Basic Structural Chemistry

Crystalline state

Structure types

Degree of Crystallinity

Amorphous · Short-range Ordered · Crypto-crystalline · Micro-crystalline · Para-crystalline · Crystalline

Less Structural Order   More Structural Order
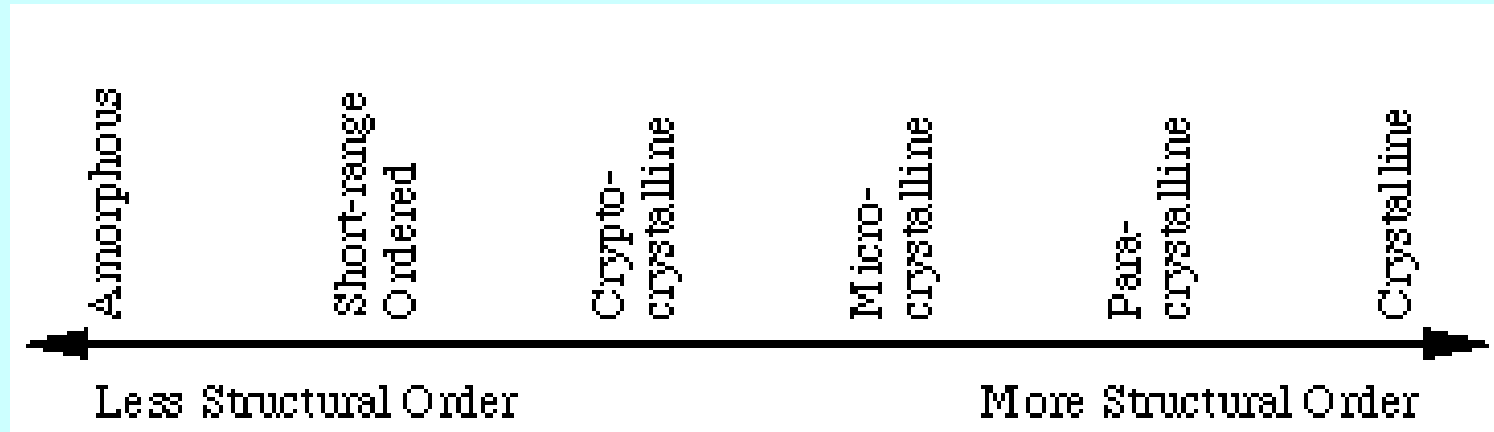
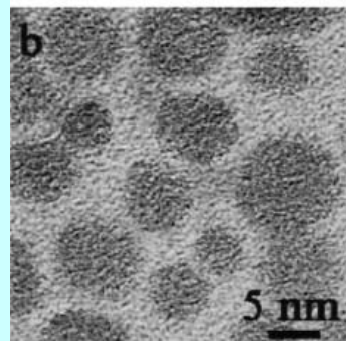**Crystalline – 3D long range order**
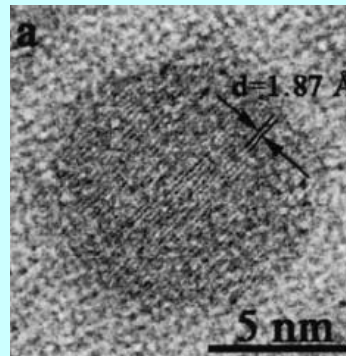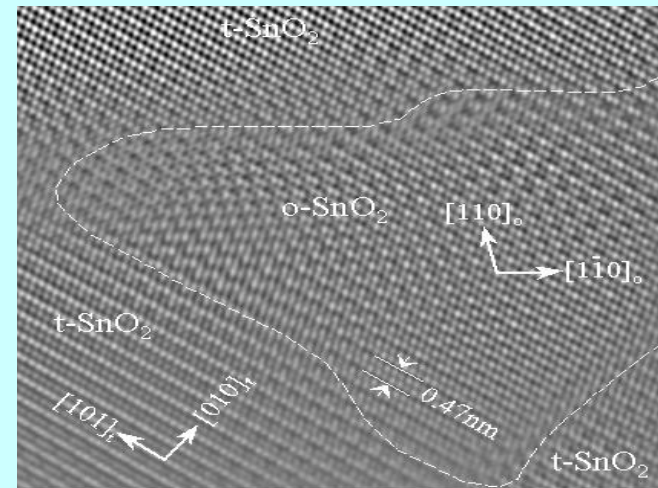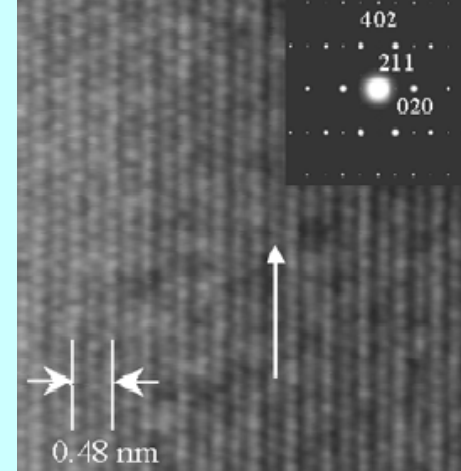 **Single-crystalline**
  Polycrystalline - many crystallites of different sizes and orientations
                (random, oriented)

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

Amorphous – no order, random
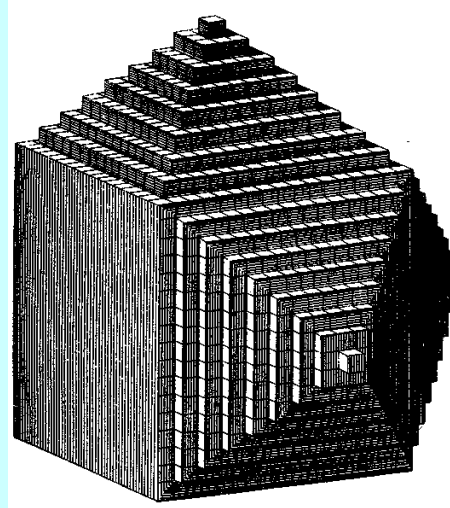
Degree of Crystallinity

