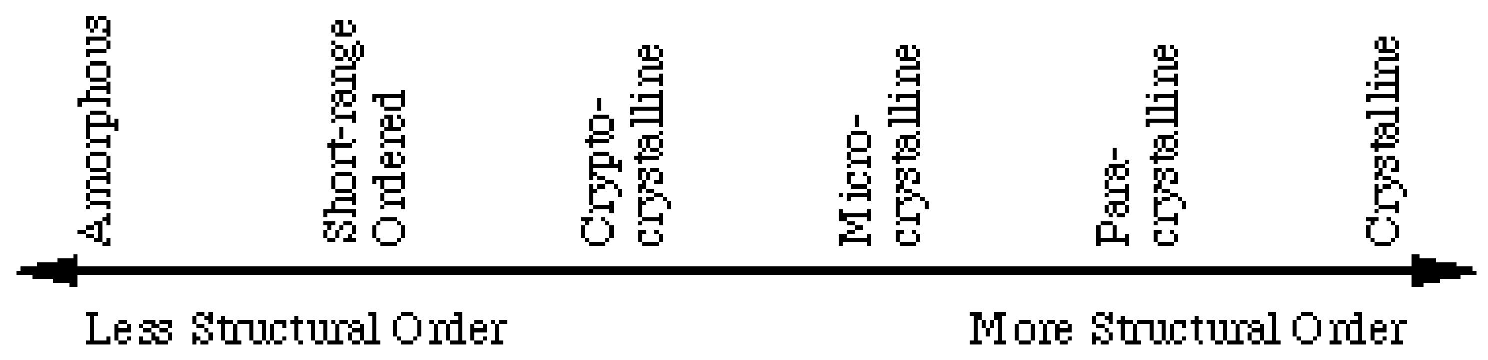
Basic Structural Chemistry

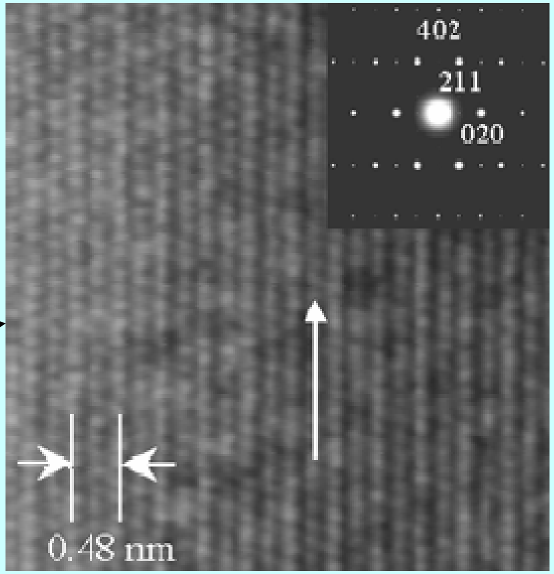
Crystalline state

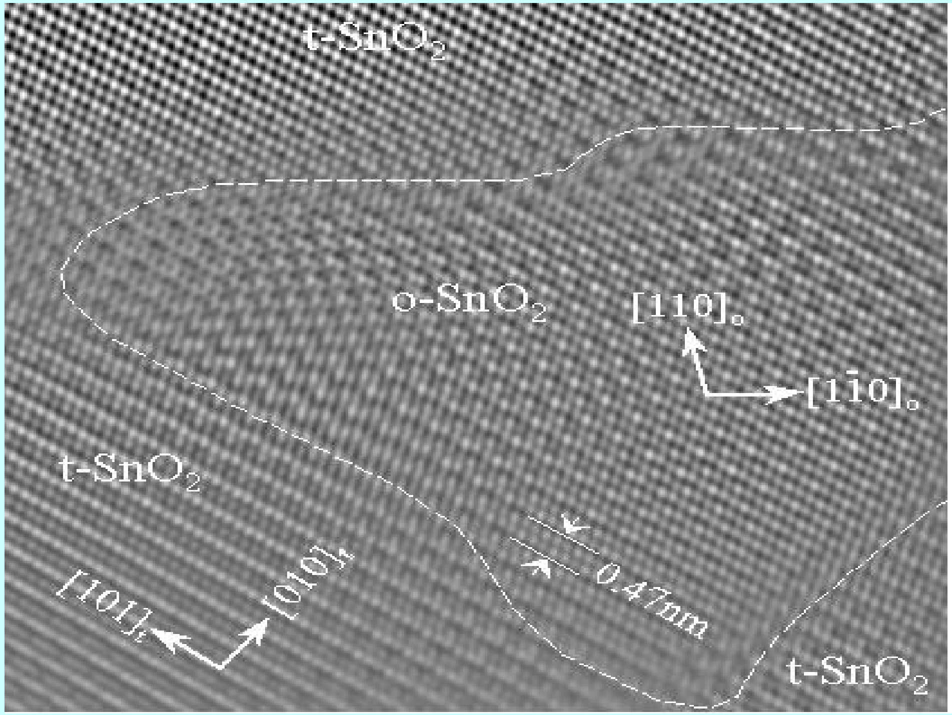
Structure types

Degree of Crystallinity



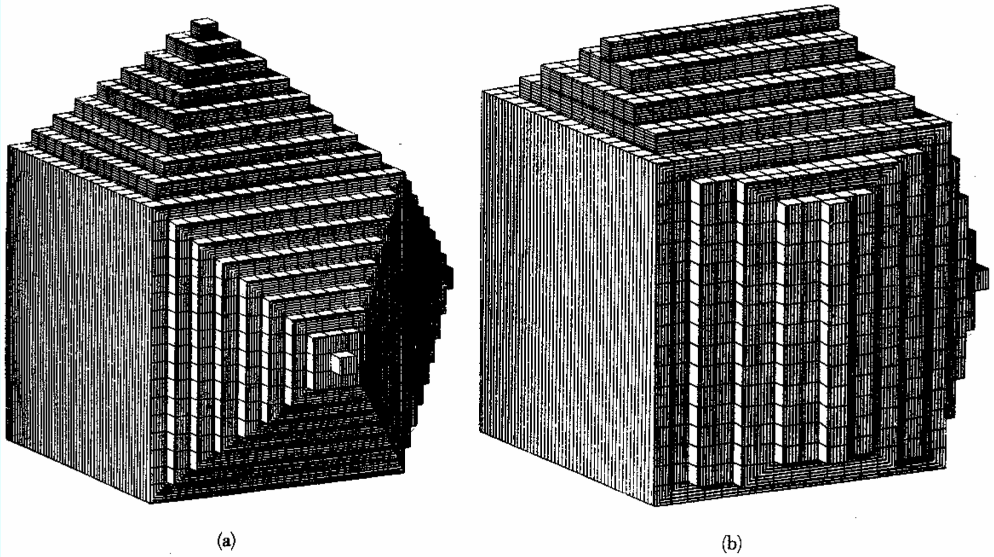
- Single Crystalline
- Polycrystalline
- Amorphous

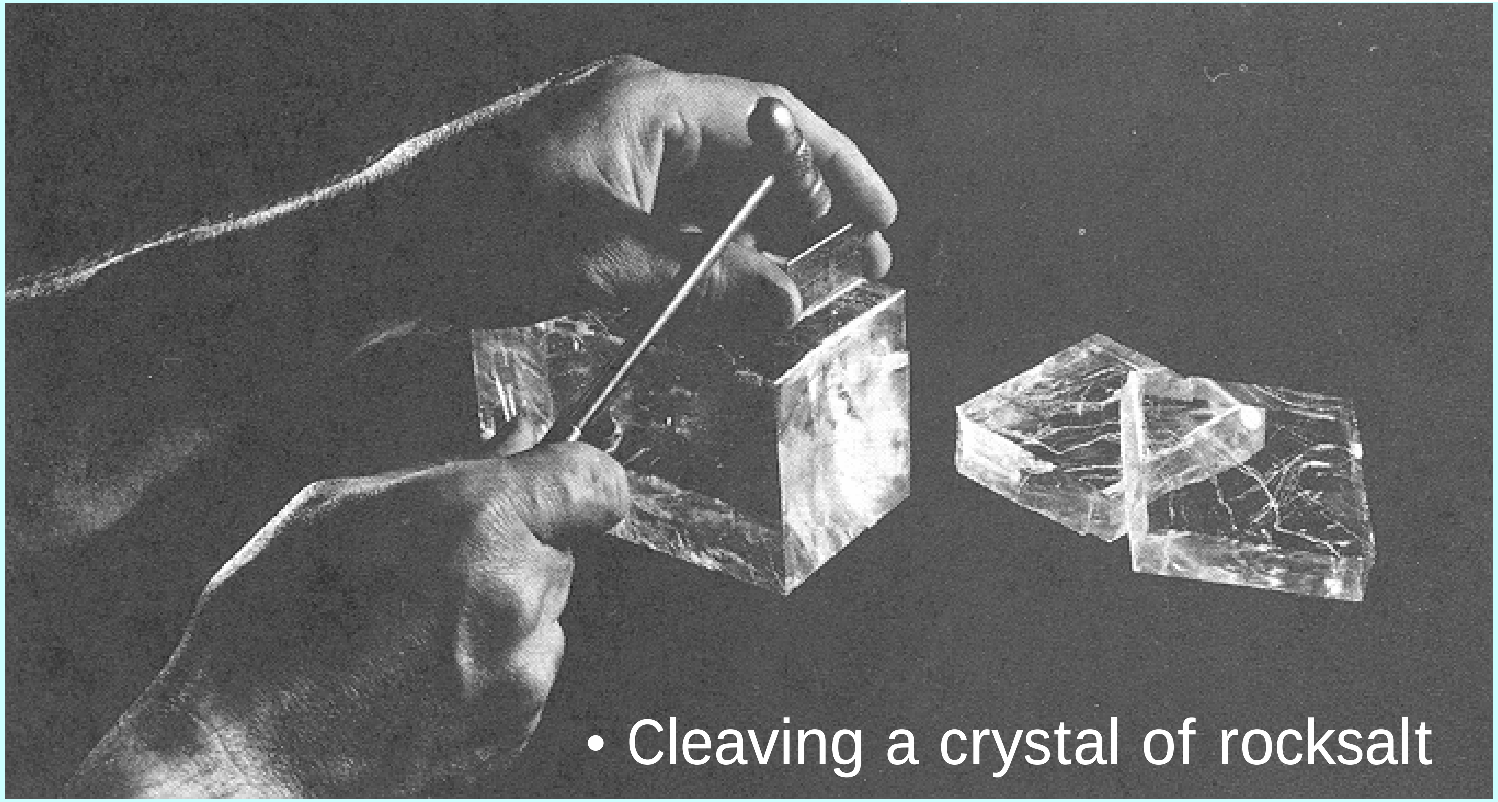




Crystal Structure

- The building blocks of these two are identical, but different crystal faces are developed





- Cleaving a crystal of rocksalt

Crystals

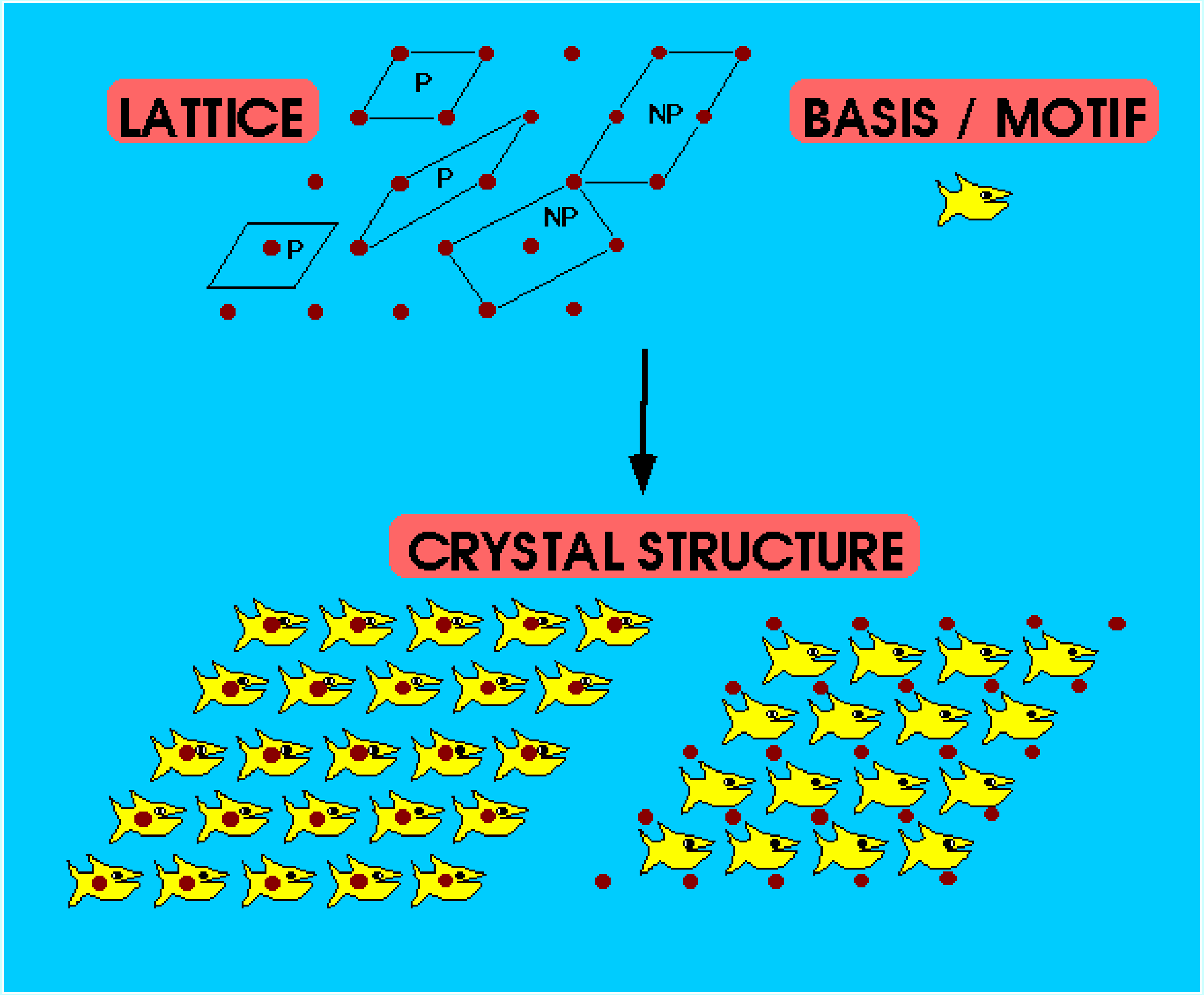
- **Crystal consist of a periodic arrangement of structural motifs = building blocks**
- **Building block is called a basis: an atom, a molecule, or a group of atoms or molecules**
- **Such a periodic arrangement must have translational symmetry such that if you move a building block by a distance:**

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

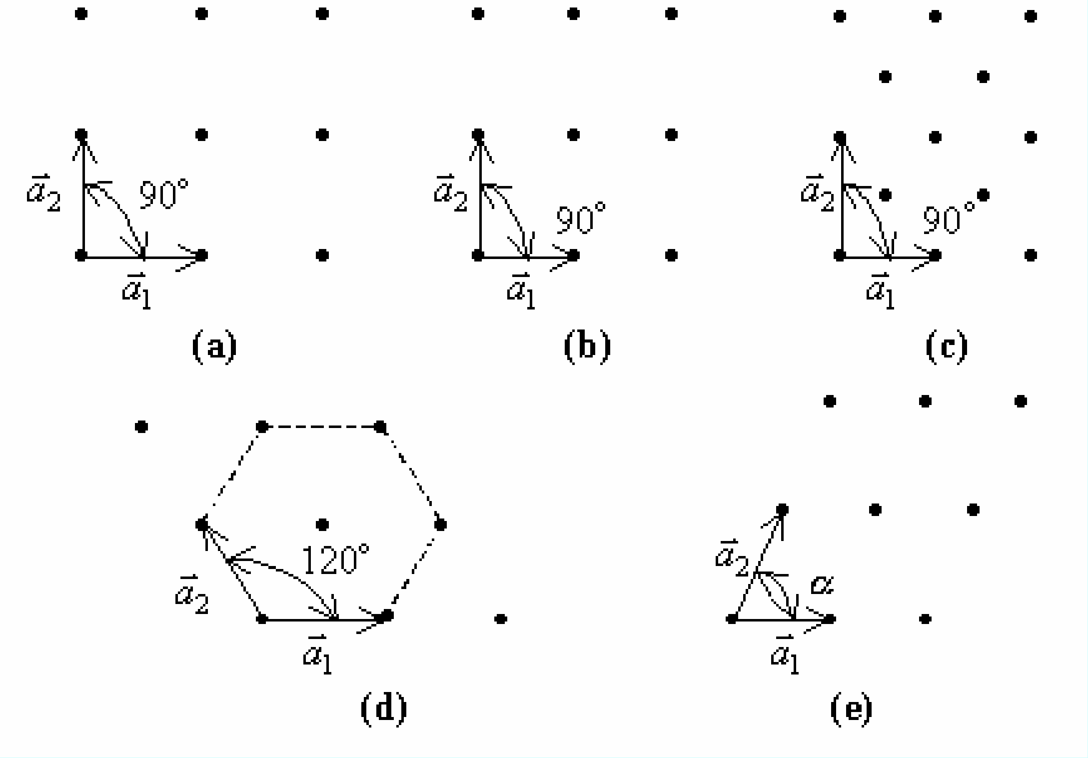
  where n_1, n_2, and n_3 are integers, and $\overline{a}, \overline{b}, \overline{c}$ are vectors.

  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.**

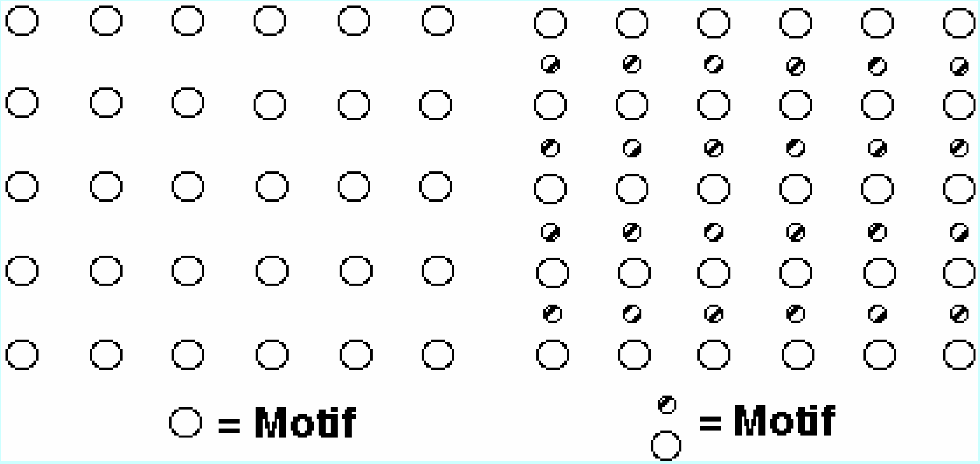
Planar Lattice 2D

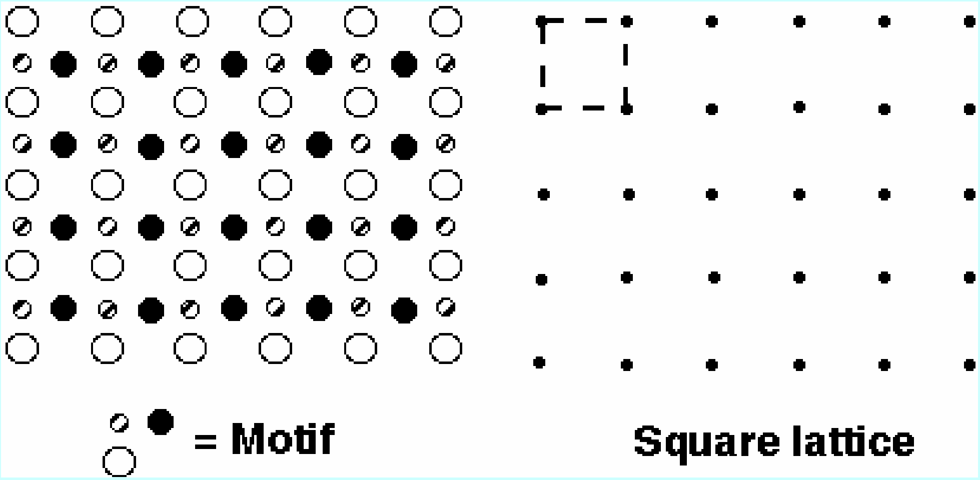


Five Planar Lattices

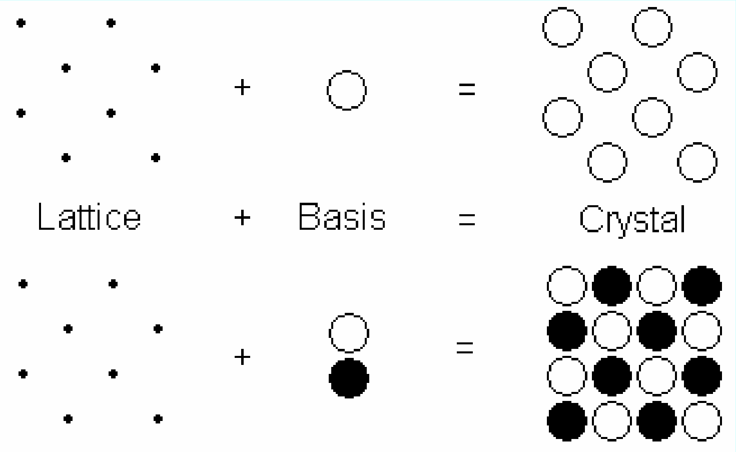


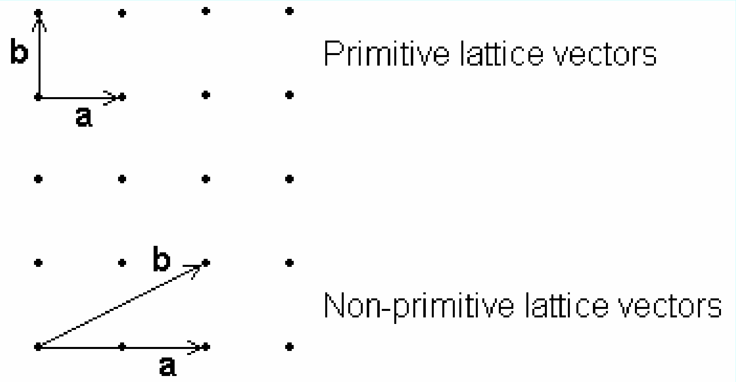
Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2$, $\alpha = 90°$
Rectangular	2	$a_1 \neq a_2$, $\alpha = 90°$
Hexagonal	1	$a_1 = a_2$, $\alpha = 120°$
Oblique	1	$a_1 \neq a_2$, $\alpha \neq 120°$, $\alpha \neq 90°$





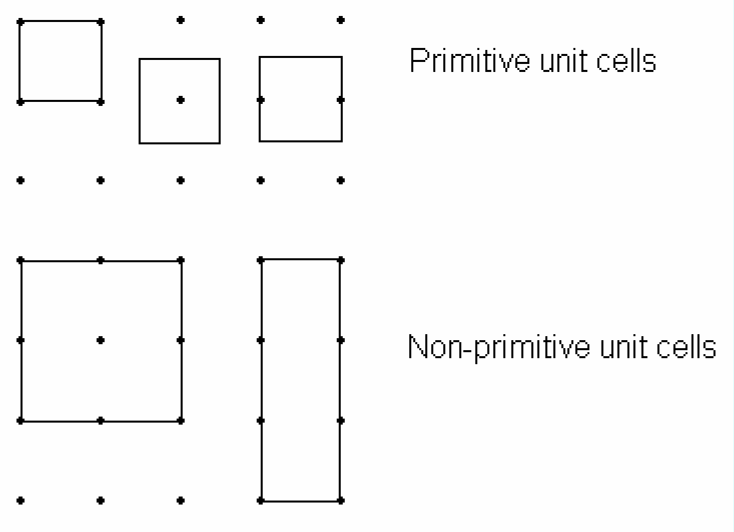
Square lattice


Lattice + Basis = Crystal

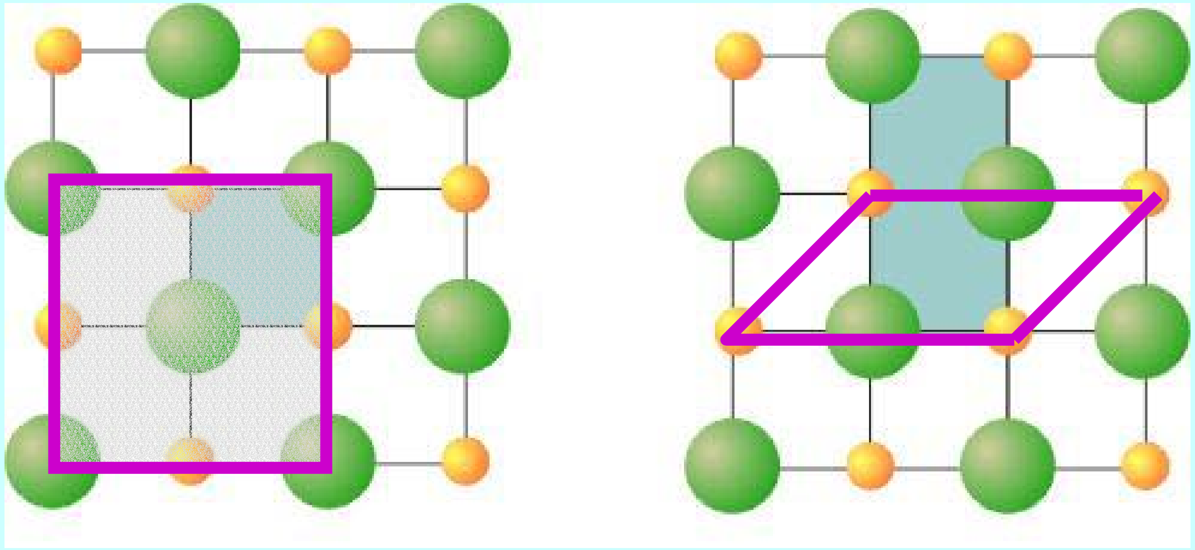


Primitive lattice vectors

Non-primitive lattice vectors


Primitive unit cells

Non-primitive unit cells

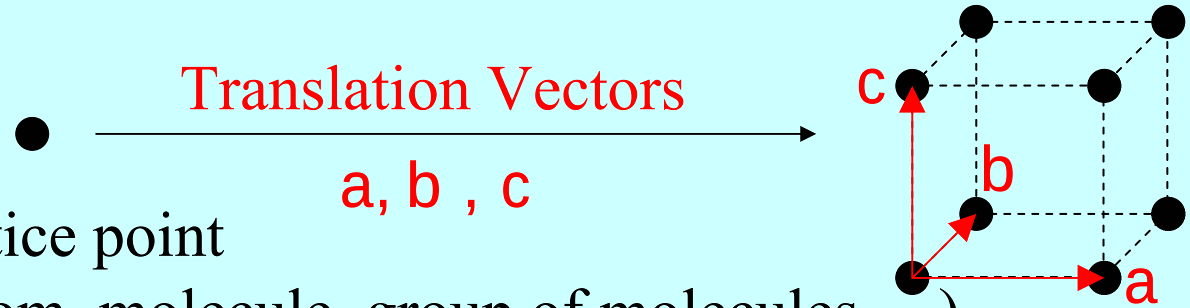


Unit Cell: An „imaginary“ parallel sided region of a structure from which the entire crystal can be constructed by purely translational displacements
Contents of unit cell represents chemical composition

Space Lattice: A pattern that is formed by the lattice points that have identical environment.

Coordination Number (CN): Number of direct neighbours of a given atom (first coordination sphere)

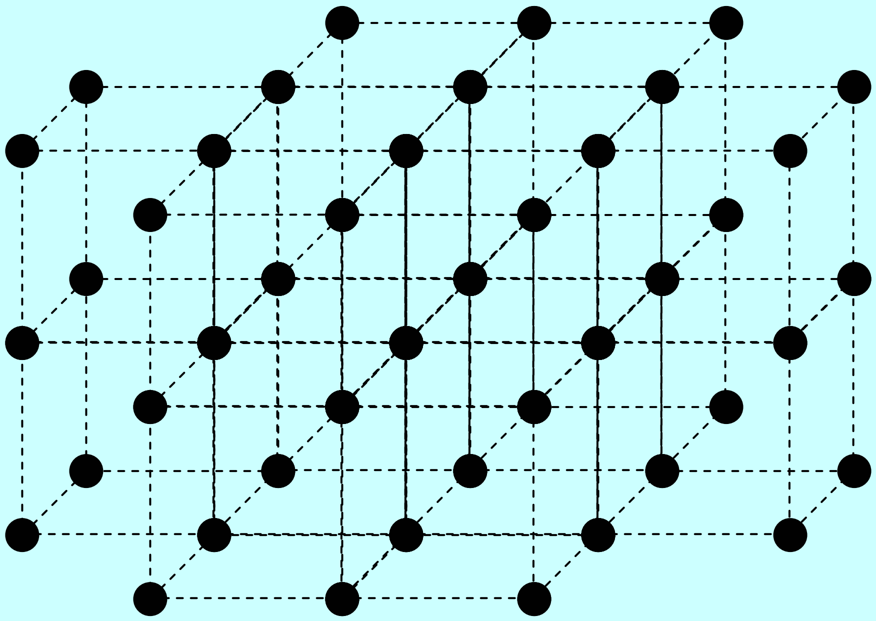
Crystal = Periodic Arrays of Atoms



Translation Vectors

a, b , c

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

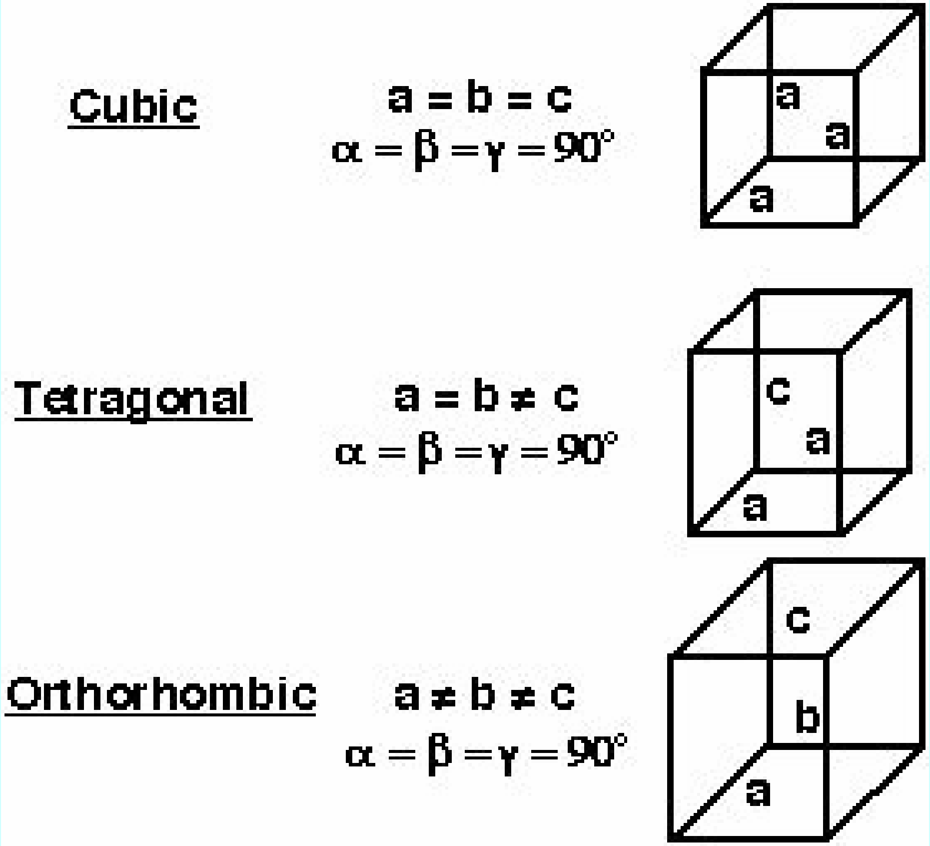


Primitive Cell:

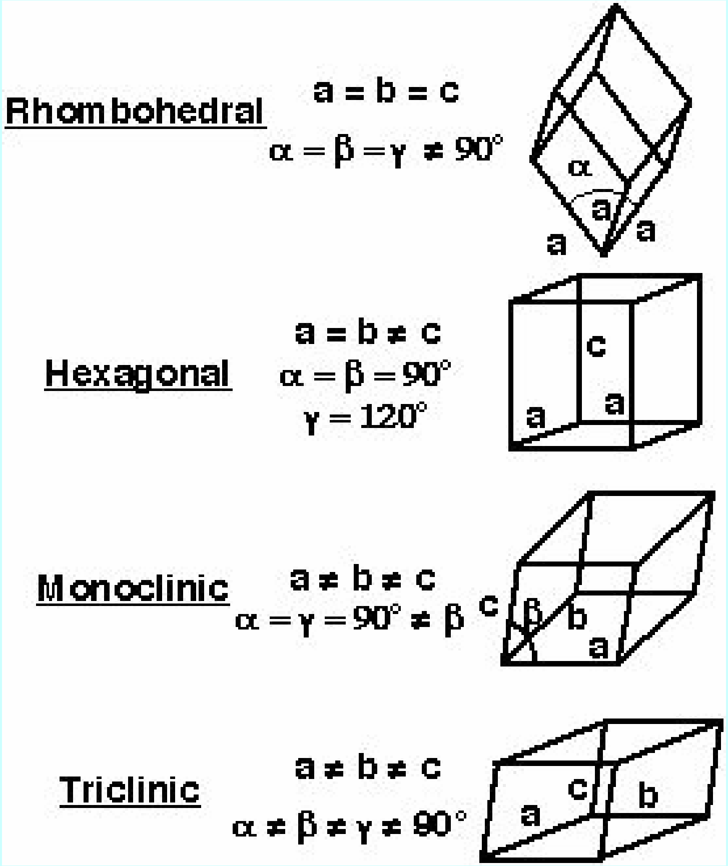
- Smallest building block for the crystal lattice.
- Repetition of the primitive cell gives a crystal lattice

	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)**

Seven Crystal Systems

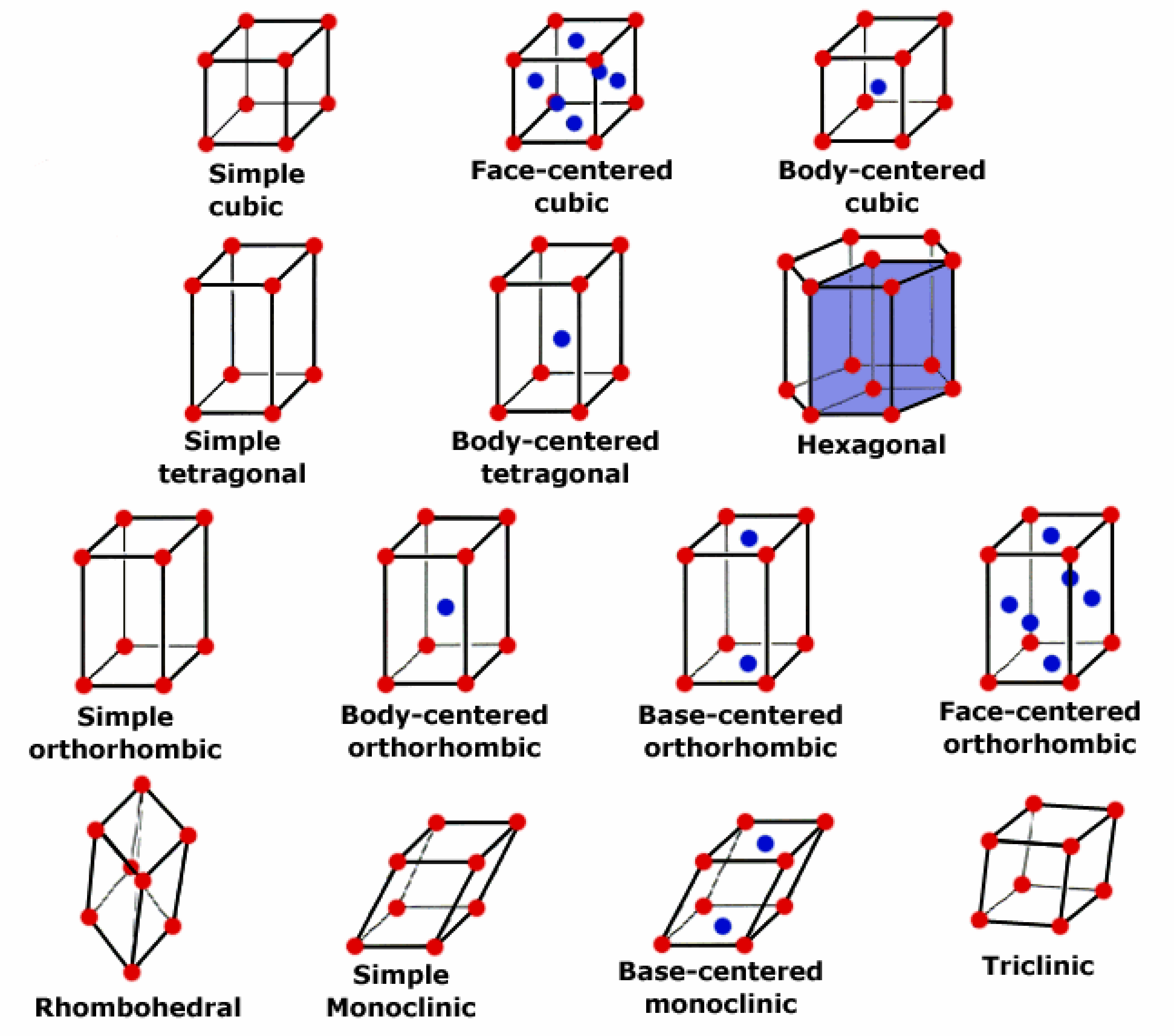


Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$



Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

Fourteen Bravais Lattices

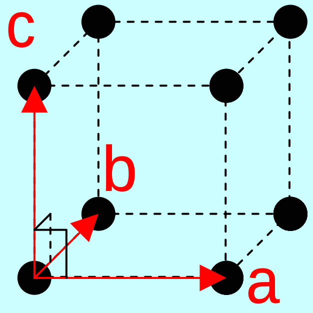


Simple Cubic (SC)

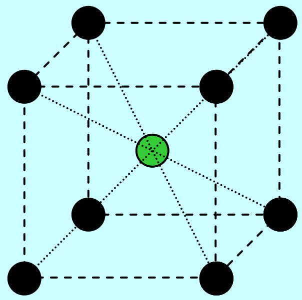
$a = b = c$

$a \perp b \perp c$

Conventional Cell = Primitive Cell

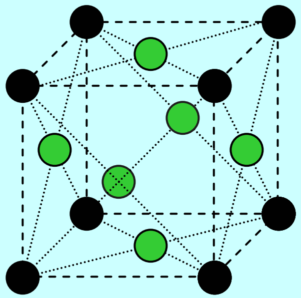


Add one atom at the center of the cube



Body-Centered Cubic (BCC)

Add one atom at the center of each face



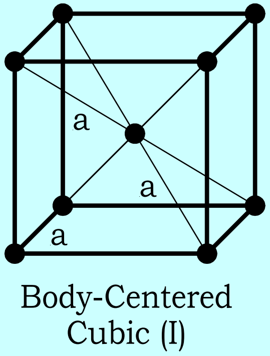
Face-Centered Cubic (FCC)

Conventional Unit Cell ≠ Primitive Cell

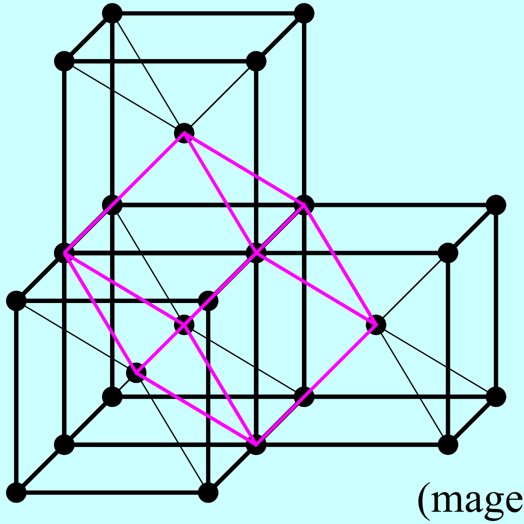
Primitive Cell

A volume of space translated through all the vectors in a lattice just fills all of space without overlapping or leaving voids is called a *primitive cell* of the lattice.

A primitive cell contains just one Bravais lattice point.
The primitive cell is the smallest cell that can be translated throughout space to completely recreate the entire lattice.
There is not one unique shape to a primitive cell and many possible shapes fulfill the definition.
The primitive cell for the simple cubic lattice is equal to the simple cubic unit cell (they are identical).
A common choice for the primitive cell of the body-centered cubic lattice is shown below.



