $MnCr_2O_4$

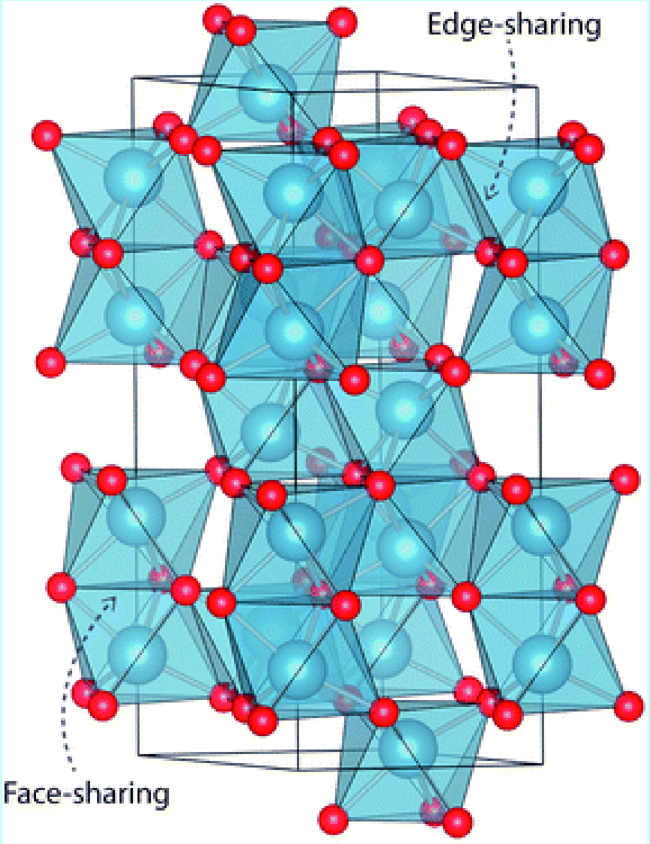
AB_2X_4 Spinel inverse: As for spinel but A cations and 1/2 of B cations interchanged

$MgFe_2O_4$, $NiFe_2O_4$, $MgIn_2O_4$, $MgIn_2S_4$, Mg_2TiO_4, Zn_2TiO_4, Zn_2SnO_4, $FeCo_2O_4$.

δ = the inversion parameter
$(A_\delta B_{1-\delta})_A[A_{1-\delta}B_{1+\delta}]_BO_4$

Values from $\delta = 1$ (normal) to $\delta = 0$ (inverse)
May depend on synthesis conditions

Corundum, Al_2O_3



Al_2O_3 lattice consists of HCP array of O^{2-} ions

Al^{3+} ions fill ……. of all octahedral holes

The Al centres are surrounded by ……. oxides

Oxides are coordinated by …… Al^{3+} ions

Garnets

Naturally occuring garnets $A_3B_2Si_3O_{12} = A_3B_2(SiO_4)_3$

A_3 = divalent cation (Mg, Fe, Mn or Ca) dodecahedral
B_2 = trivalent (Al, Fe^{3+}, Ti, or Cr) octahedral
Si_3 = tetravalent, tetrahedral
Since Ca is much larger in radius than the other divalent cations, there are two series of garnets: one with calcium and one without:
pyralspite contain Al (pyrope, almandine, spessartine)
ugrandite contain Ca (uvarovite, grossular, andradite)

Synthetic garnets $A_3B_5O_{12}$

A_3 = trivalent cations, large size (Y, La,…)
B_5 = trivalent (Al, Fe^{3+}, Ti, or Cr) 2B octahedral, 3B tetrahedral
$Y_3Al_5O_{12}$
$Y_3Fe_5O_{12}$