- Single Crystalline

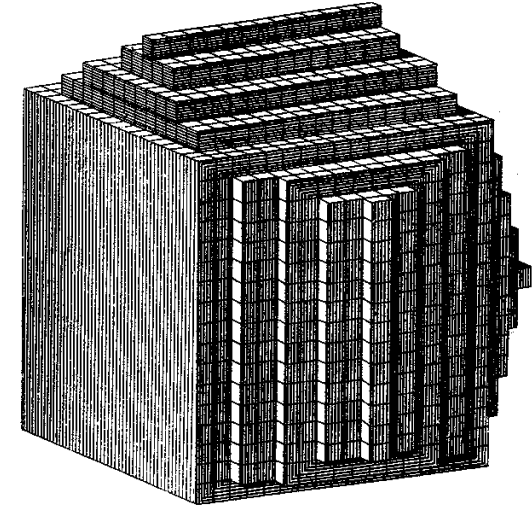- Polycrystalline

- Semicrystalline
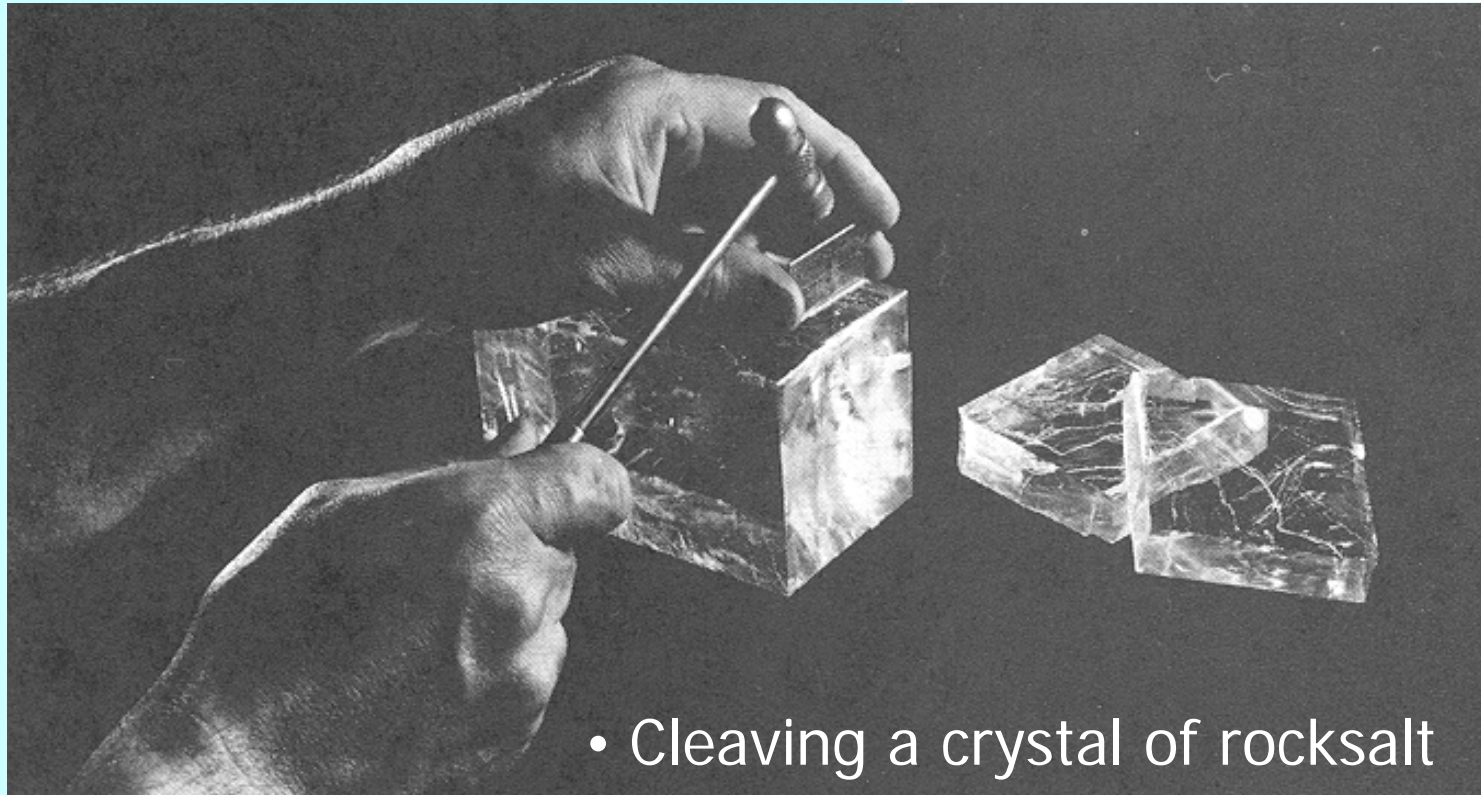
- Amorphous

Grain boundaries

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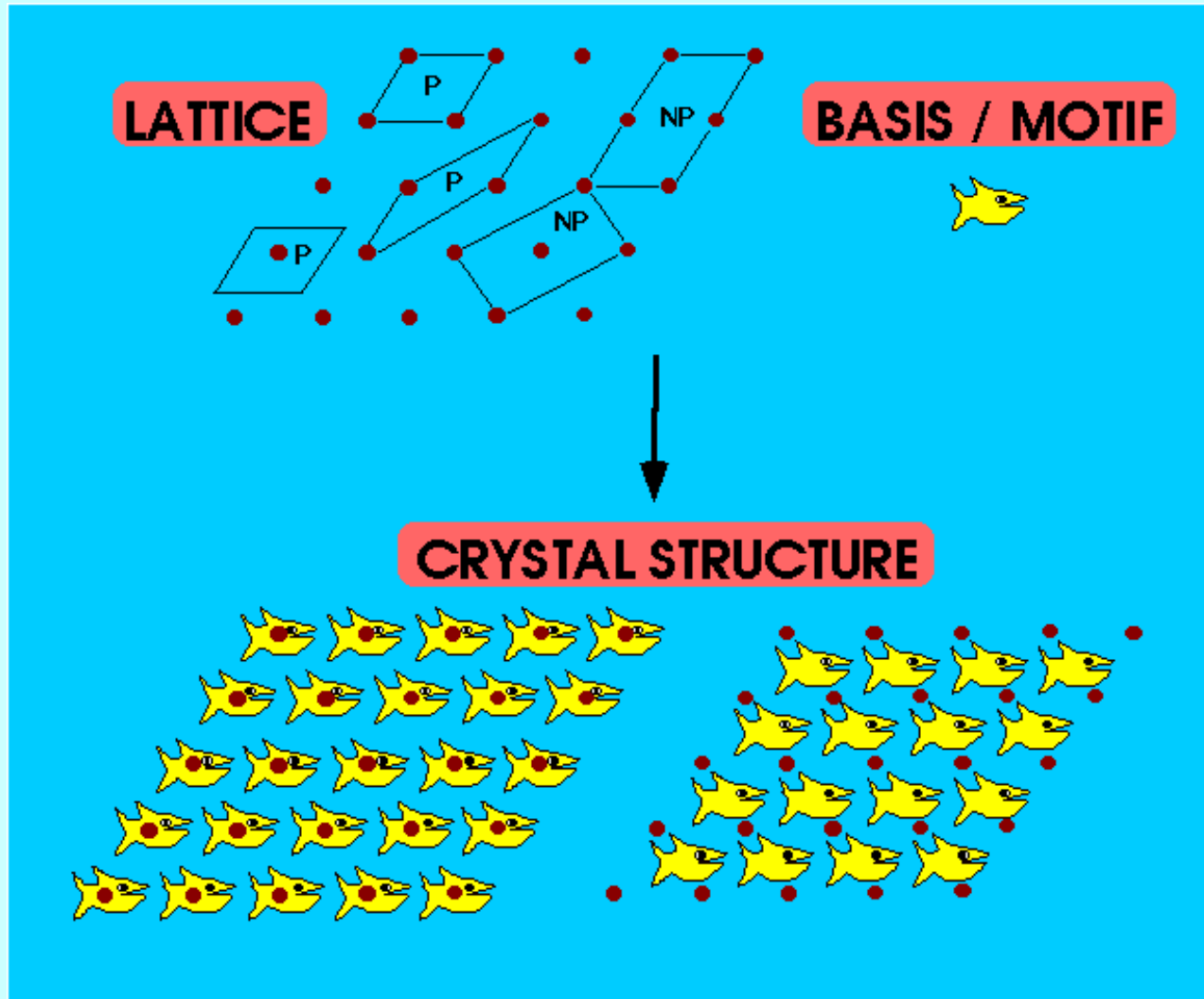
$$\overline{T} = n_1\overline{a} + n_2\overline{b} + n_3\overline{c}$$

where n_1, n_2, and n_3 are integers, and $\overline{a}$, $\overline{b}$, $\overline{c}$ are vectors.
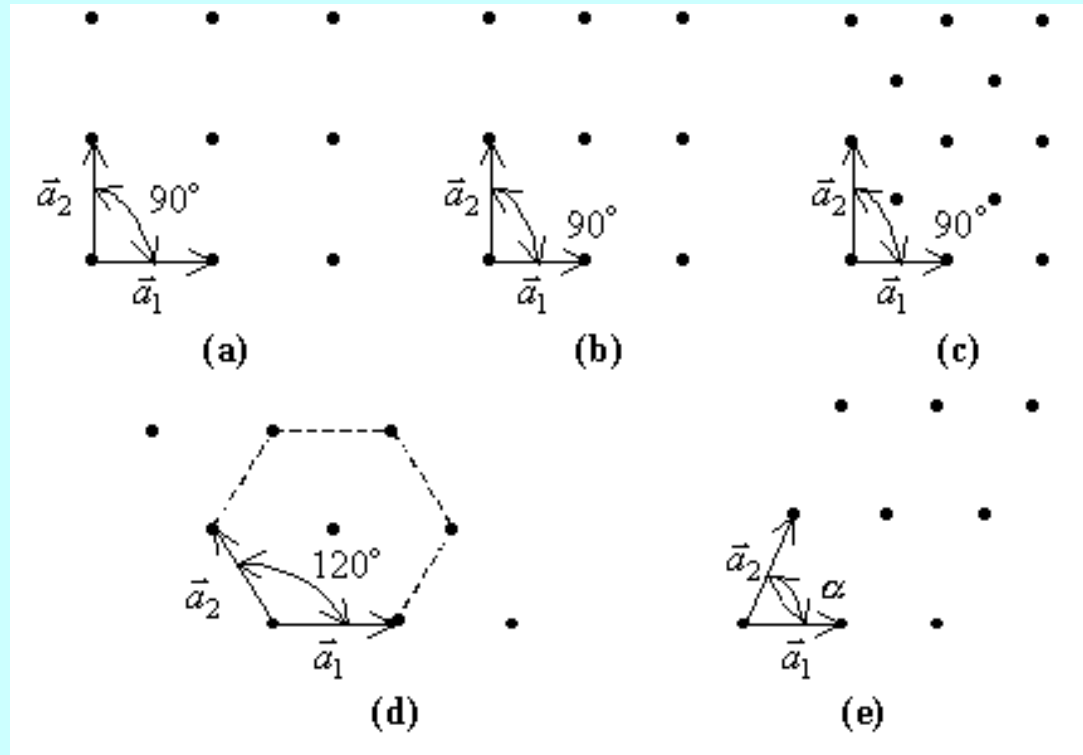
- **then it falls on another identical building block with the same orientation.**
- **If we remove the building blocks and replace them with points, then we have *a point lattice* or Bravais lattice.**
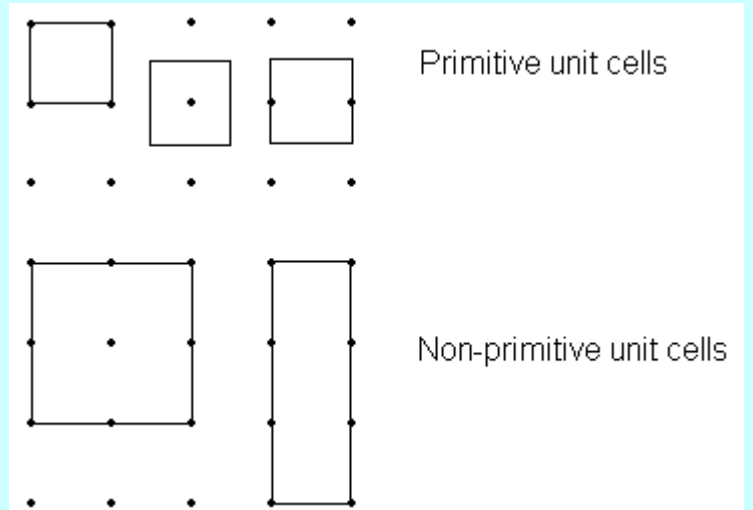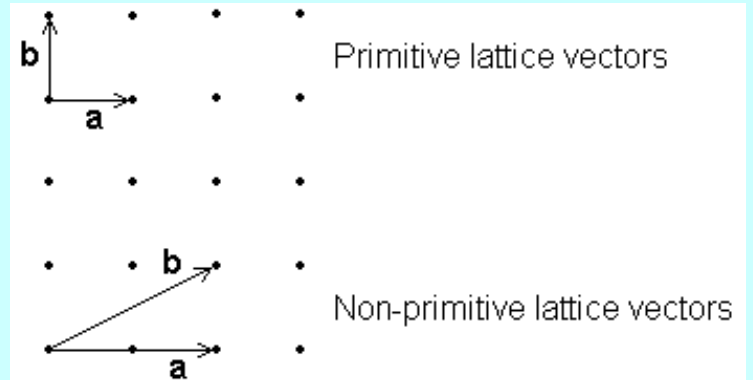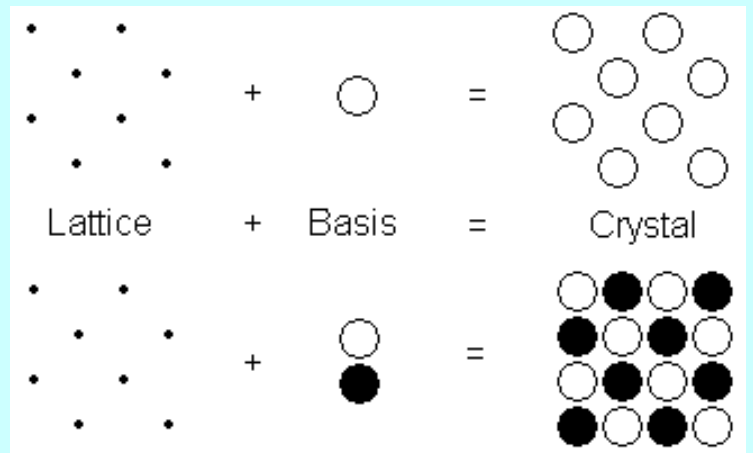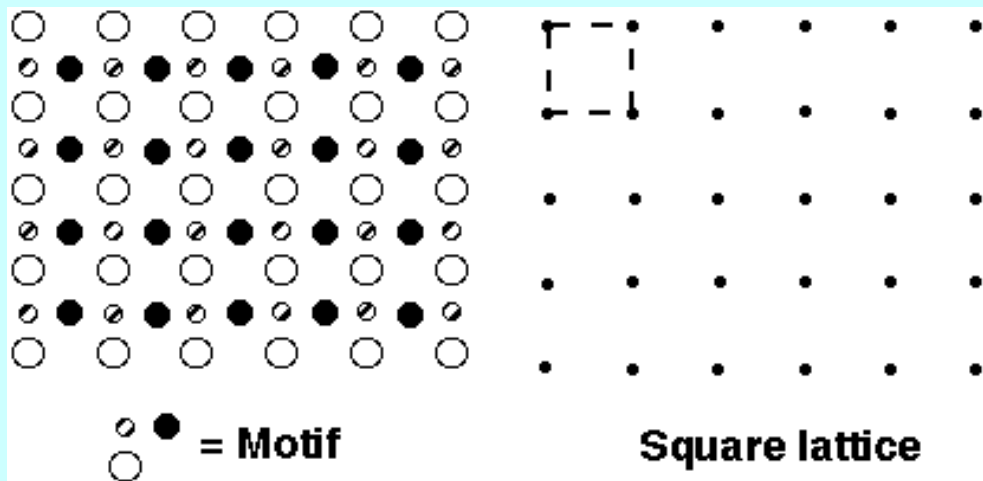
Planar Lattice 2D

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	$a_1 \neq a_2$, $\alpha \neq 120°$, $\alpha \neq 90°$