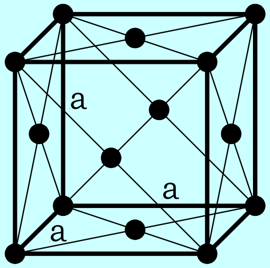
Unit Cell



(magenta)

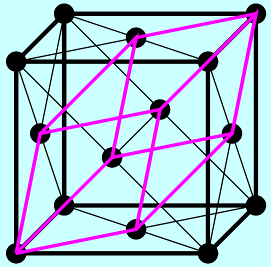
Primitive Cell

Nonprimitive Unit Cell vs. Primitive Cell

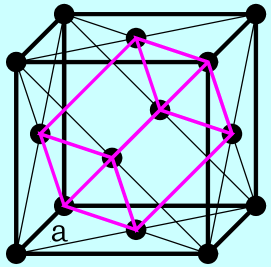


Face-Centered
Cubic (F)

Unit Cell



Primitive Cell

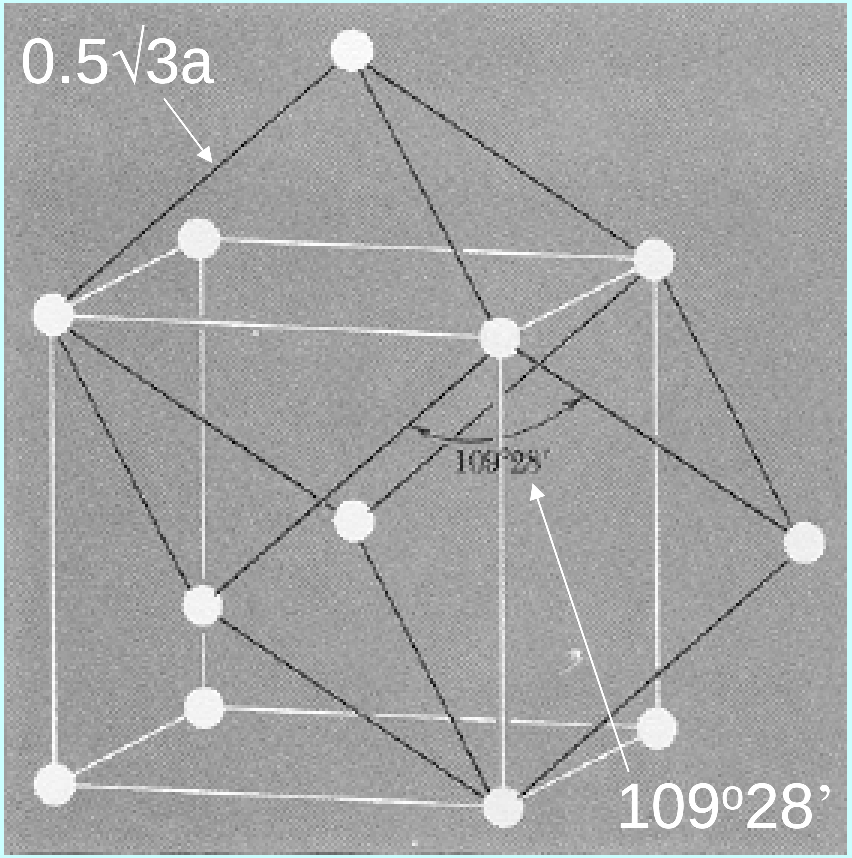


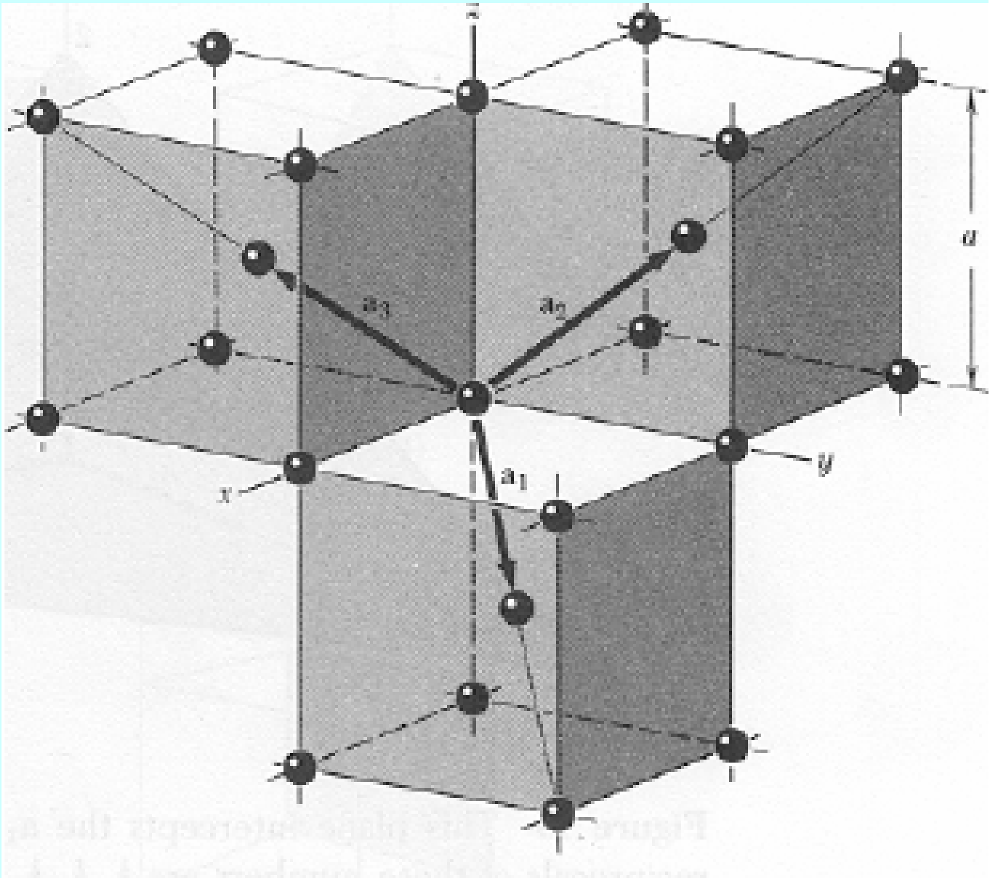
Rotated 90°

The primitive cell is smaller or equal in size to the unit cell. The unit cells help to remind us of the symmetry (ie. Cubic).

Primitive Cell of BCC

- Rhombohedron primitive cell



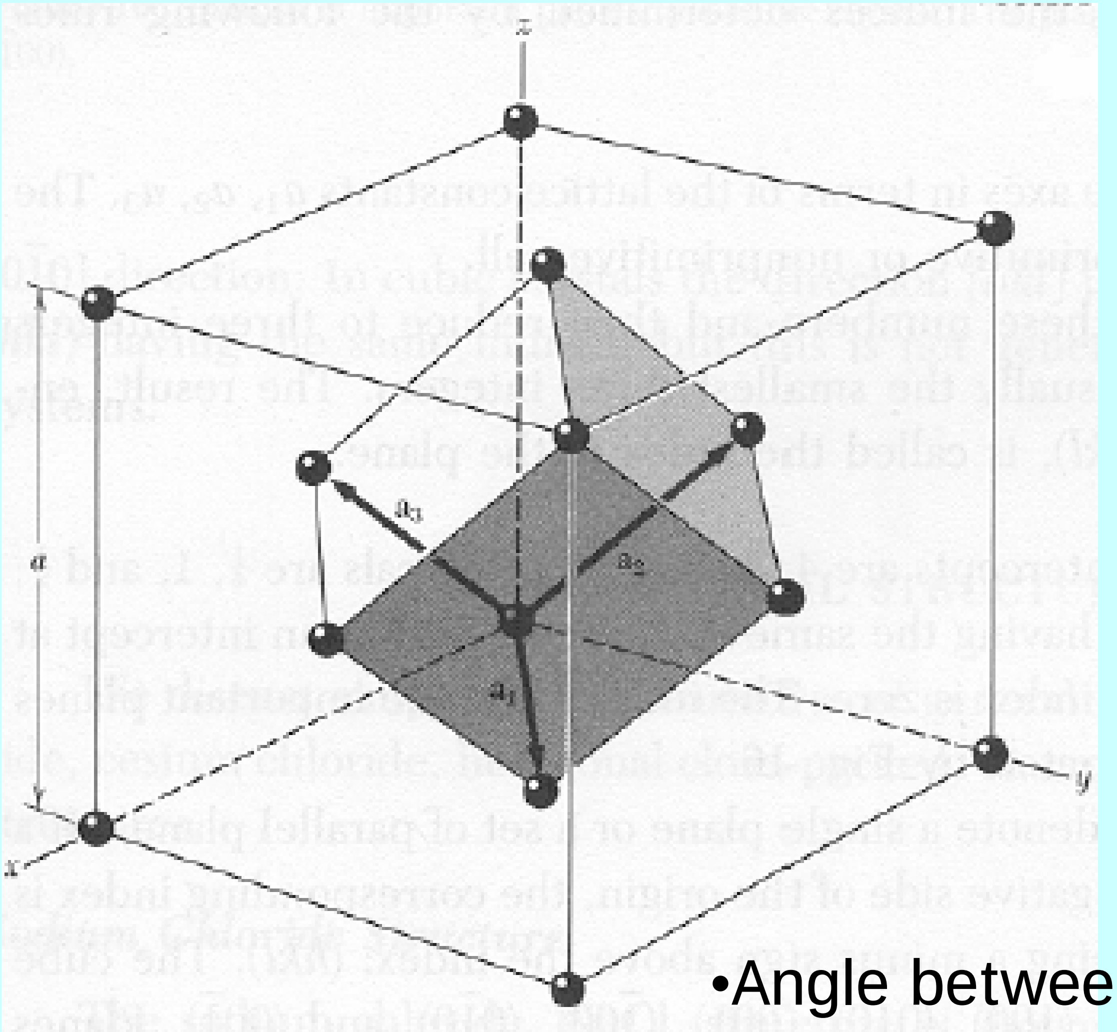


- Primitive Translation Vectors:

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ;$$

$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; .$$

Primitive Cell of FCC



- Angle between a_1, a_2, a_3: 60^o

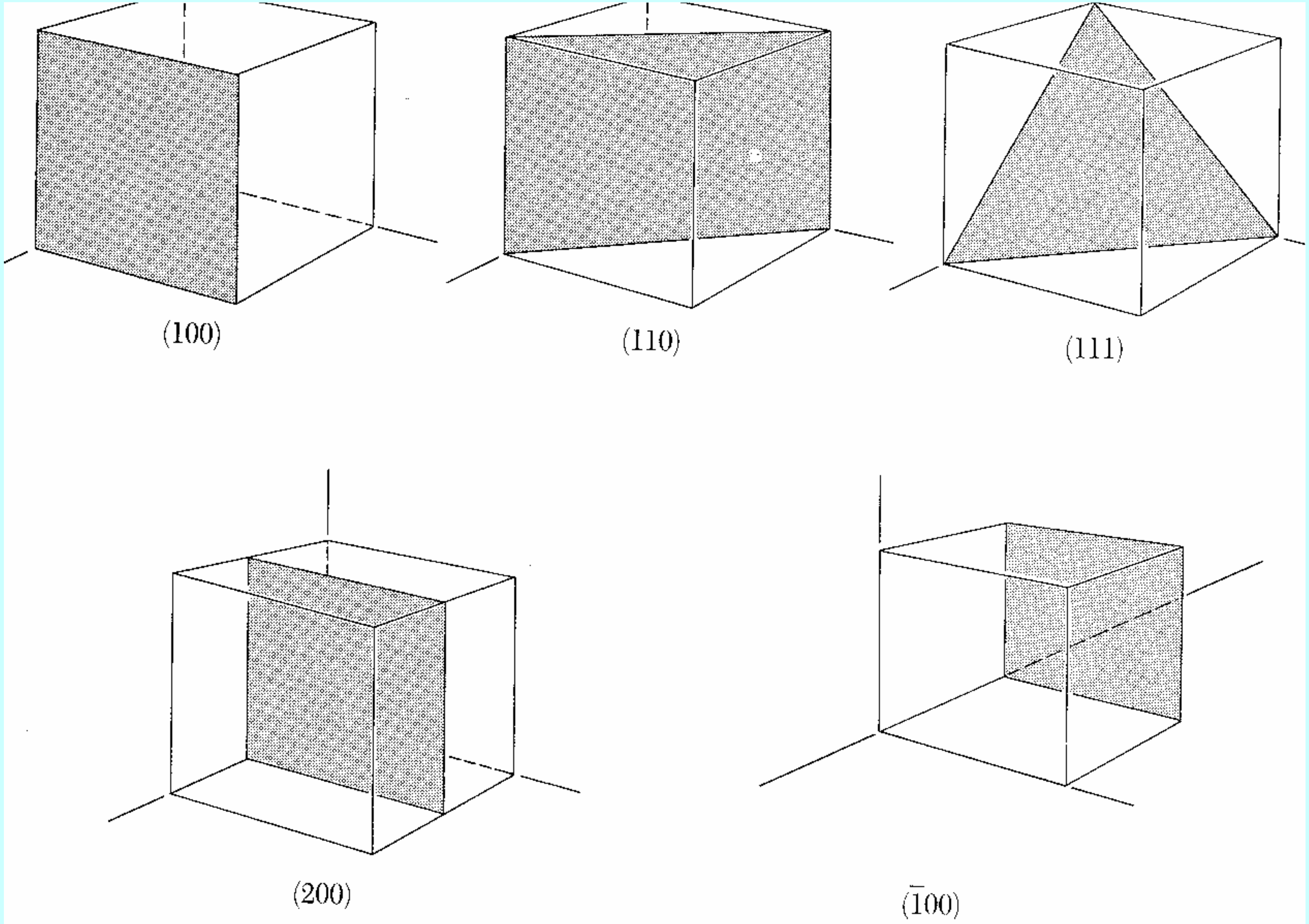
$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{x}+\hat{y}) \ ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{y}+\hat{z}) \ ; \qquad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{z}+\hat{x}) \ .$$

Index System for Crystal Planes (Miller Indices)

1) **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.**

2) **Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result enclosed in parenthesis (*hkl)*, is called the index of the plane.**

Miller Indices



(100)

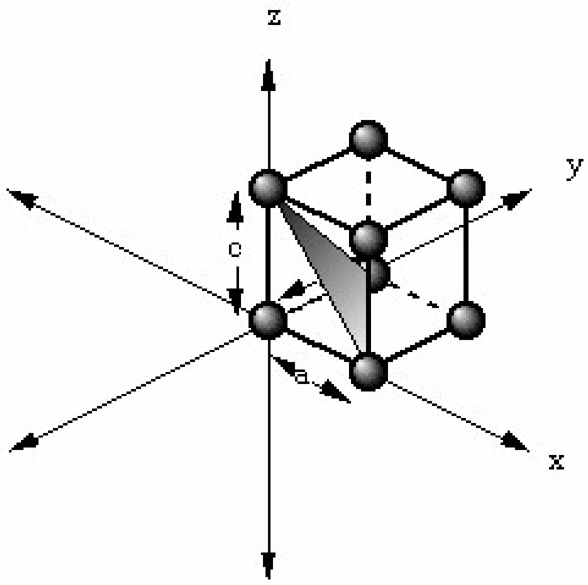
(110)

(111)

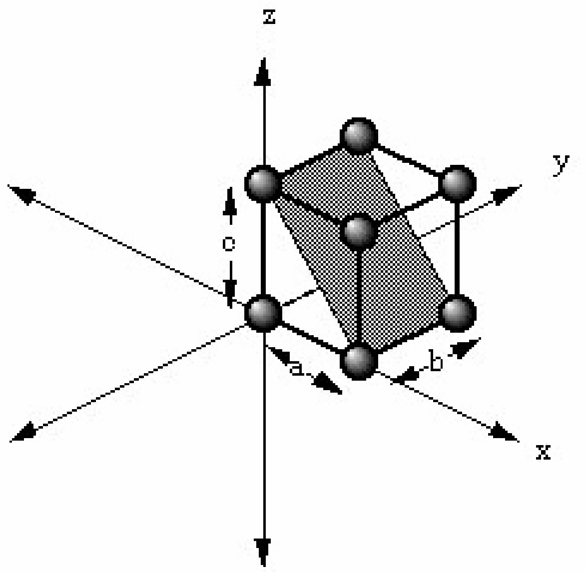
(200)

($\bar{1}00$)

Miller Indices

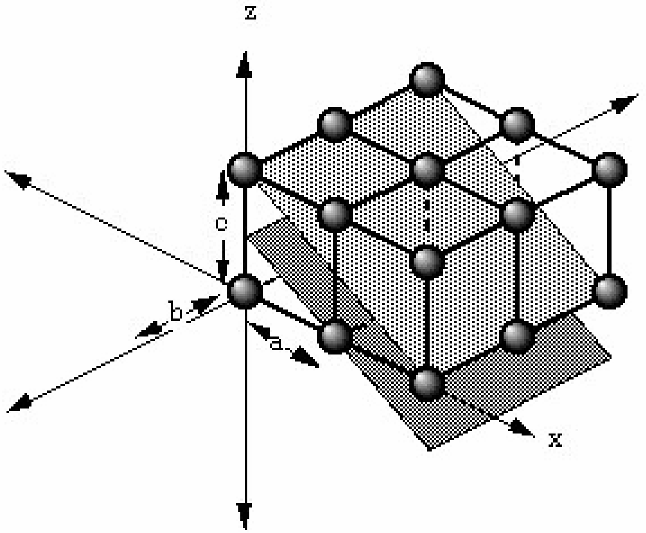


	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1
Miller indice	(111)		

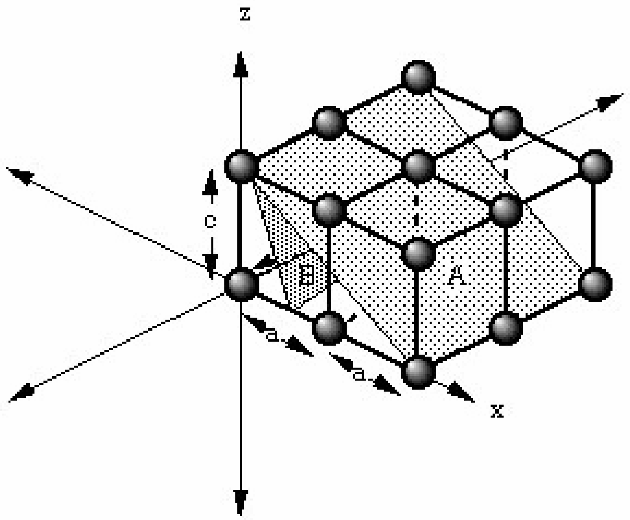


	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		

Miller Indices



	a	b	c
intercept length	1	∞	1/2
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2
Miller indice	(102)		



	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	∞	$\frac{1}{2}$	$\frac{1}{2}$	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	(102)			(201)		

Crystals

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

- ionic (NaCl, CsCl, CaF_2, ...)
  cations and anions, electrostatic interactions

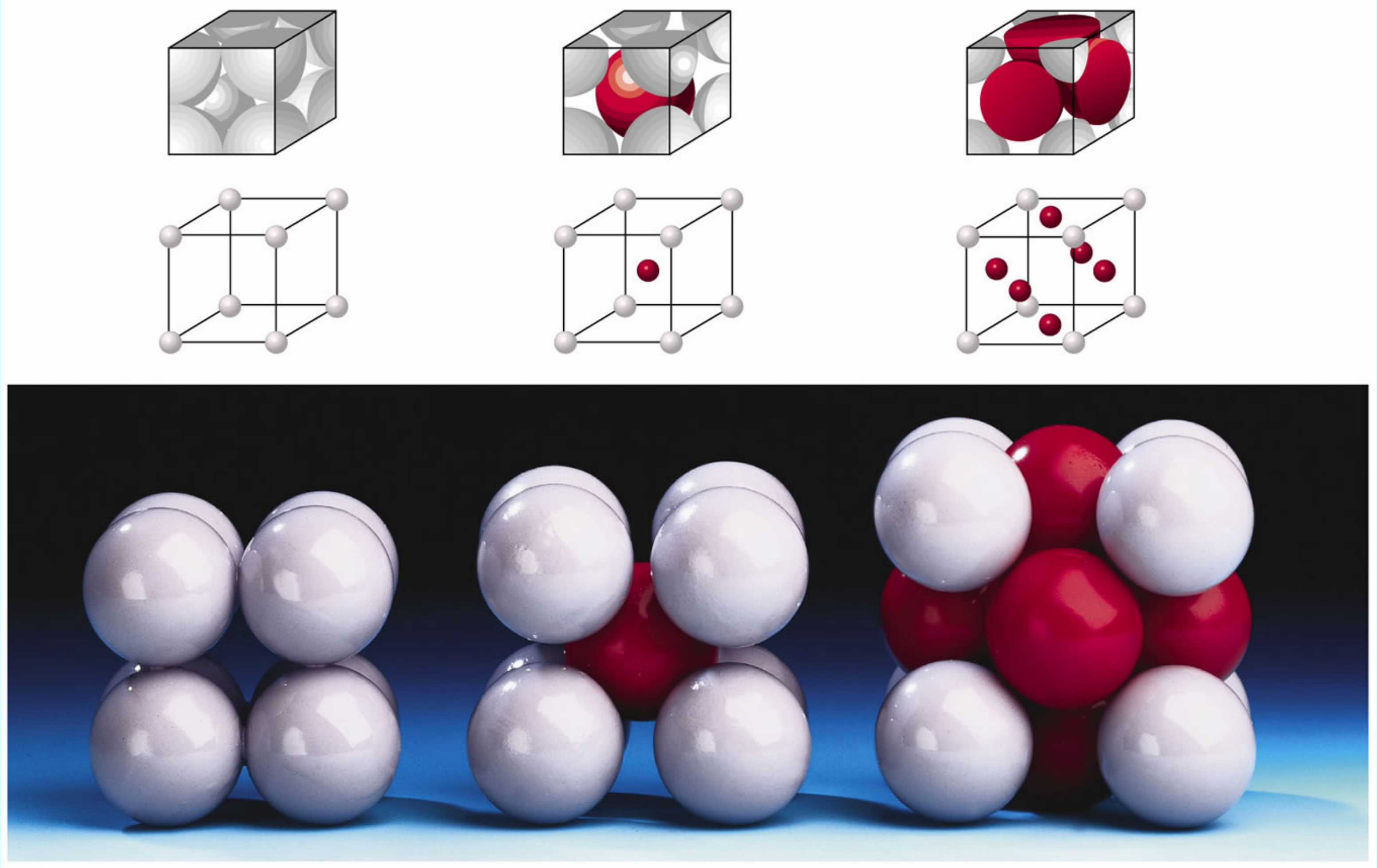
- covalent (diamond, graphite, SiO_2, AlN,...)
  atoms, covalent bonding

- molecular (Ar, C_{60}, HF, H_2O, organics, proteins)
  molecules, van der Waals and hydrogen bonding

Crystal Bonding

- van der Waals bonds
- Ionic bonds
- Hydrogen bonds
- Metallic bonds
- Covalent bonds

Three Cubic Cells



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

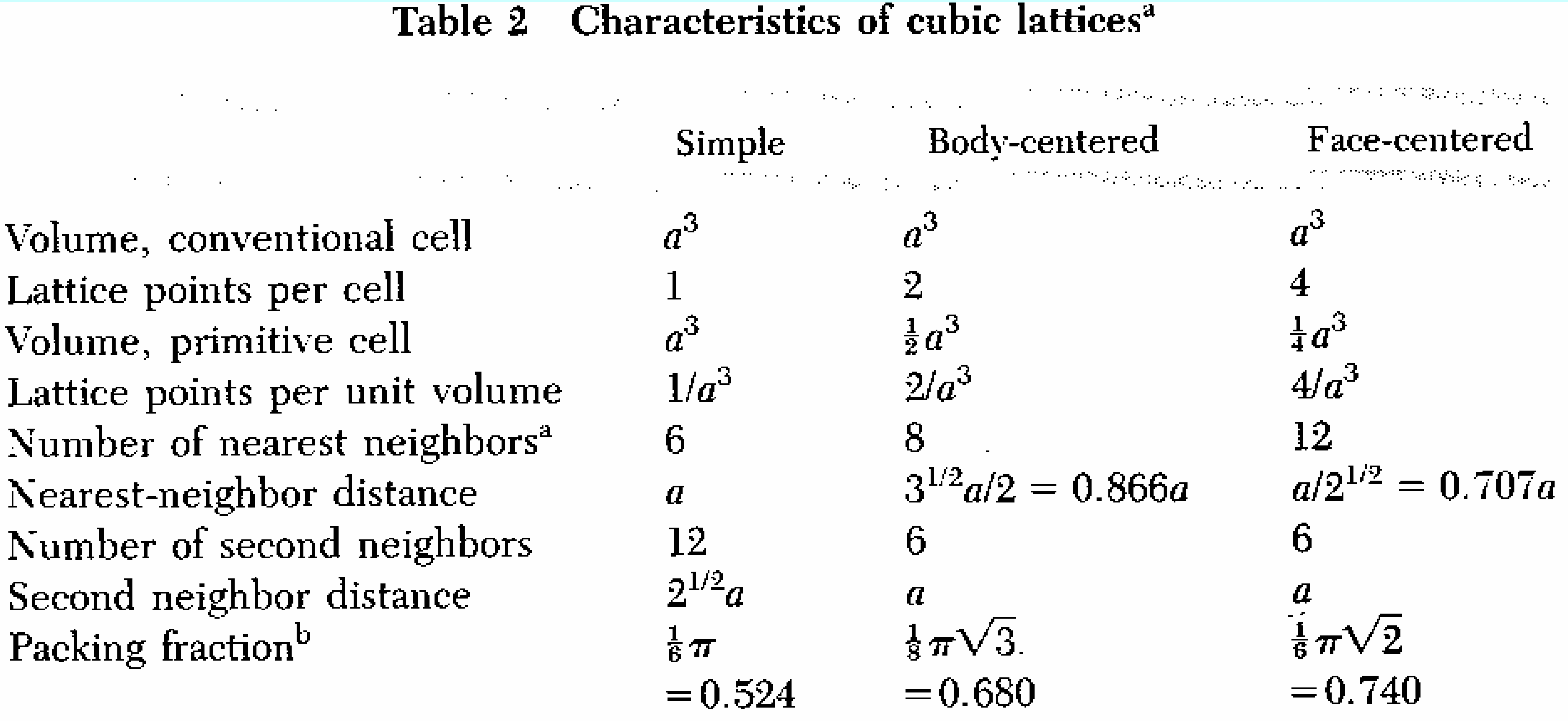
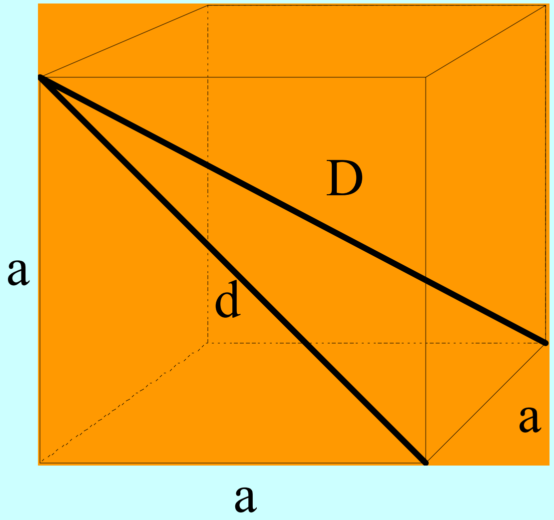


Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

Cube



a = edge

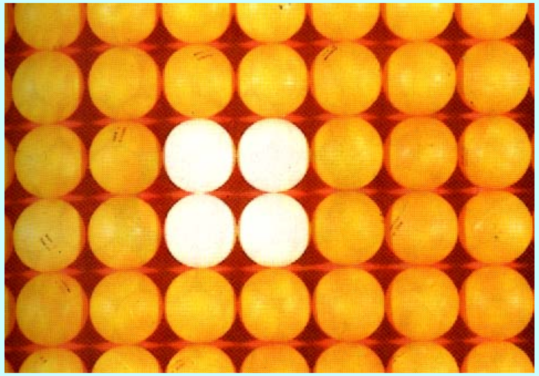
d = face diagonl
$(d^2 = a^2 + a^2 = 2a^2)$

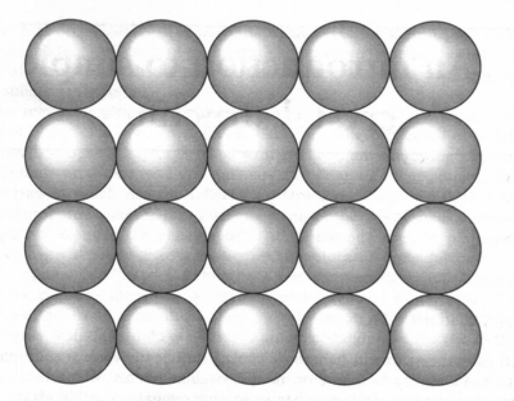
D = body diagonal
$(D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2)$