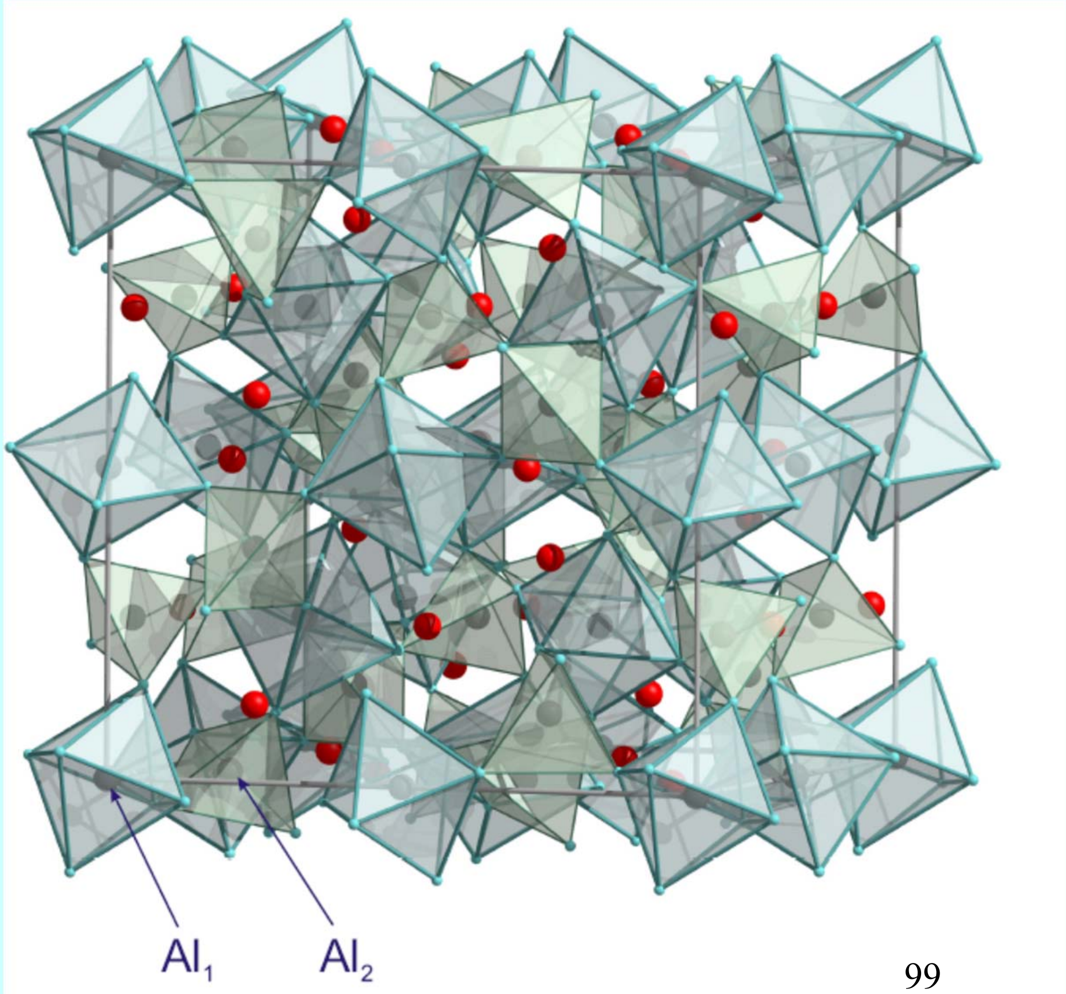
Synthetic Garnets $A_3B_5O_{12}$

YAG
Garnet $Y_3Al_5O_{12}$

Y_3 = red - dodecahedral trivalent cations, large size

Al_5 = blue
2 octahedral
3 tetrahedral

O_{12}



Fullerides

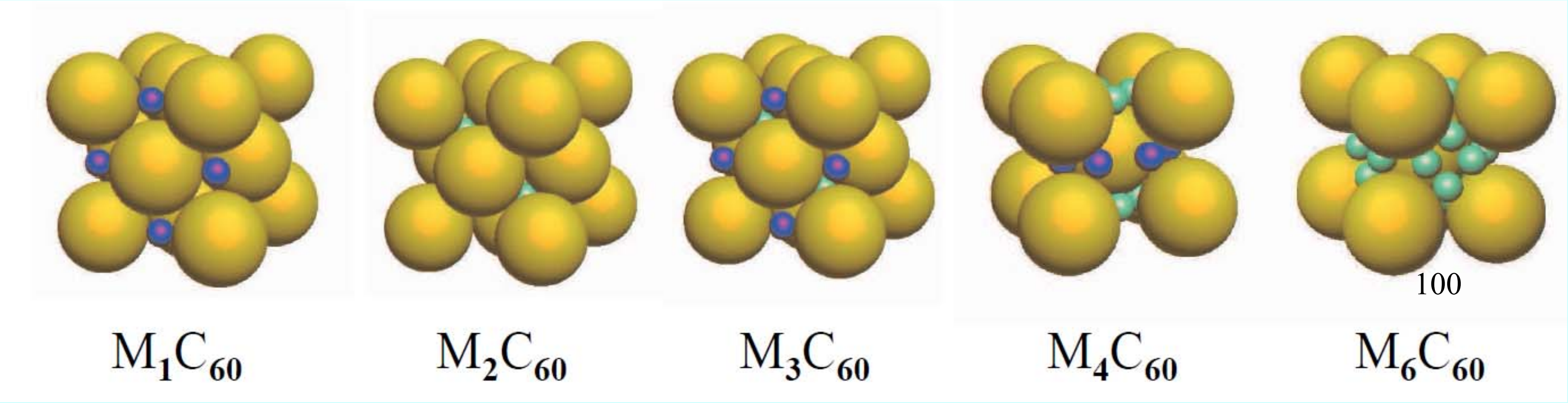
M_1C_{60} all the octahedral (O) sites (dark blue) are occupied (NaCl)