○ = Motif

○ = Motif

● = Motif

Square lattice

Lattice + Basis = Crystal

Primitive lattice vectors

Non-primitive lattice vectors

Primitive unit cells

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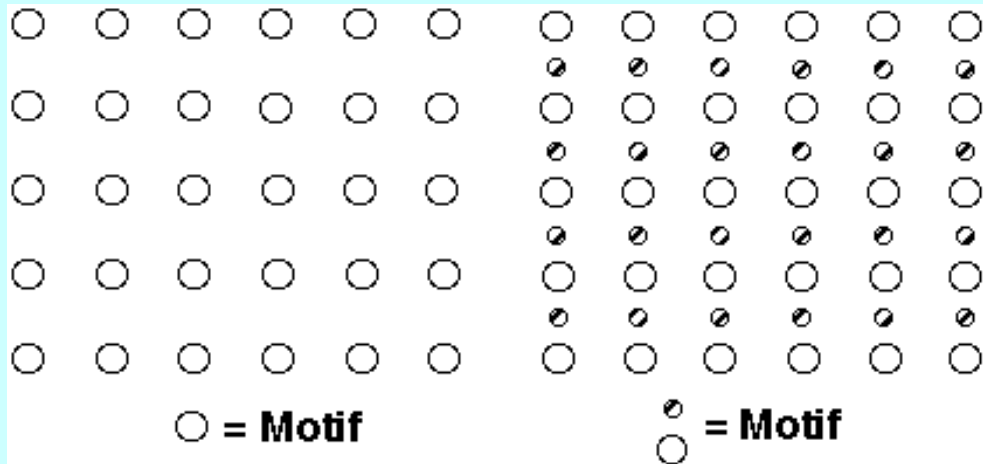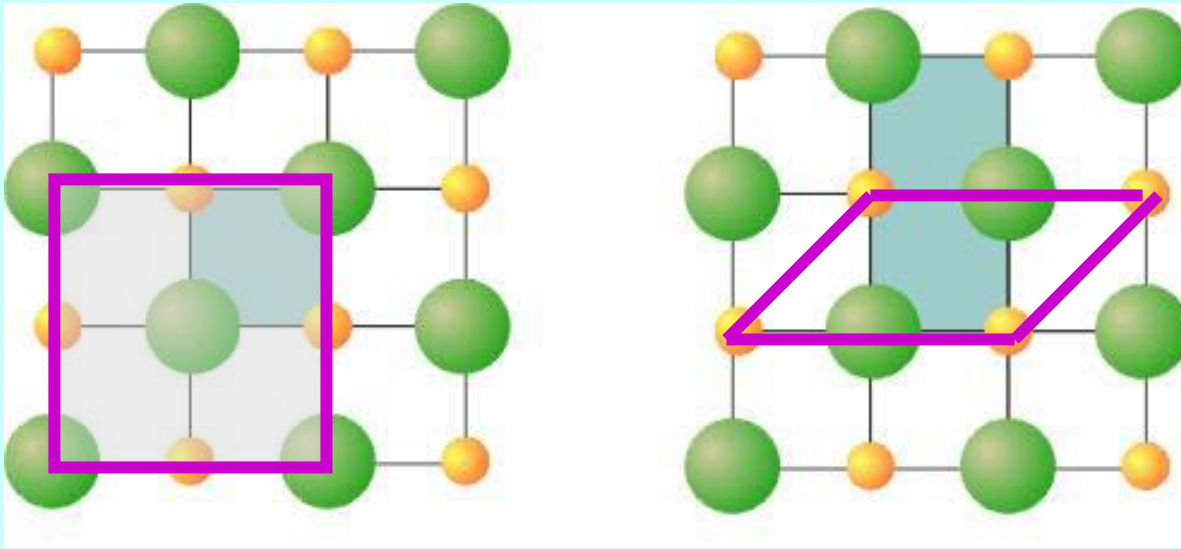
Unit Cell: An „imaginary" parallel sided region of a structure from which the entire crystal can be constructed by purely translational displacements
Contents of unit cell represents chemical composition

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,…)
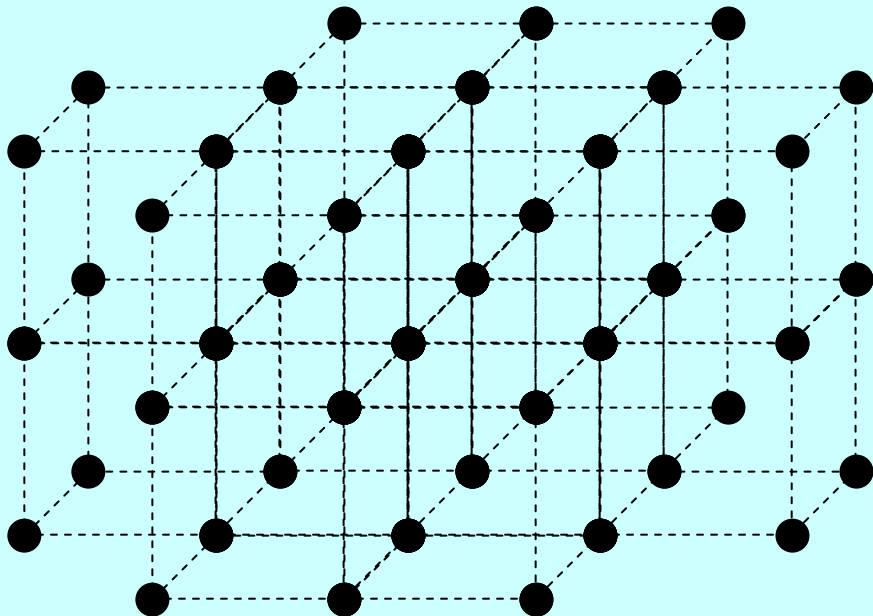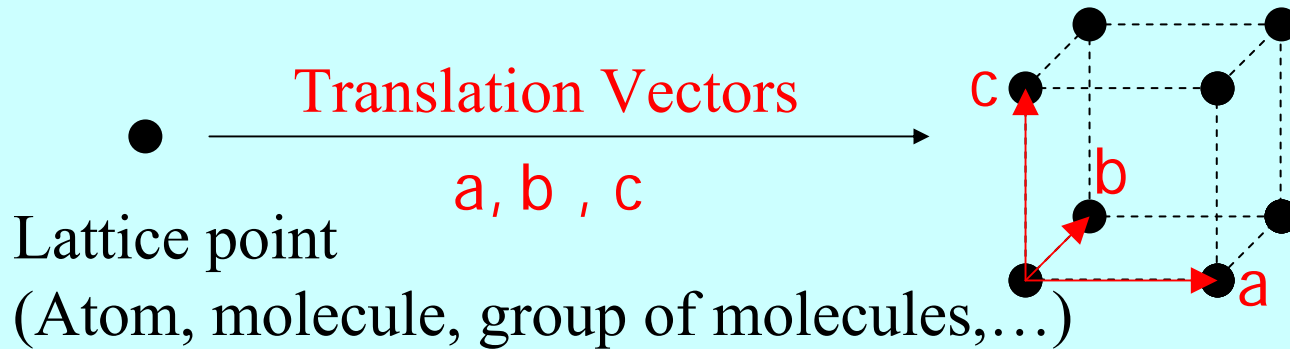
Primitive Cell:
• Smallest building block for the crystal lattice.
• Repetition of the primitive cell gives a crystal lattice
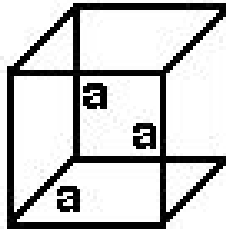
Lattices and Space Groups

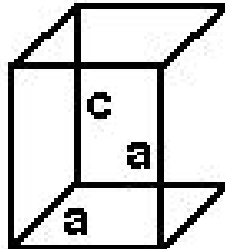|	Bravais Lattice (Lattice point = Basis of Spherical Symmetry)	Crystal Structure (Structural motif = Basis of Arbitrary Symmetry)
Number of point groups:	7 (7 crystal systems)	32 (32 crystallographic point groups)
Number of space groups:	14 (14 Bravais lattices)	230 (230 space groups)

Seven Crystal Systems
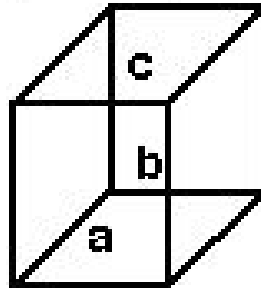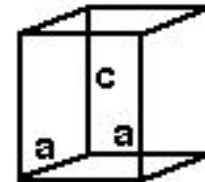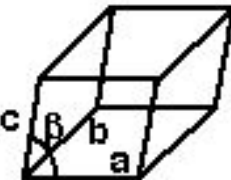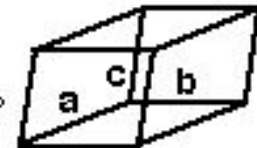
Fourteen Bravais Lattices
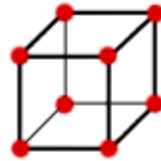
Simple cubic
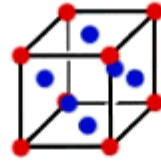
Face-centered cubic

Body-centered cubic

Simple tetragonal

Body-centered tetragonal
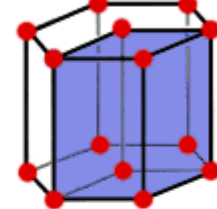
Hexagonal
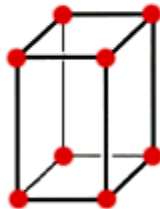
Simple orthorhombic
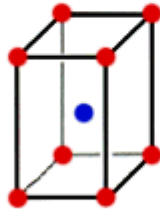
Body-centered orthorhombic
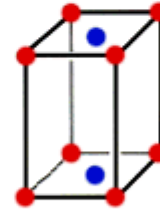
Base-centered orthorhombic
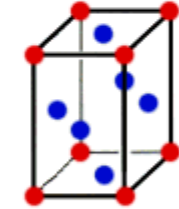
Face-centered orthorhombic
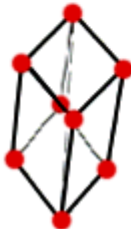
Rhombohedral
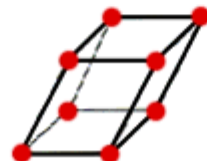
Simple Monoclinic
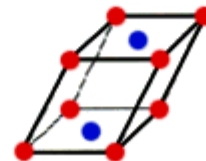
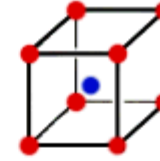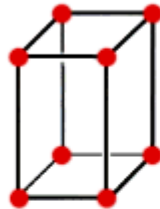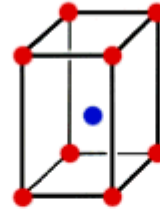Base-centered monoclinic
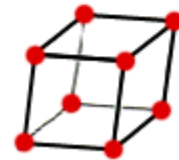
Triclinic

Simple Cubic (SC)

Conventional Cell = Primitive Cell

$a = b = c$

$a \perp b \perp c$
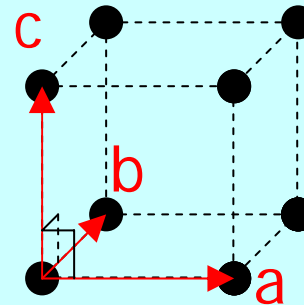
Add one atom at the center of the cube
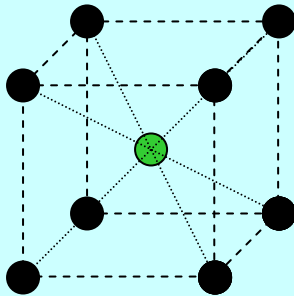
Add one atom at the center of each face

Body-Centered Cubic (BCC)
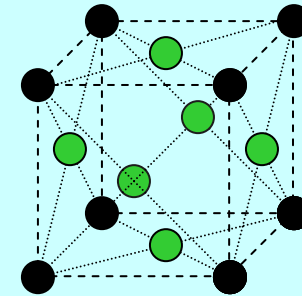
Face-Centered Cubic (FCC)

Conventional Unit Cell ≠ Primitive Cell

Primitive Cell

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

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 of a primitive cell, many possible shapes.