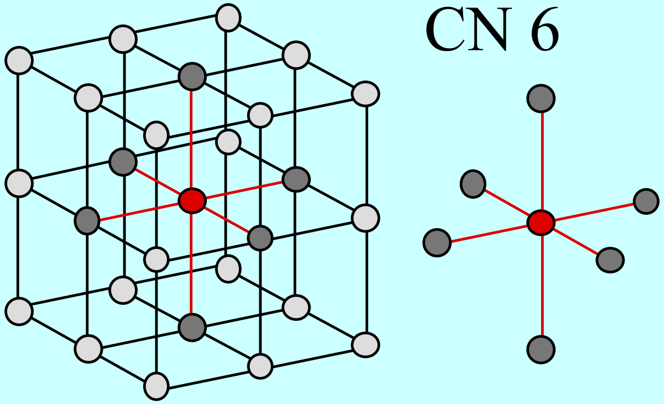
$$d = \sqrt{2} \cdot \mathrm{a}$$

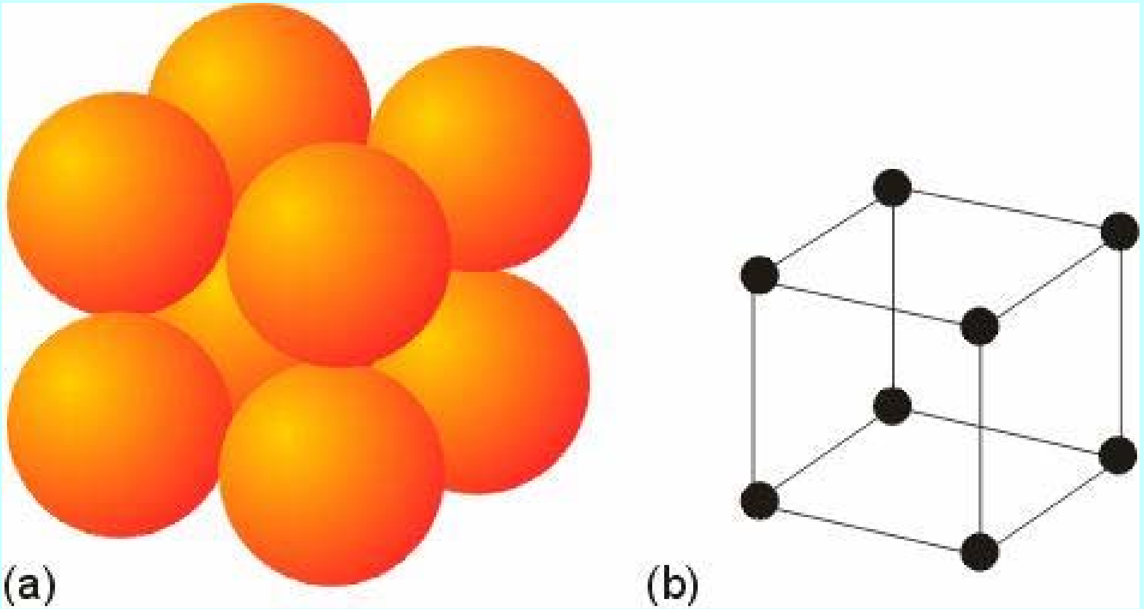
$$D = \sqrt{3} \cdot \mathrm{a}$$

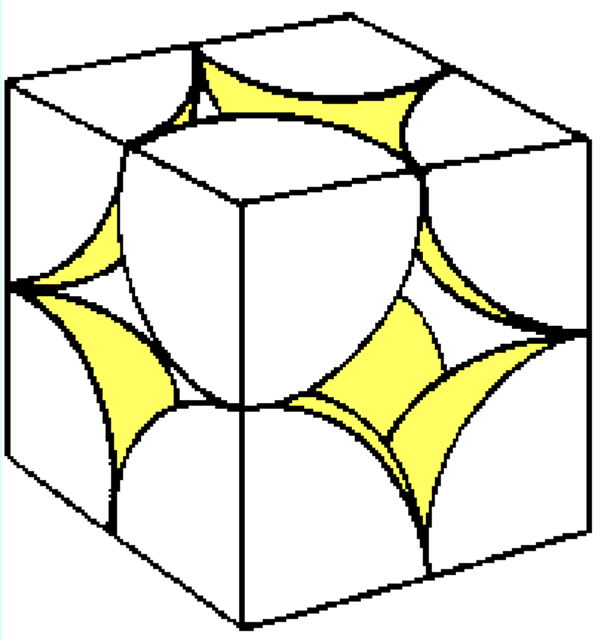
SC = Polonium





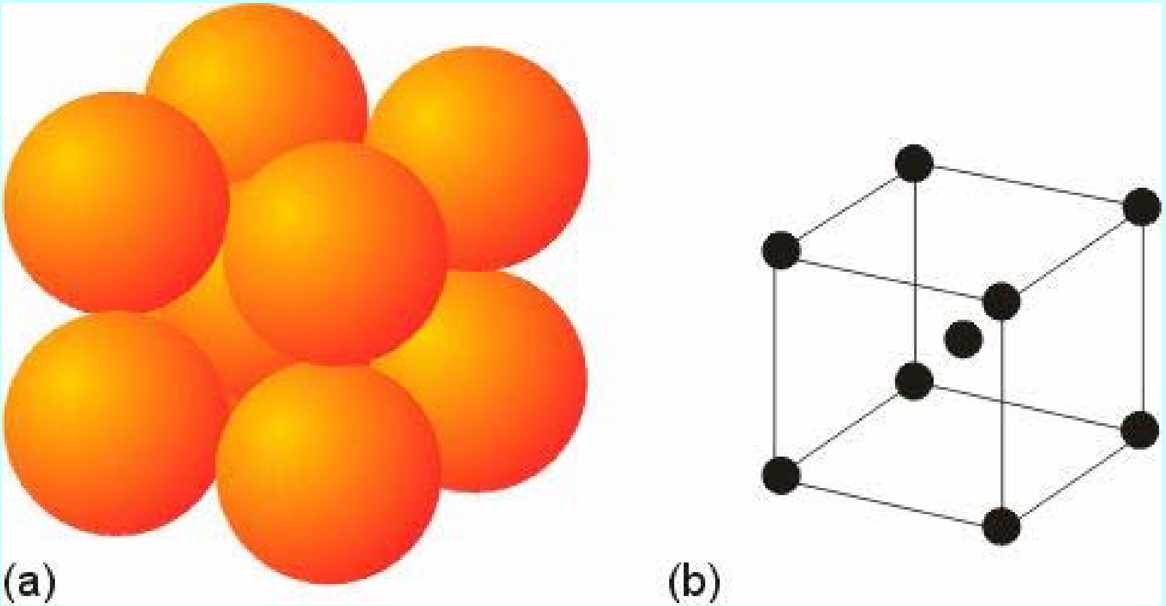


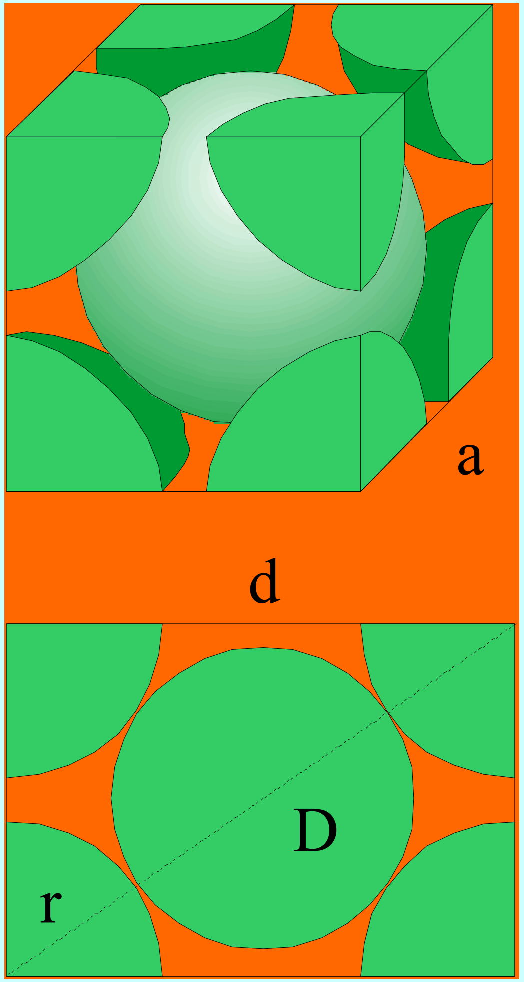




Space filling 52%

BCC = W, Tungsten



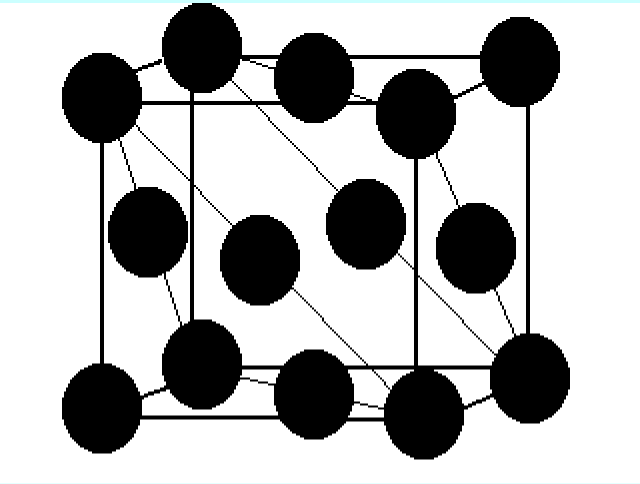


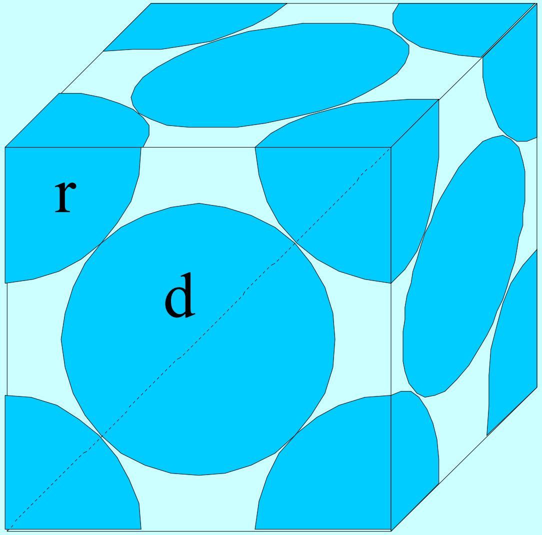
Space filling 68%

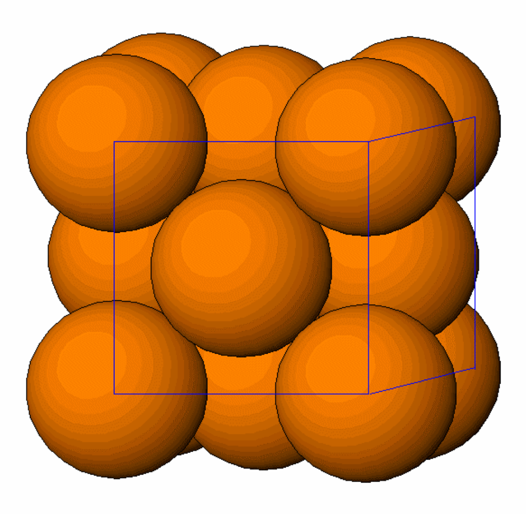
CN 8

Fe, Cr, V, Li-Cs, Ba

FCC = Copper, Cu = CCP



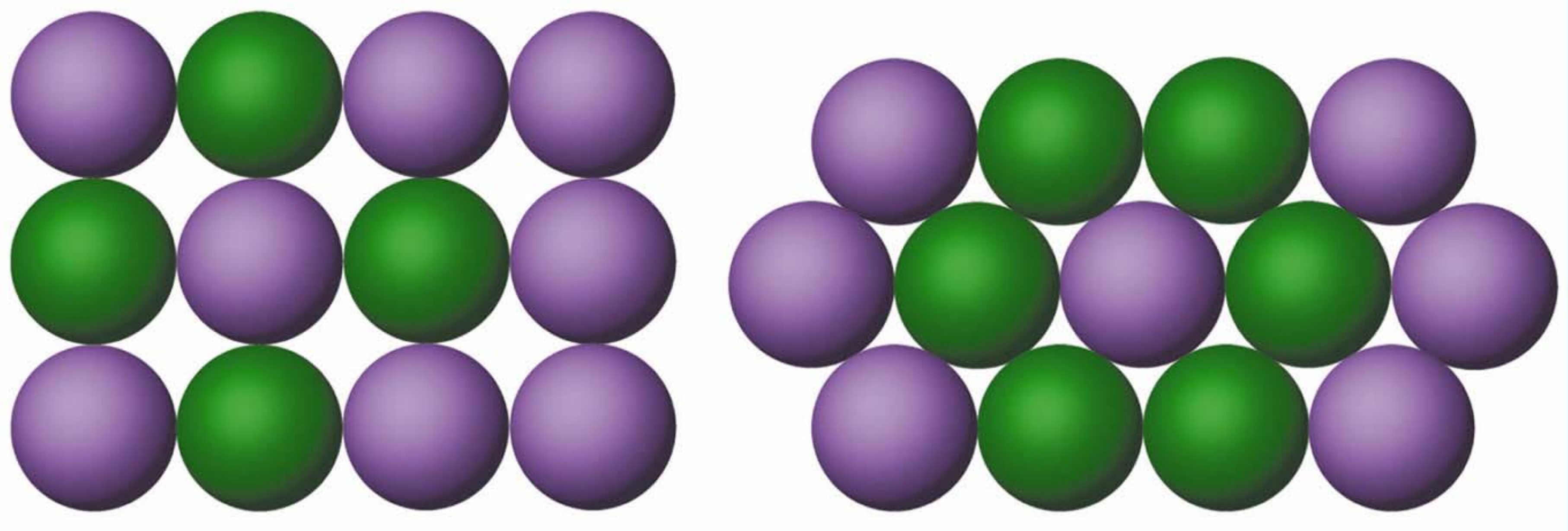




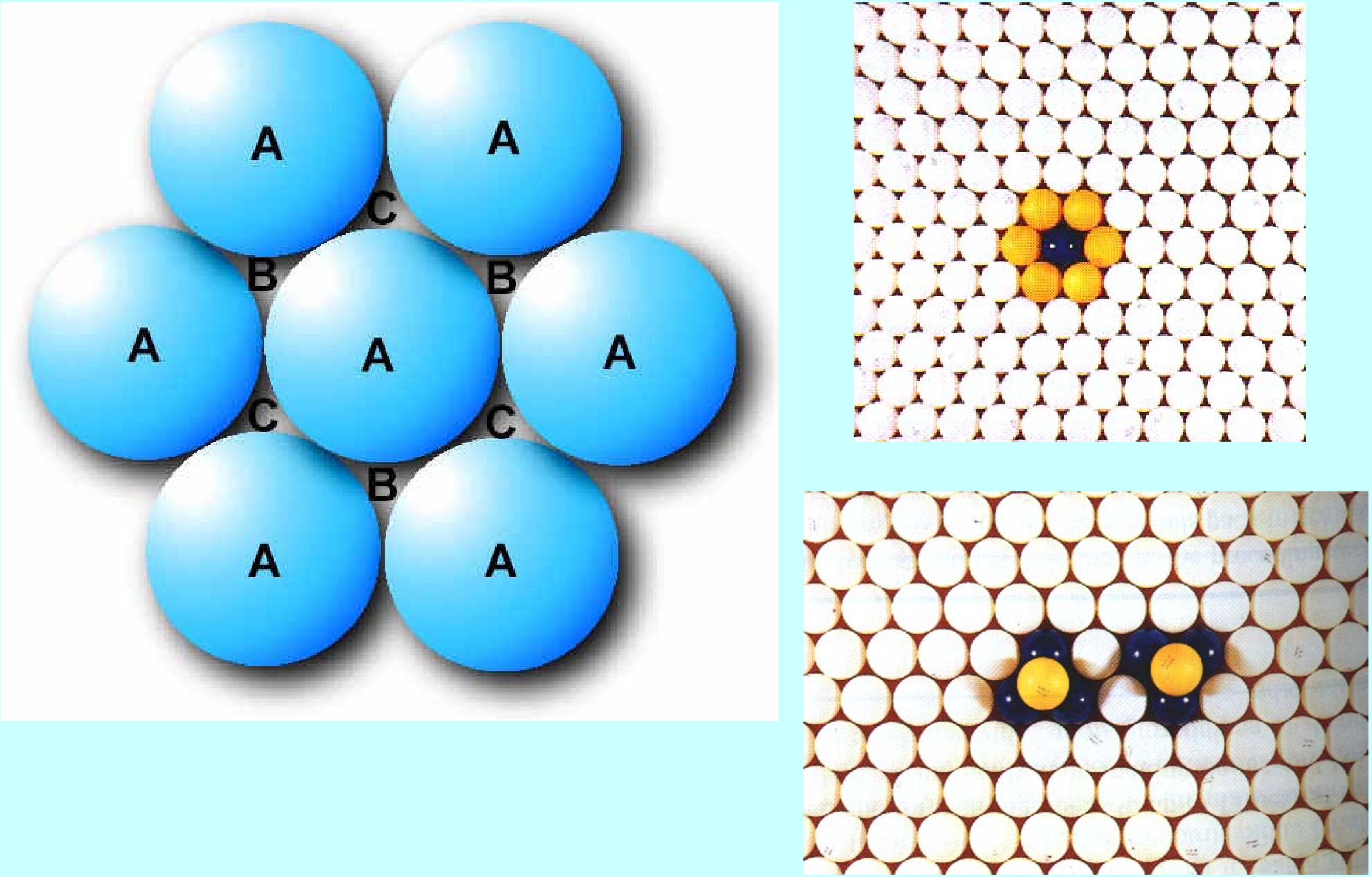
Space filling 74%

CN 12

Close Packing in Plane 2D

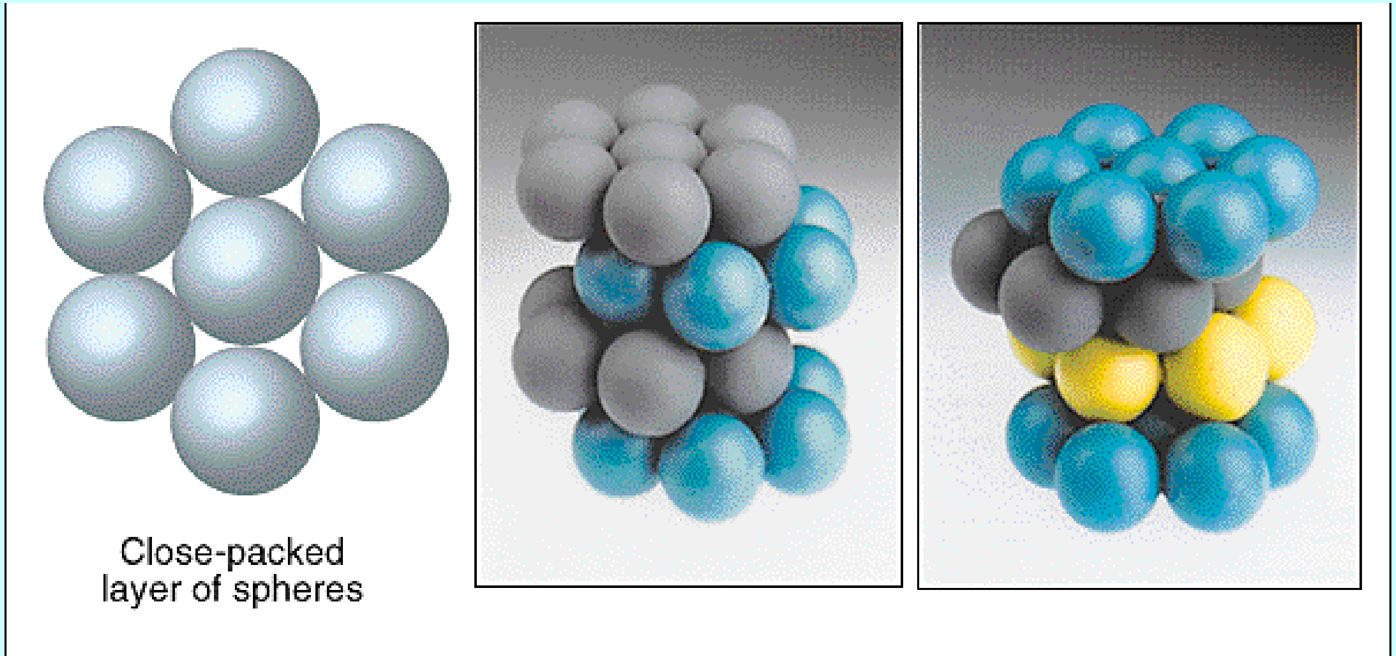


(a) An "open" packing **(b)** Close packing



B and C holes cannot be occupied at the same time

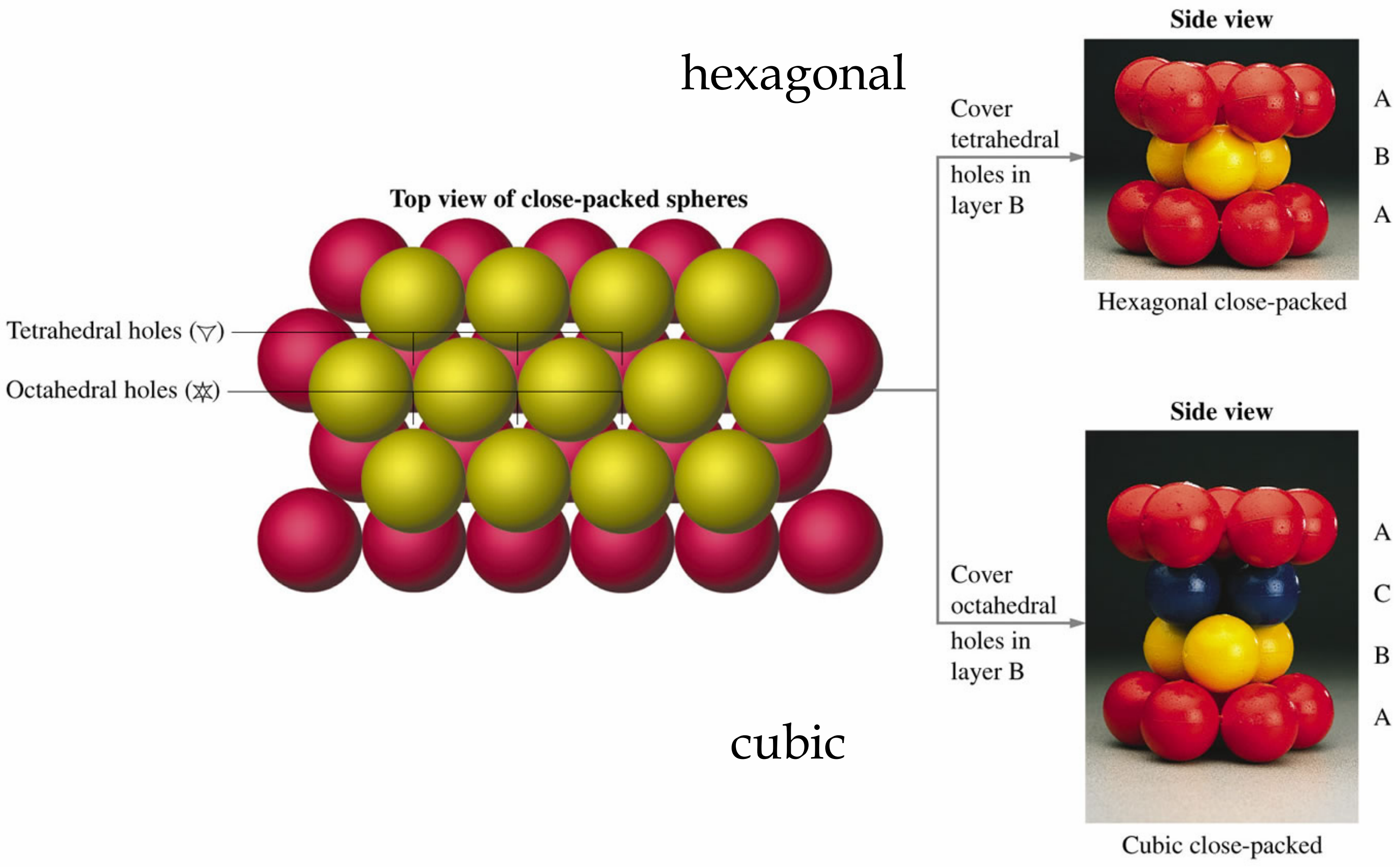
Close Packing in Space 3D



Hexagonal
HCP

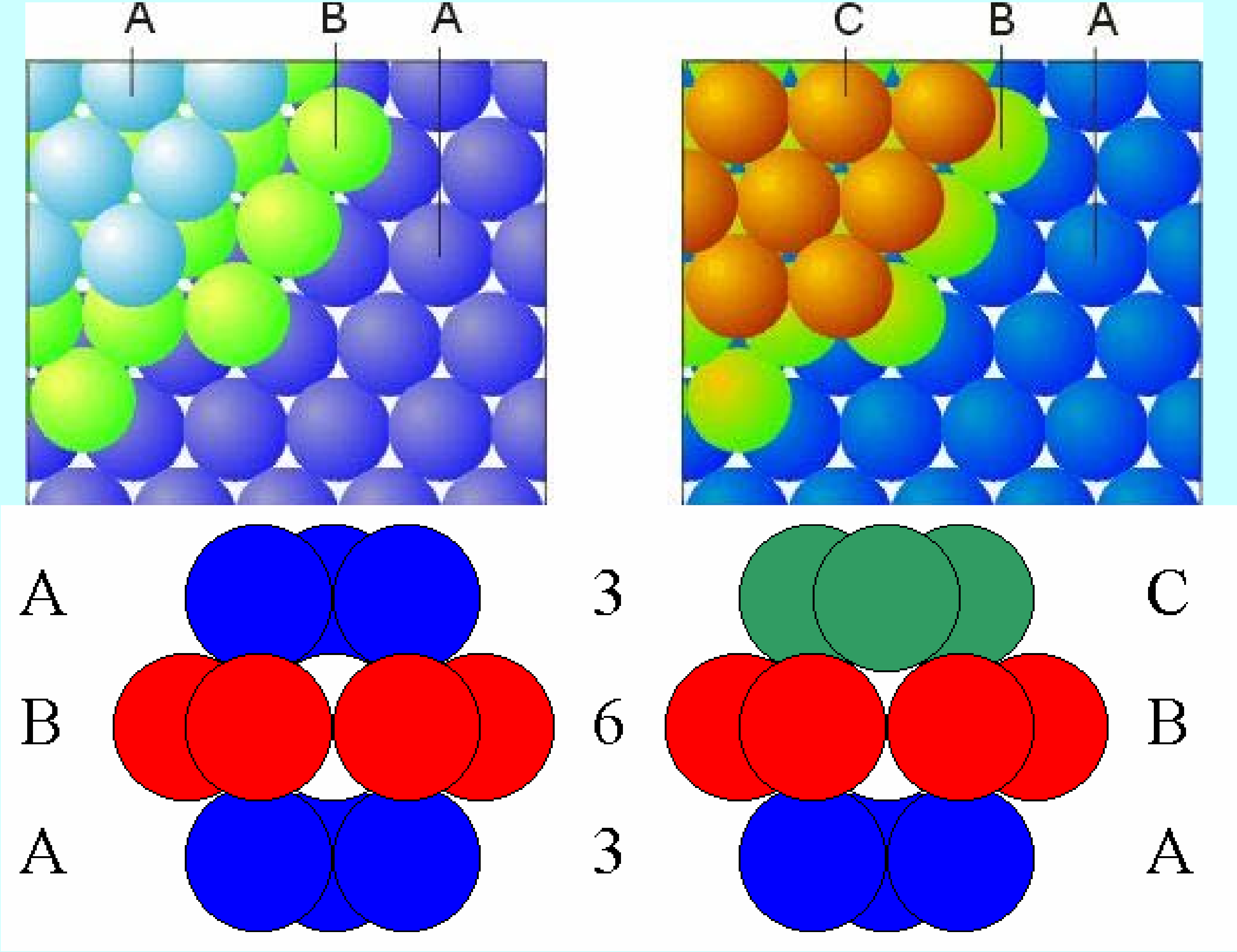
Cubic
CCP

hexagonal



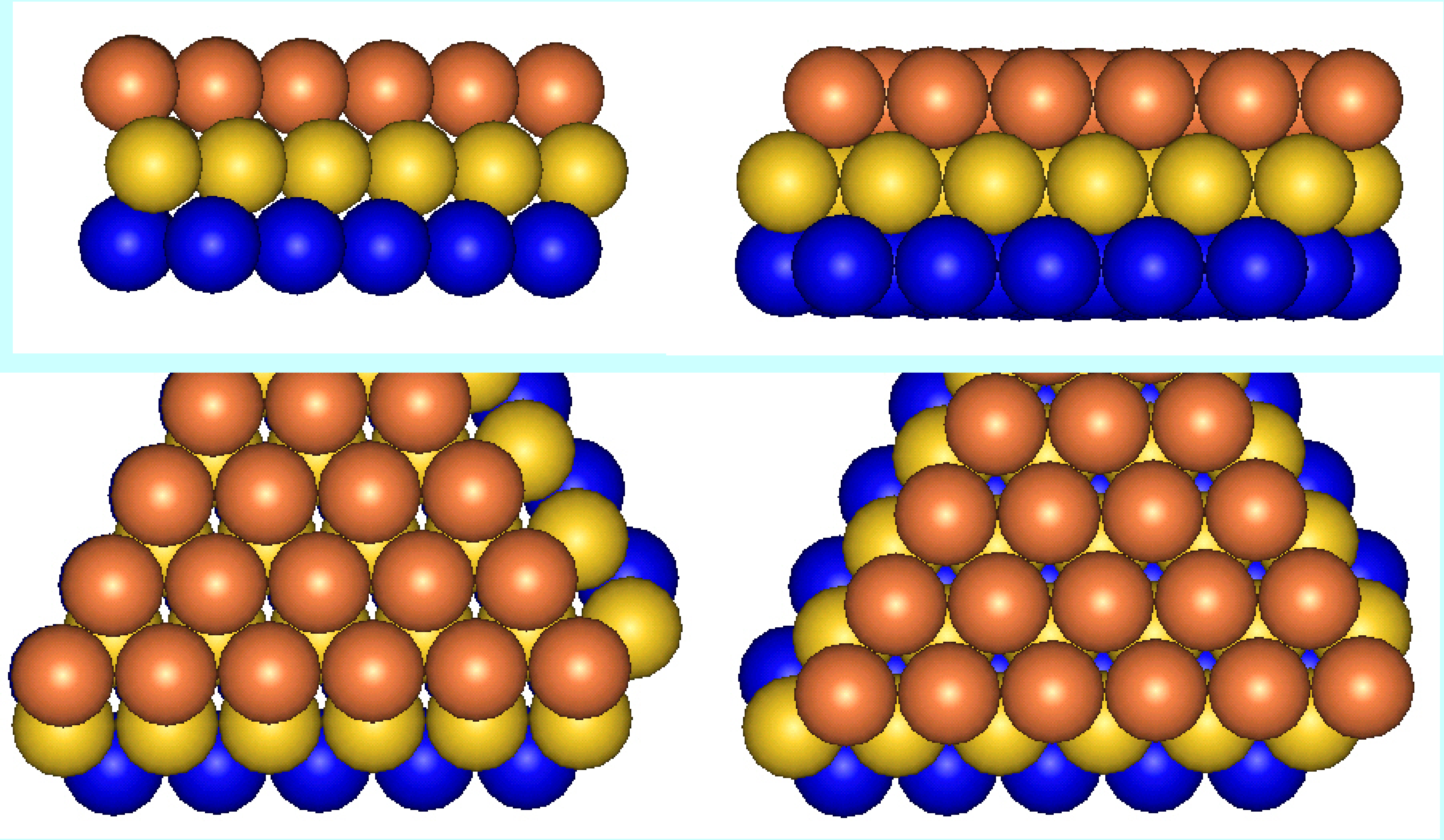
cubic

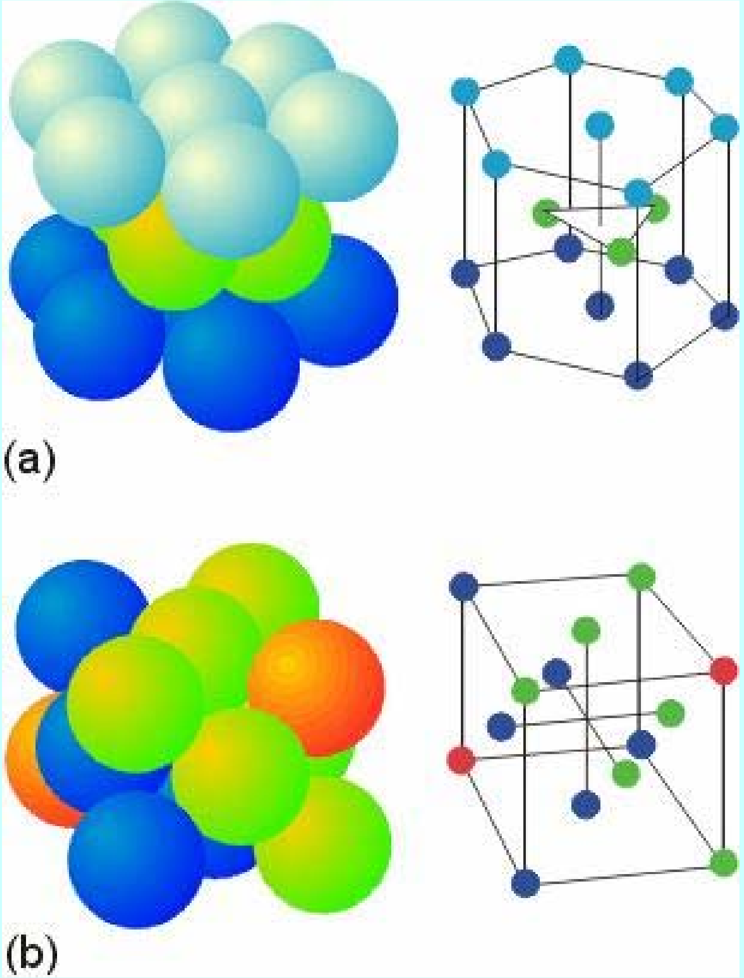
hexagonal cubic



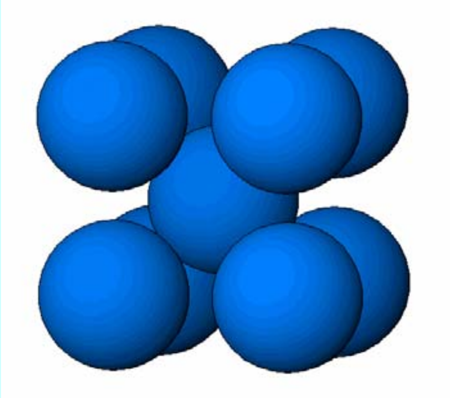
hexagonal

cubic

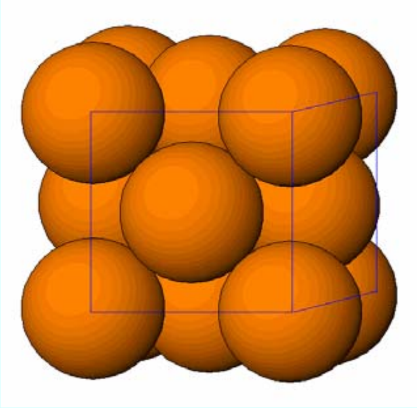




**Mg, Be, Zn, Ni, Li, Be, Os, He,
Sc, Ti, Co, Y, Ru**



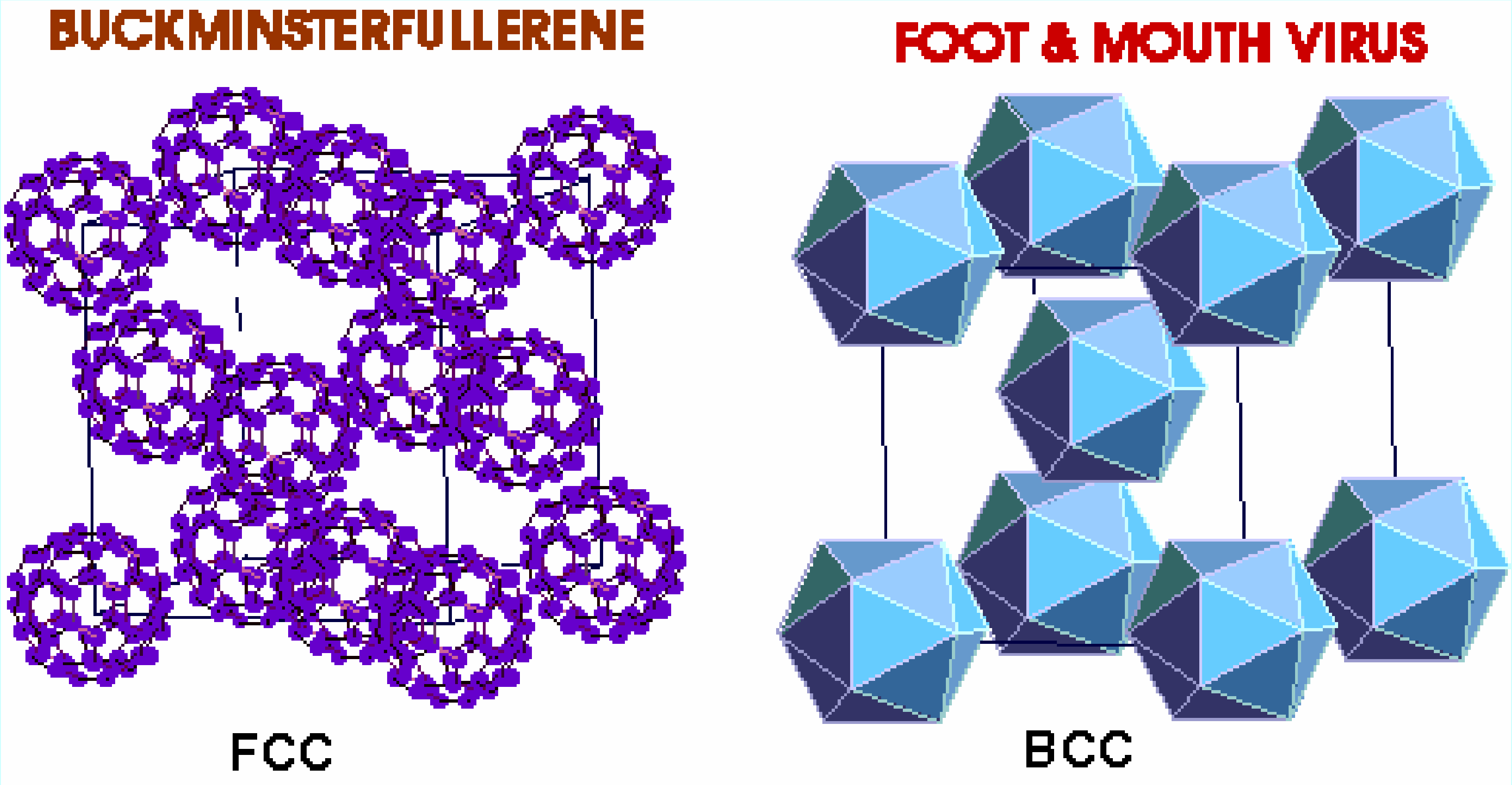
hexagonal



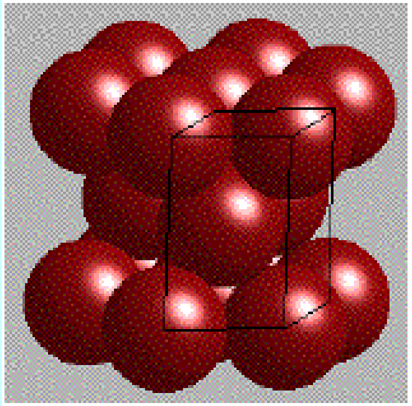
cubic

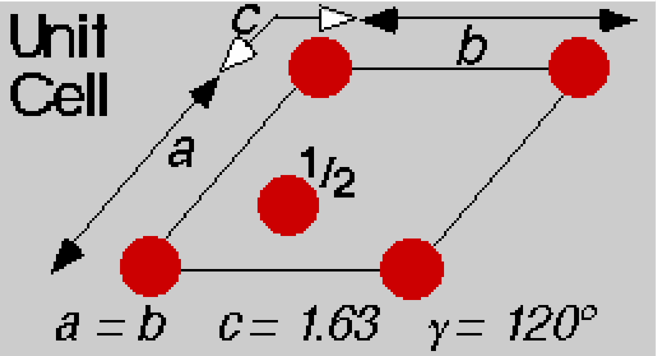
**Cu, Ca, Sr, Ag, Au, Ni, Rh, solid
Ne-Xe, F_2, C_{60}, opal (300 nm)**

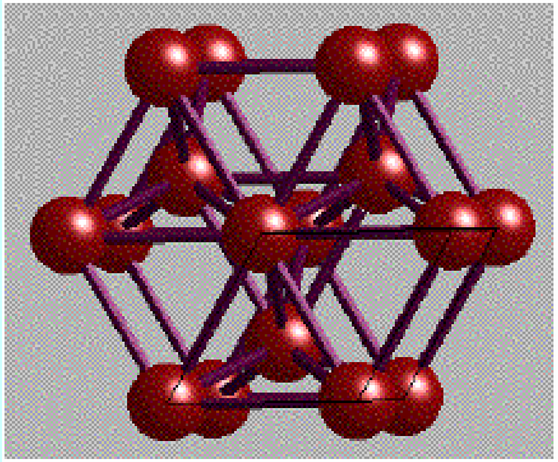
Structures with Larger Motifs

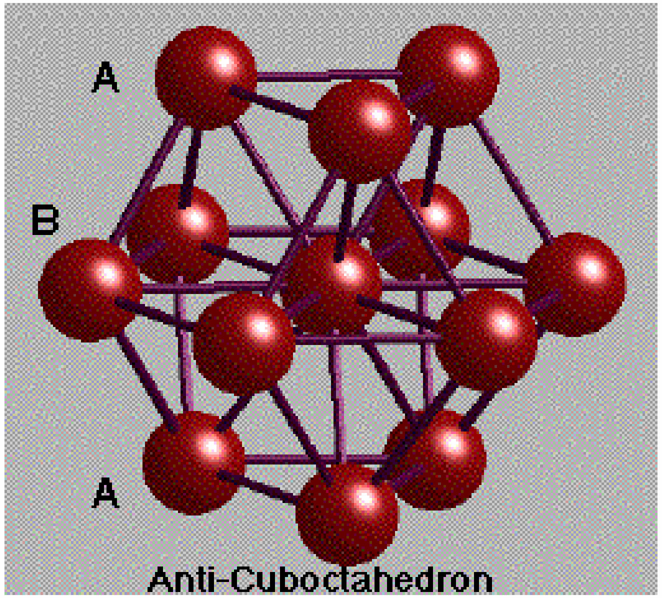


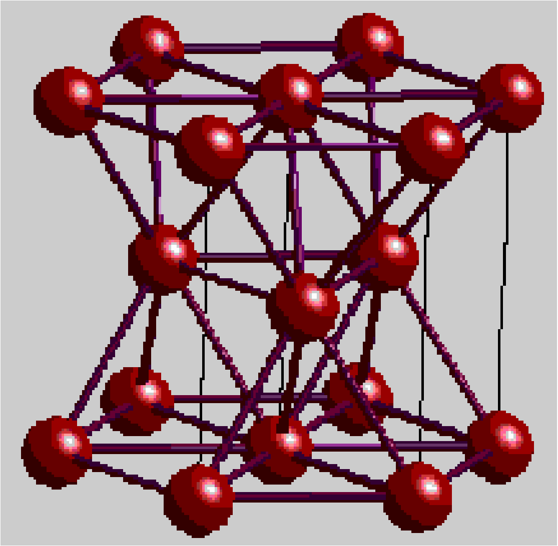
HEXAGONAL CLOSE-PACKING





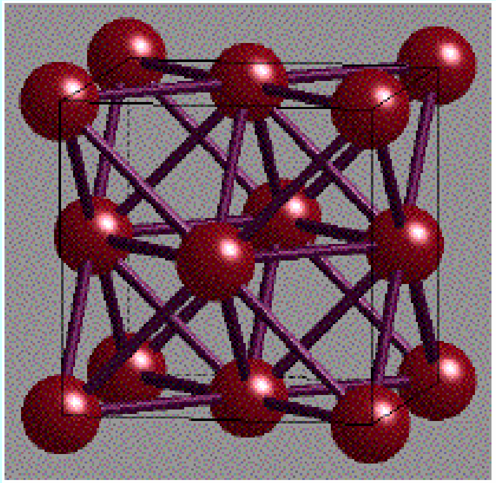


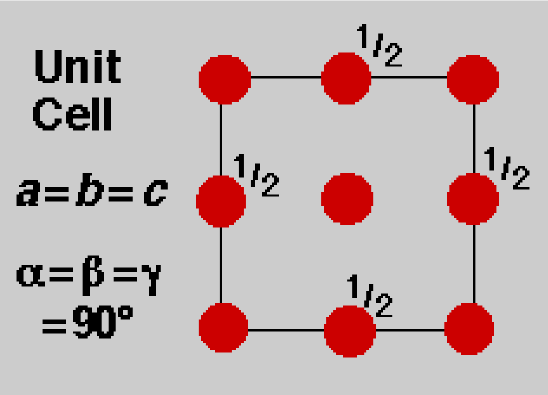




CUBIC CLOSE-PACKING

Face-Centred Cubic (FCC) Unit Cell

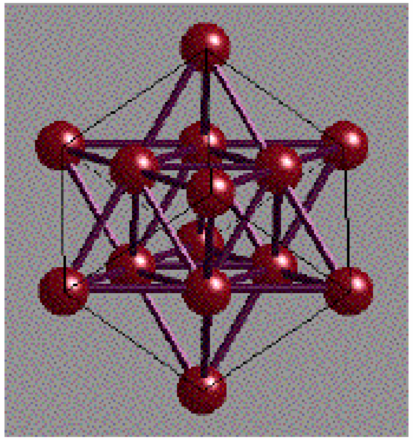


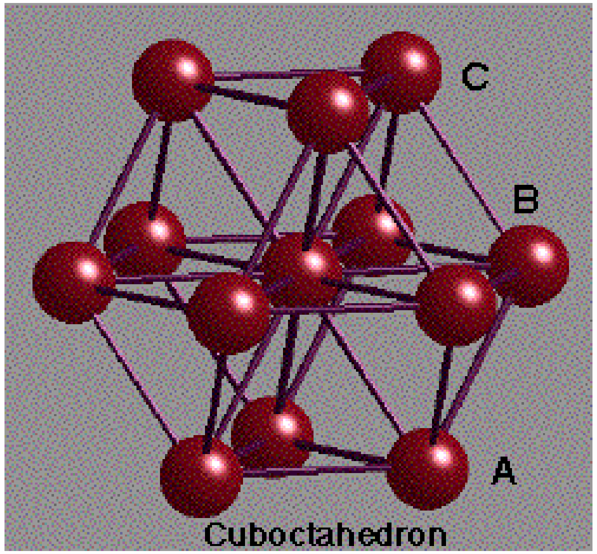


Unit Cell

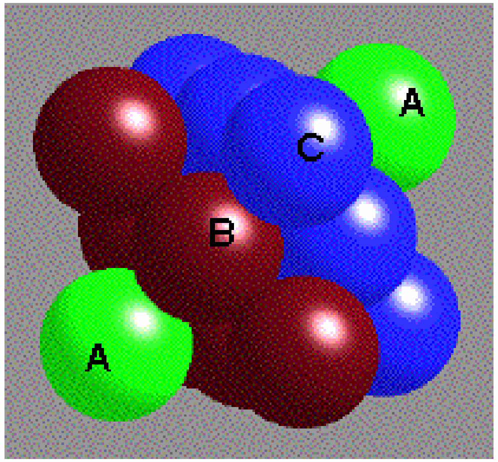
$a = b = c$

$\alpha = \beta = \gamma = 90°$

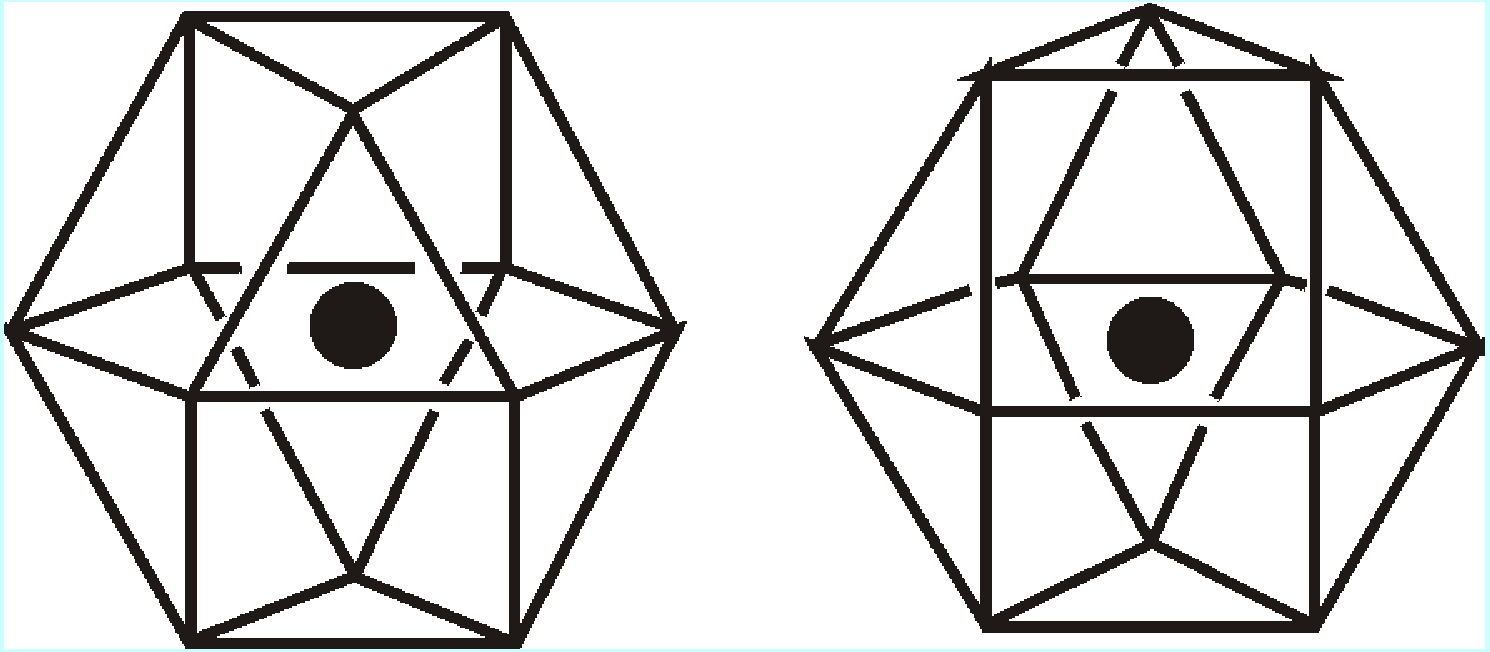




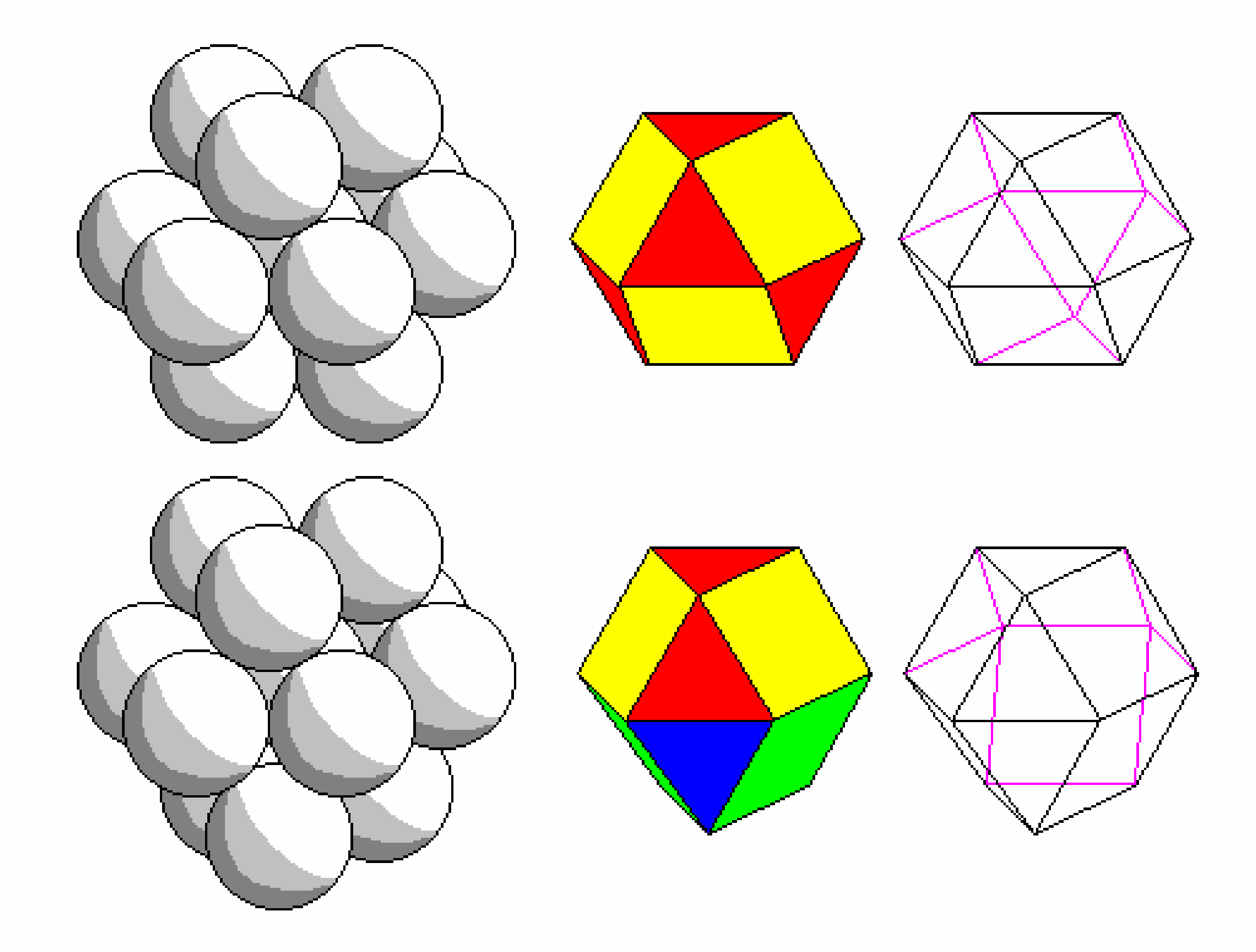
Cuboctahedron



Coordination Polyhedrons

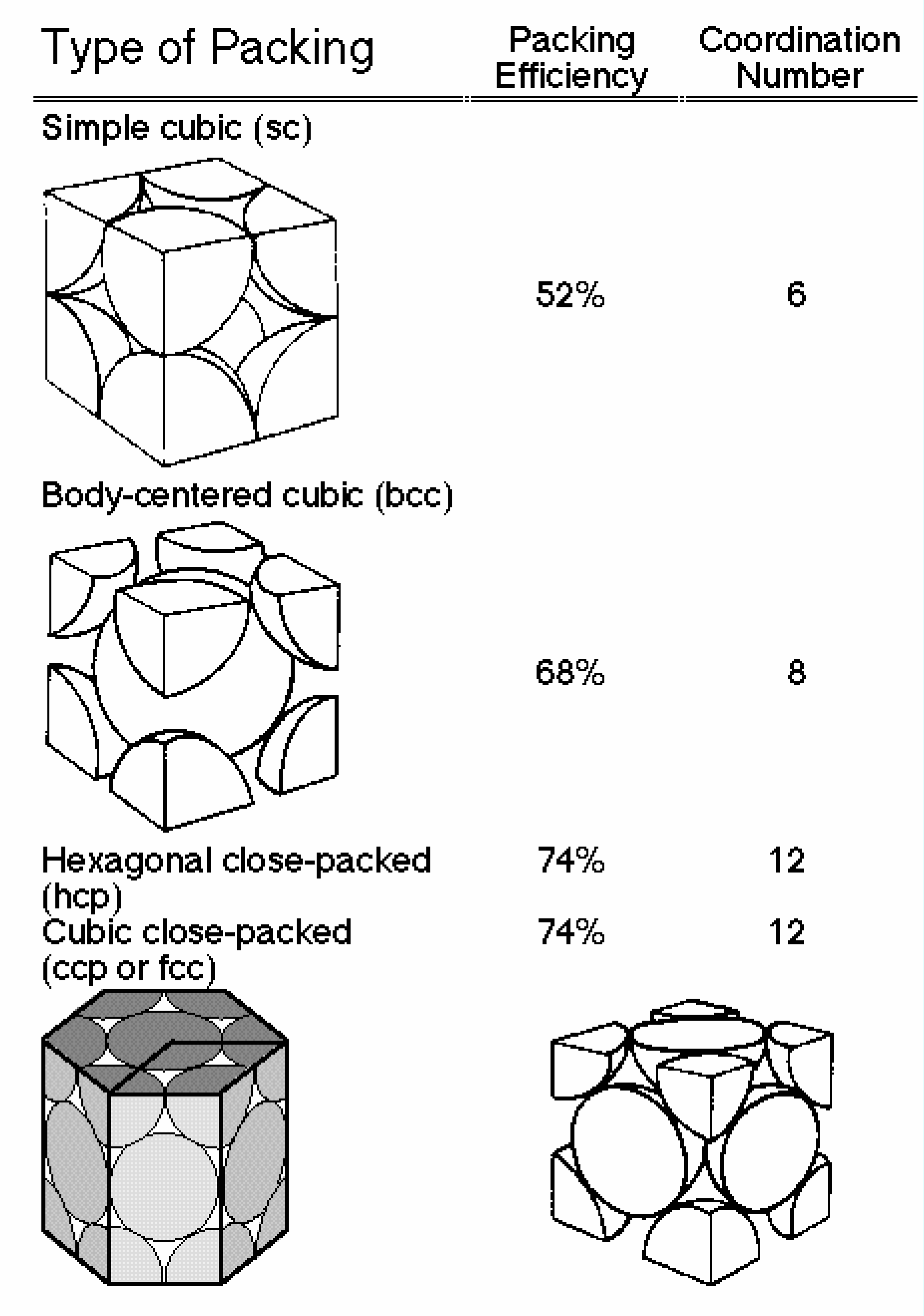


Coordination Polyhedrons



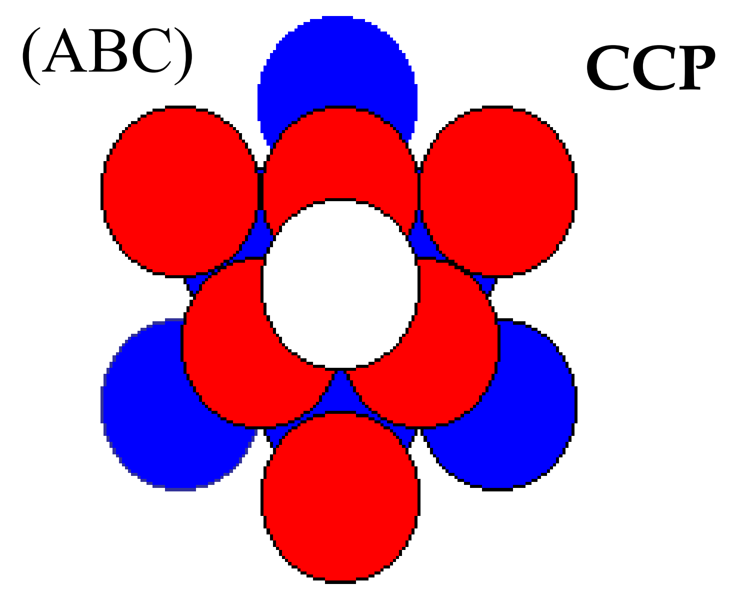
Space Filling

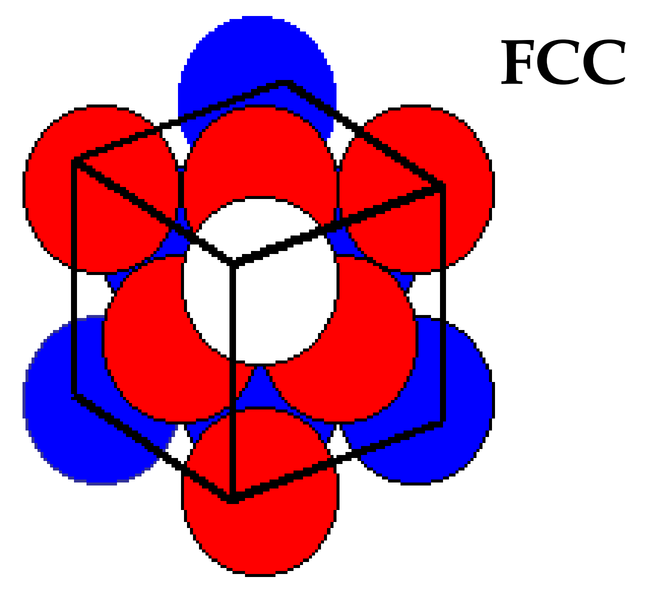
	Atom Radius	Number of Atoms (lattice points)	Space filling
SC	a/2	1	52%
BCC	$\sqrt{3}a/4$	2	68%
FCC	$\sqrt{2}a/4$	4	74%
Diamond	$\sqrt{3}a/8$	8	34%