M_2C_{60} all the tetrahedral (T) sites (light blue) are occupied (CaF_2)

M_3C_{60} both the O and the T sites are occupied (BiF_3)

M_4C_{60} rearranged to a body-centered tetragonal (bct) cell and both the O and the T sites of the bct lattice are occupied

M_6C_{60} a bcc lattice and all its T sites are occupied



M_1C_{60} M_2C_{60} M_3C_{60} M_4C_{60} M_6C_{60}

Layered Structures

CdI_2

Hexagonal close packing of anions with 1/2 octahedral holes filled by cations

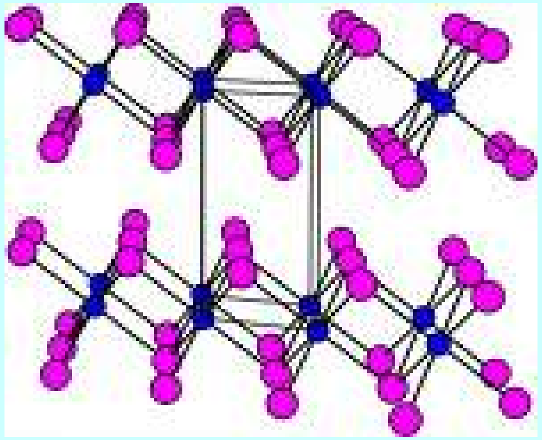
CoI_2, FeI_2, MgI_2, MnI_2, PbI_2, ThI_2, TiI_2, TmI_2, VI_2, YbI_2, ZnI_2, VBr_2, $TiBr_2$, $MnBr_2$, $FeBr_2$, $CoBr_2$, $TiCl_2$, TiS_2, TaS_2
$Mg(OH)_2$ - brucite

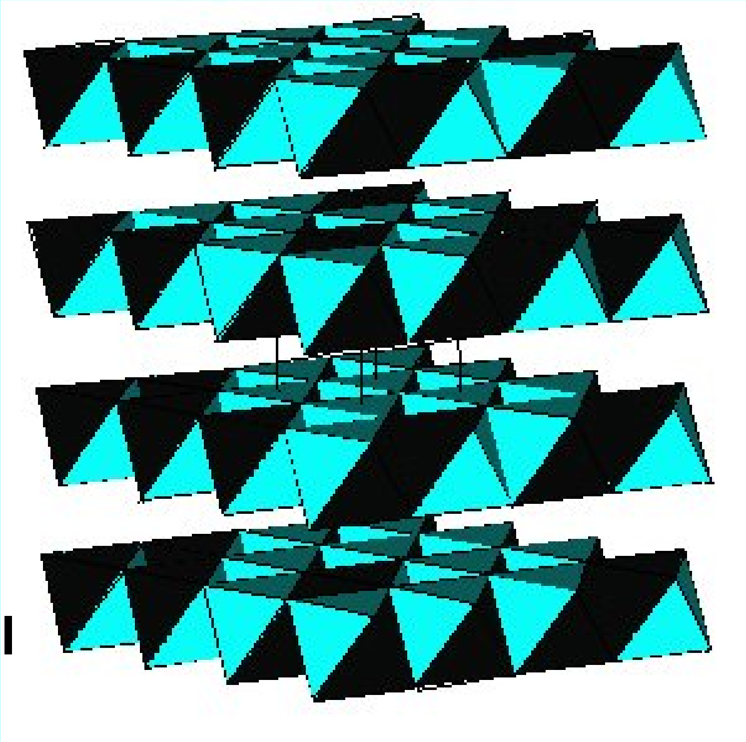
$CdCl_2$

Cubic close packing of anions with 1/2 octahedral holes filled by cations

$CdCl_2$, $CdBr_2$, $CoCl_2$, $FeCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$, NiI_2, $ZnBr_2$, ZnI_2, Cs_2O* (anti-$CdCl_2$ structure)