The primitive cell for the simple cubic lattice is equal to the simple cubic unit cell (they are identical).
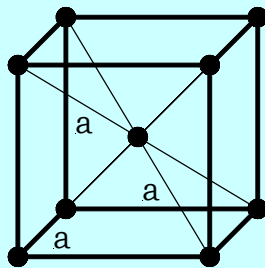
Body-Centered
Cubic (I)

Unit Cell
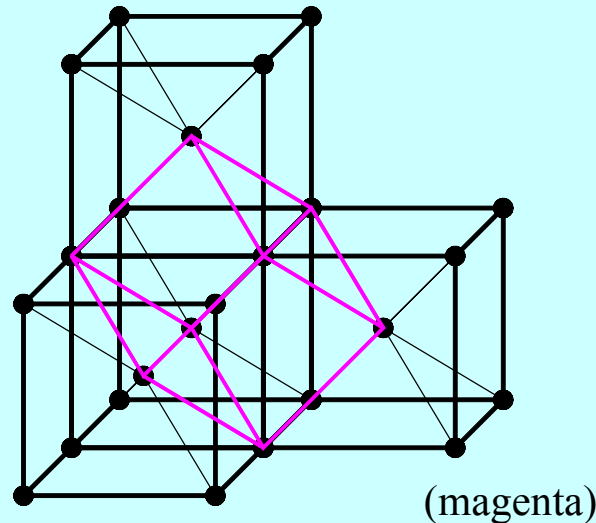
(magenta)

Primitive Cell

Primitive Cell of BCC

•Rhombohedron primitive cell
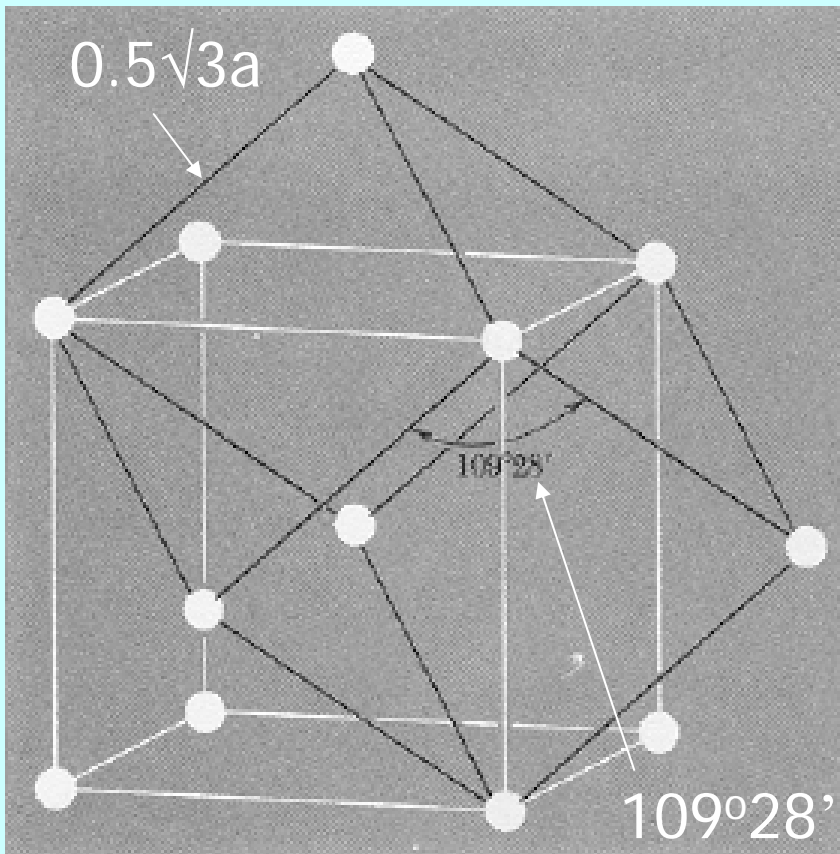
0.5√3a

109°28'

109°28'

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).

Nonprimitive Unit Cell vs. Primitive Cell
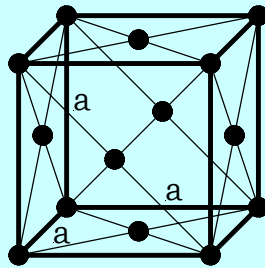
Face-Centered
Cubic (F)

Unit Cell
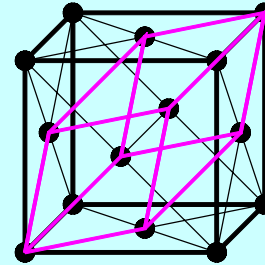
Primitive Cell
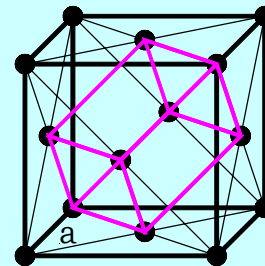
Rotated 90º

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 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.**

(100)   (110)   (111)

(200)   ($\bar{1}$00)
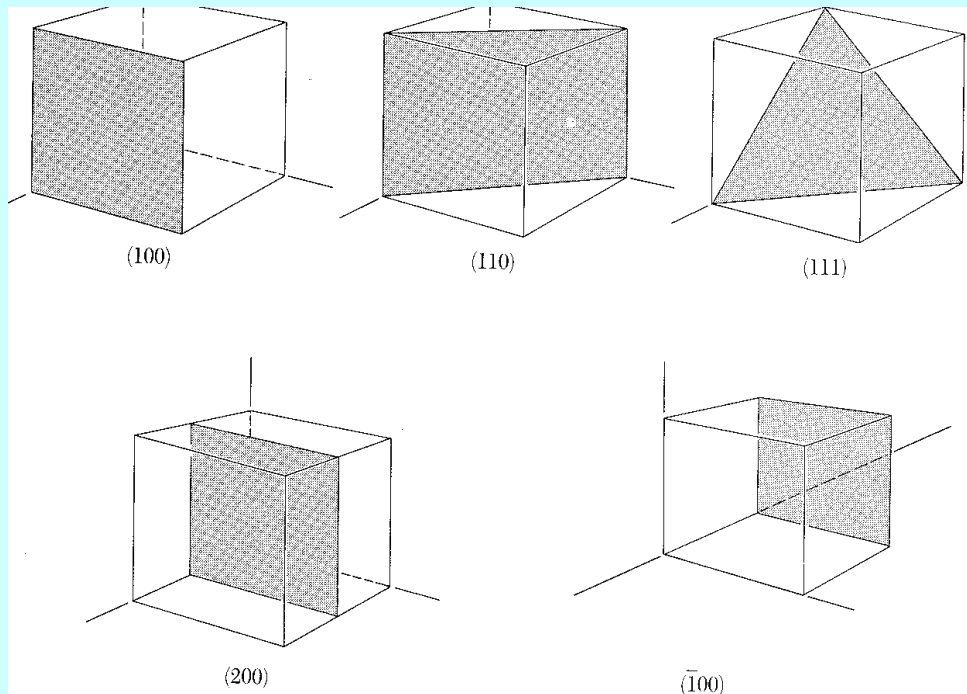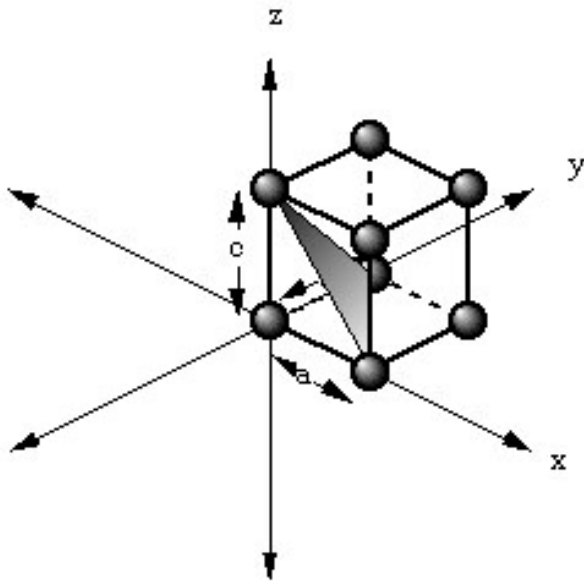
Miller Indices

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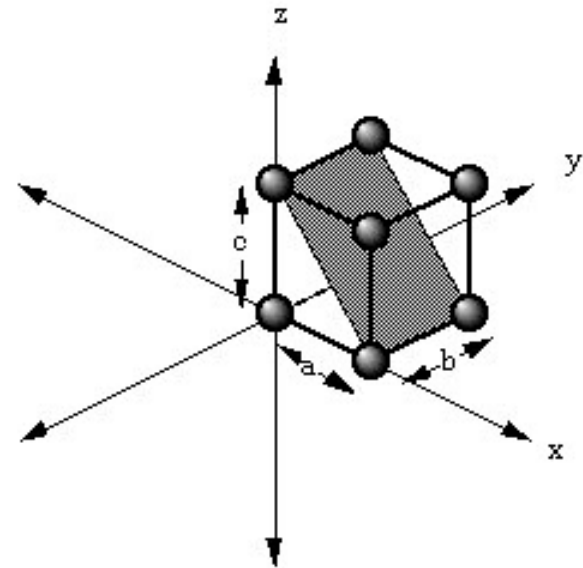
	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		

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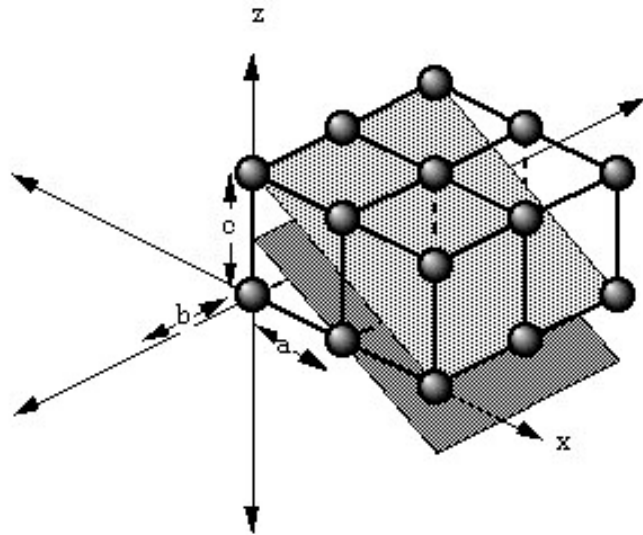
	a	b	c
intercept length	1	∞	1/2
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2
Miller indice		(102)	
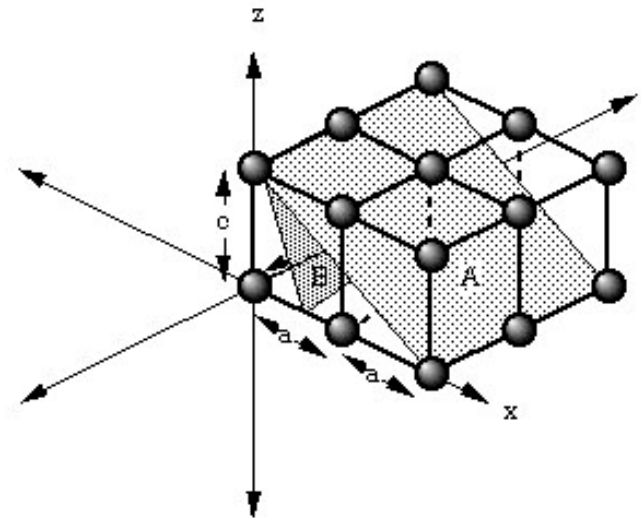
	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	∞	$\frac{1}{2}$	$\frac{1}{2}$	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice		(102)			(201)	