Type of Packing	Packing Efficiency	Coordination Number
Simple cubic (sc)	52%	6
Body-centered cubic (bcc)	68%	8
Hexagonal close-packed (hcp)	74%	12
Cubic close-packed (ccp or fcc)	74%	12

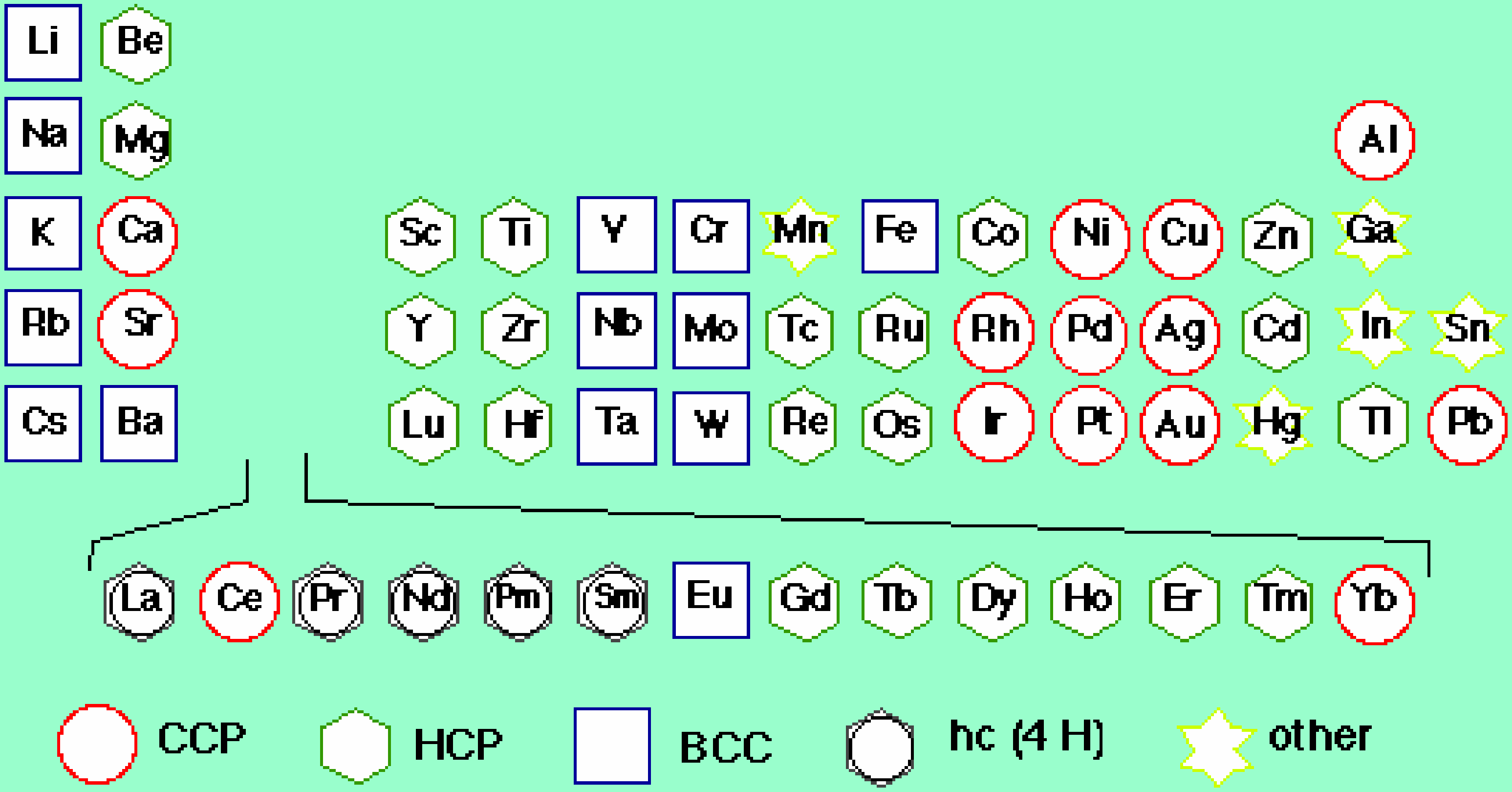
CCP = FCC



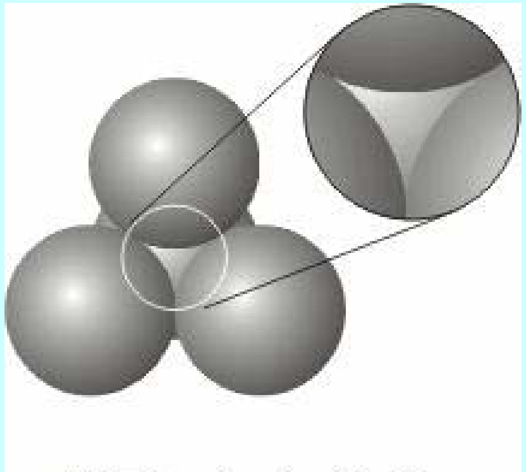


Close packed layers of CCP are oriented perpendicularly to the body diagonal of the cubic cell of FCC

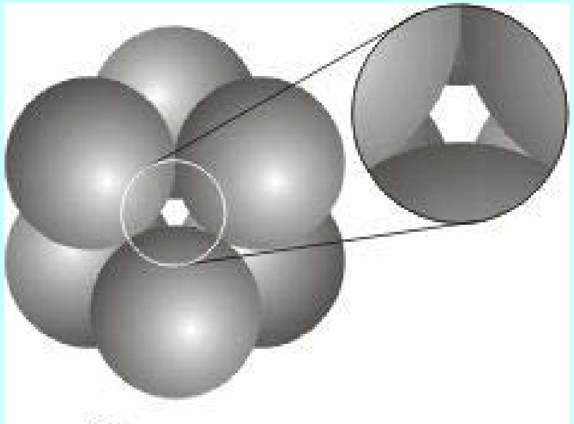
Periodic Table of Metal Structures



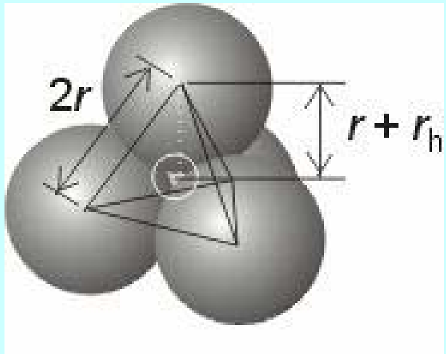
Two Types of Voids (Holes)

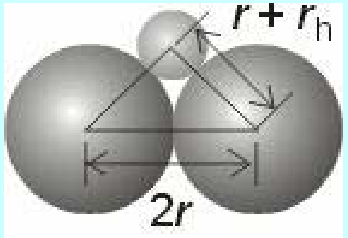


5 Tetrahedral hole

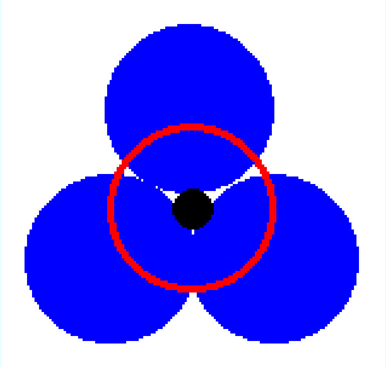


2 Octahedral hole

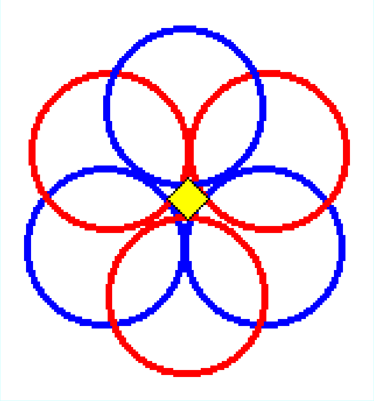




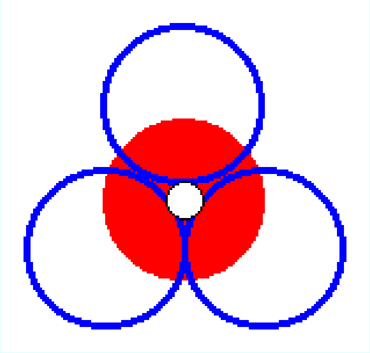
3



Tetrahedral Holes T+



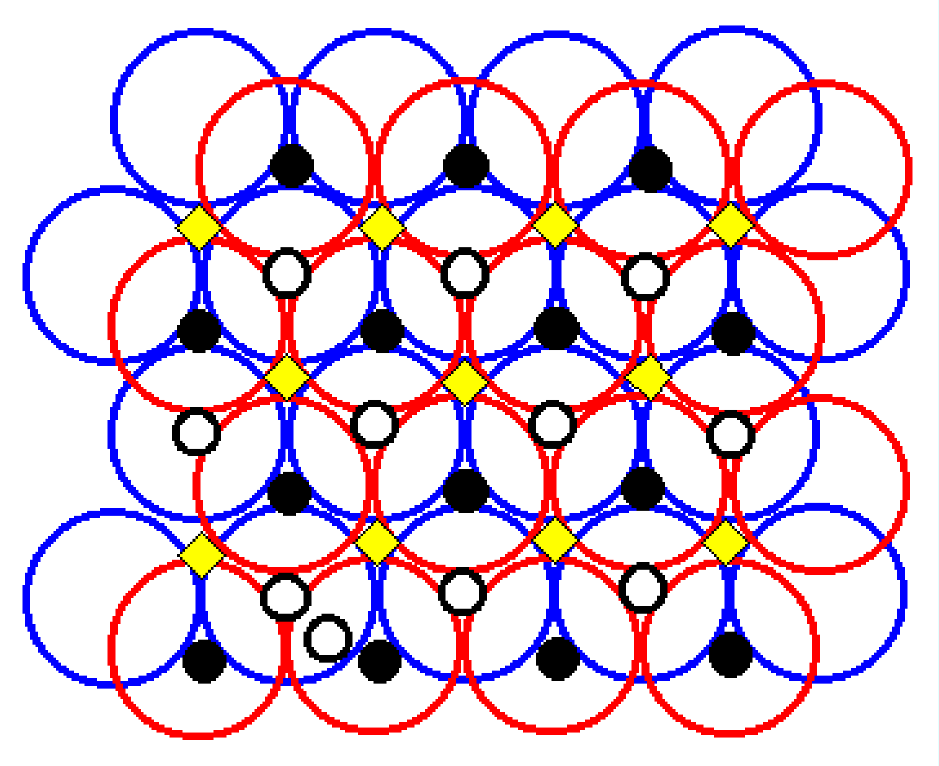
Octahedral Holes



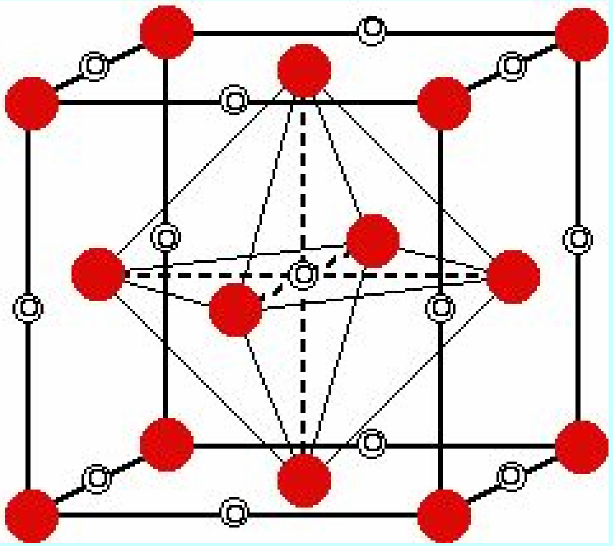
Tetrahedral Holes T-

N cp atoms in lattice cell

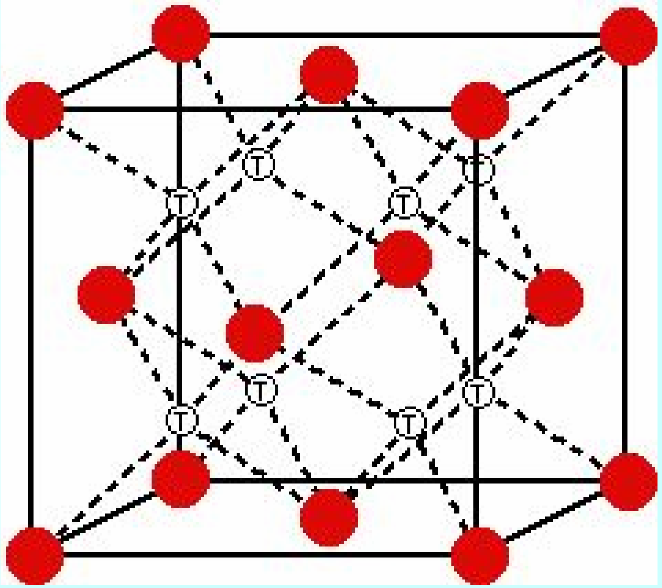
N Octahedral Holes
2N Tetrahedral Holes



Two Types of Voids (Holes)

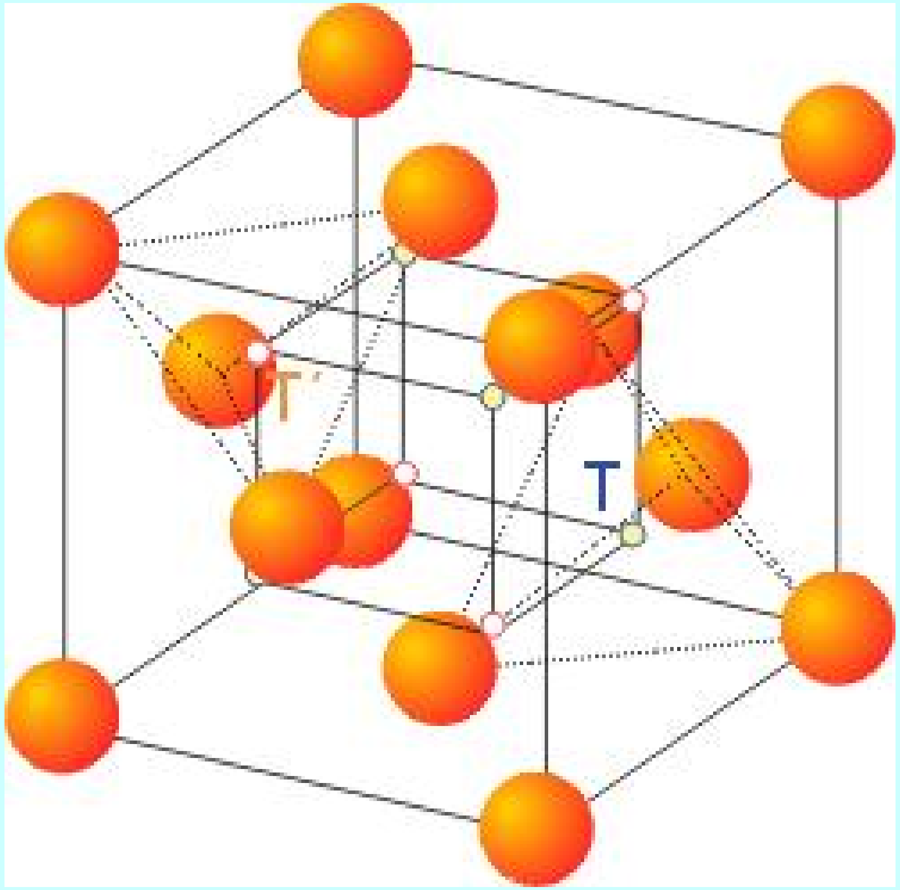


Octahedral Holes



Tetrahedral Holes

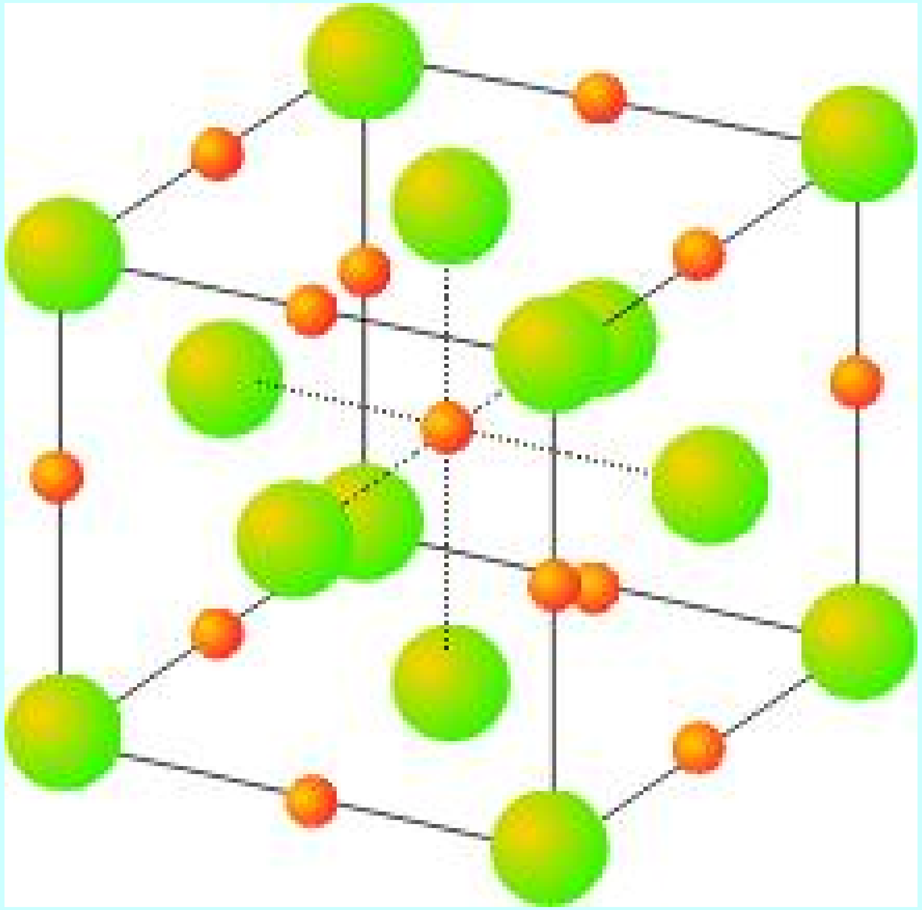
Tetrahedral Holes (2N)



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

N = 8
number of tetrahedral holes (2N)

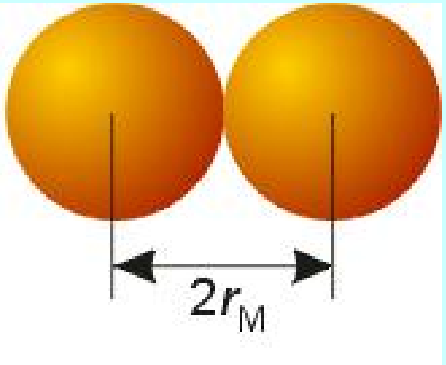
Octahedral Holes (N)



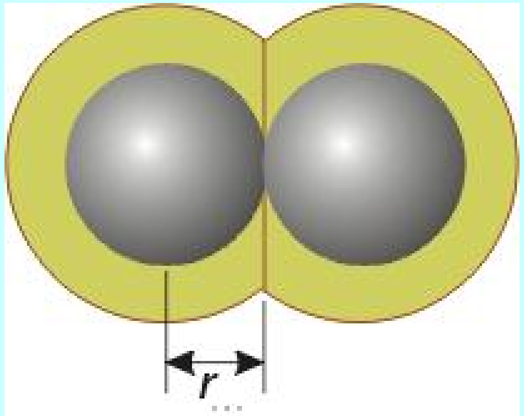
Z = 4
number of atoms in the cell (N)

N = 4
number of octahedral holes (N)

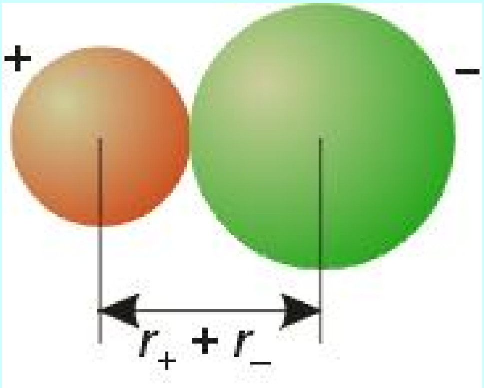
Different Types of Radii



1 Metallic radius



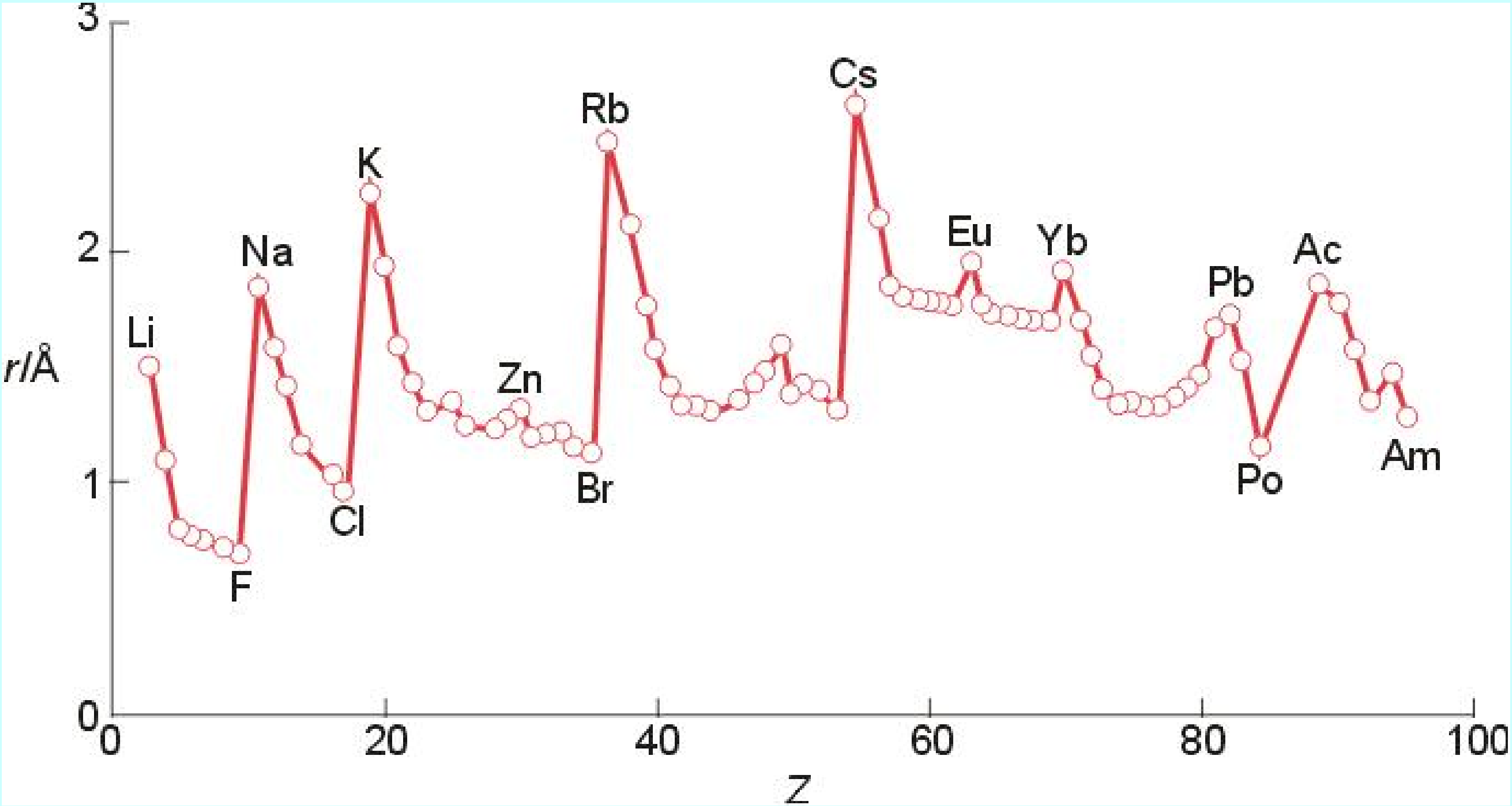
2 Covalent radius



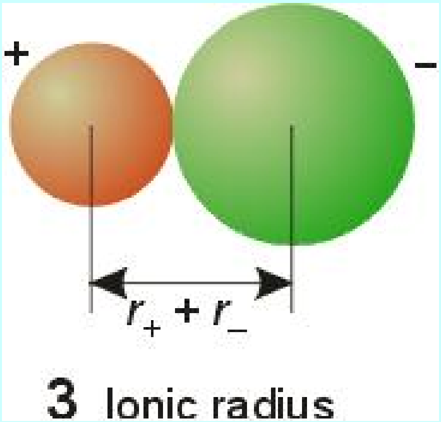
3 Ionic radius

Variation of atomic radii

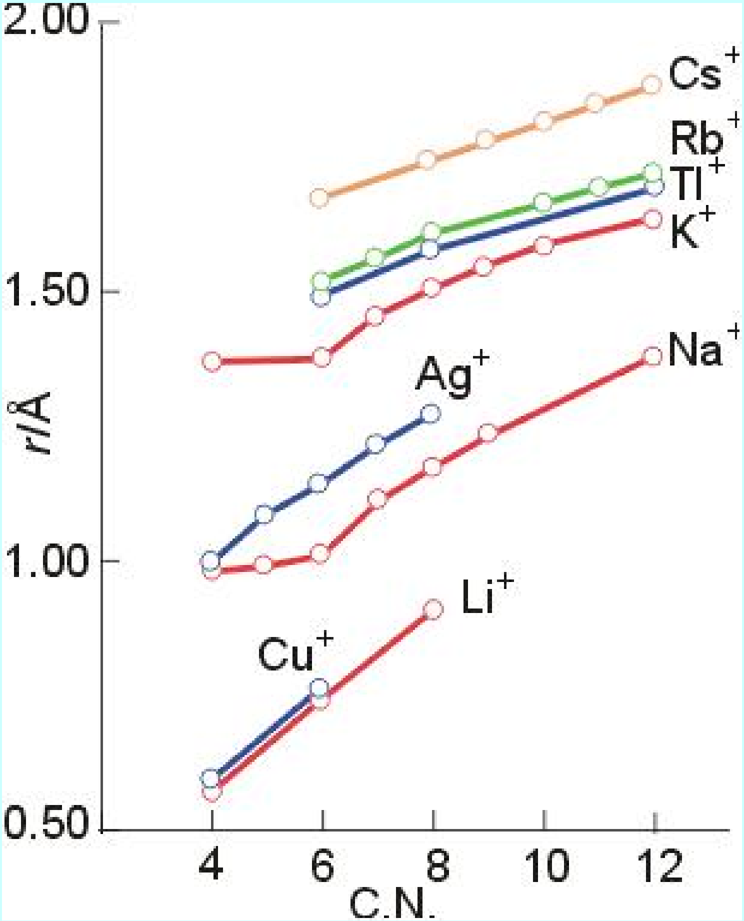
through the Periodic table



Variation of ionic radii with coordination number



3 Ionic radius



The radius of one ion was fixed to a reasonable value

($r(O^{2-})$ = 140 pm) (Linus Pauling)

That value is then used to compile a set of self consistent values for all other ions.

General trends for ionic radii

1. Ionic radii increase down a group.(Lanthanide contraction restricts the increase of heavy ions)

2. Radii of equal charge ions decrease across a period

3. Ionic radii increase with increasing coordination number

   the higher the CN the bigger the ion

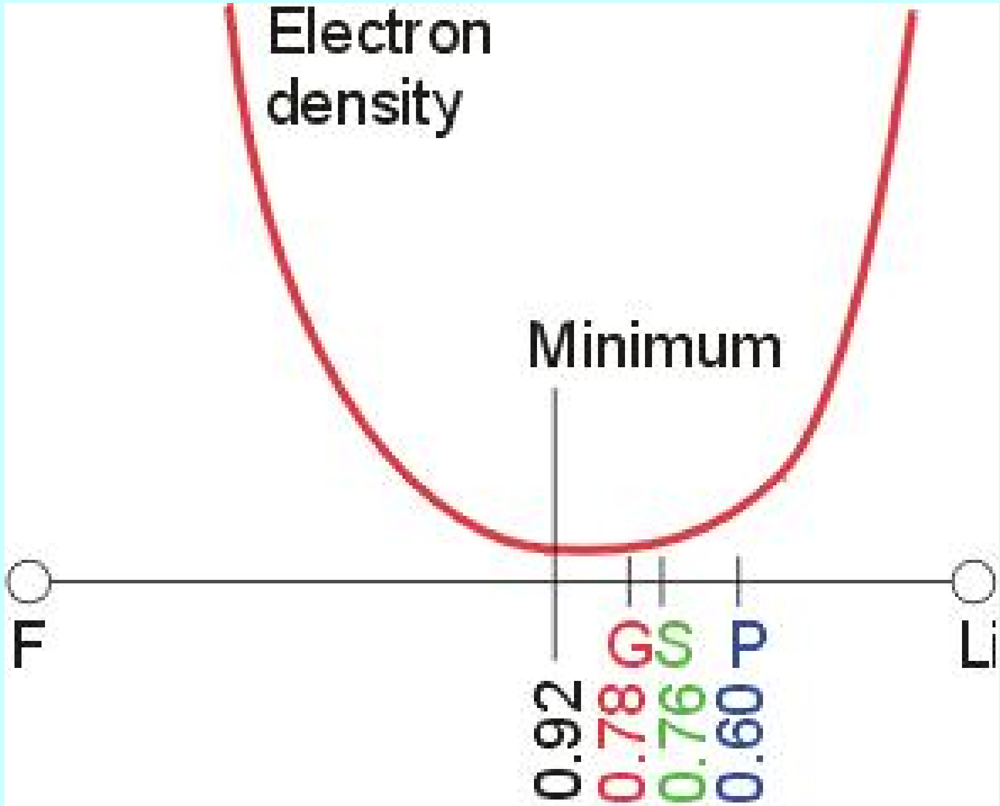
4. The ionic radius of a given atom decreases with increasing charge
   ($r(Fe^{2+}) > r(Fe^{3+})$)

5. Cations are usually the smaller ions in a cation/anion combination (exceptions: $r(Cs^+) > r(F^-)$)

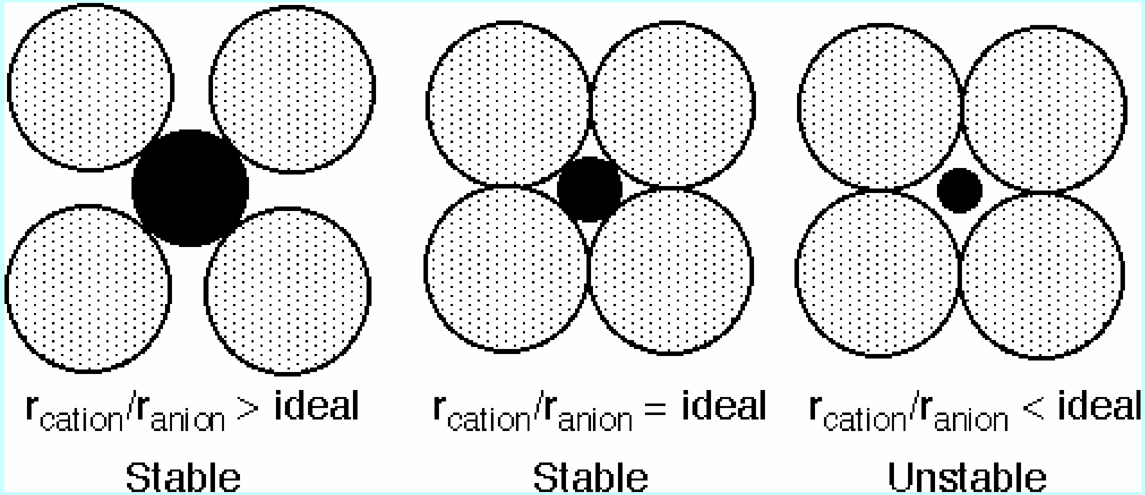
6. Frequently used for rationalization of structures:
   „radius ratio“ r(cation)/r(anion) (< 1)

Variation of the electron density along the Li – F axis in LiF

P – Pauling radius
G – Goldschmidt radius
S – Shannon radius.



Cation/anion Radius Ratio

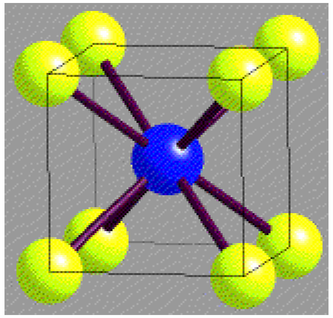


CN	r/R
12 – hcp/ccp	1.00 (substitution)
8 – cubic	0.732 – 1.00
6 – octahedral	0.414 – 0.732
4 – tetrahedral	0.225 – 0.414

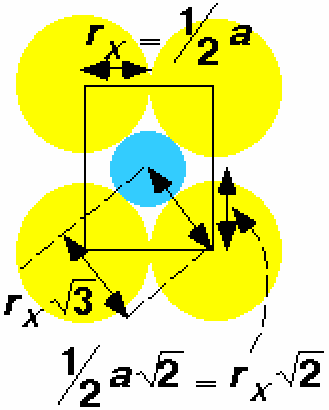
optimal radius
ratio for
given CN
ions are in touch

Limiting Radius Ratios

CsCl 8:8

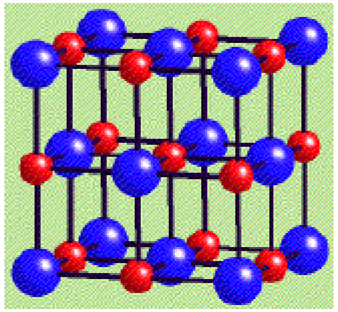

unit cell

cell side a

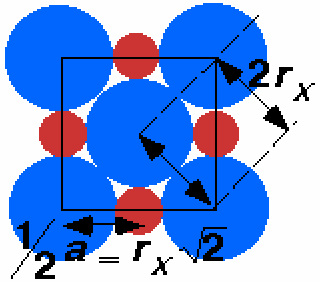


$$r_M + r_X = r_X\sqrt{3}$$
$$r_M / r_X = \sqrt{3} - 1$$
$$= 0.732$$

NaCl 6:6

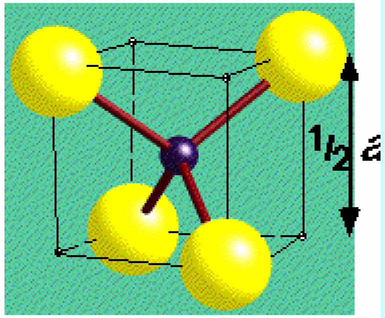

unit cell

face diagonal $a\sqrt{2}$



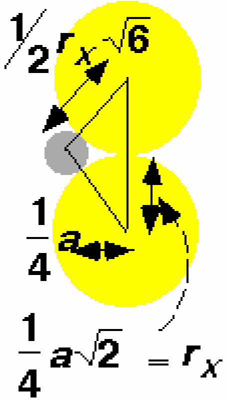
$$r_M + r_X = r_X\sqrt{2}$$
$$r_M / r_X = \sqrt{2} - 1$$
$$= 0.414$$

ZnS 4:4

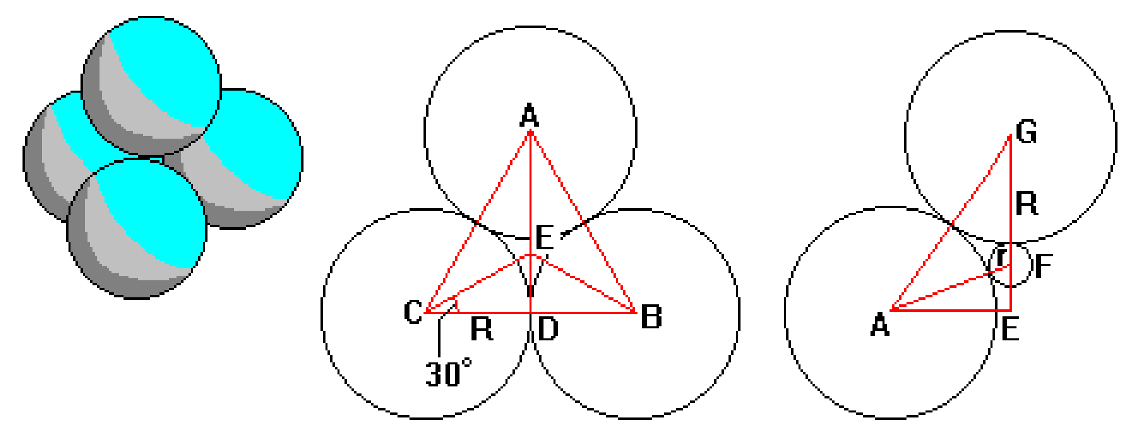


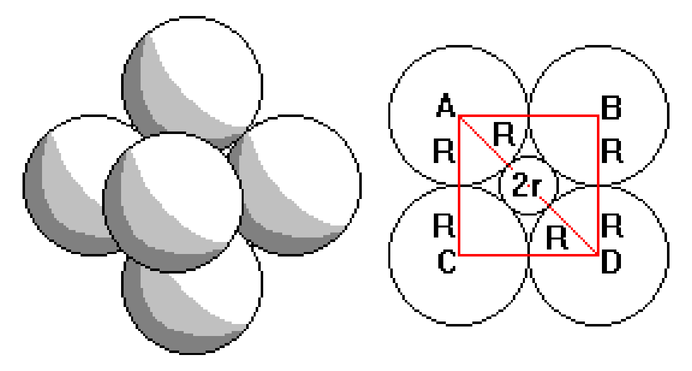
$\frac{1}{8}$th unit cell

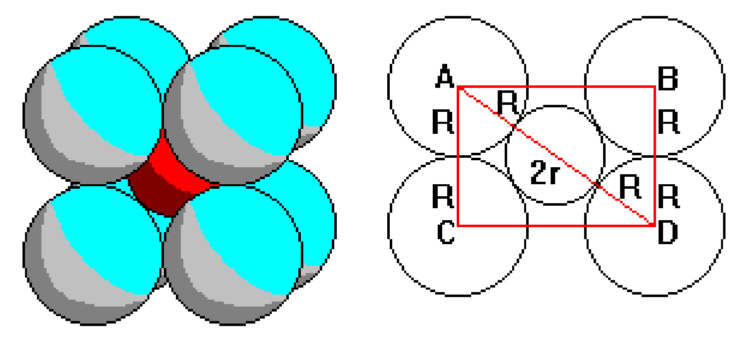
body diagonal $a\sqrt{3}$

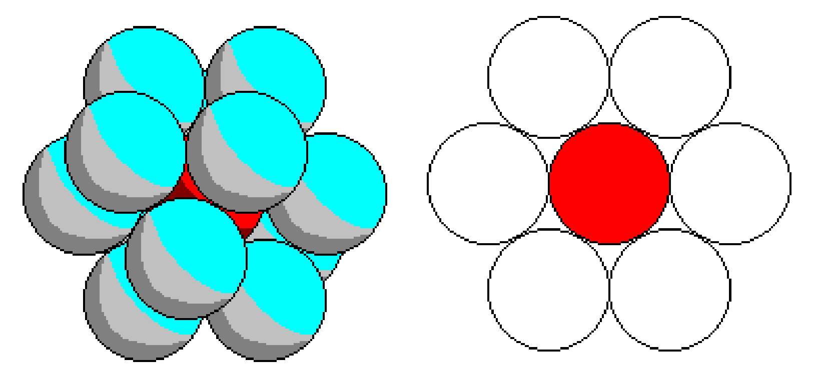


$$r_M + r_X = \frac{1}{2} r_X\sqrt{6}$$
$$r_M / r_X = \frac{1}{2}\sqrt{6} - 1$$
$$= 0.225$$


A
E
C
R
D
B
30°
G
R
r
F
A
E


A
R
B
R
R
2r
R
R
R
C
D

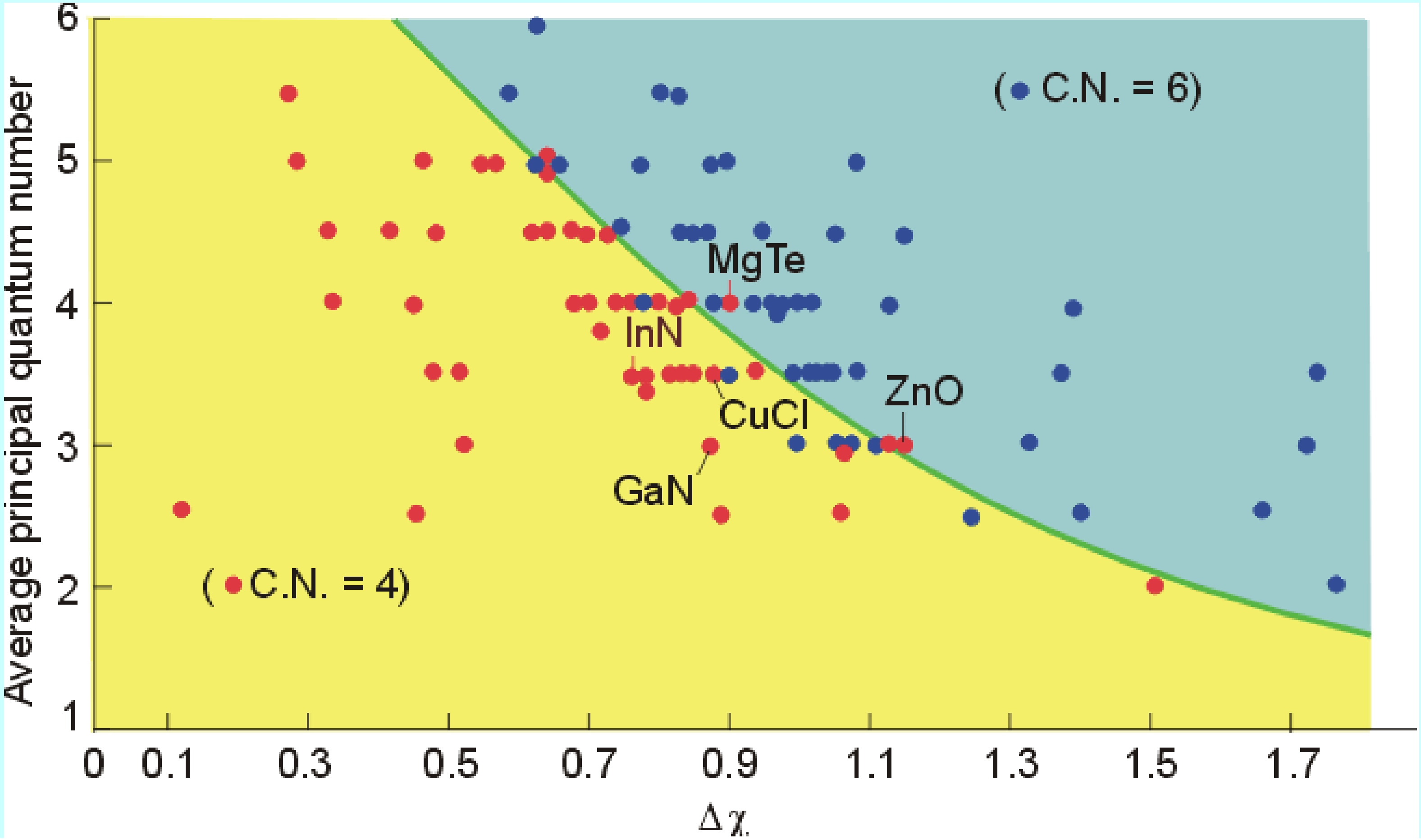

A
B
R
R
R
2r
R
R
R
C
D



Structure map:

Dependence of the structure type (coordination number) on the electronegativity difference and the average principal quantum number (size and polarizability)

AB compounds



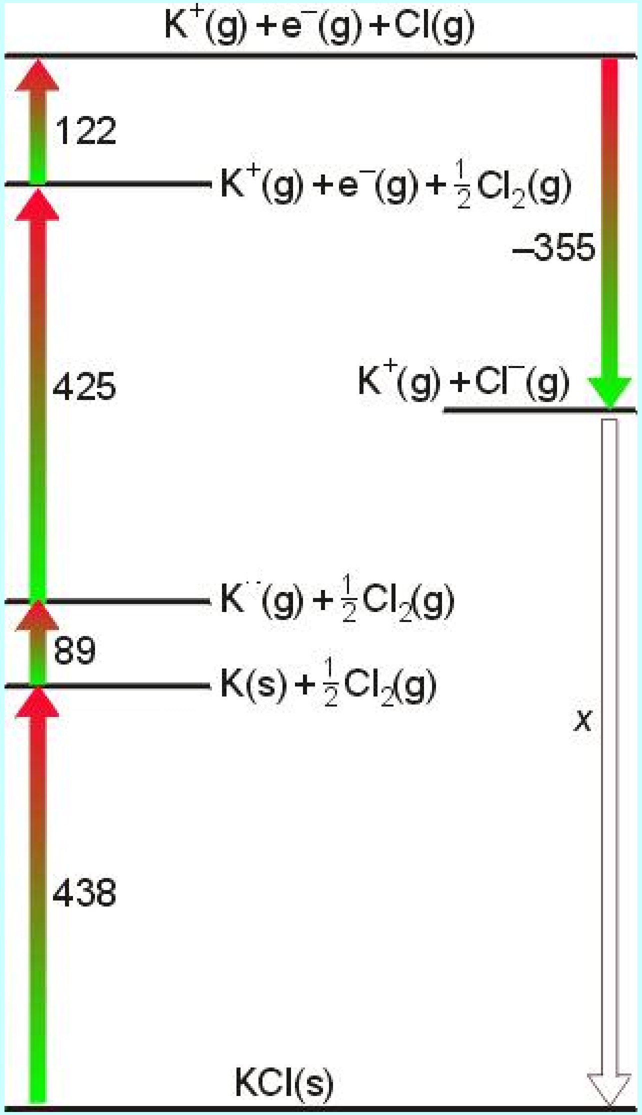
Lattice Enthalpy

The lattice enthalpy change ΔH_L^0 is the standard molar enthalpy change for the following process:

$$M^+_{(gas)} + X^-_{(gas)} \rightarrow MX_{(solid)} \qquad \Delta H_L^0$$

Because the formation of a solid from a „gas of ions" is always exothermic lattice enthalpies (defined in this way) are usually negative.
If entropy considerations are neglected the most stable crystal structure of a given compound is the one with the highest lattice enthalpy.