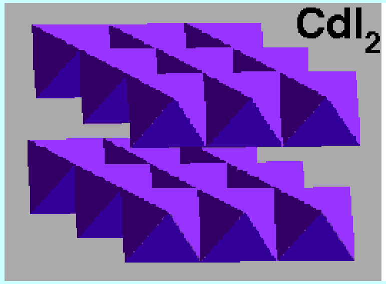
CdI_2 Hexagonal Close Packing

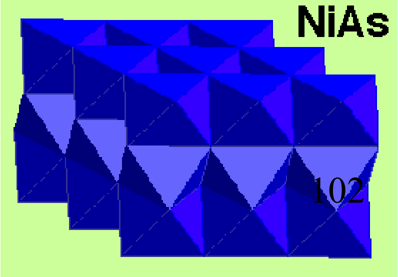




HCP of anions with 1/2 octahedral holes filled by cations

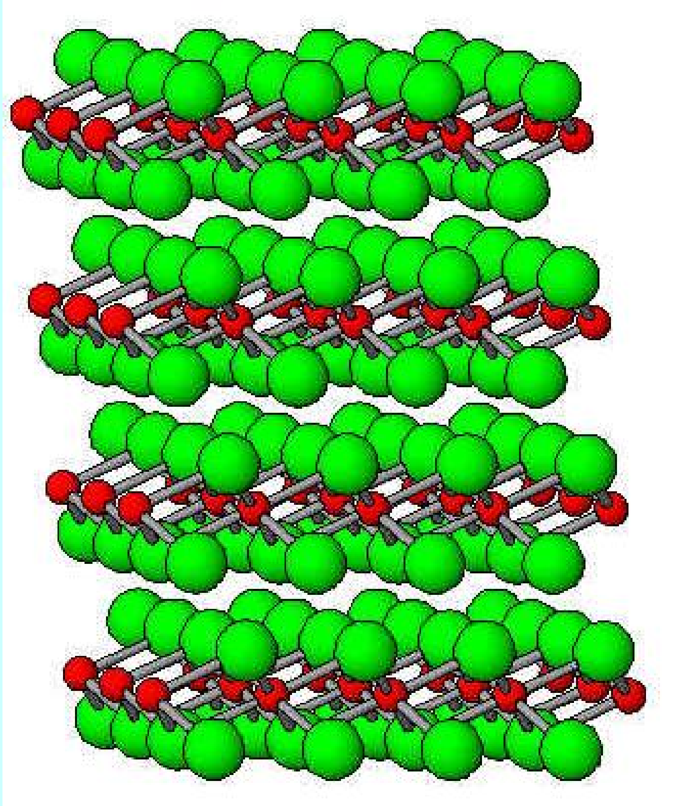
Fully occupied and completely empty planes alternate

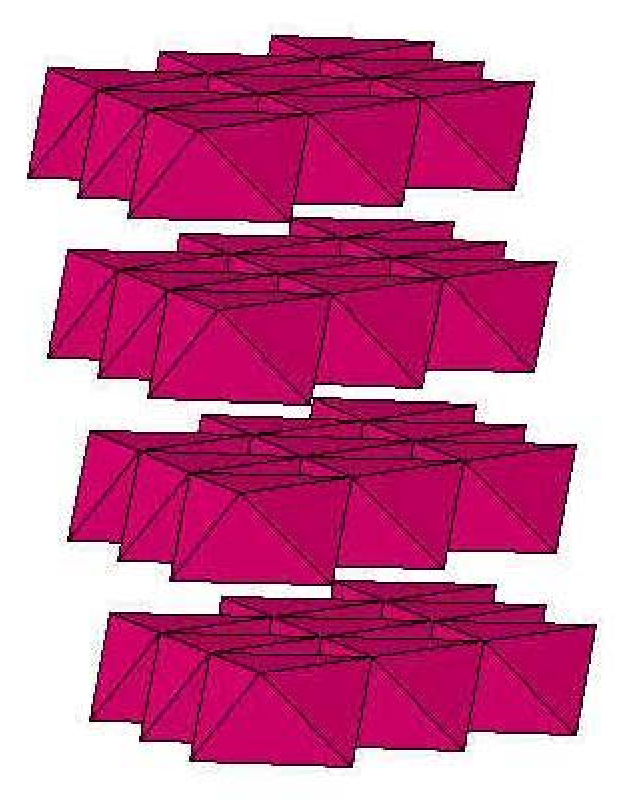




$CdCl_2$ Cubic Close Packing

CCP of anions with 1/2 octahedral holes filled by cations, fully occupied and completely empty planes alternate





Vocabulary of terms

Parallelepiped = rovnoběžnostěn