Crystals and Crystal Bonding

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

- ionic (NaCl, CsCl, CaF_2, ...)
  Ionic bonds, 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

Three Cubic Cells
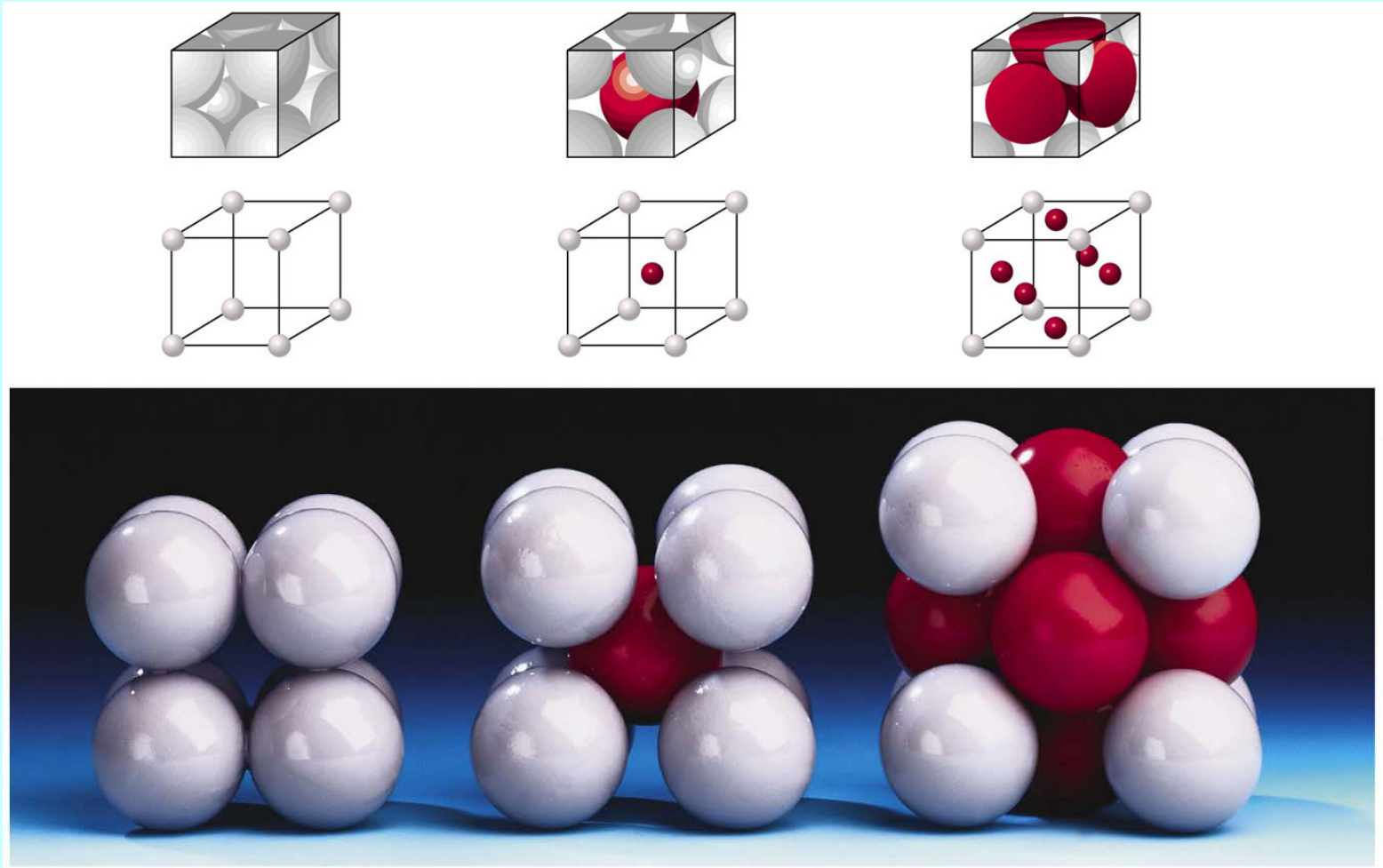
**SC or Primitive (P)**   **BCC (I)**   **FCC (F)**

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]	$\frac{1}{6}\pi$	$\frac{1}{8}\pi\sqrt{3}$	$\frac{1}{6}\pi\sqrt{2}$
	$= 0.524$	$= 0.680$	$= 0.740$

Cube
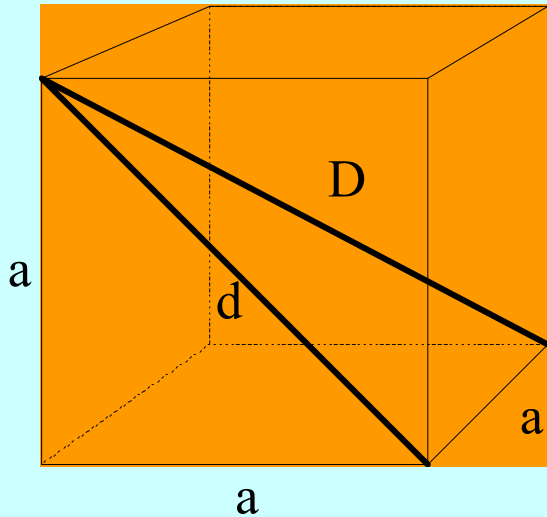
a = edge

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

D = body diagonal
    $(D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2)$
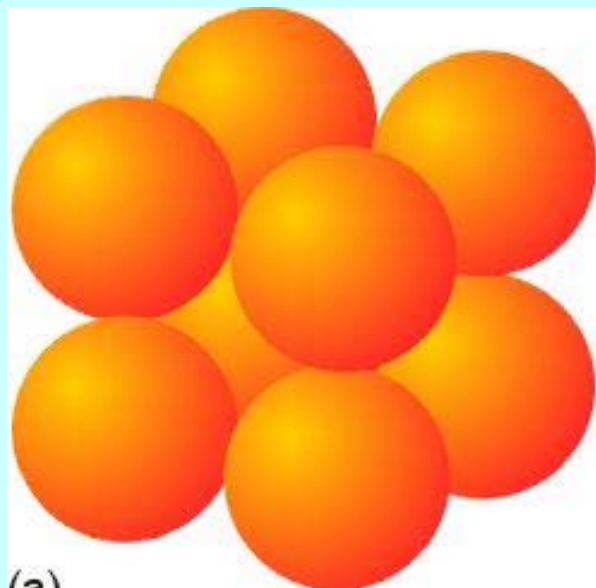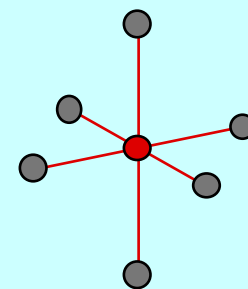
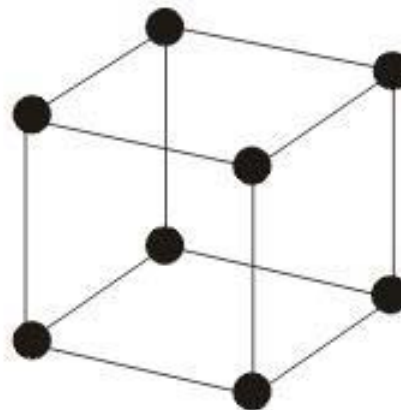$$d = \sqrt{2} \cdot a$$

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

SC = Polonium

CN 6

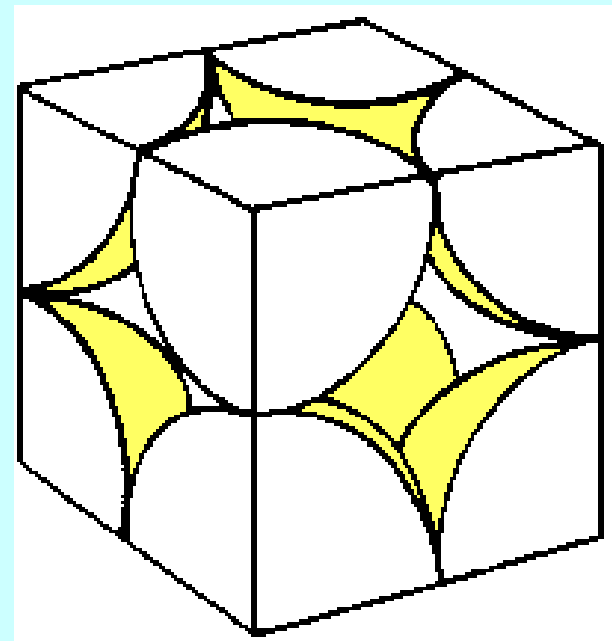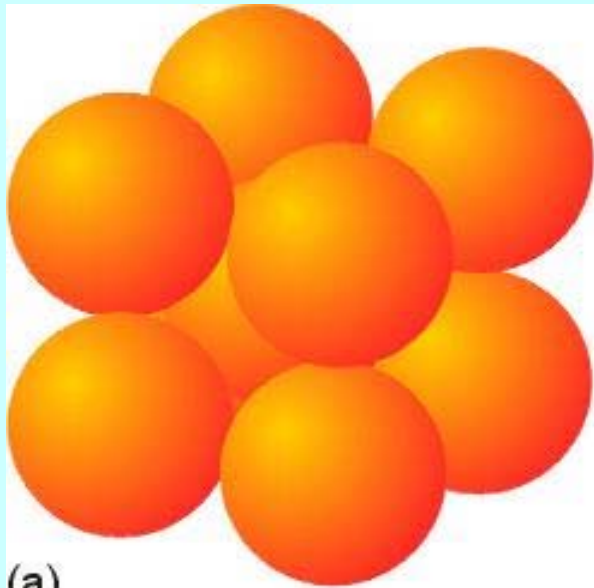Z = 1
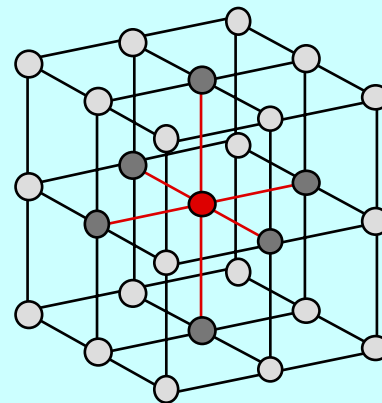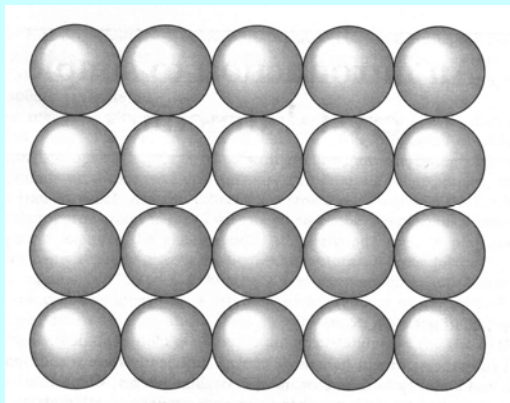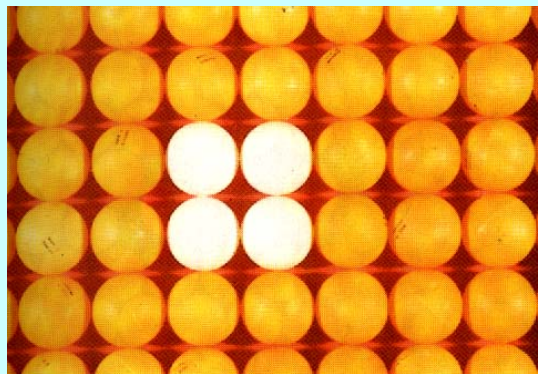
Space filling 52%