Lattice enthalpies can be determined by a thermodynamic cycle → Born-Haber cycle



A Born-Haber cycle for KCl

(all enthalpies: kJ mol^{-1} for <u>normal conditions</u> → standard enthalpies)

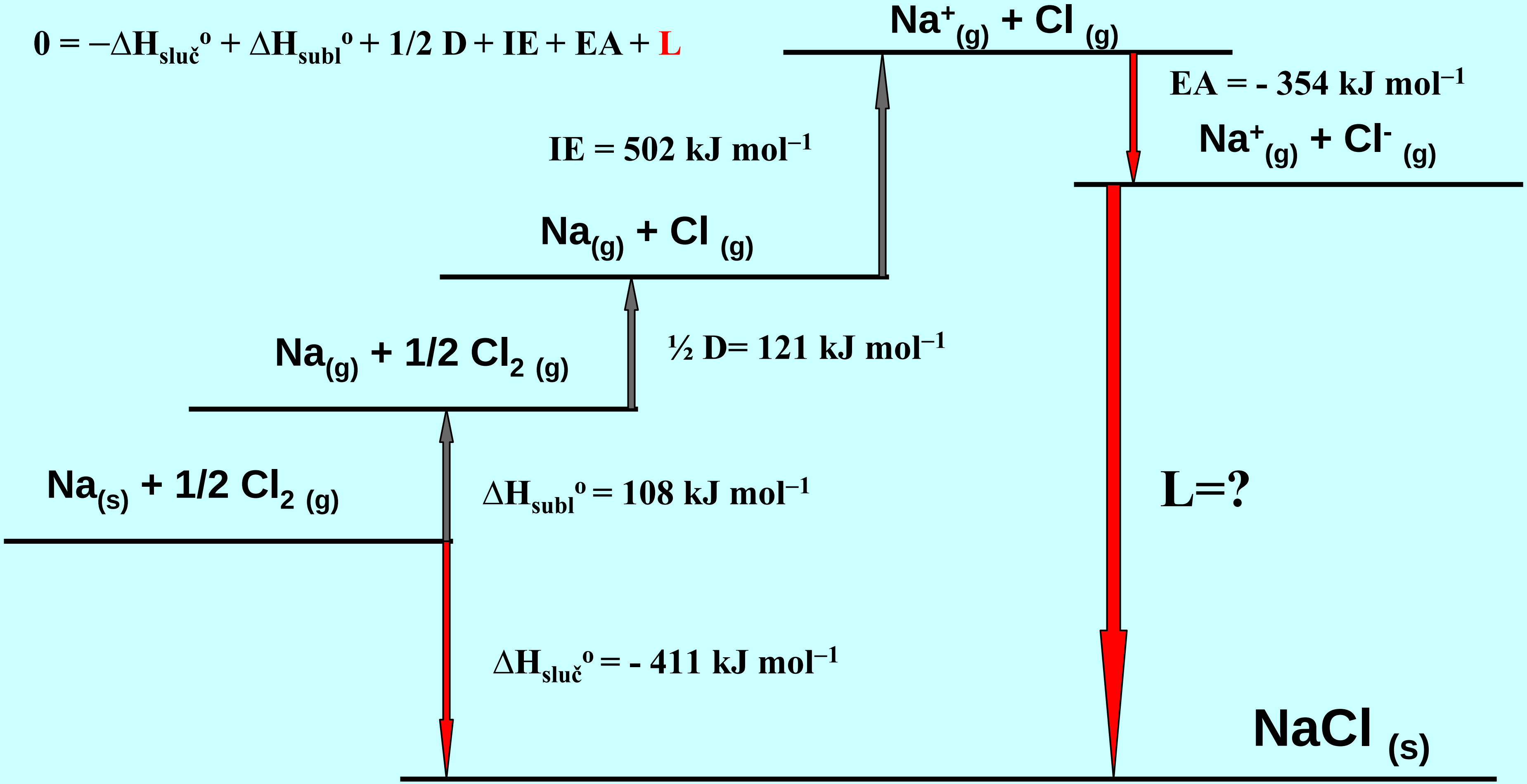
standard enthalpies of

- formation: 438

- sublimation: +89 (K)
- ionization: + 425 (K)
- atomization: +244 (Cl_2)
- electron affinity: -355 (Cl)
- lattice enthalpy: x

Born-Haber cycle

$0 = -\Delta H_{\text{sluč}}^{o} + \Delta H_{\text{subl}}^{o} + 1/2\ D + IE + EA + L$



$Na^{+}_{(g)} + Cl_{(g)}$

$EA = -354\ \text{kJ mol}^{-1}$

$Na^{+}_{(g)} + Cl^{-}_{(g)}$

$IE = 502\ \text{kJ mol}^{-1}$

$Na_{(g)} + Cl_{(g)}$

$½\ D = 121\ \text{kJ mol}^{-1}$

$Na_{(g)} + 1/2\ Cl_{2\ (g)}$

$Na_{(s)} + 1/2\ Cl_{2\ (g)}$

$\Delta H_{\text{subl}}^{o} = 108\ \text{kJ mol}^{-1}$

L=?

$\Delta H_{\text{sluč}}^{o} = -411\ \text{kJ mol}^{-1}$

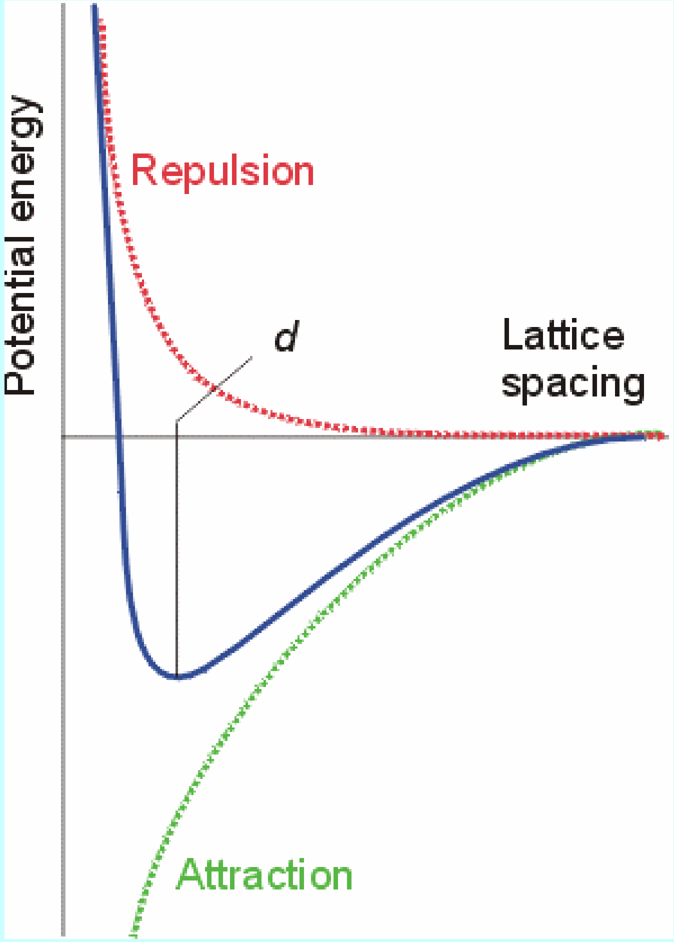
$NaCl_{(s)}$

$0 = 411 + 108 + 121 + 502 + (-354) + L$

$L = -788\ \text{kJ mol}^{-1}$

all enthalpies: kJ mol^{-1} for normal conditions → standard enthalpies

Lattice Enthalpy



$$L = E_{coul} + E_{rep}$$

One ion pair

$E_{coul} = (1/4\pi\varepsilon_0)\ z_A\ z_B / d$

$E_{rep} = B / d^n$

n = Born exponent
(experimental measurement of compressibilty)

Lattice Enthalpy

1 mol of ions

$E_{coul} = N_A\ (e^2\ /\ 4\ \pi\ \varepsilon_0)\ (z_A\ z_B\ /\ d)\ A$

$E_{rep} = N_A\ B\ /\ d^n$

$$L = N_A A \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d} + N_A \frac{B}{d^n}$$

$L = E_{coul} + E_{rep}$

Find minimum $dL/d(d) = 0$

Calculation of lattice enthalpies

Coulombic contributions to lattice enthalpies

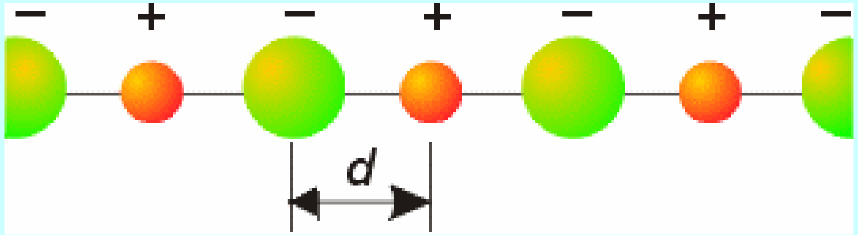
$$V_{AB} = -A \boxed{\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}}} N$$

Coulomb potential of an ion pair

V_{AB}: Coulomb potential (electrostatic potential)
A: <u>Madelung constant</u> (depends on structure type)
N: Avogadro constant
z: charge number
e: elementary charge
ε_o: dielectric constant (vacuum permittivity)
r_{AB}: shortest distance between cation and anion

Madelung Constant

Count all interactions in the crystal lattice

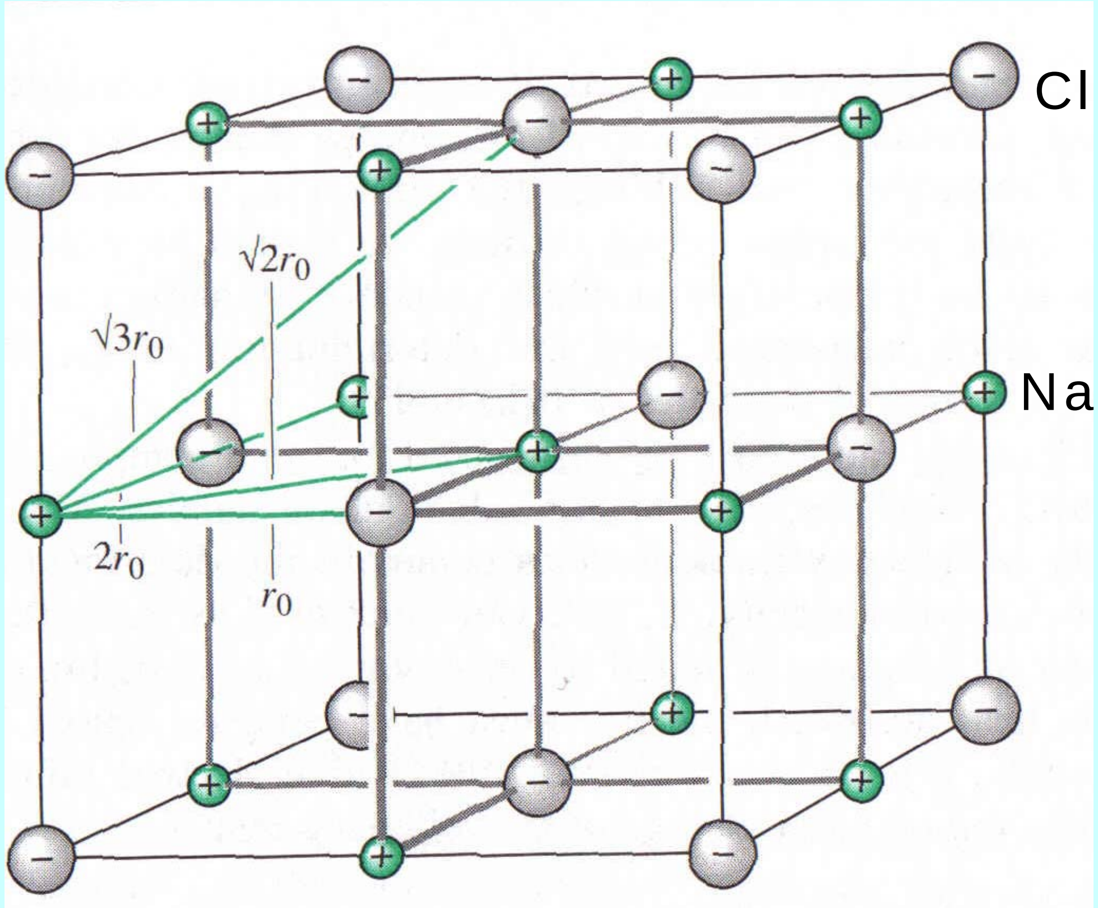


$$E_{coul} = (e^2 / 4\,\pi\,\varepsilon_0)*(z_A\,z_B / d)*[+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + ...]$$

$$E_{coul} = (e^2 / 4\,\pi\,\varepsilon_0)*(z_A\,z_B / d)*(2\ln 2)$$

Madelung constant A
(for linear chain of ions)
= sum of convergent series

Calculation of the Madelung constant



3D ionic solids:
Coulomb attraction and
repulsion

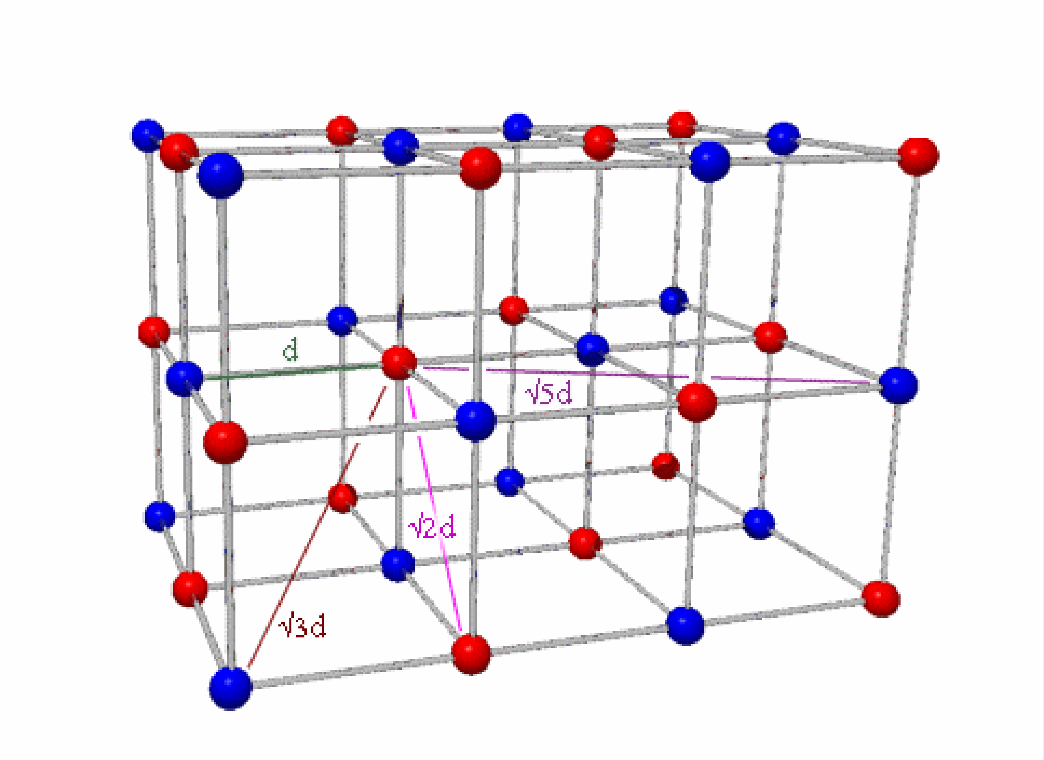
Madelung constants:

CsCl:	1.763
NaCl:	1.748
ZnS:	1.641 (wurtzite)
ZnS:	1.638 (sphalerite)
ion pair:	1.0000 (!)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \dots$$

= 1.748... (NaCl)
(infinite summation)

Madelung constant for NaCl



$$E_{coul} = (e^2 / 4 \pi \varepsilon_0) * (z_A z_B / d) * [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) \ldots.]$$

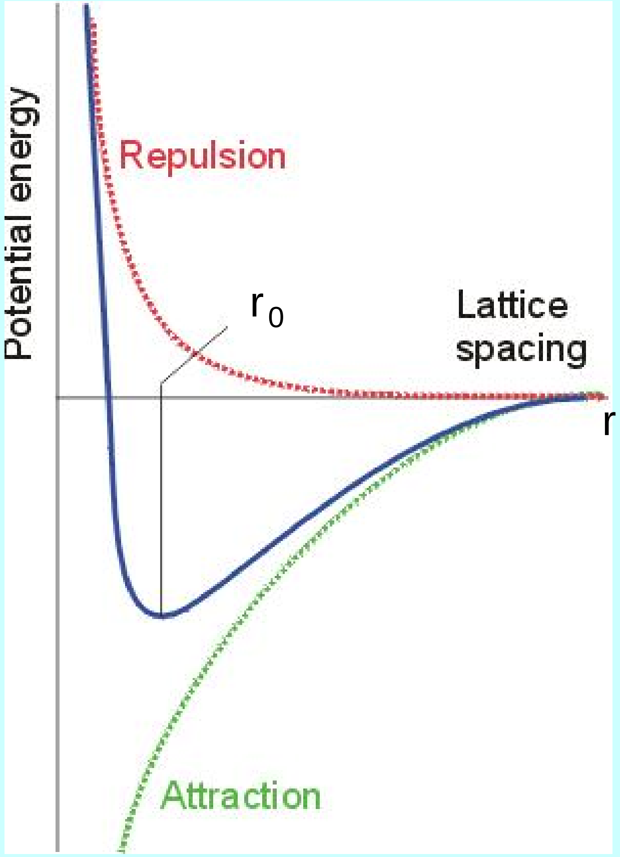
convergent series

$$E_{coul} = (e^2 / 4 \pi \varepsilon_0) * (z_A z_B / d) * A$$

Madelung Constants for other Structural Types

Structural Type	A
NaCl	1.74756
CsCl	1.76267
CaF_2	2.519
ZnS Sfalerite	1.63805
ZnS Wurtzite	1.64132

Born repulsion V_{Born}



Repulsion arising from overlap of electron clouds

Because the electron density of atoms decreases exponentially towards zero at large distances from the nucleus the Born repulsion shows the same behavior

approximation:

$$\boxed{V_{Born} = \frac{B}{r^n}}$$

B and n are constants for a given atom type; n can be derived from compressibility measurements (~8)

Total lattice enthalpy from Coulomb interaction and Born repulsion

$$\Delta H_L^0 = Min.(V_{AB} + V_{Born})$$

(set first derivative of the sum to zero)

$$\boxed{\Delta H^0_L = -A\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} N(1-\frac{1}{n})}$$

Measured (calculated) lattice enthalpies (kJ mol^{-1}):
NaCl: –772 (-757); CsCl: -652 (-623)
(measured from Born Haber cycle)

The Kapustinskii equation

Kapustinskii found that if the Madelung constant for a given structure is divided by the number of ions in one formula unit (ν) the resulting values are almost constant:

Structure	**Madel. const.(A)**	**A/ν**	**Coordination**
CsCl	1.763	0.88	8:8
NaCl	1.748	0.87	6:6
CaF_2	2.519	0.84	8:4
α-Al_2O_3	4.172	0.83	6:4

→ general lattice energy equation that can be applied to any crystal regardless of the crystal structure

$$\boxed{\Delta H_L^0 = -\frac{1.079 \cdot 10^5 \nu \cdot z_+ z_-}{r_+ \cdot r_-}}$$

Most important advantage of the Kapustinski equation

→ it is possible to apply the equation for lattice calculations of crystals with polyatomic ions (e.g. KNO_3, $(NH_4)_2SO_4$ ...).

→ a set of „thermochemical radii“ was derived for further calculations of lattice enthalpies

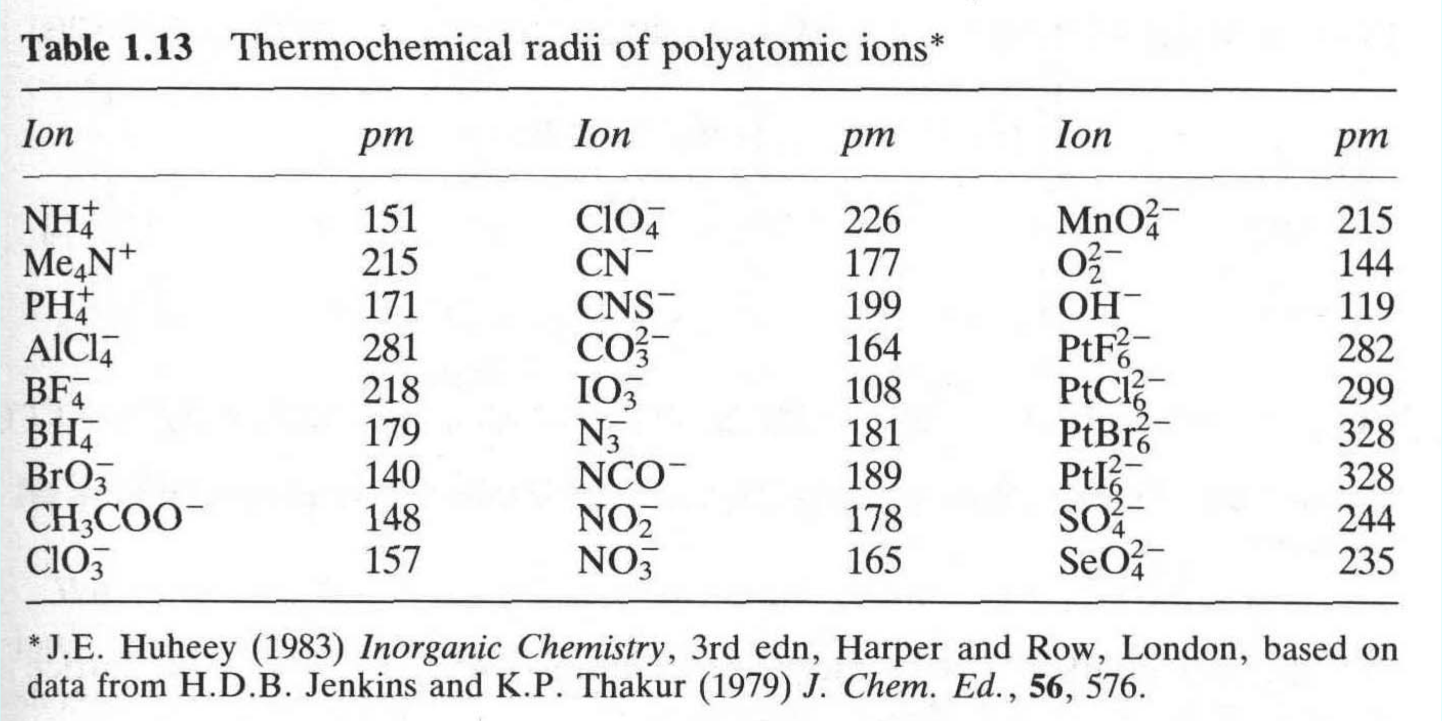


Table 1.13 Thermochemical radii of polyatomic ions*

Ion	*pm*	*Ion*	*pm*	*Ion*	*pm*
NH_4^+	151	ClO_4^-	226	MnO_4^{2-}	215
Me_4N^+	215	CN^-	177	O_2^{2-}	144
PH_4^+	171	CNS^-	199	OH^-	119
$AlCl_4^-$	281	CO_3^{2-}	164	PtF_6^{2-}	282
BF_4^-	218	IO_3^-	108	$PtCl_6^{2-}$	299
BH_4^-	179	N_3^-	181	$PtBr_6^{2-}$	328
BrO_3^-	140	NCO^-	189	PtI_6^{2-}	328
CH_3COO^-	148	NO_2^-	178	SO_4^{2-}	244
ClO_3^-	157	NO_3^-	165	SeO_4^{2-}	235

*J.E. Huheey (1983) *Inorganic Chemistry*, 3rd edn, Harper and Row, London, based on data from H.D.B. Jenkins and K.P. Thakur (1979) *J. Chem. Ed.*, **56**, 576.

Lattice Enthalpy

Born – Lande

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}\left(1 + \frac{1}{n}\right)$$

El. config.	n
He	5
Ne	7
Ar	9
Kr	10
Xe	12

Born – Mayer

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)$$

$d^* = 0.345$ Å

Lattice Enthalpy

Kapustinski

M/v je přibližně konstantní pro všechny typy struktur
v = počet iontů ve vzorcové jednotce

M nahrazeno 0.87 v, není nutno znát strukturu

$$L = 1210 v \frac{Z_A Z_B}{d}\left(1 - \frac{0{,}345}{d}\right)$$

Kapustinski

structure	***M***	**CN**	**stoichm**	***M / v***
CsCl	1.763	(8,8)	AB	0.882
NaCl	1.748	(6,6)	AB	0.874
ZnS sfalerite	1.638	(4,4)	AB	0.819
ZnS wurtzite	1.641	(4,4)	AB	0.821
CaF_2 fluorite	2.519	(8,4)	AB_2	0.840
TiO_2 rutile	2.408	(6,3)	AB_2	0.803
CdI_2	2.355	(6,3)	AB_2	0.785
Al_2O_3	4.172	(6,4)	A_2B_3	0.834

v = the number of ions in one formula unit

Lattice Enthalpy of NaCl

Born – Lande calculation L = -765 kJ mol^{-1}
Only ionic contribution

Experimental Born – Haber cycle L = -788 kJ mol^{-1}
Lattice Enthalpy consists of ionic and covalent contribution

Applications of lattice enthalpy calculations:

→ thermal stabilities of ionic solids

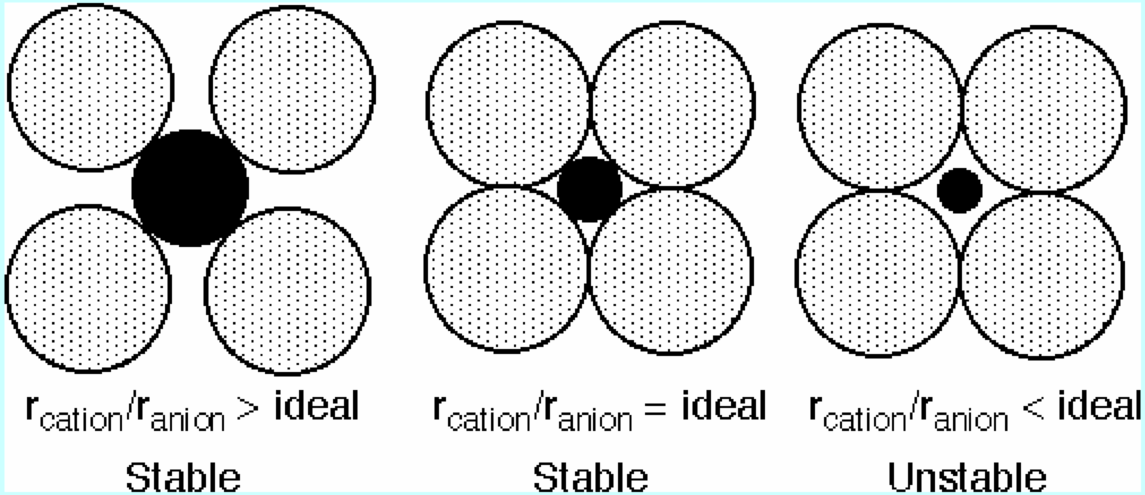
→ stabilities of oxidation states of cations

→ Solubility of salts in water

→ calculations of electron affinity data

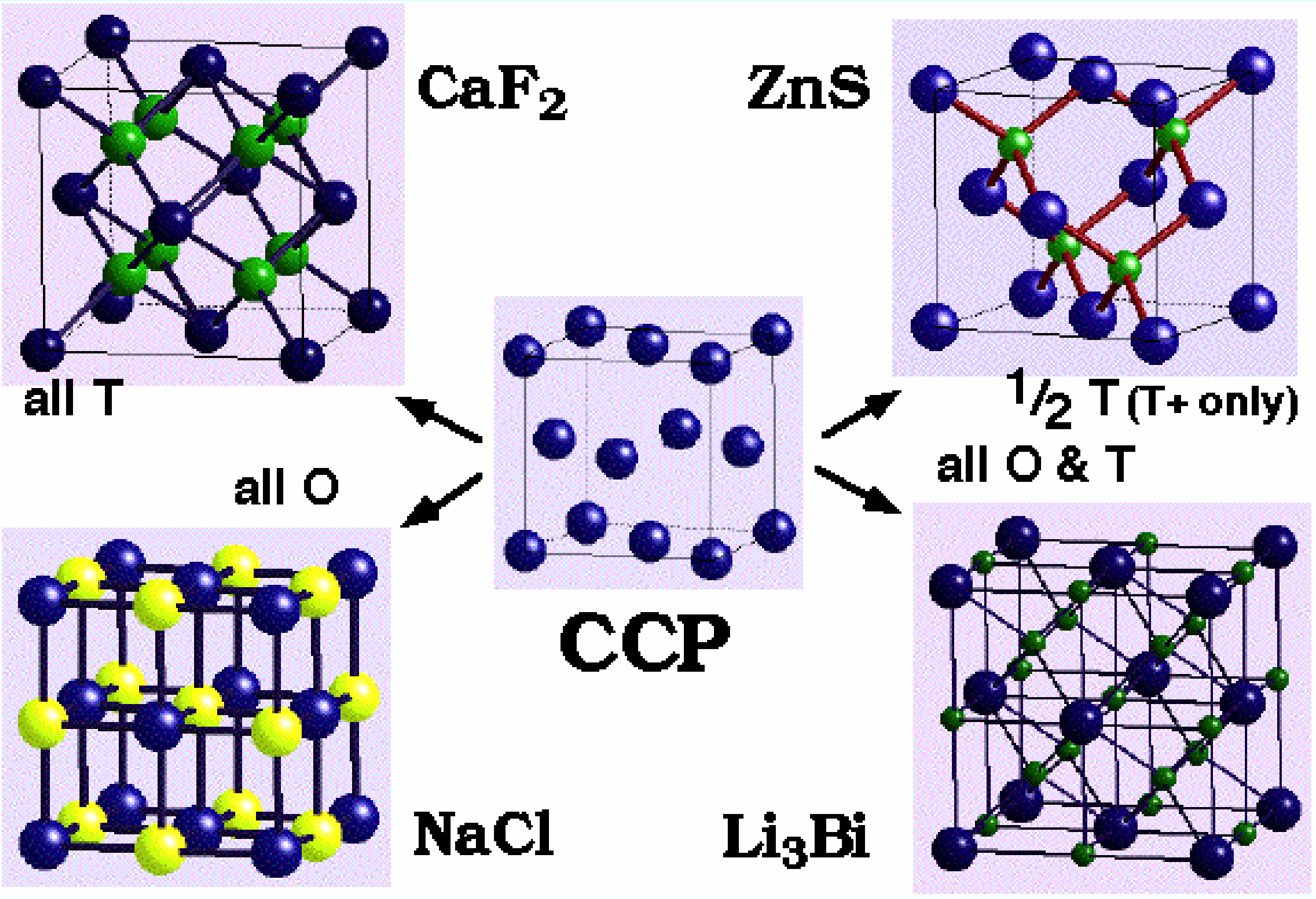
→ lattice enthalpies and stabilities of „non existent“ compounds

Cation/anion Radius Ratio



CN	r/R
12 – hcp/ccp	1.00 (substitution)
8 – cubic	0.732 – 1.00
6 – octahedral	0.414 – 0.732
4 – tetrahedral	0.225 – 0.414

Structure Types Derived from CCP = FCC



CaF_2

all T

ZnS

$^1/_2$ T (T+ only)

CCP

all O

NaCl

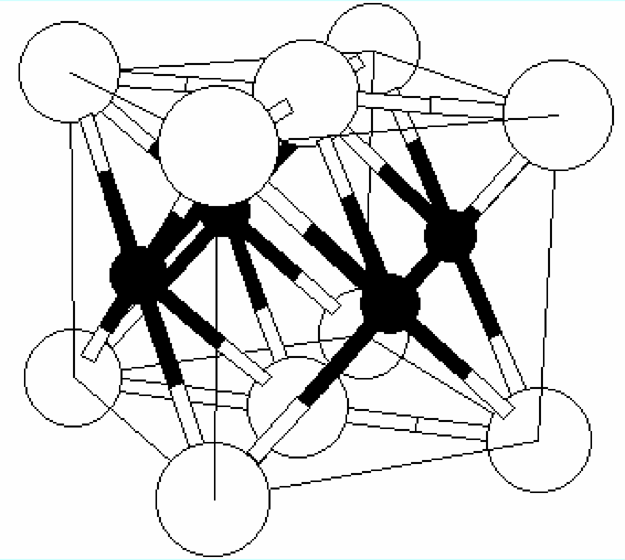
all O & T

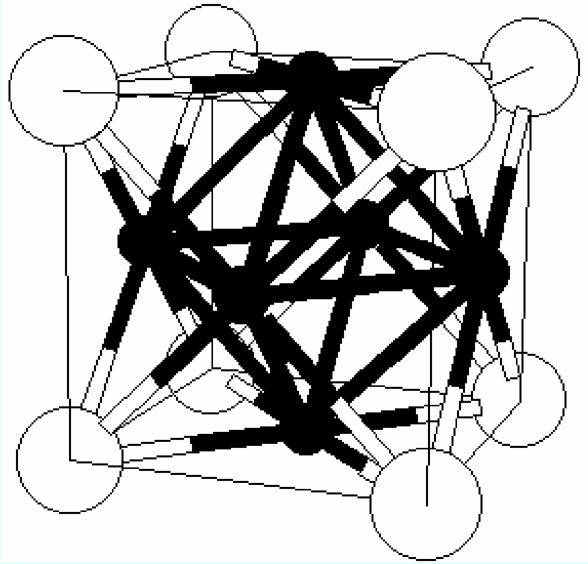
Li_3Bi

Pauling Rules

- Cation-Anion distance is determined by sums of ionic radii. Cation coordination environment is determined by radius ratio.
- The bond valence sum of each ion should equal oxidation state.
- Avoid shared polyhedral edges and/or faces.
(particularly for cations with high oxidation state & low coordination number)
- In a crystal containing different cations those with large valence and small coord. number tend not to share anions.
- The number of chemically different coordination environments for a given ion tends to be small.

Structure Types Derived from CCP = FCC





Characteristic Structures of Solids = Structure Types

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

Fluorite $\underline{CaF_2}$ $BaCl_2$, K_2O, PbO_2 ...

Lithium bismutide $\underline{Li_3Bi}$

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

Nickel arsenide NiAs FeS, PtSn, CoS ...

Wurtzite ZnS ZnO, MnS, SiC

Rhenium diboride ReB_2

Structure Types Derived from CCP = FCC

Anions/cell (= 4)	Oct. (Max 4)	Tet. (Max 8)	Stoichiometry	Compound
4	100% = 4	0	$M_4X_4 = MX$	NaCl (6:6 coord.)
4	0	100% = 8	$M_8X_4 = M_2X$	Li_2O (4:8 coord.)
4	0	50% = 4	$M_4X_4 = MX$	ZnS, sfalerite (4:4 coord.)
4	50% = 2	0	$M_2X_4 = MX_2$	$CdCl_2$
4	100% = 4	100% = 8	$M_{12}X_4 = M_3X$	Li_3Bi
4 spinel	50% = 2	12.5% = 1	M_3X_4	$MgAl_2O_4$,

Comparison between structures with filled octahedral and tetrahedral holes

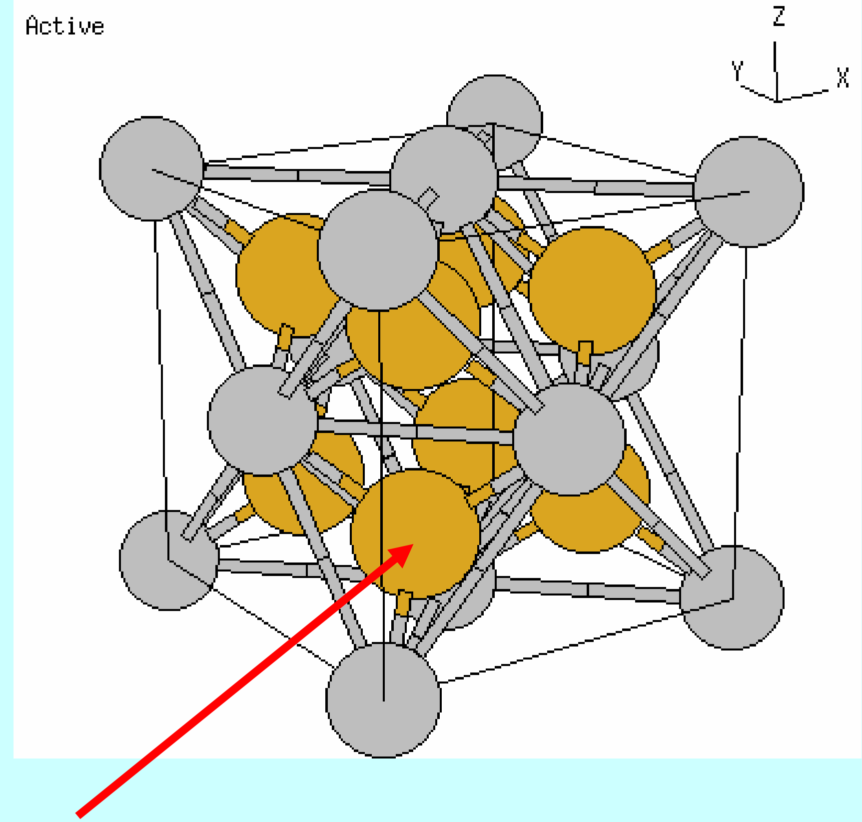
o/t	fcc(ccp)	hcp
all oct.	NaCl	NiAs
all tetr.	CaF_2	ReB_2
o/t (all)	Li_3Bi	(Na_3As) (!) problem
½ t	sphalerite (ZnS)	wurtzite (ZnS)
½ o	$CdCl_2$	CdI_2

Fluorite (CaF_2, antifluorite Li_2O)

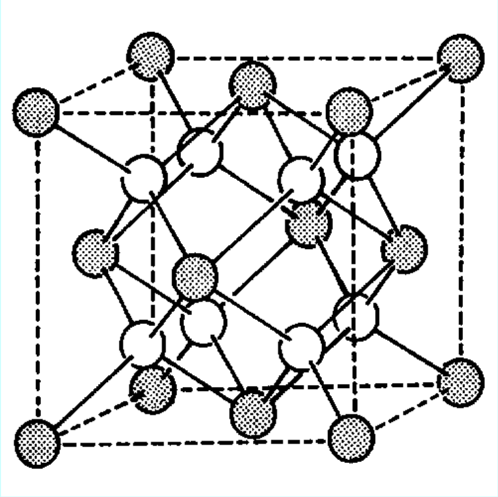
Fluorite structure = a face-centered cubic array (FCC) of cations = cubic close packing (CCP) of cations with all tetrahedral holes filled by anions = a simple cubic (SC) array of anions.

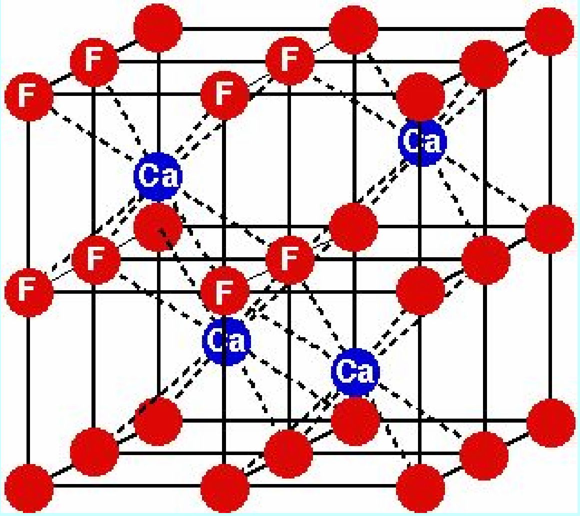
Antifluorite structure = a face-centred cubic (FCC) array of anions = cubic close packing (CCP) of anions, with cations in all of the tetrahedral holes (the reverse of the fluorite structure).

Fluorite (CaF_2, antifluorite Li_2O)



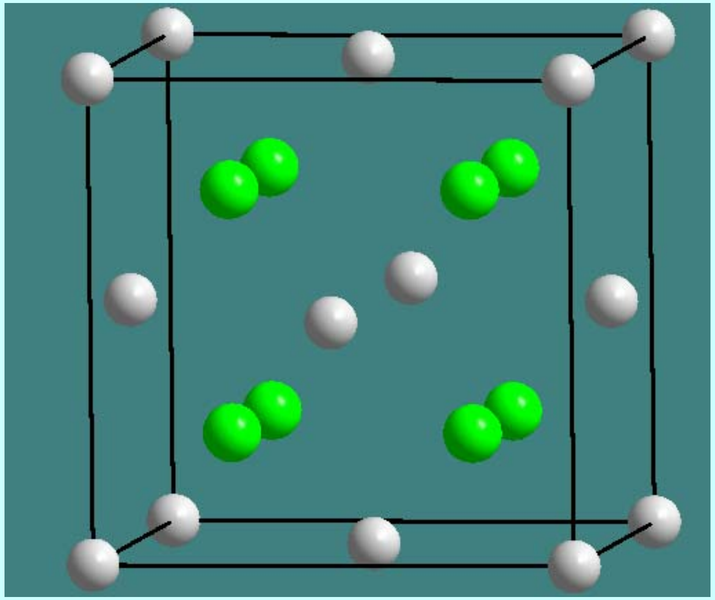
F / Li





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

Fluorite structures (CaF_2, antifluorite Li_2O)



Oxides: Na_2O, K_2O, UO_2, ZrO_2, ThO_2

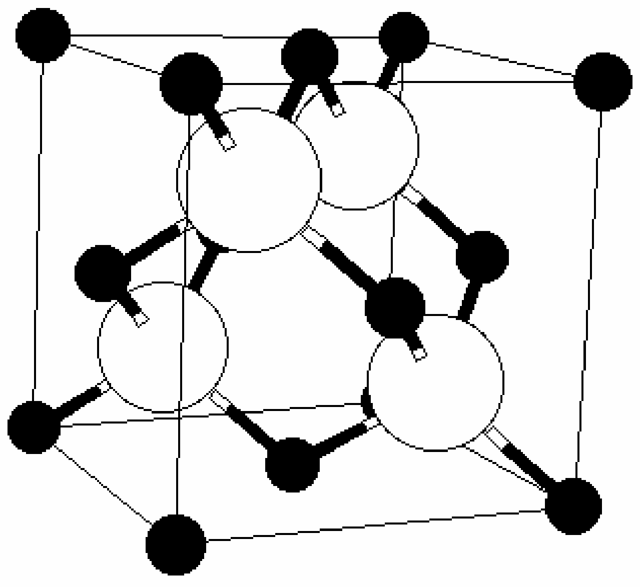
alkali metal sulfides, selenides and tellurides

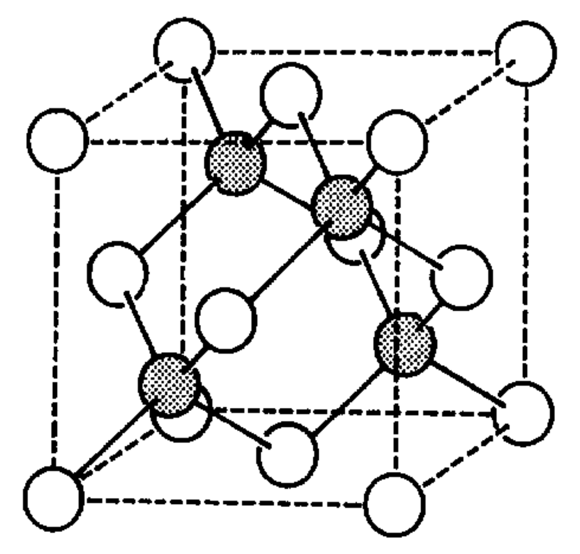
$K_2[PtCl_6]$, $(NH_4)_2[PtCl_6]$, $Cs_2[SiF_6]$, $[Fe(NH_3)_6][TaF_6]_2$.

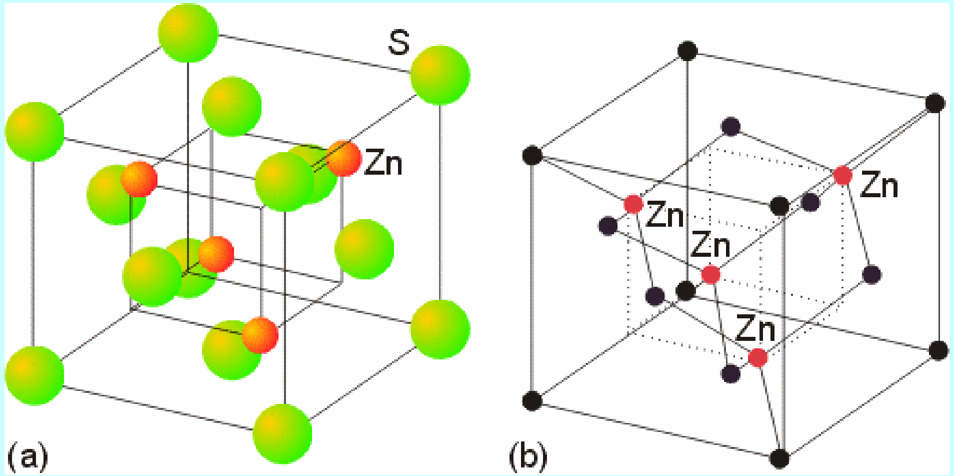
CaF_2, SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, CdF_2, HgF_2, EuF_2, β-PbF_2, PbO_2

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

Sphalerite (zincblende, ZnS)

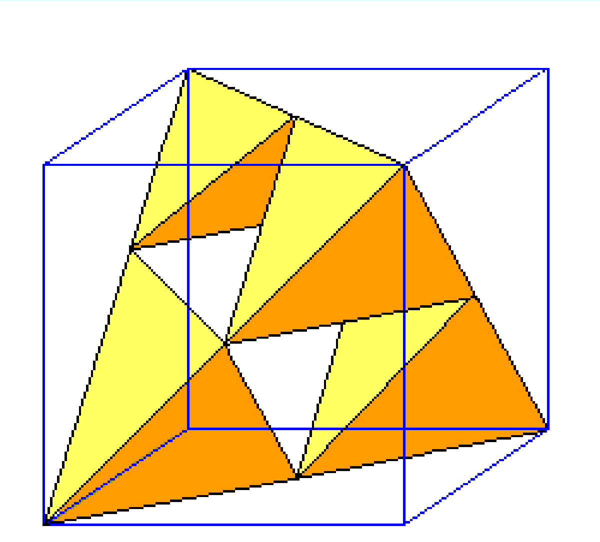


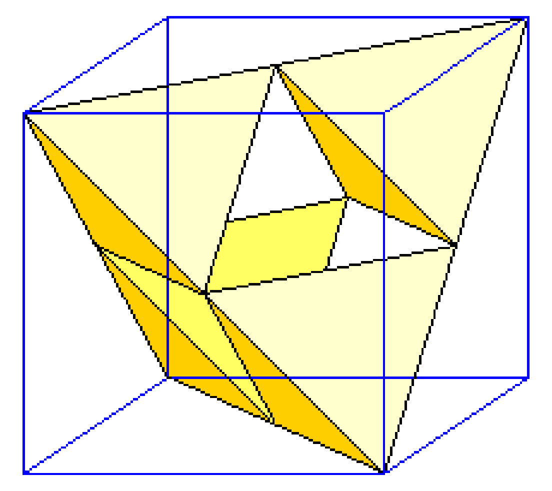


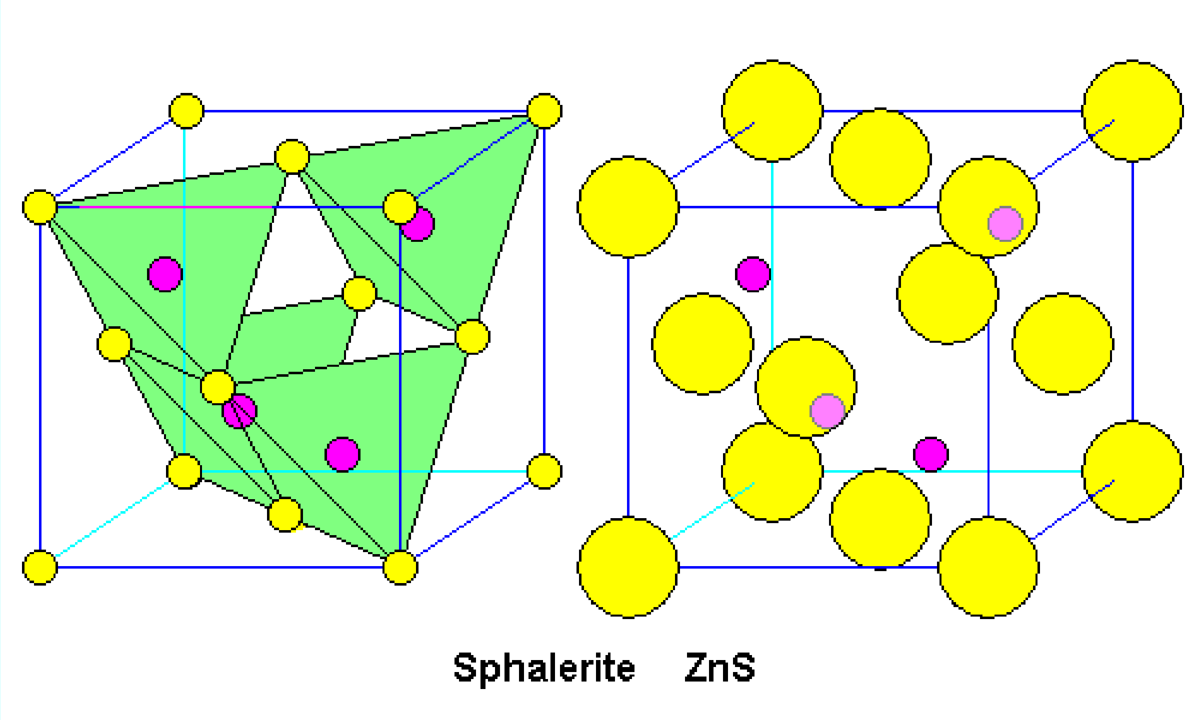


Cubic close packing of anions with 1/2 tetrahedral holes filled by cations

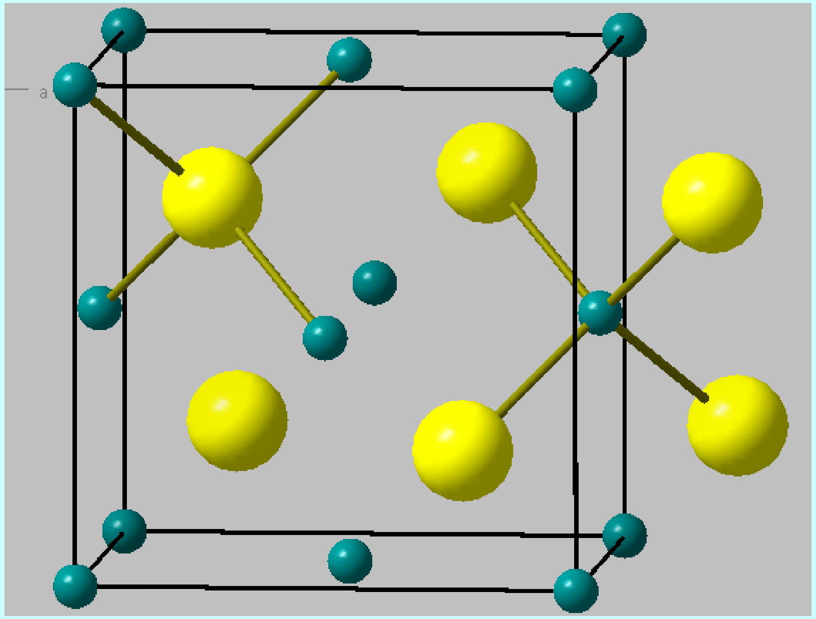
Sphalerite (zincblende, ZnS)







Sphalerite (zincblende, ZnS)



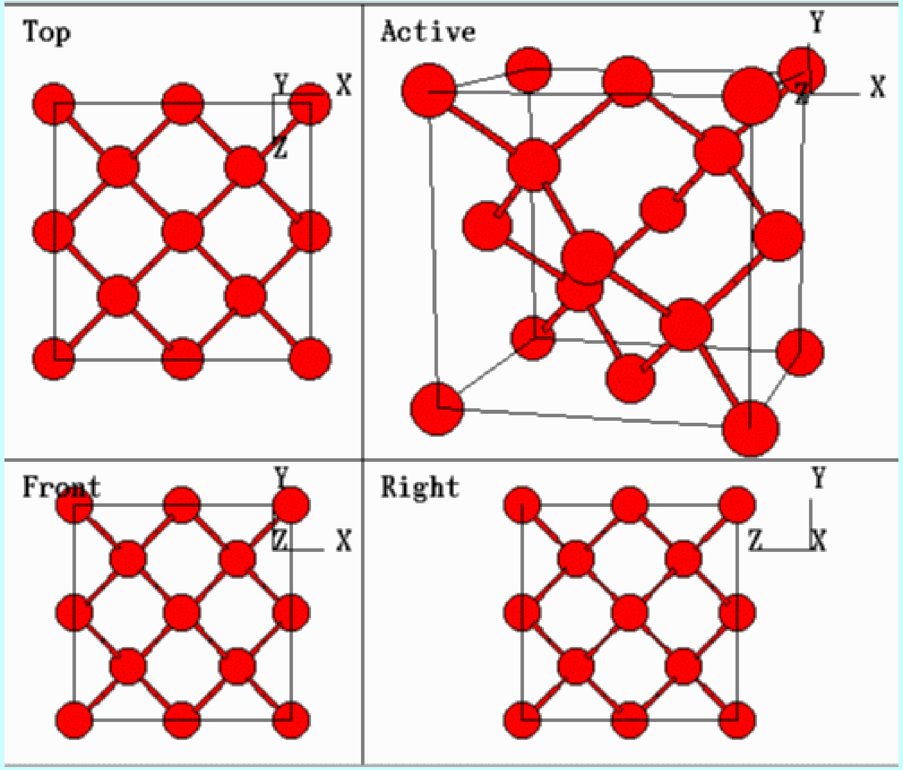
13-15 compounds: BP, BAs, AlP, AlAs, GaAs, GaP, GaSb, AlSb, InP, InAs, InSb

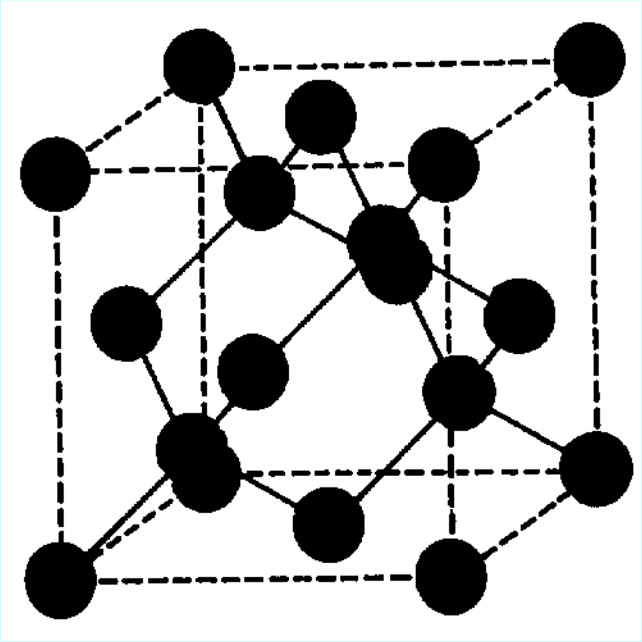
12-16 compounds: BeS, BeSe, BeTe, β-MnS (red), β-MnSe, β-CdS, CdSe, CdTe, HgS, HgSe, HgTe, ZnSe, ZnTe

Halogenides: AgI, CuF, CuCl, CuBr, CuI, NH4F

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

Diamond

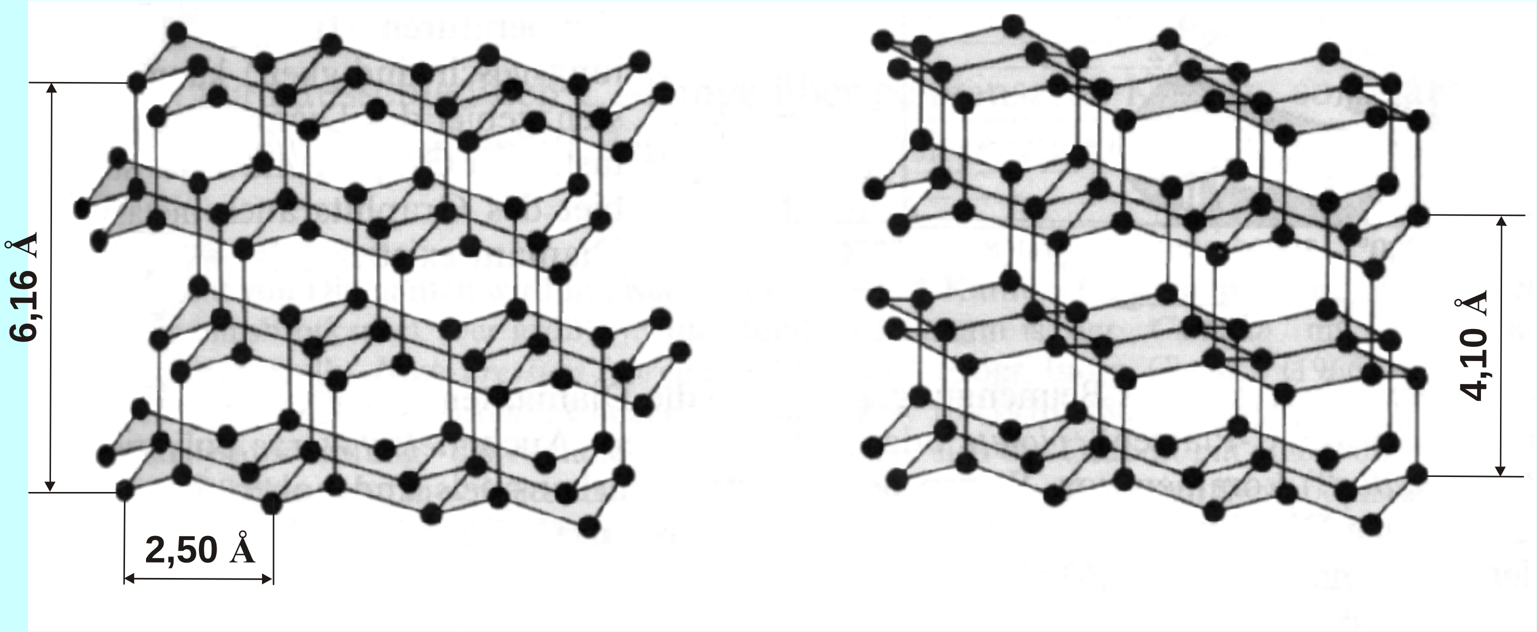




Diamond

cubic

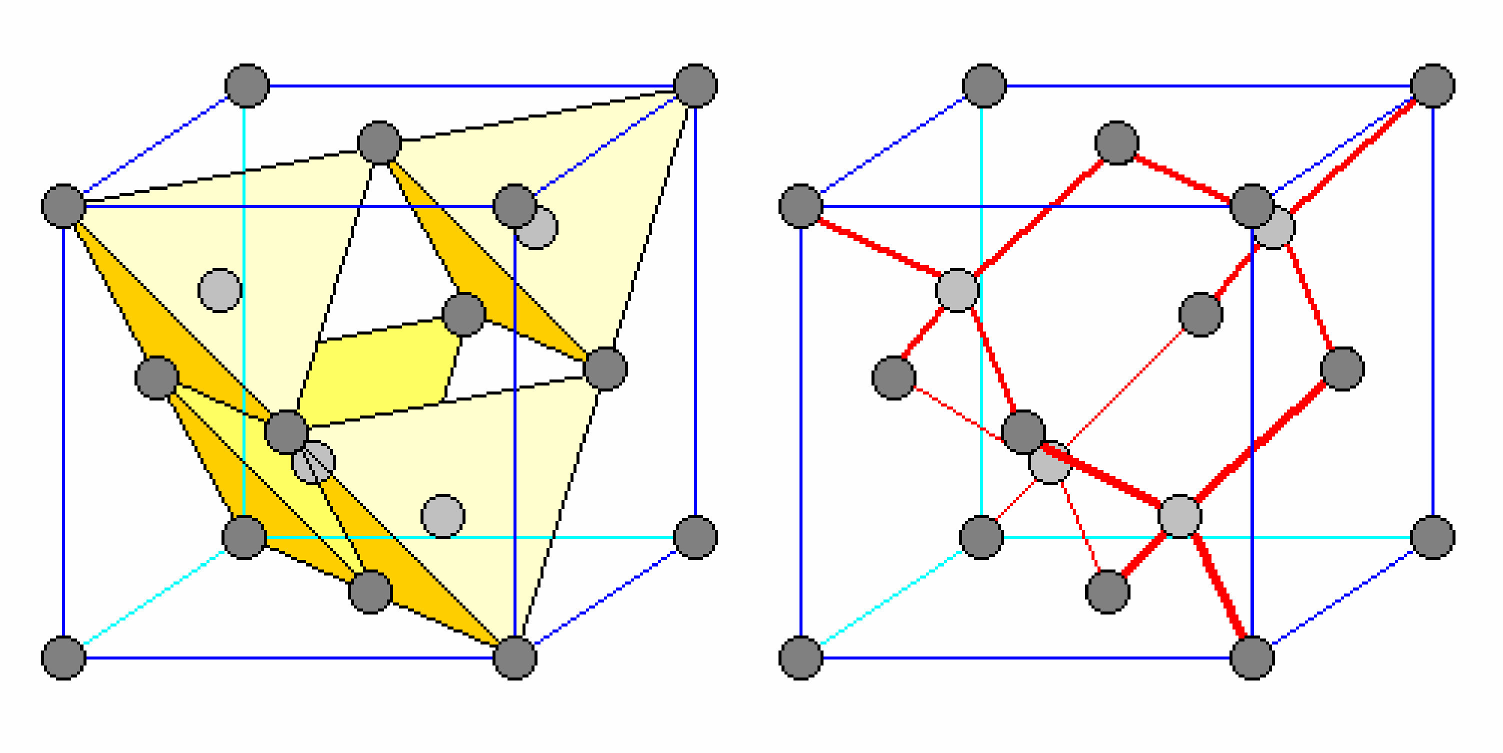
hexagonal



SiO_2 cristobalite

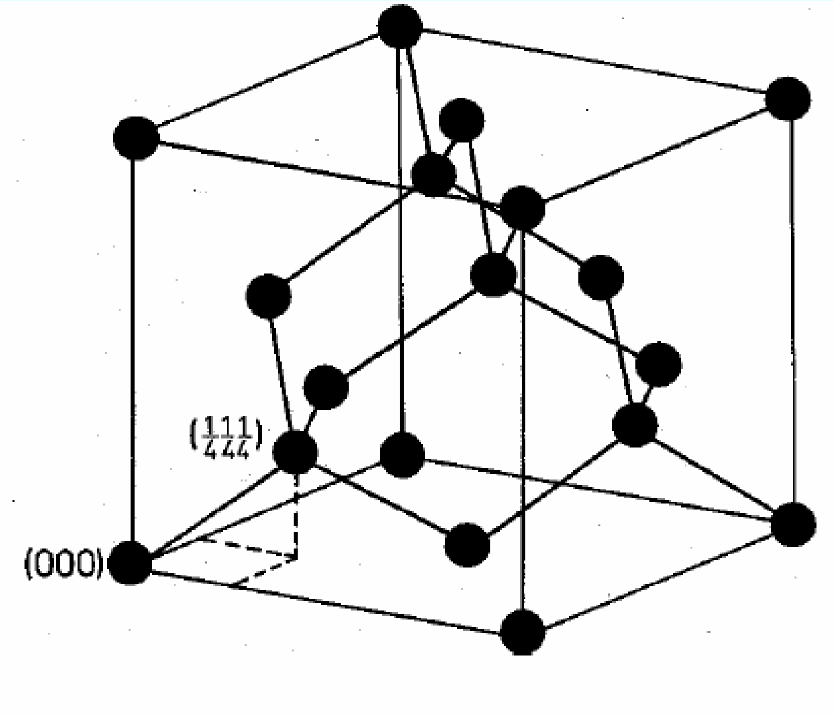
SiO_2 tridymite
ice

Cubic Diamond



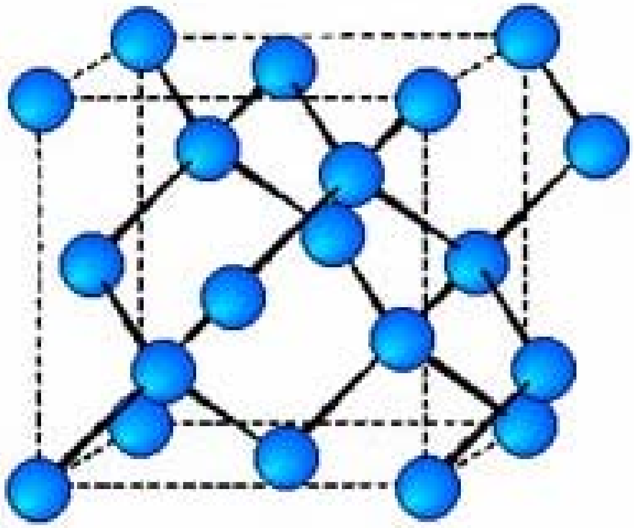
Diamond Structure

C, Si, Ge, α-Sn



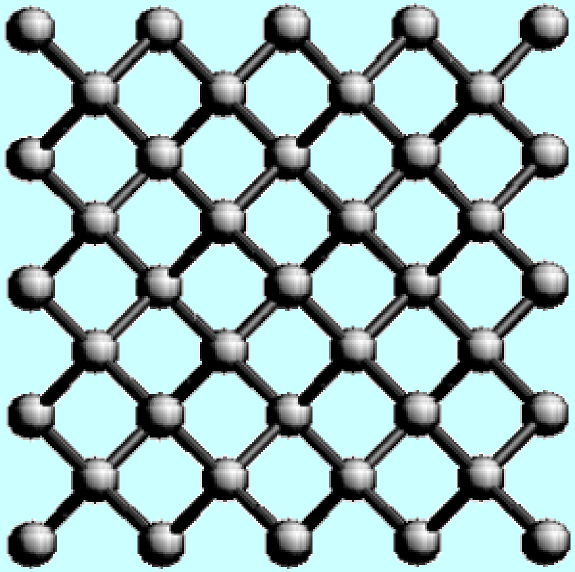
- Add 4 atoms to a FCC
- Tetrahedral bond arrangement
- Each atom has 4 nearest neighbors and 12 next nearest neighbors

Elements of the 14th Group

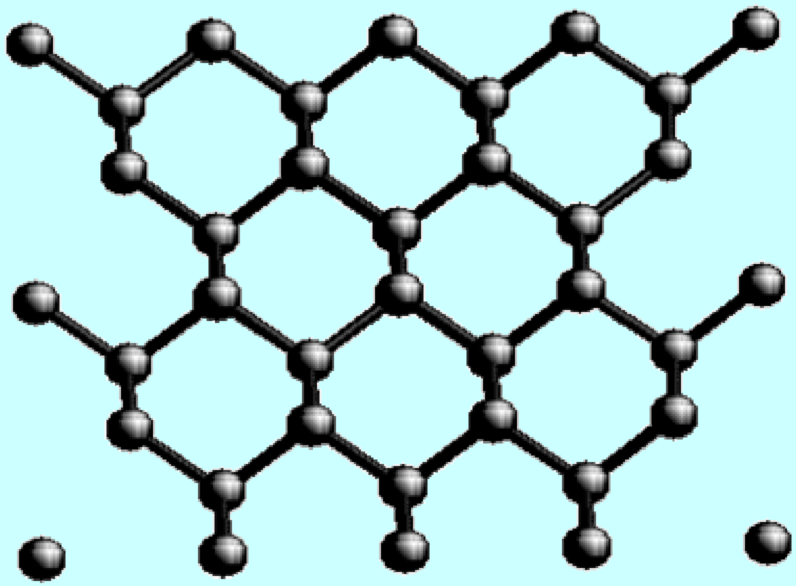


	a (Å)	d (g.cm^{-3})
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
a-Sn	6.489	7.285

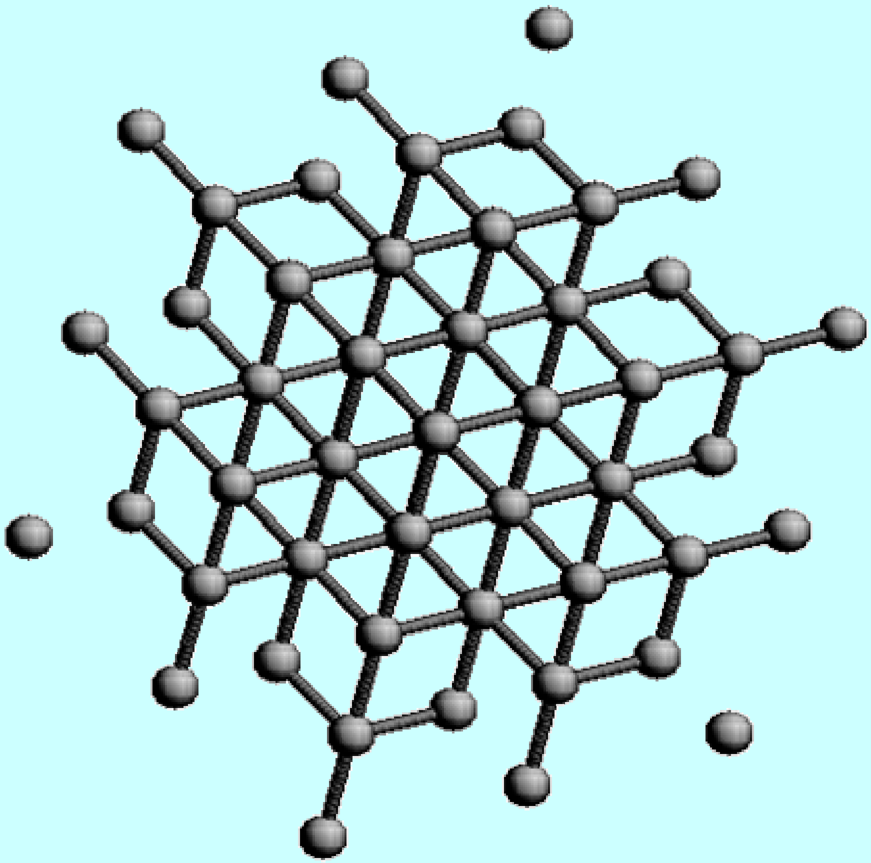
Diamond Lattice (100)



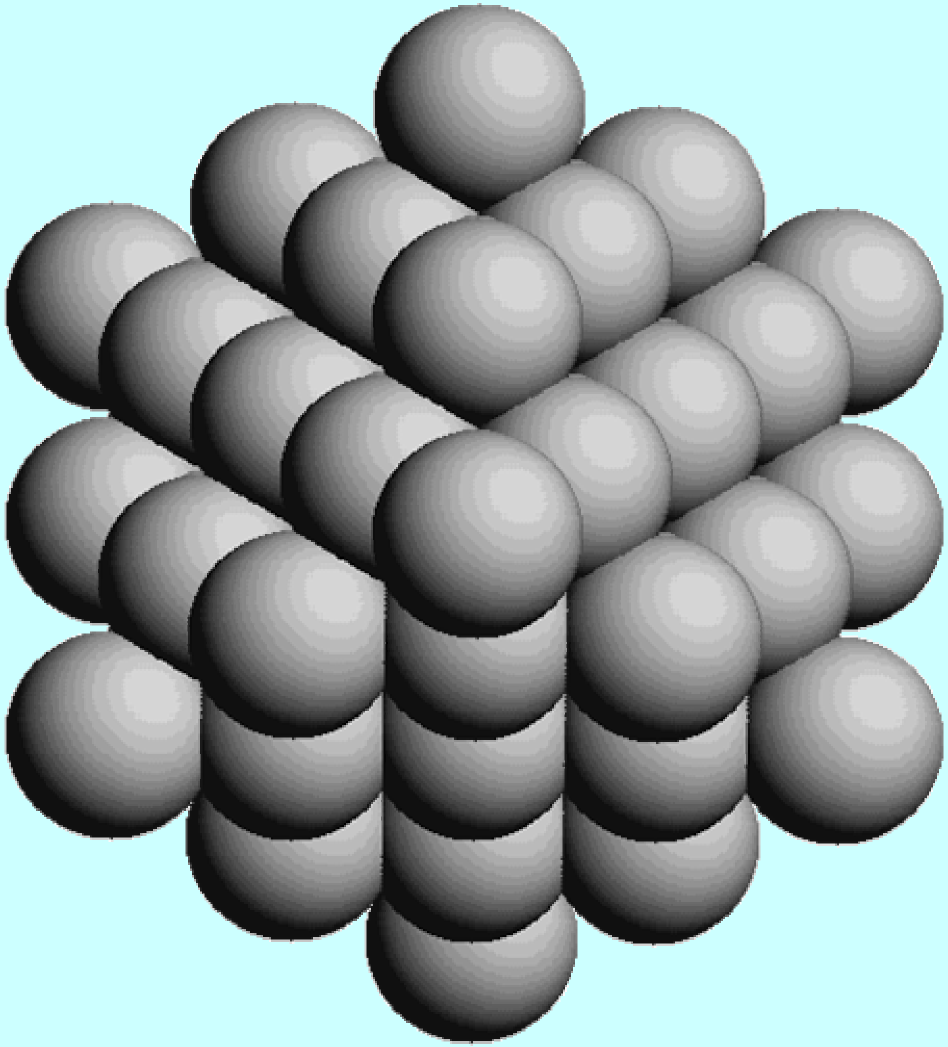
Diamond Lattice (110)



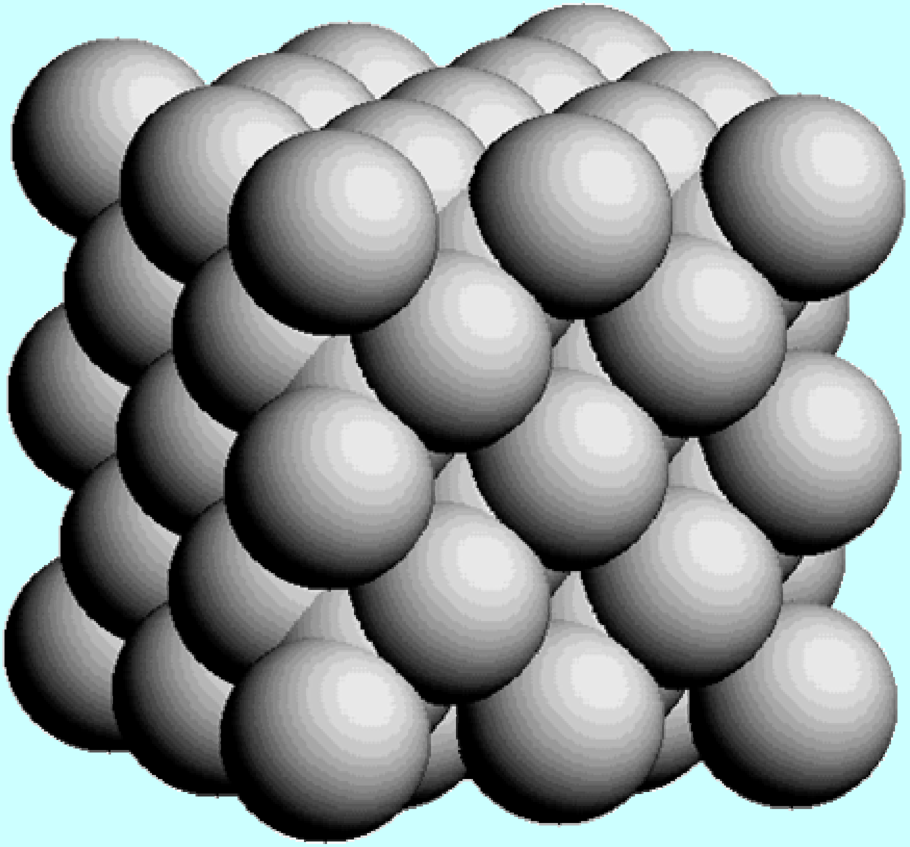
Diamond Lattice (111)



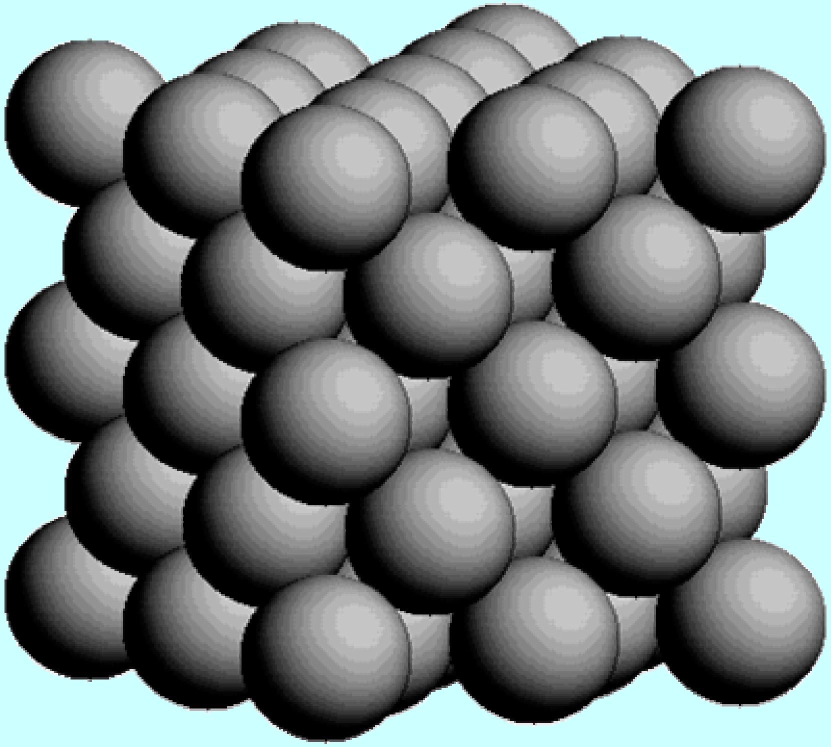
Diamond Lattice (111) Hard Sphere Model



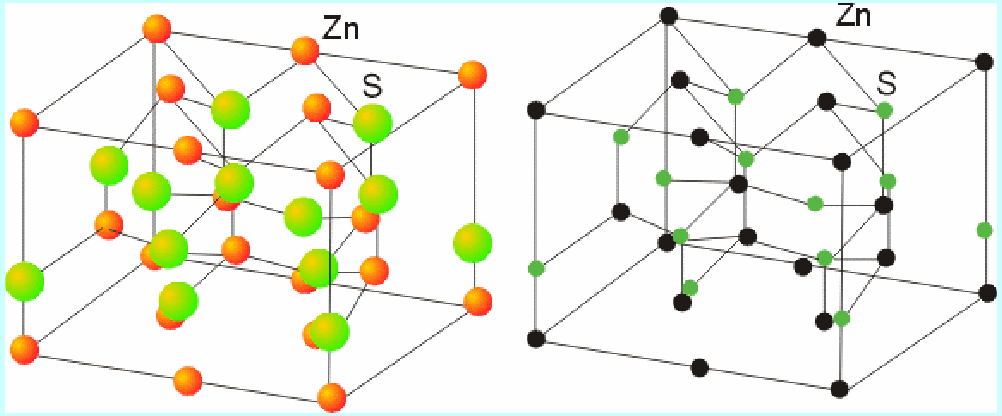
Diamond Lattice (111) Hard Sphere Model

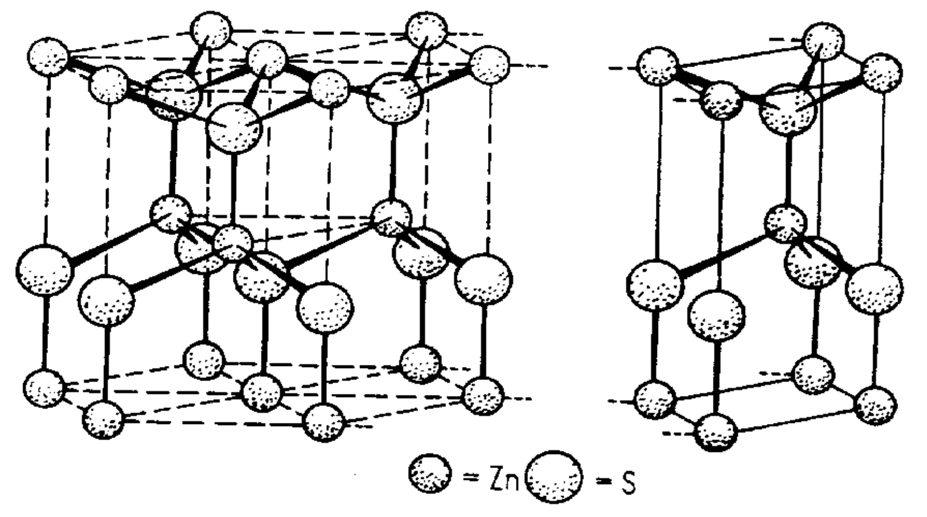


Face Centered Cubic Lattice (111) Hard Sphere Model



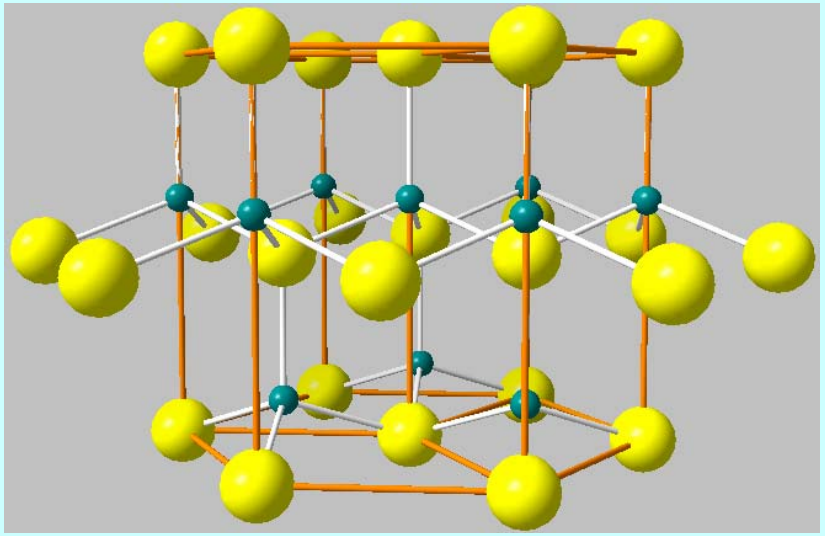
Wurzite, ZnS





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

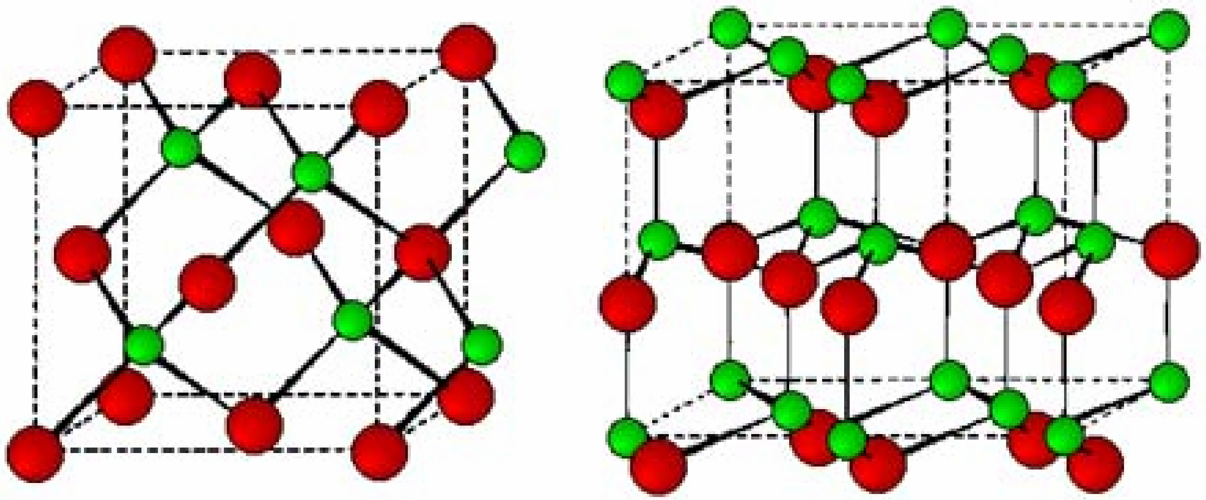
Wurzite, ZnS



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

Semiconductors of 13-15 and 12-16 type

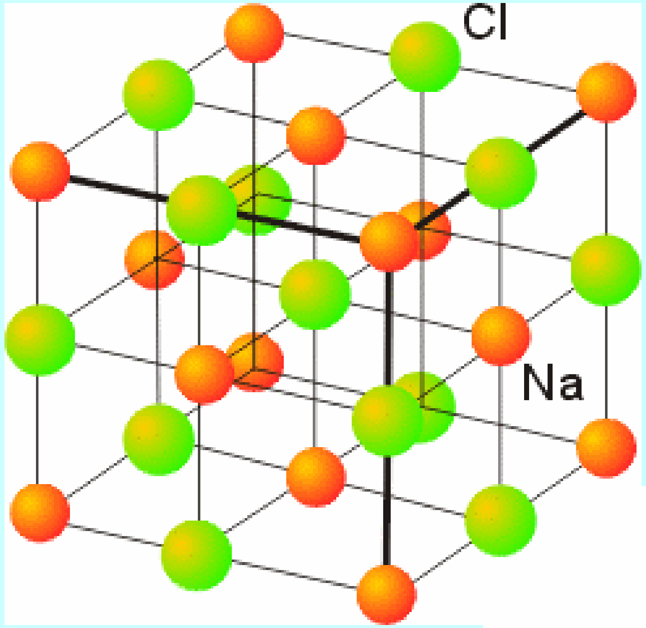
Structure of III-V and II-VI Compound Semiconductors