BCC = W, Tungsten

Z = 2
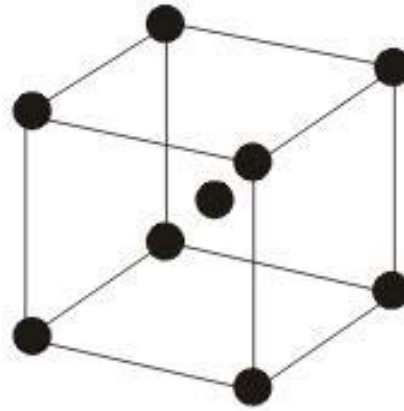
Space filling 68%

CN 8

Fe, Cr, V, Li-Cs, Ba
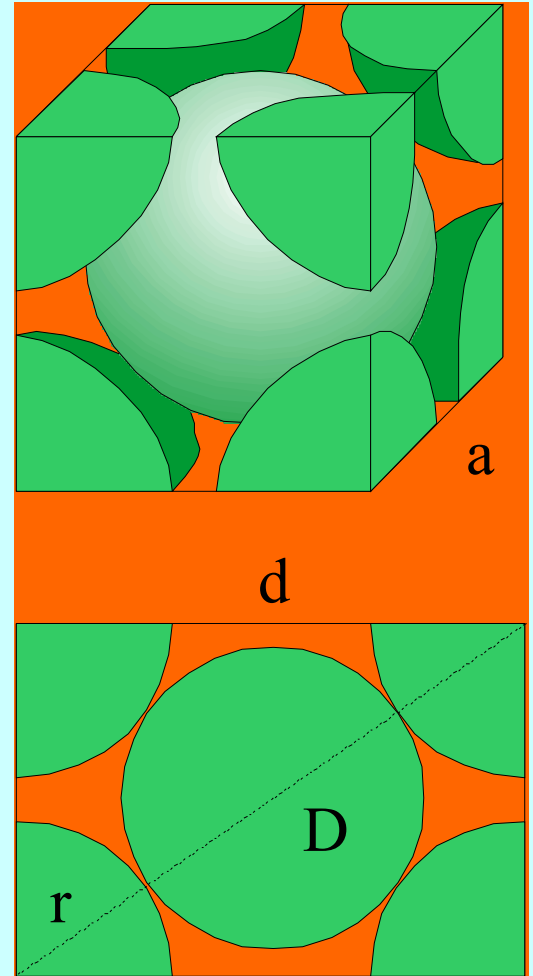
BCC
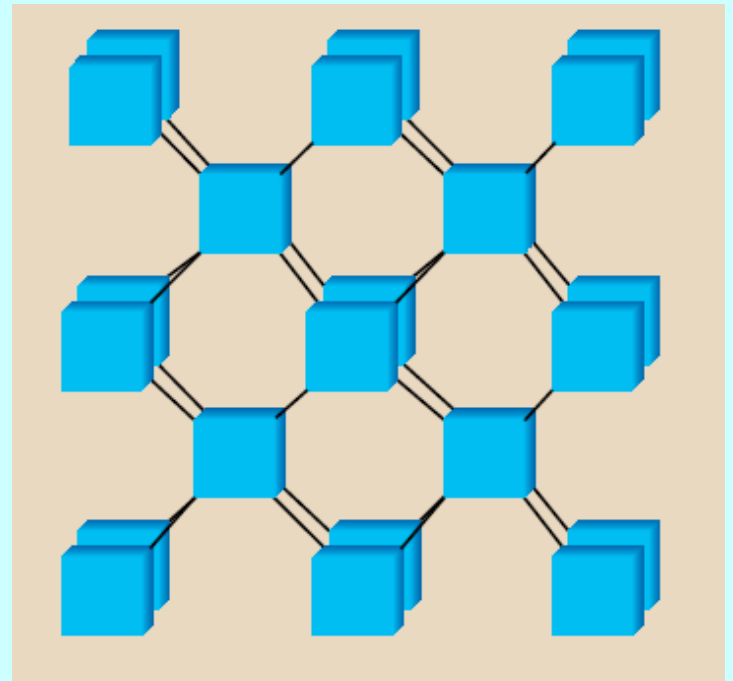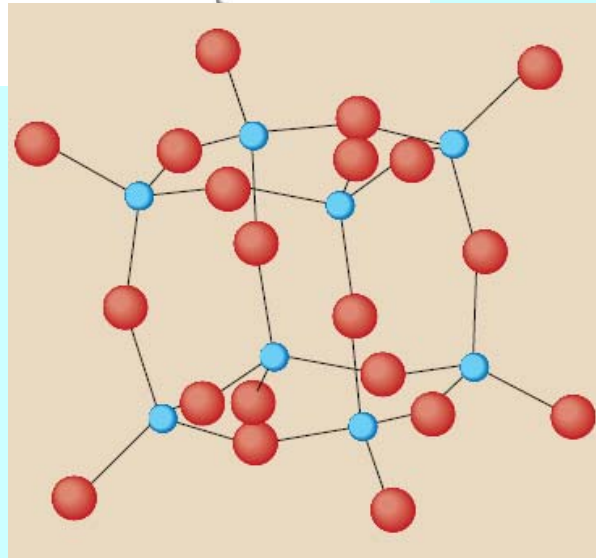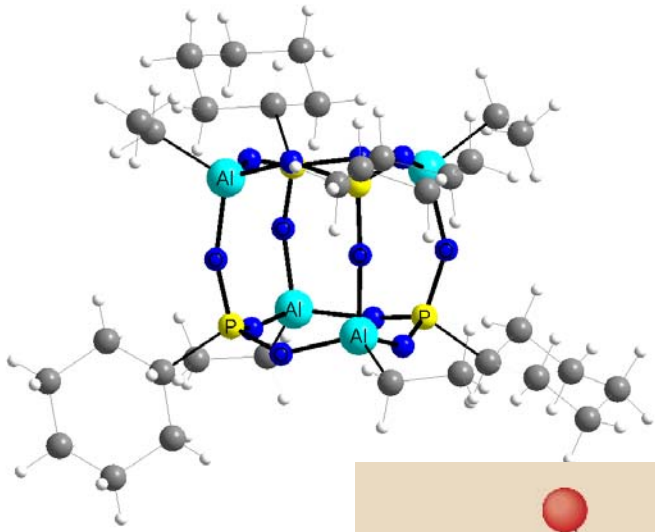
FCC = Copper, Cu = CCP
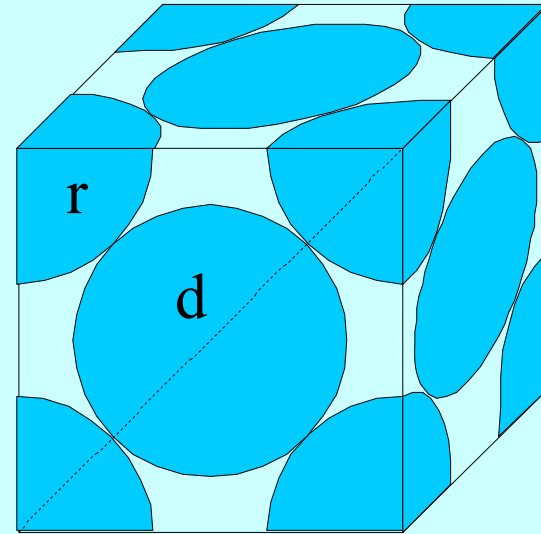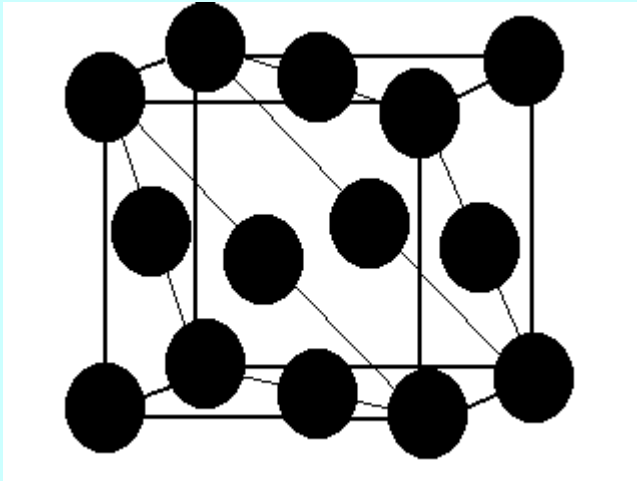
Z = 4
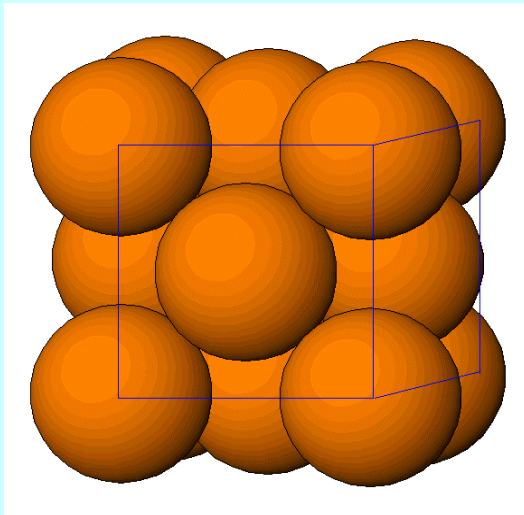
Space filling 74%