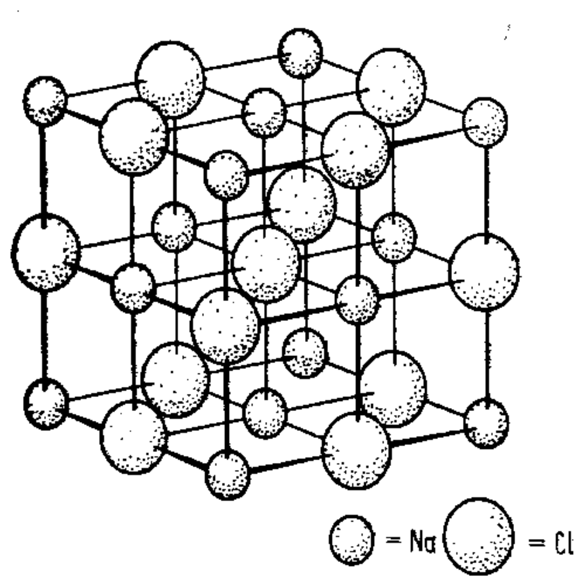


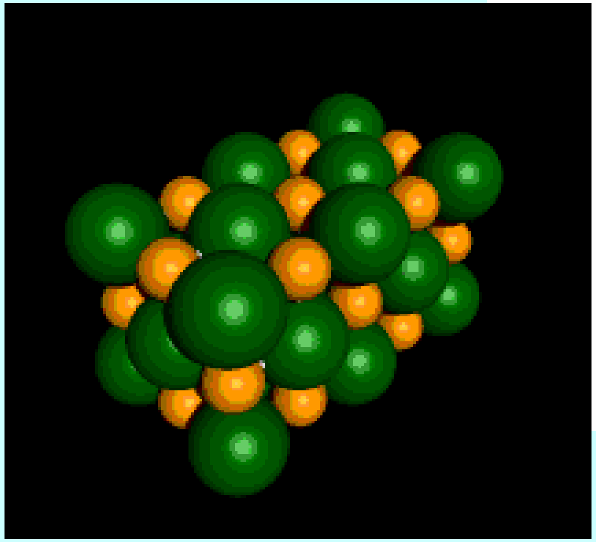
Zinc blende

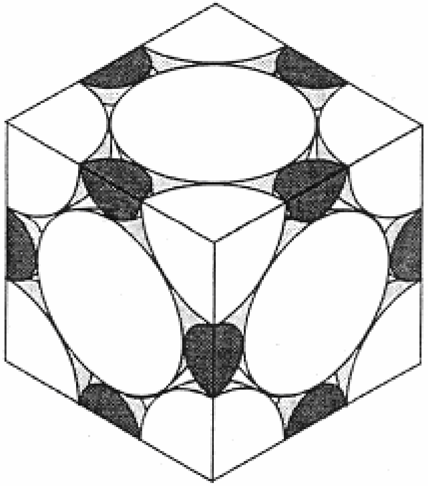
Wurtzite

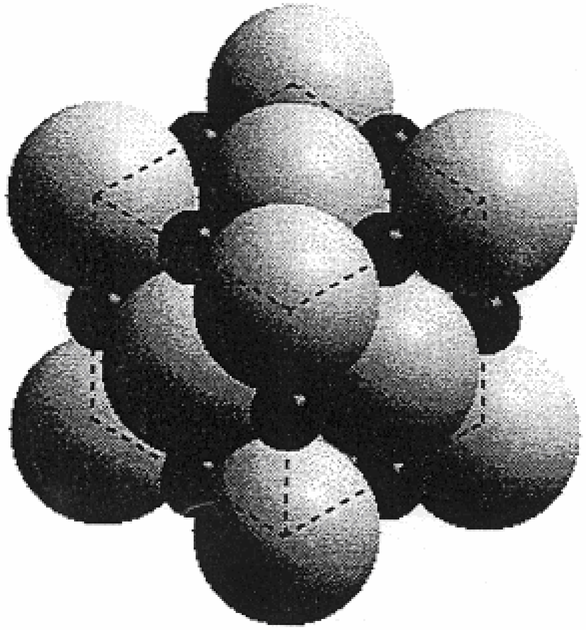
Rock Salt, NaCl





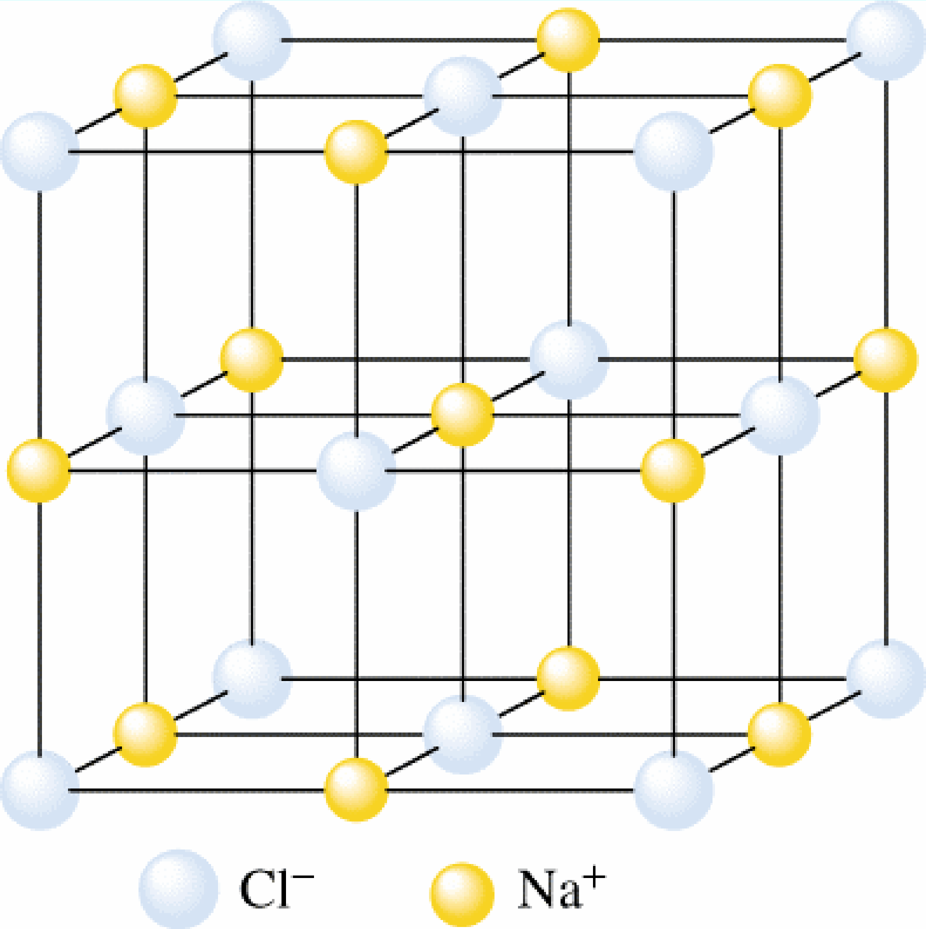


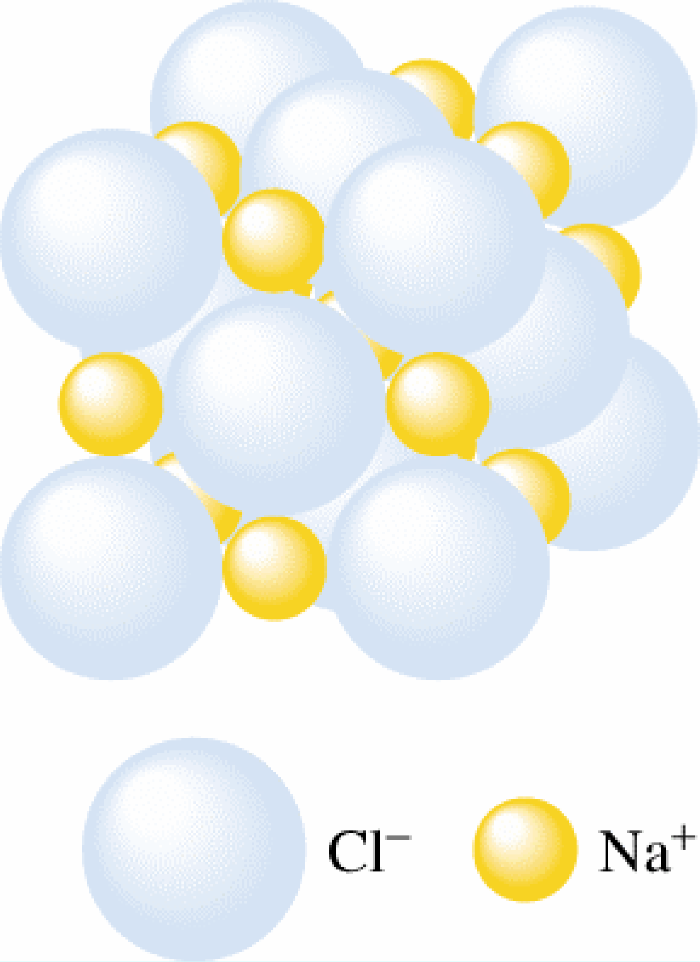




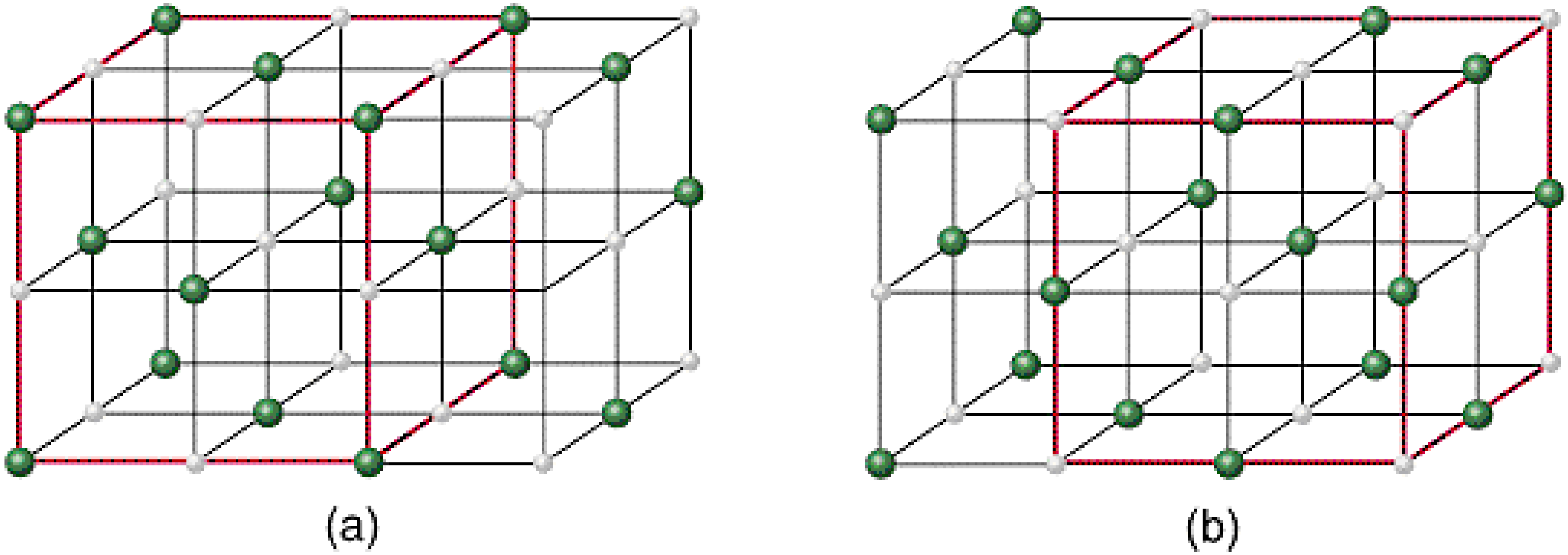
Cubic close packing of anions with all octahedral holes filled by cations

Rock Salt, NaCl



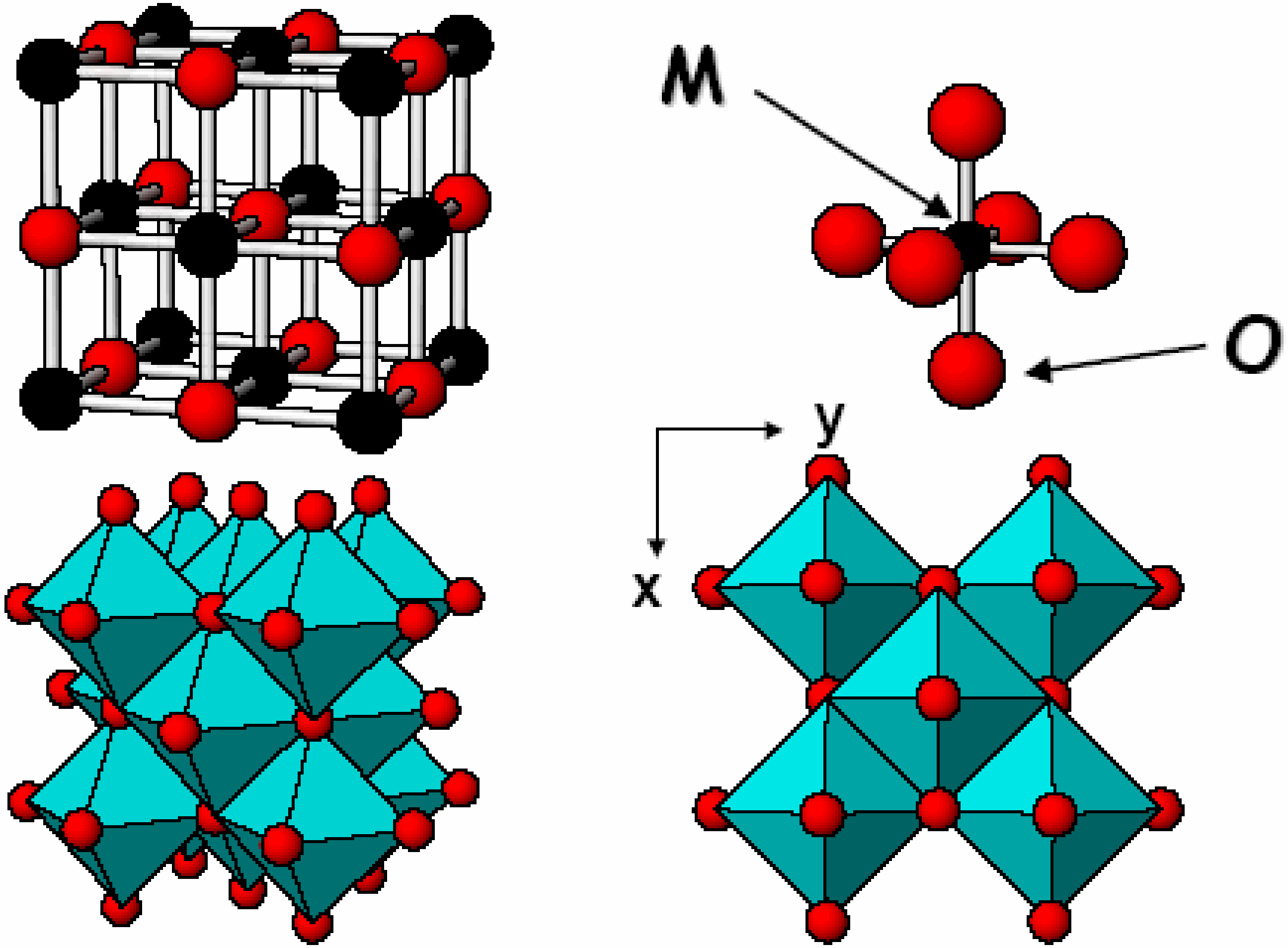


Rock Salt, NaCl

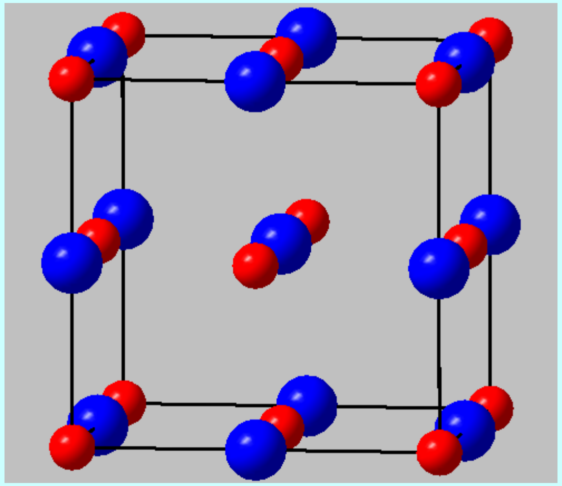


Anion and cation sublattices

Rock Salt Crystal Structure



Rock salt structures (NaCl)



Hydrides: LiH, NaH, KH

Borides: ZrB, HfB

Carbides: TiC, ZrC, VC, UC

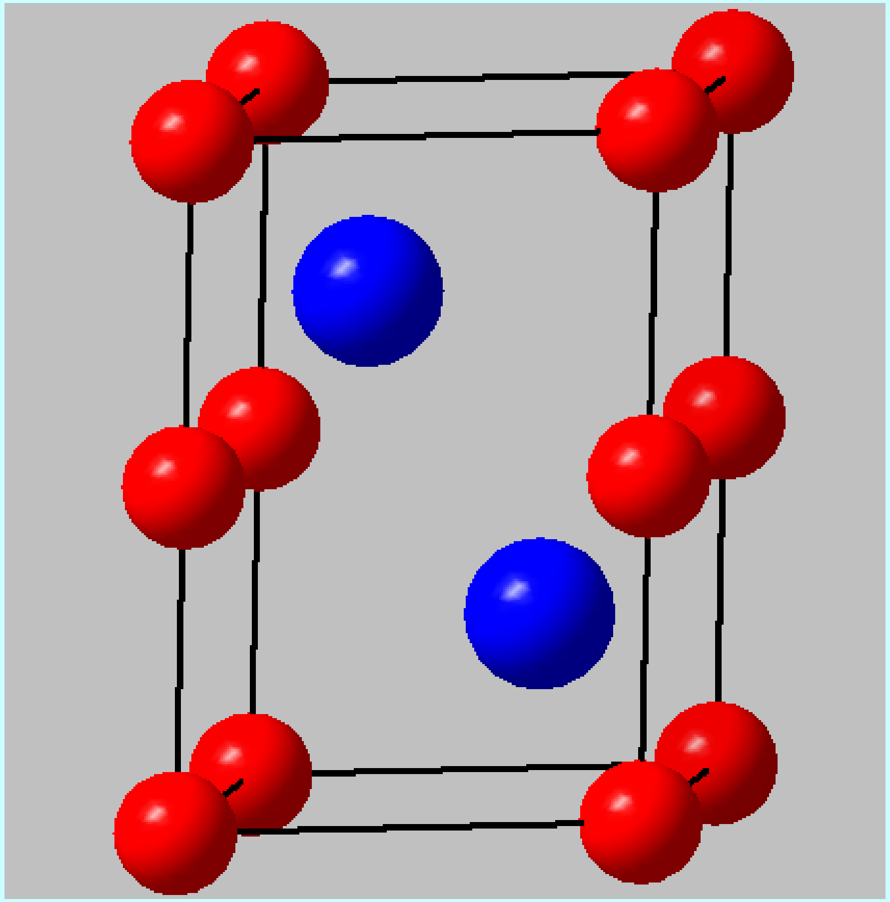
Nitrides: ScN, TiN, UN, CrN, VN, ZrN

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

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

Intermetallics: SnAs
Other
FeS_2 (pyrite), CaC_2

NiAs - type

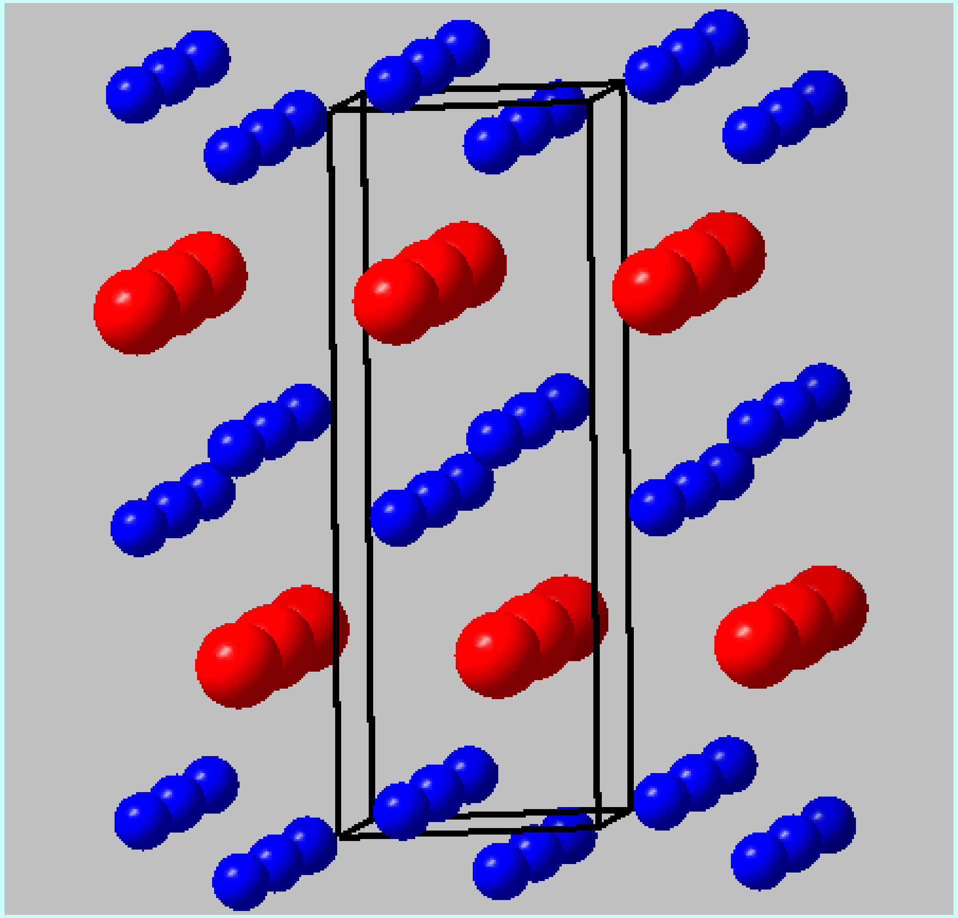


Hexagonal close packing of anions with all octahedral holes filled by cations

NiS, NiAs, NiSb, NiSe, NiSn, NiTe, FeS, FeSe, FeTe, FeSb, PtSn, CoS, CoSe, CoTe, CoSb, CrSe, CrTe, CoSb,

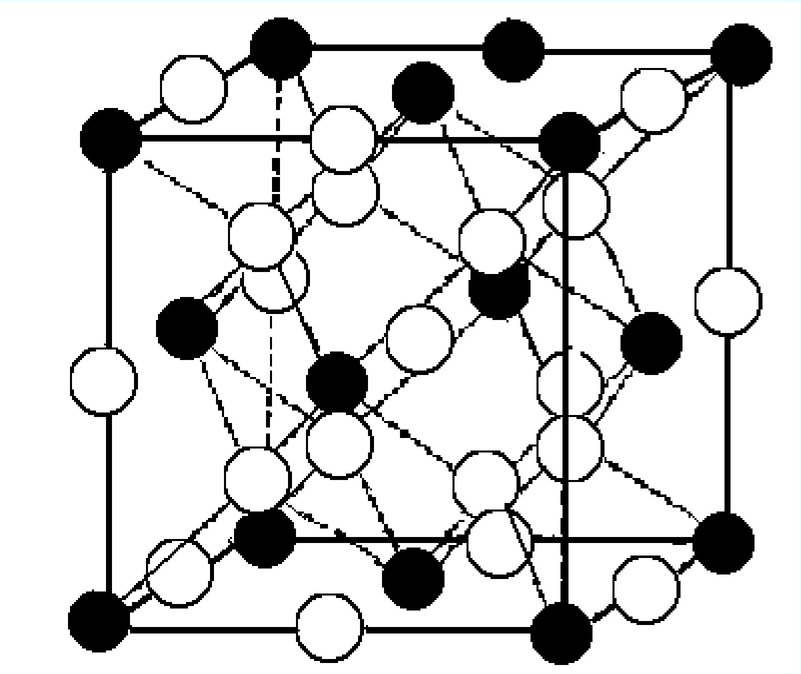
PtB (anti-NiAs structure)

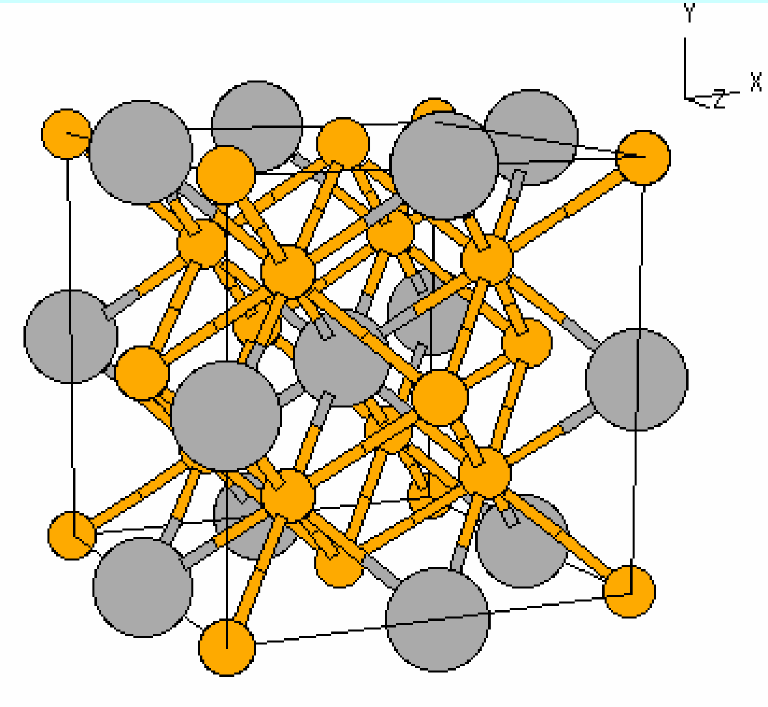
ReB_2 - type



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

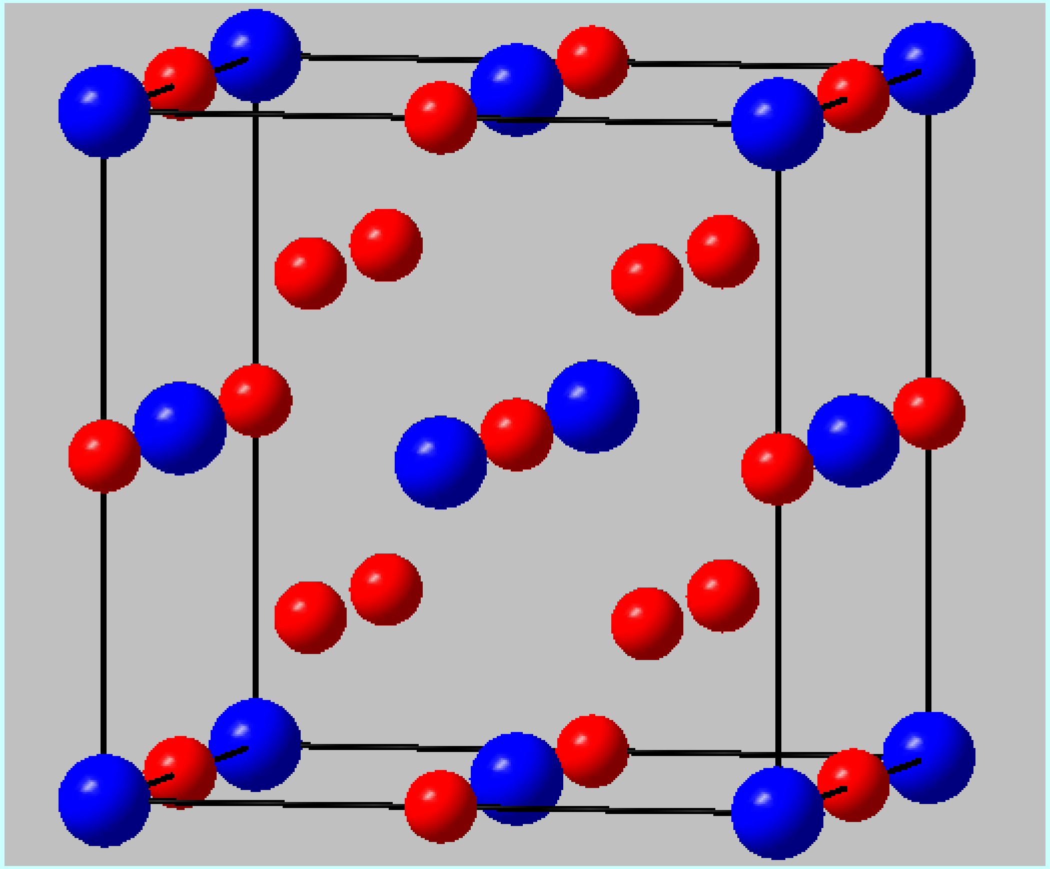
Li_3Bi - type (anti BiF_3)





$[Cr(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$
bcc

Li_3Bi - type (anti BiF_3)

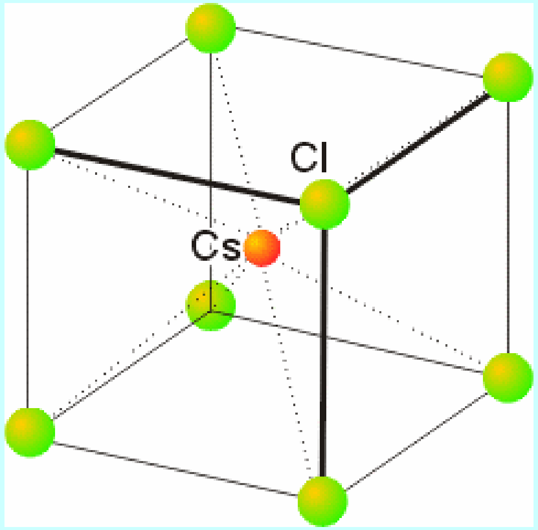


Fe_3Al

$[Cr(NH_3)_6]Cl_3$

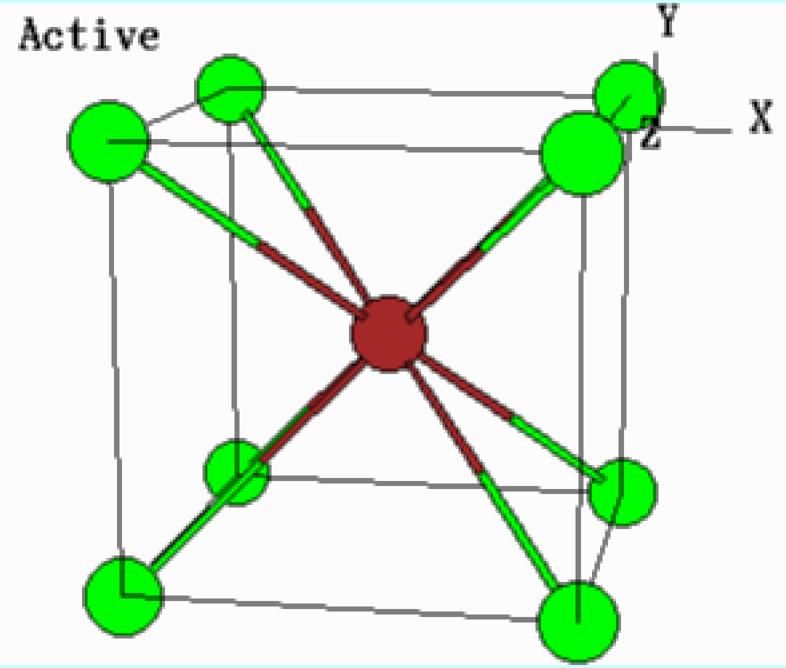
$K_3[Fe(CN)_6]$

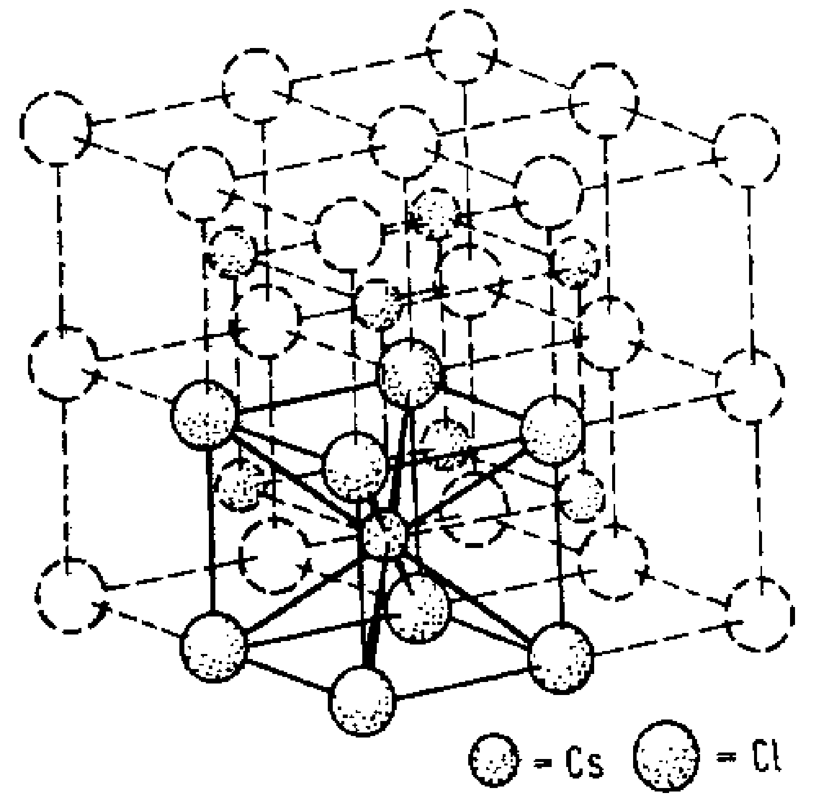
Cubic close packing of anions with all tetrahedral and octahedral holes filled by cations



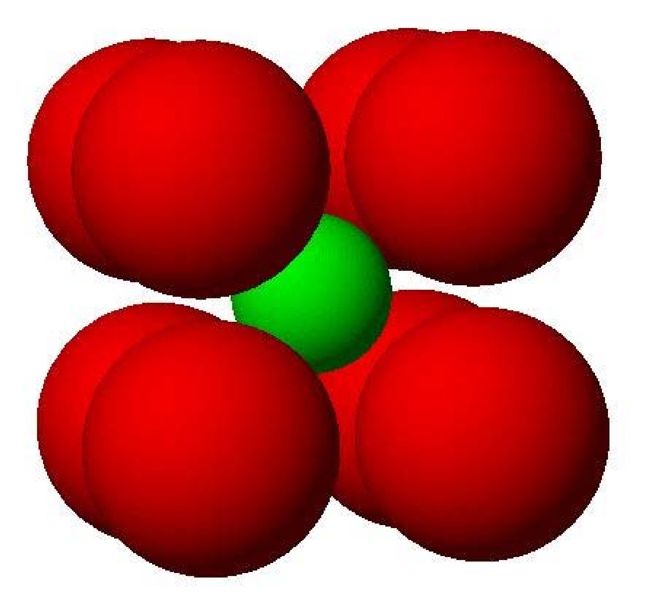
CsCl

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

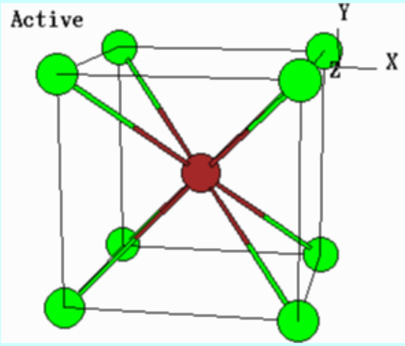


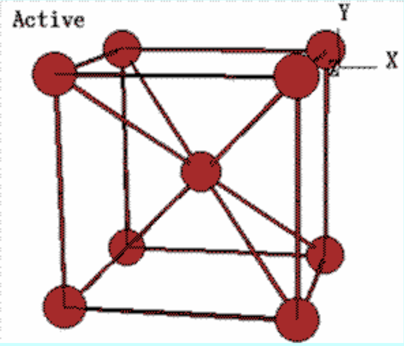


CsCl



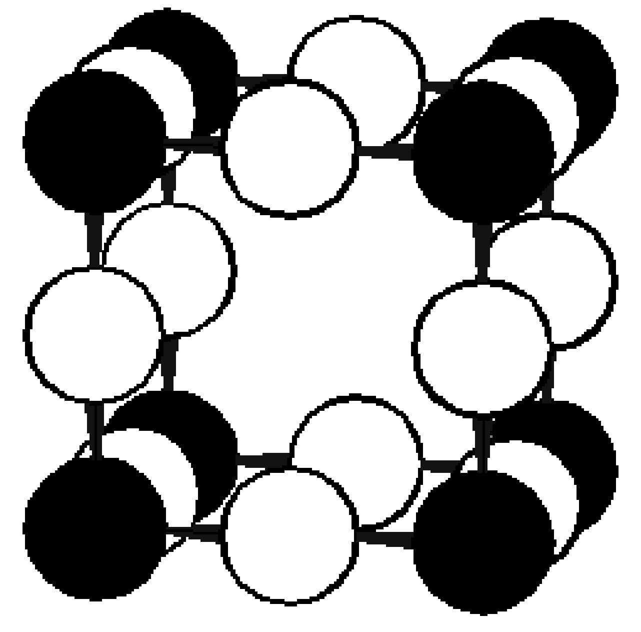
CsCl is not BCC

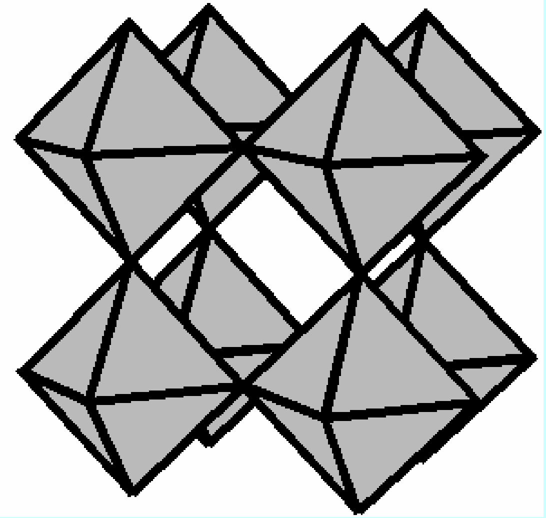




CsBr, CsI, CsCN, NH_4Cl, NH_4Br, TlCl, TlBr, TlI, CuZn, CuPd, LiHg

ReO_3





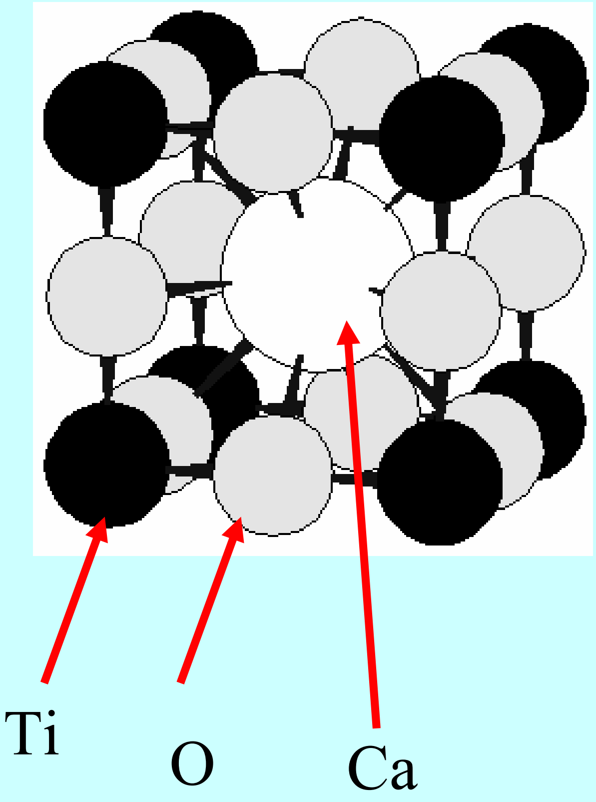
SC of ReO_6 octahedra

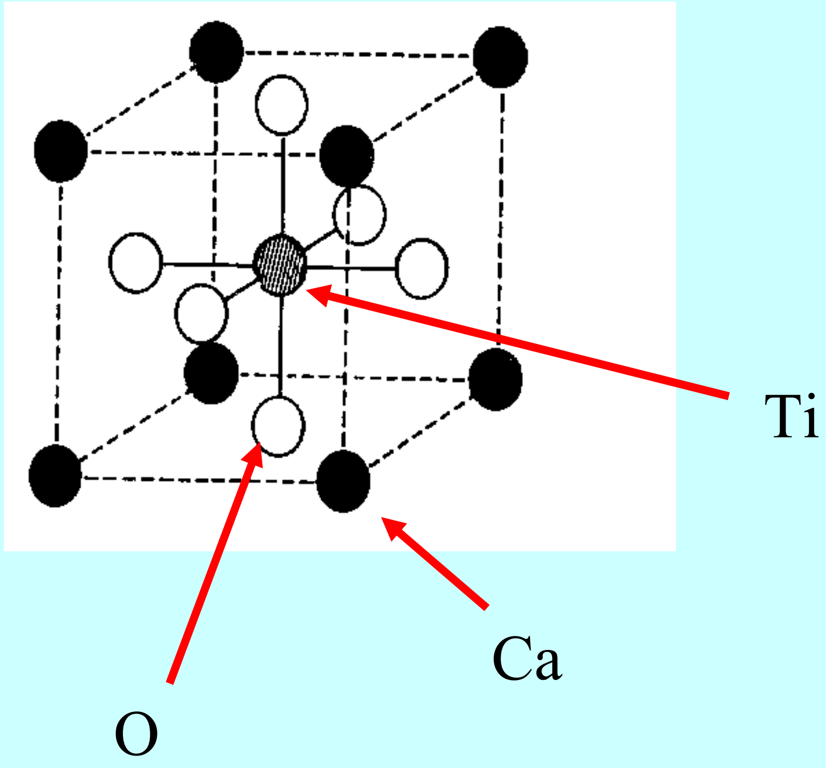
NaCl structure with 3/4 of cations removed and 1/4 of anions removed

UO_3, MoF_3, NbF_3, TaF_3, Cu_3N

Perovskite, $CaTiO_3$

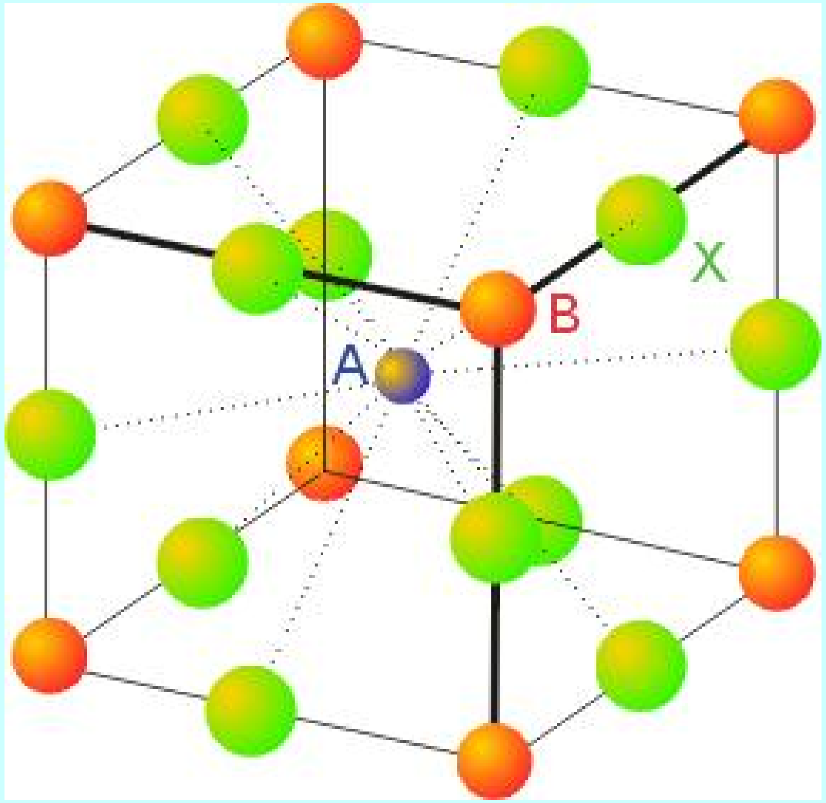
Two equvivalent views of the unit cell of perovskite





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

Perovskite structure $CaTiO_3$



TiO_6 – octahedra

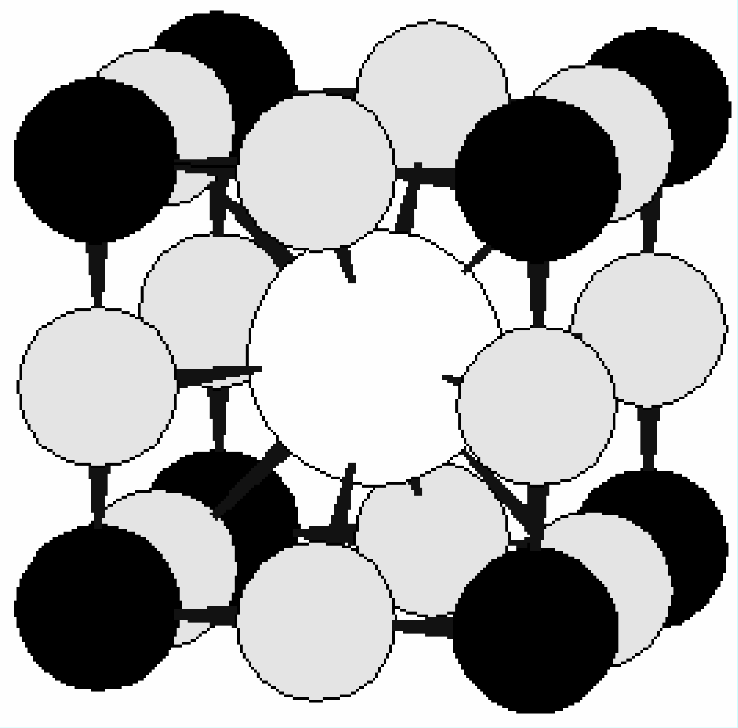
CaO_{12} – cuboctahedra

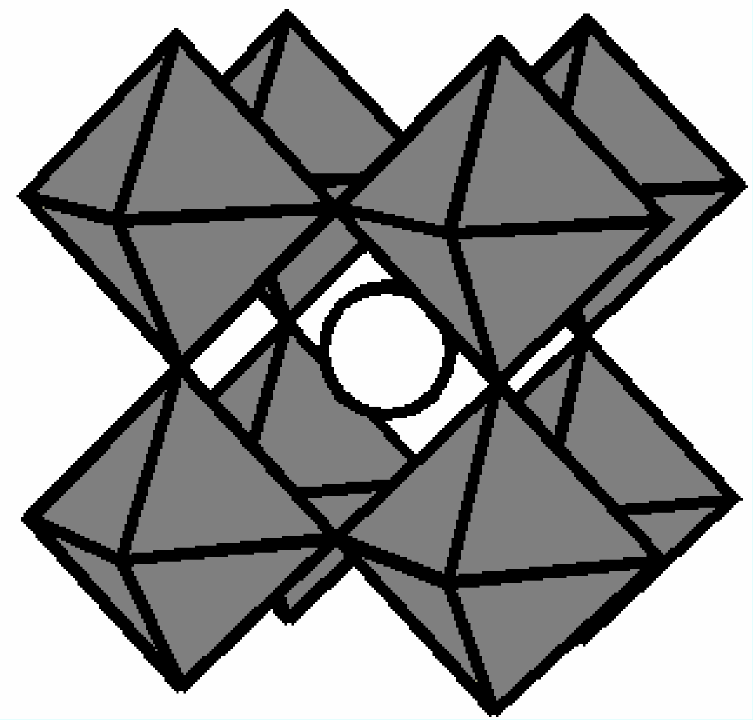
(Ca^{2+} and O^{2-} form a cubic close packing)

preferred structure of piezoelectric, ferroelectric and superconducting materials

Perovskite, $CaTiO_3$

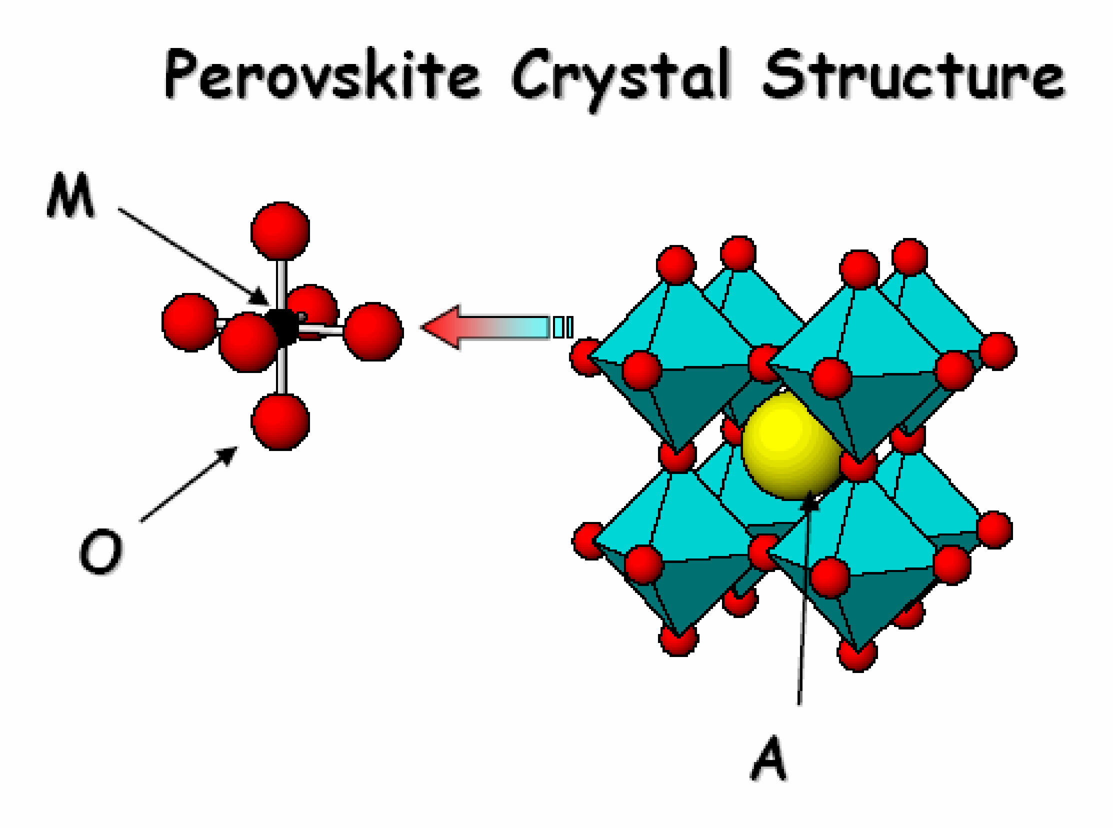
Cubic "close packing" of A and X with 1/4 octahedral holes filled by B cations





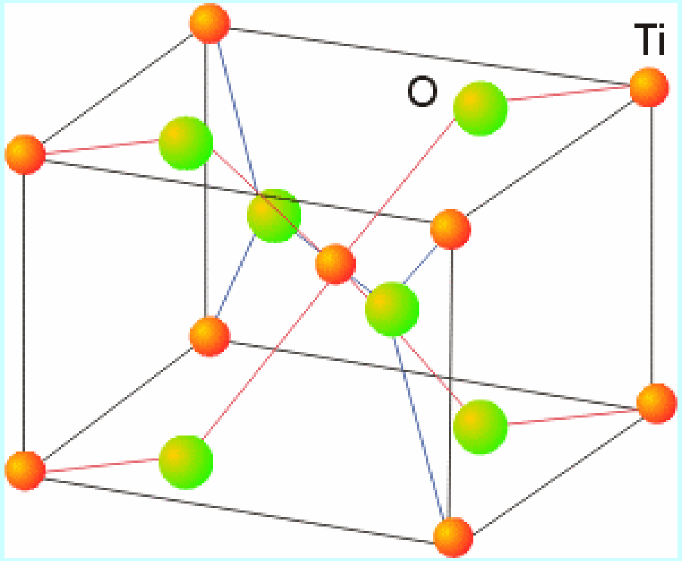
Similarity to CsCl

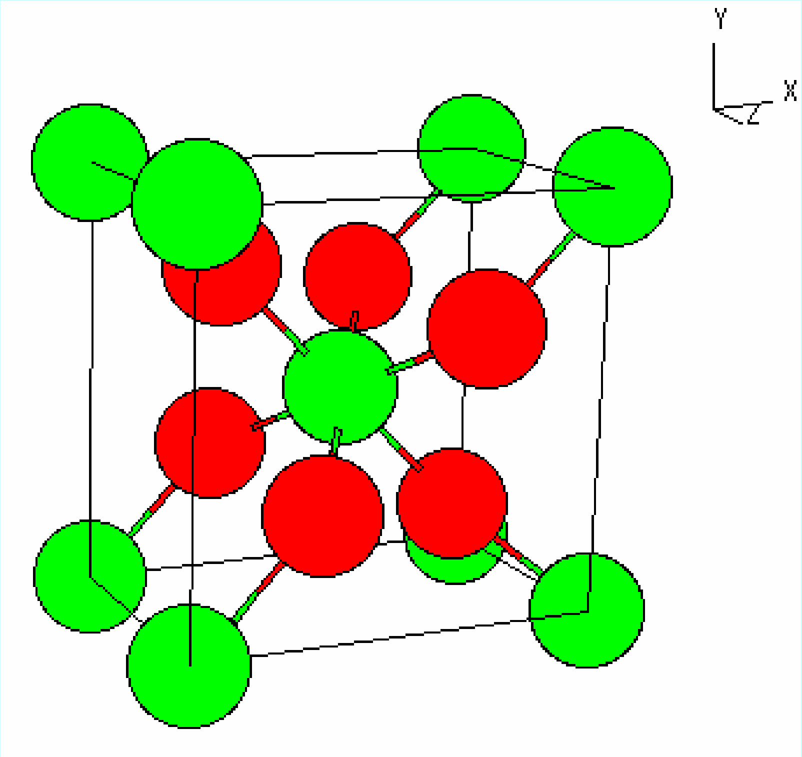
Perovskite, $CaTiO_3$



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

Rutile, TiO_2





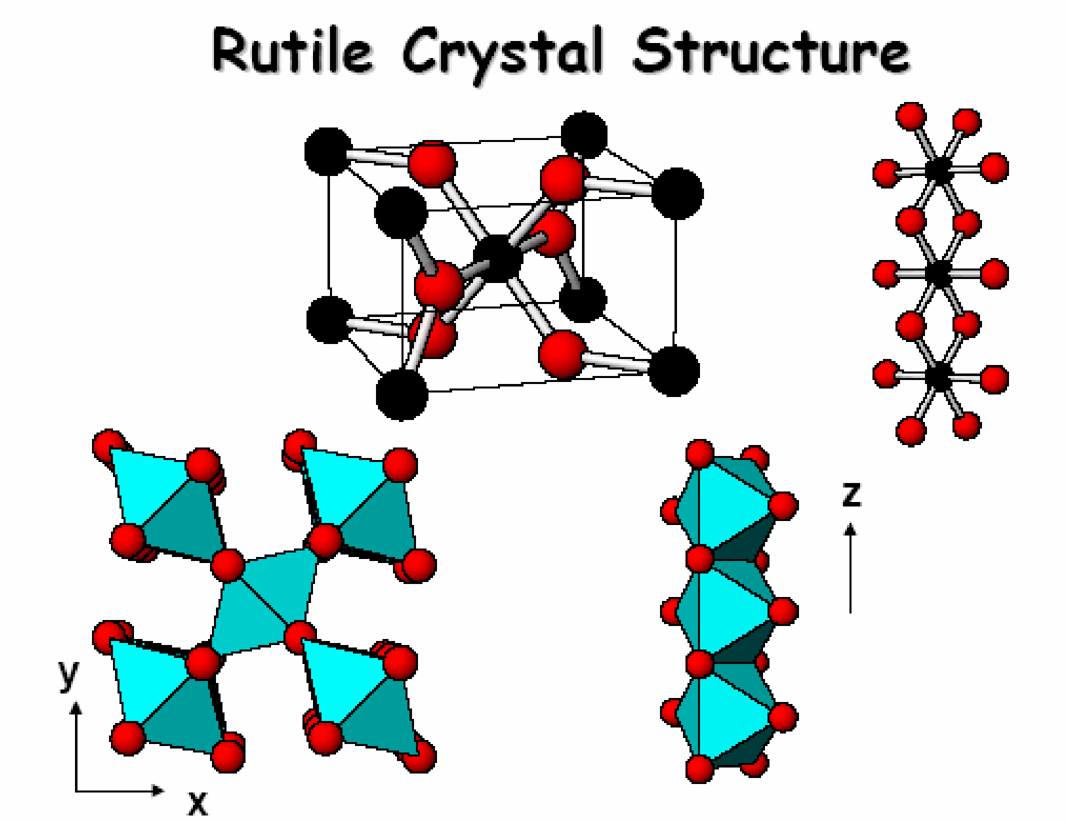
CN – stoichiometry Rule

A_xB_y

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

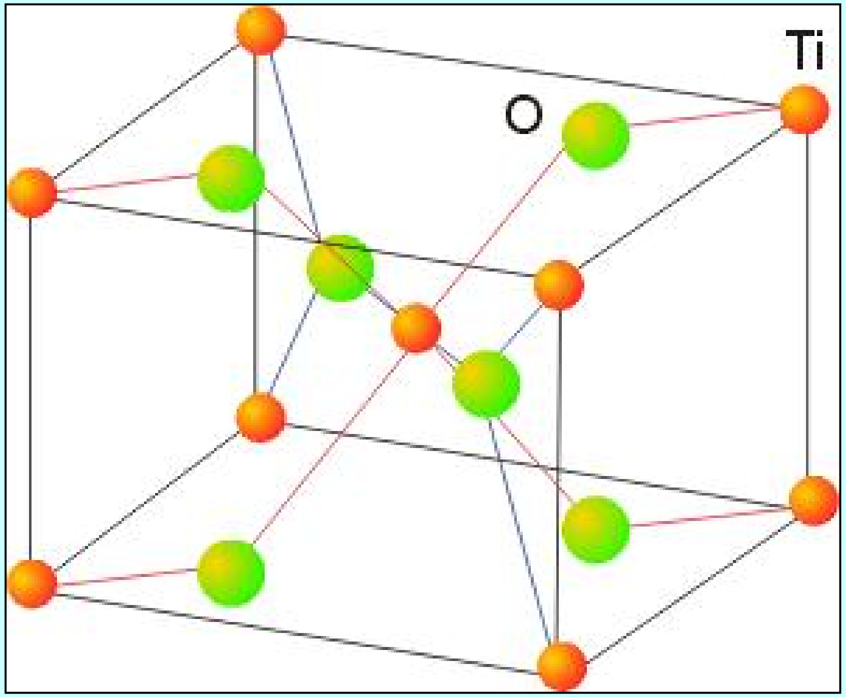
Distorted hexagonal close packing of anions with 1/2 octahedral holes filled by cations (giving a tetragonal lattice)

Rutile, TiO_2



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

The rutile structure: TiO_2

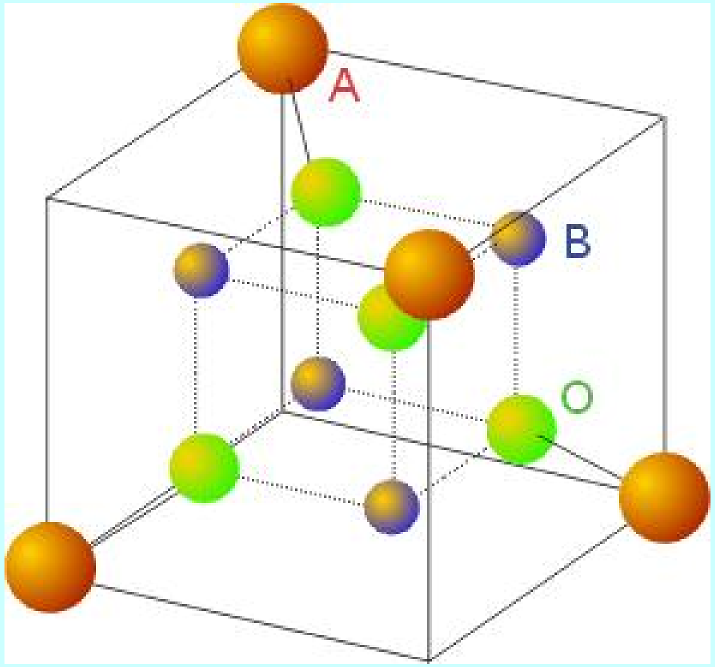


TiO_6 – octahedra

OTi_3 – trigonal planar

(alternative to CaF_2 for highly charged smaller cations)

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

Spinel

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, $FeCo_2O_4$.

Layered Structures

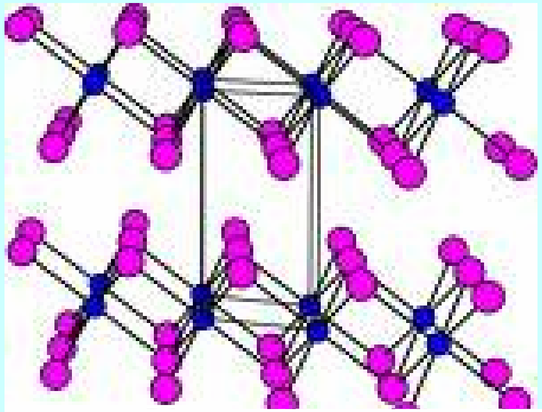
CdI_2 Hexagonal close packing of anions with 1/2 octahedral holes filled by cations

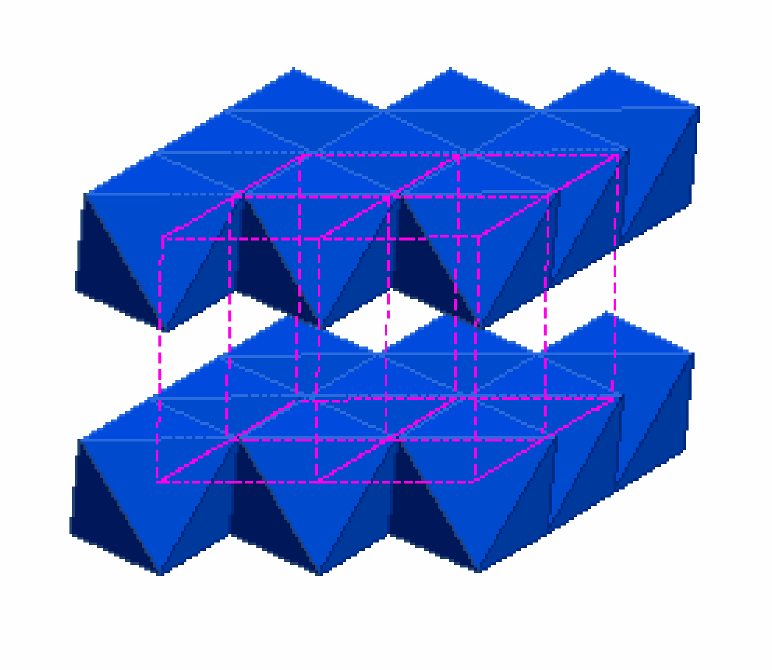
CoI_2, FeI_2, MgI_2, MnI_2, PbI_2, ThI_2, TiI_2, TmI_2, VI_2, YbI_2, ZnI_2, VBr_2, $TiBr_2$, $MnBr_2$, $FeBr_2$, $CoBr_2$, $TiCl_2$, TiS_2., TaS_2.

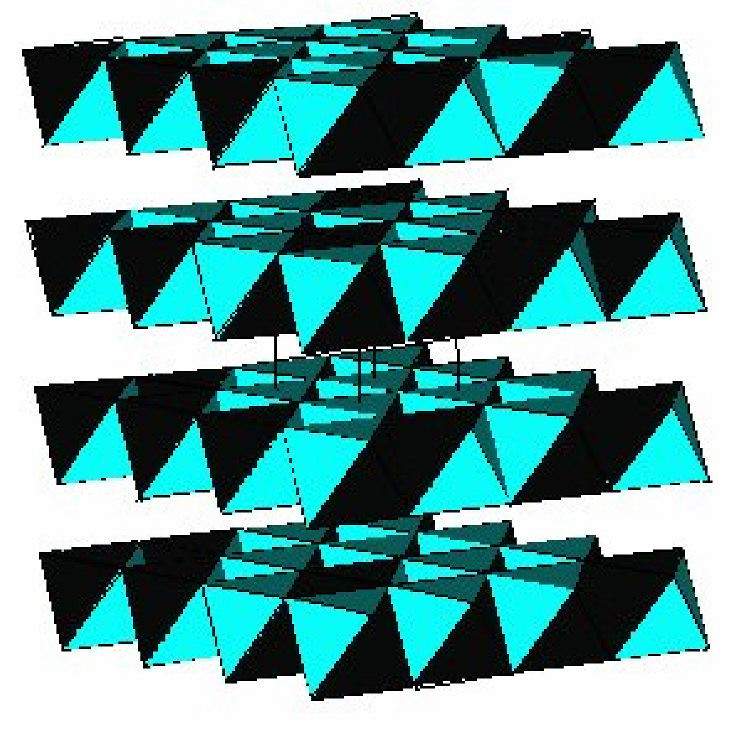
$CdCl_2$ Cubic close packing of anions with 1/2 octahedral holes filled by cations

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

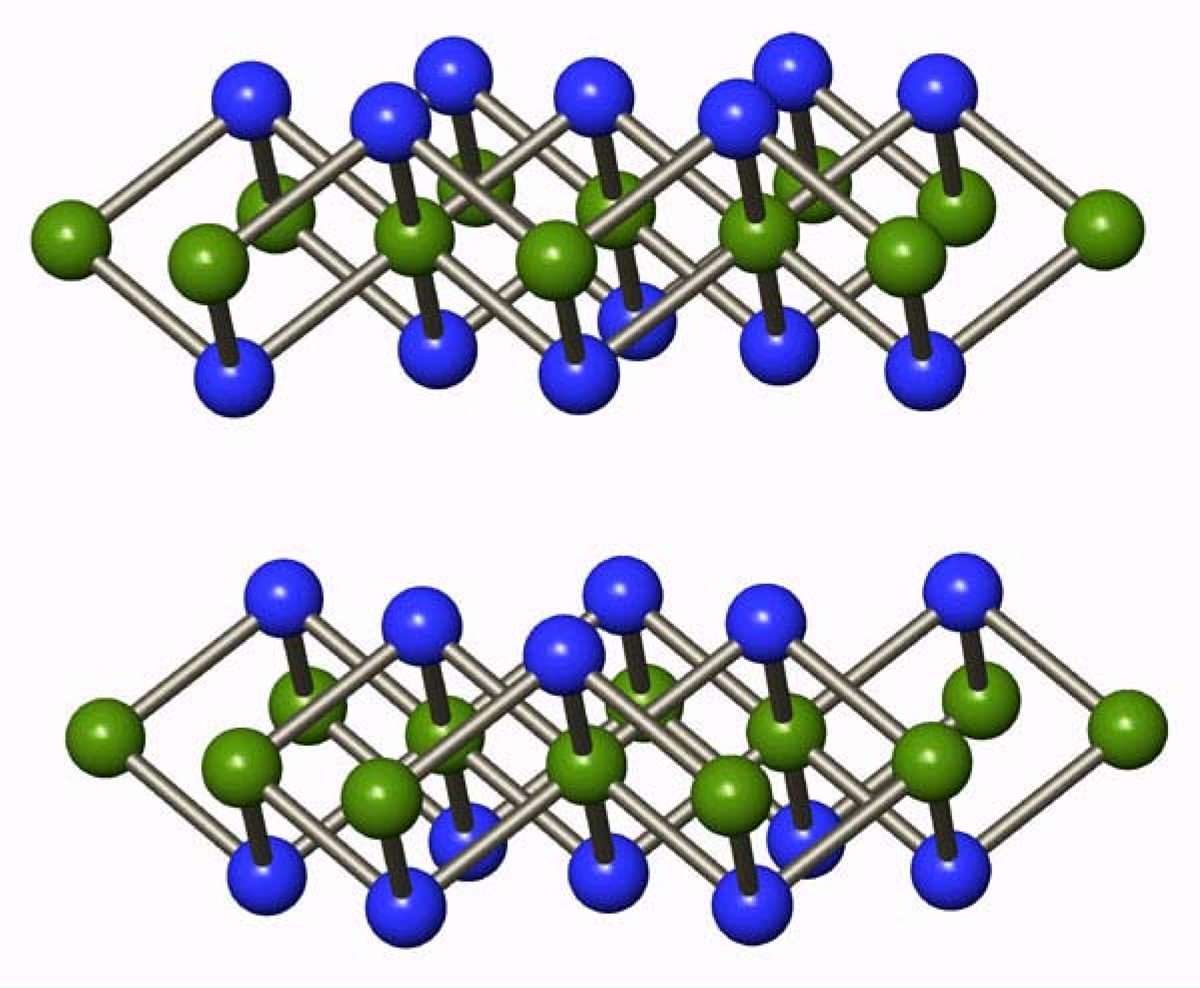
CdI_2 Hexagonal close packing



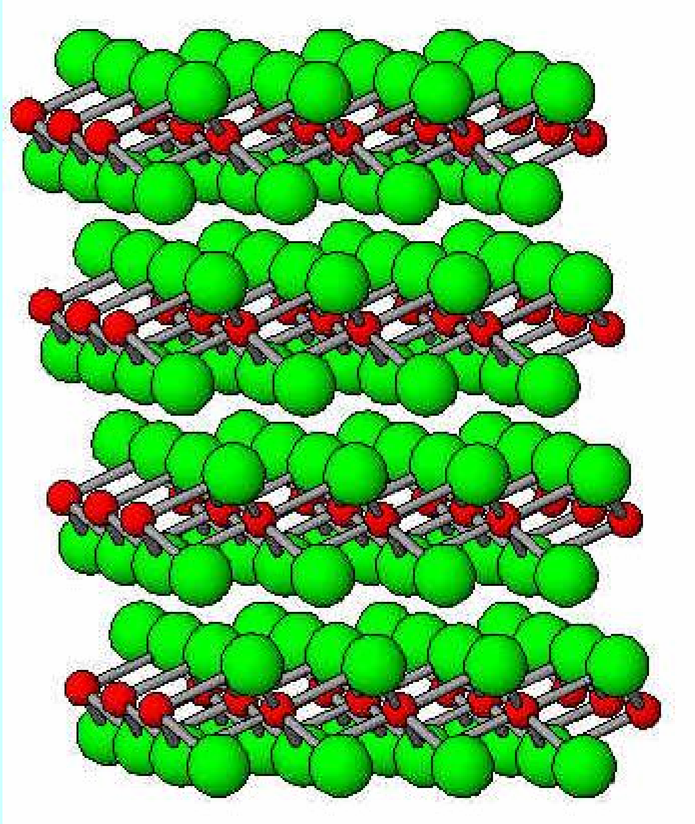


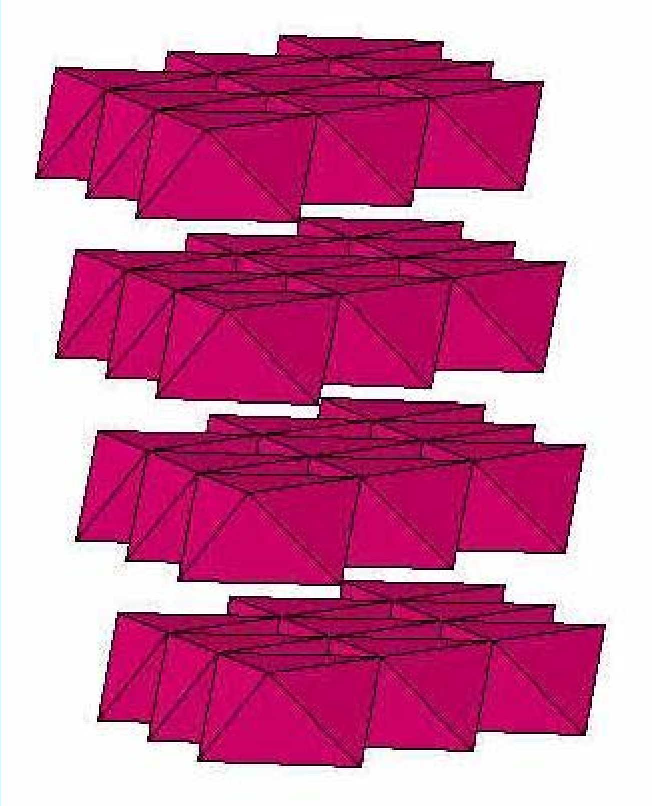


$CdCl_2$ Cubic close packing

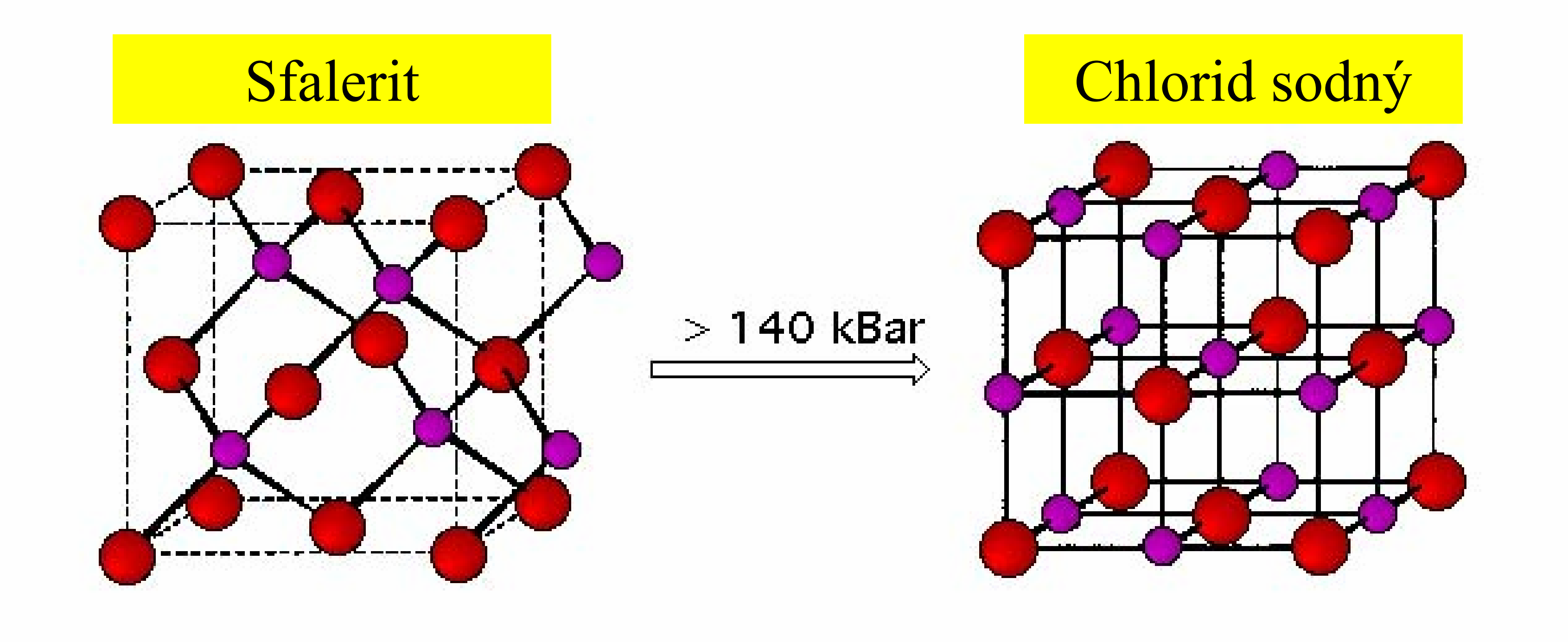


$CdCl_2$ Cubic close packing





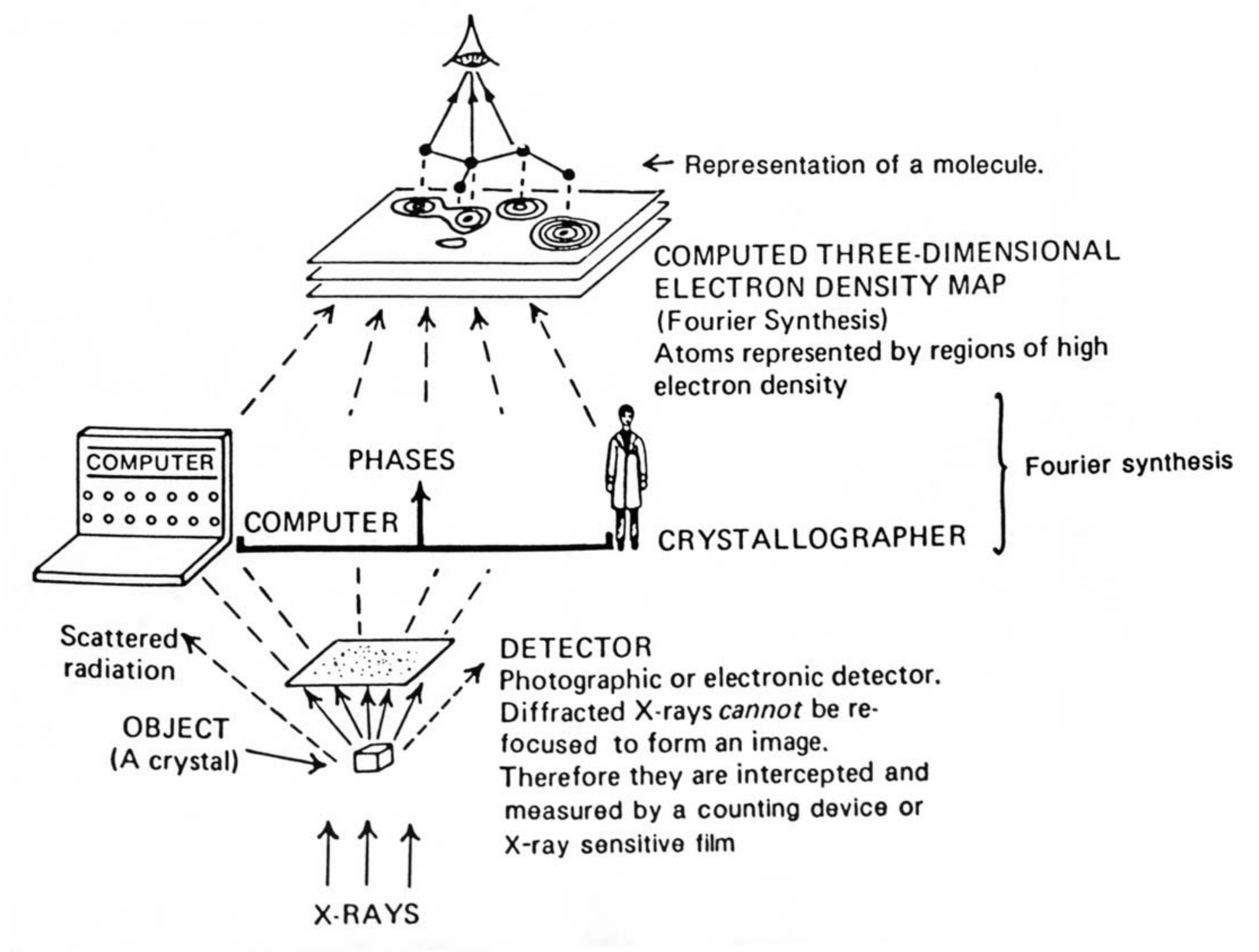
Fázové přeměny za zvýšeného tlaku



Důsledky zvýšení tlaku

- Zvýšení koordinačního čísla
- Zvýšení hustoty
- Prodloužení vazebných délek
- Přechod ke kovovým modifikacím

X-ray structure analysis with single crystals

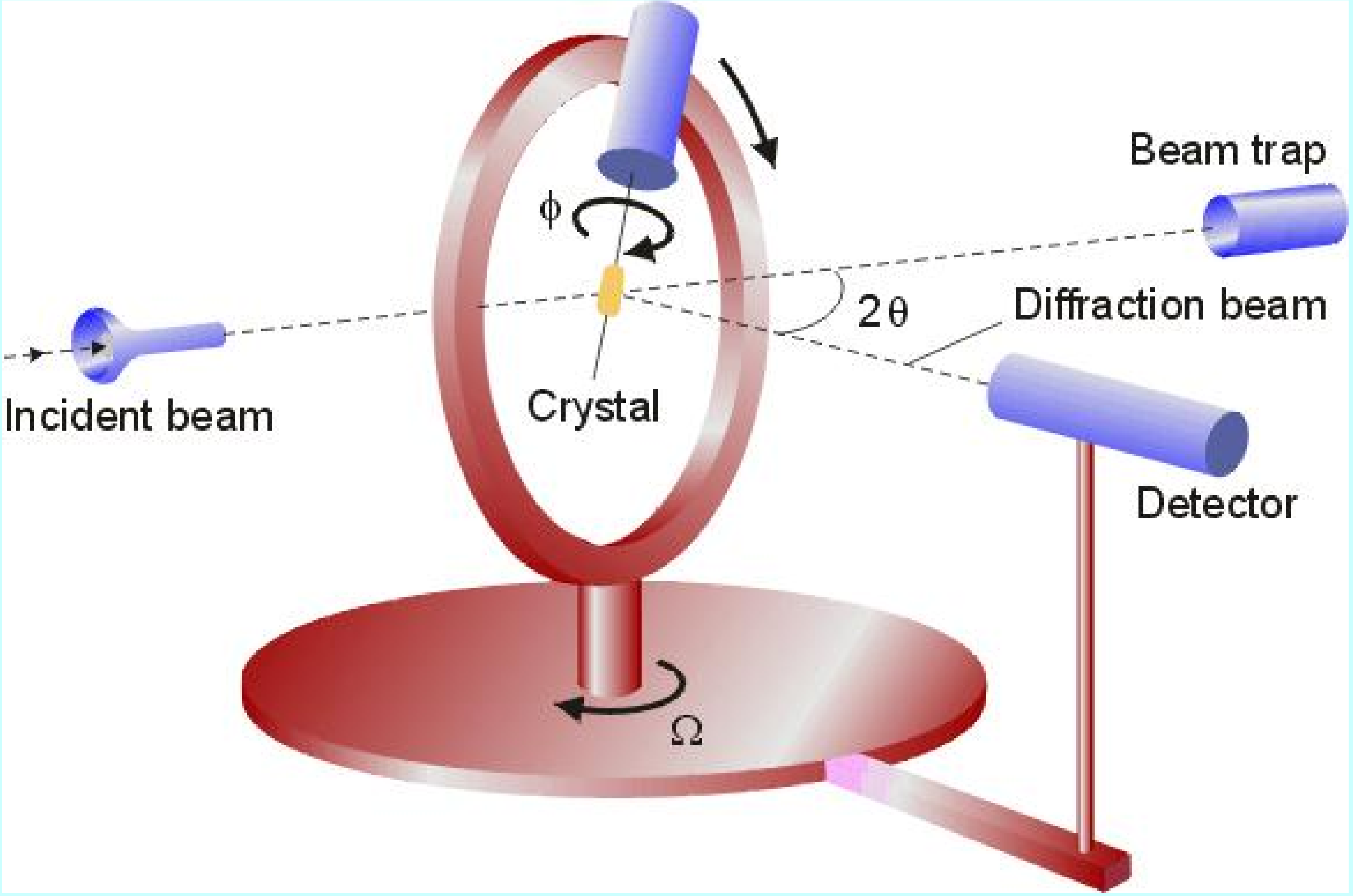


Representation of a molecule.

COMPUTED THREE-DIMENSIONAL ELECTRON DENSITY MAP (Fourier Synthesis)
Atoms represented by regions of high electron density

DETECTOR
Photographic or electronic detector.
Diffracted X-rays *cannot* be refocused to form an image.
Therefore they are intercepted and measured by a counting device or X-ray sensitive film

Principle of a four circle X-ray diffractometer for single crystal structure analysis



CAD4 (Kappa Axis Diffractometer)

IPDS (Imaging Plate Diffraction System)