CN 12

Close Packing in Plane 2D
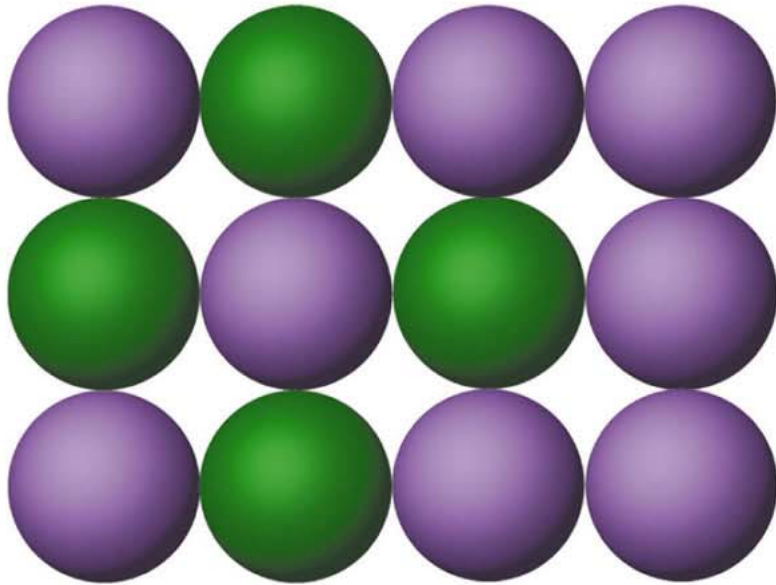
(a) An "open" packing
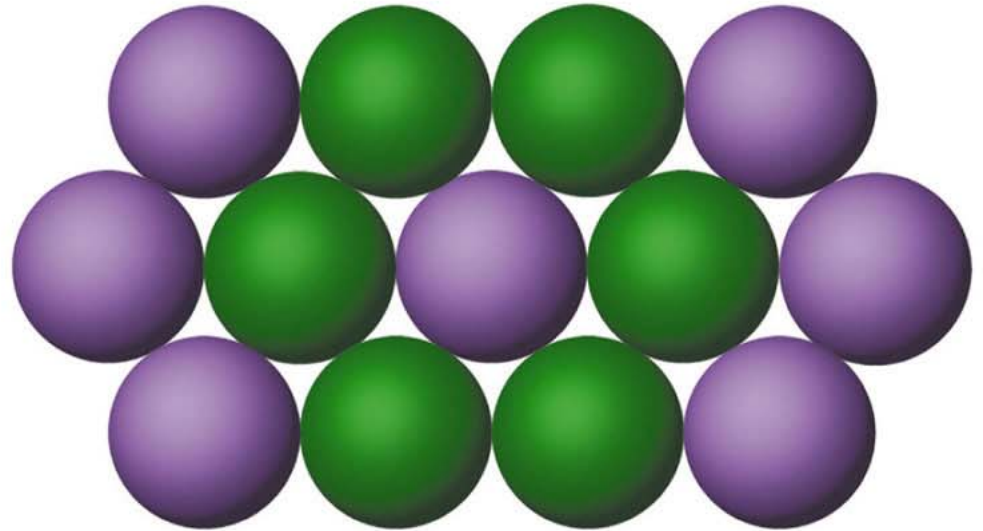
(b) Close packing
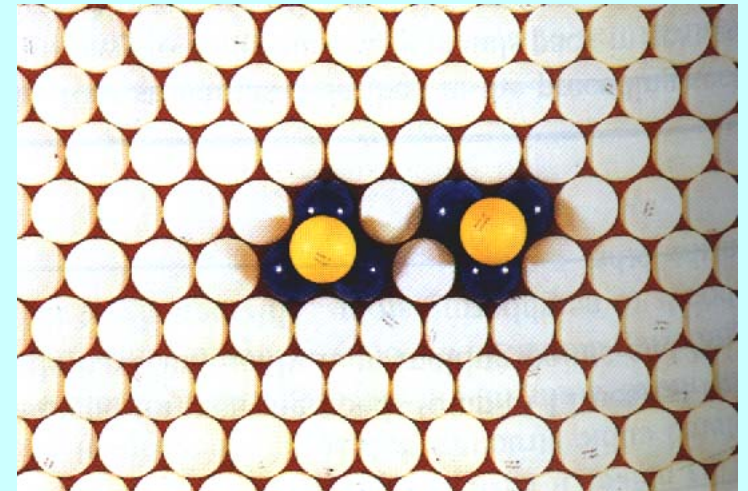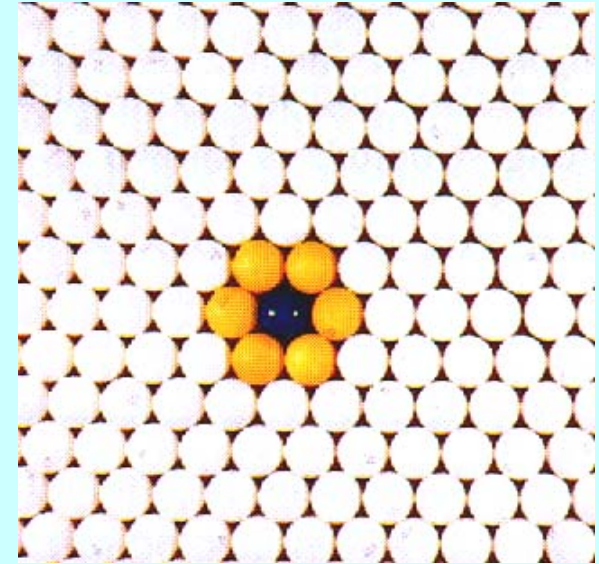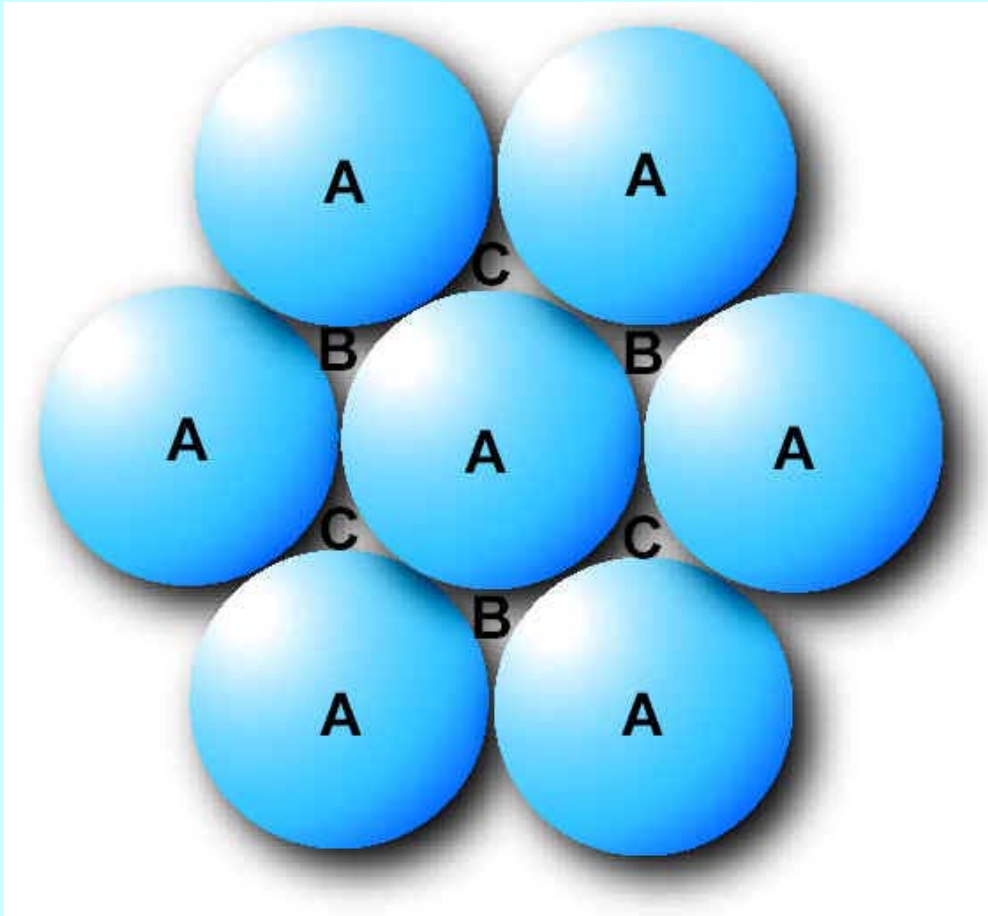
B and C holes cannot be occupied at the same time

Close Packing in Space 3D
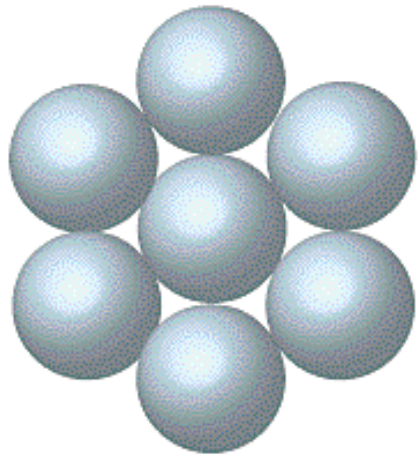
Close-packed layer of spheres
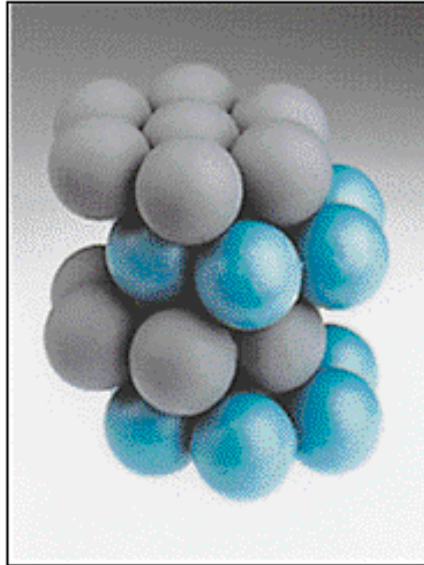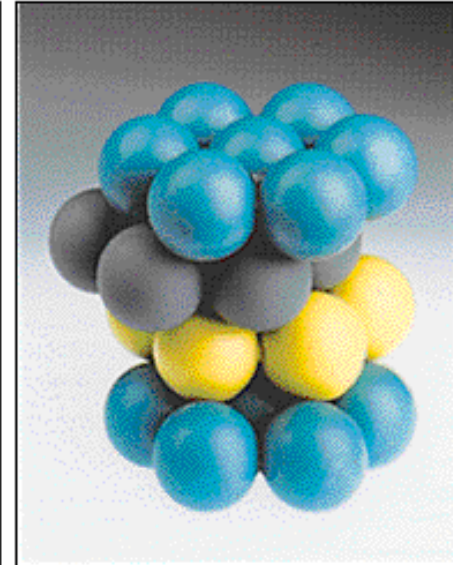
(a) (b) (c)

Hexagonal
HCP

Cubic
CCP

hexagonal

Top view of close-packed spheres

Tetrahedral holes (▽)

Octahedral holes (✡)

Side view

Cover tetrahedral holes in layer B

A
B
A

Hexagonal close-packed

Side view

Cover octahedral holes in layer B

A
C
B
A

Cubic close-packed

cubic

hexagonal

cubic

A		3
B		6
A		3

C	
B	
A	
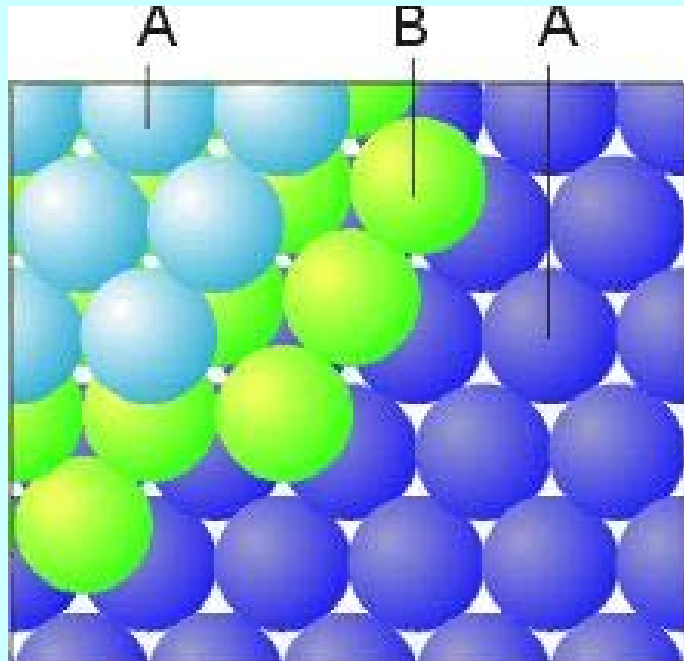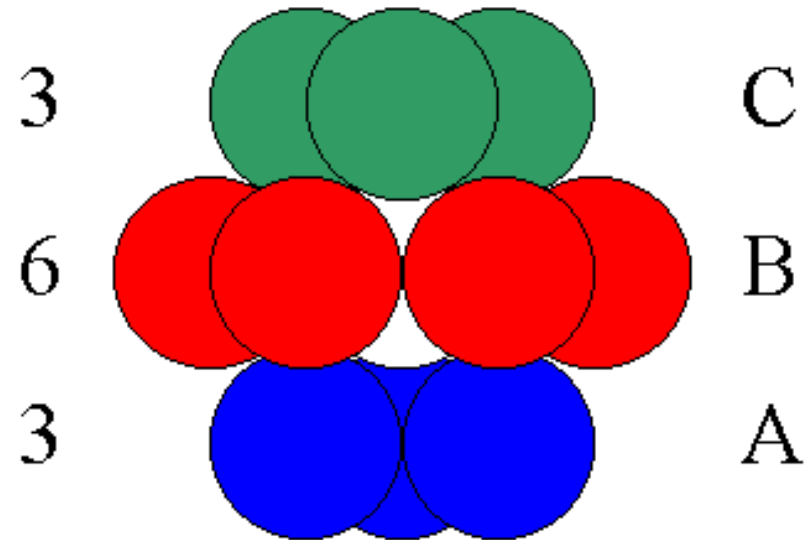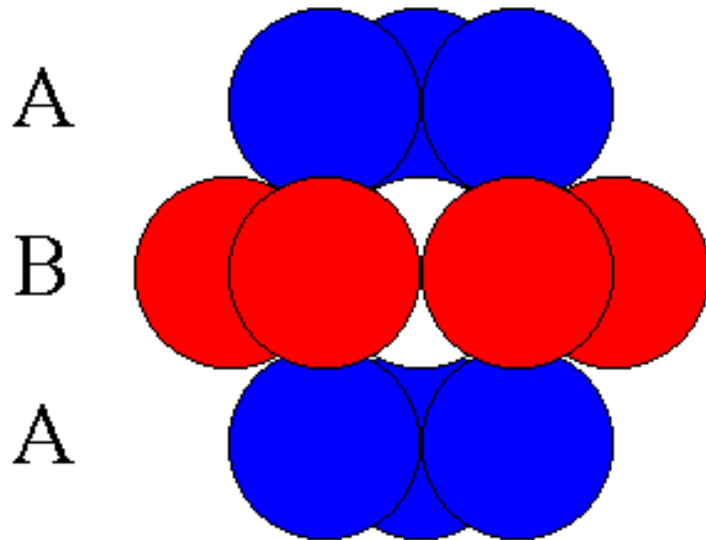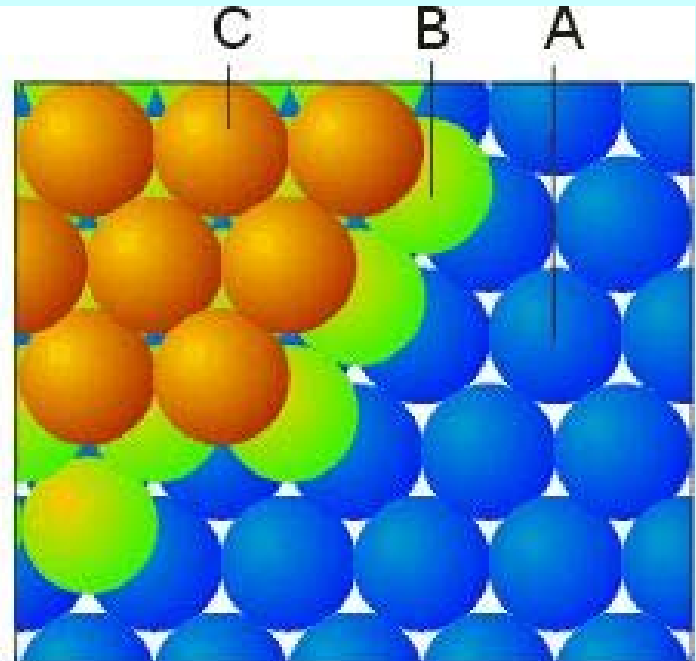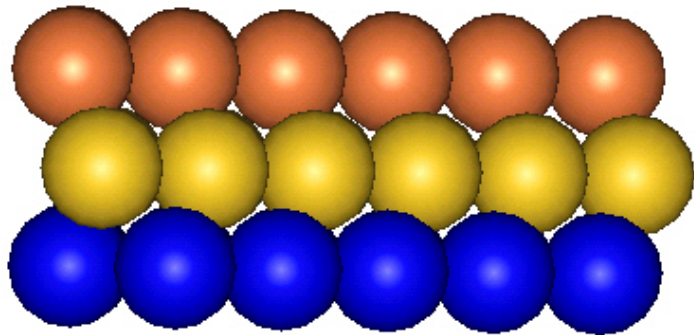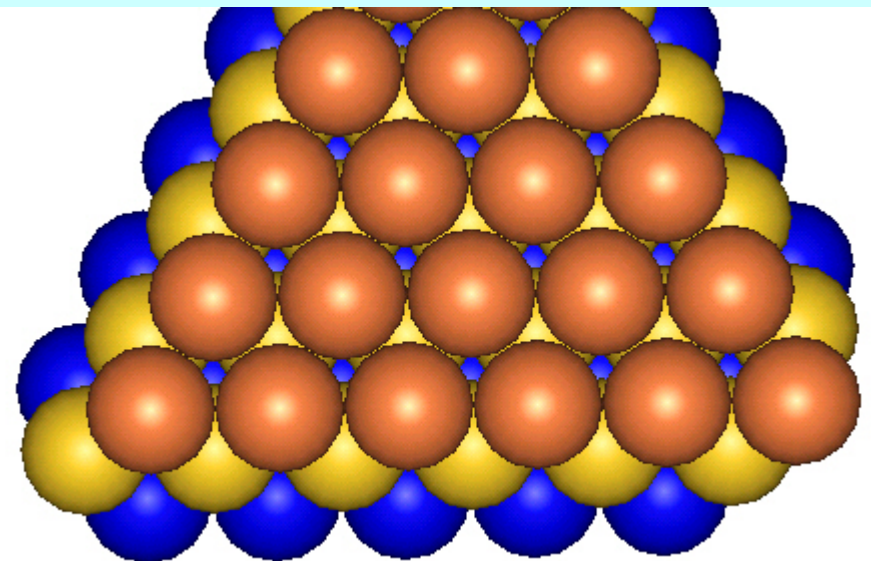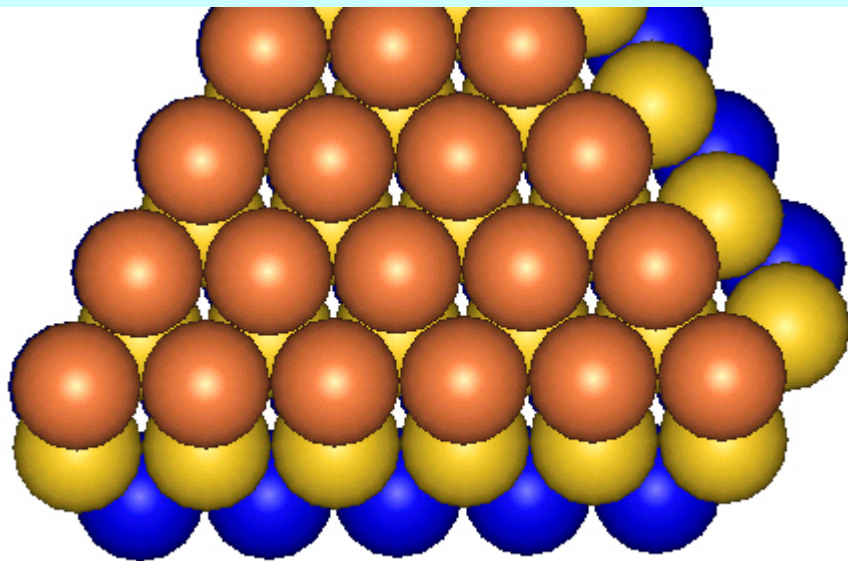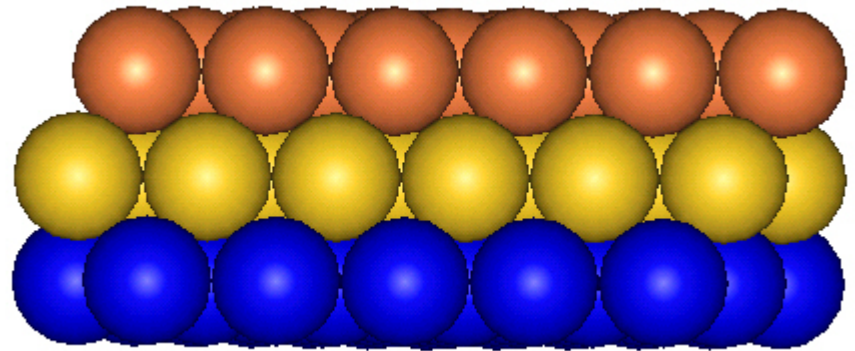
hexagonal

cubic

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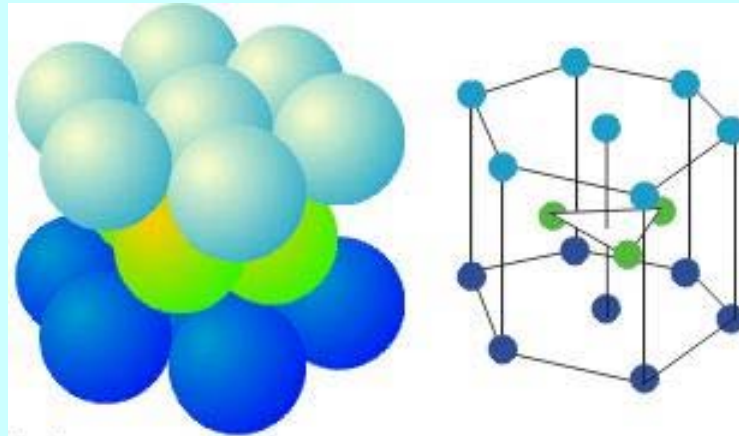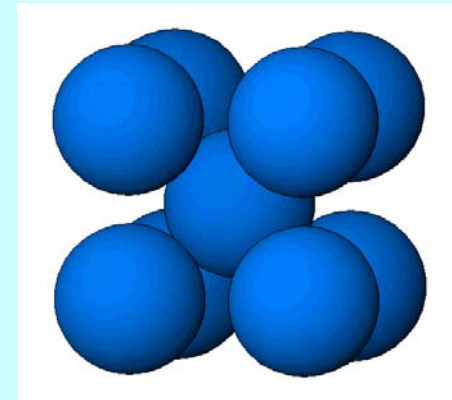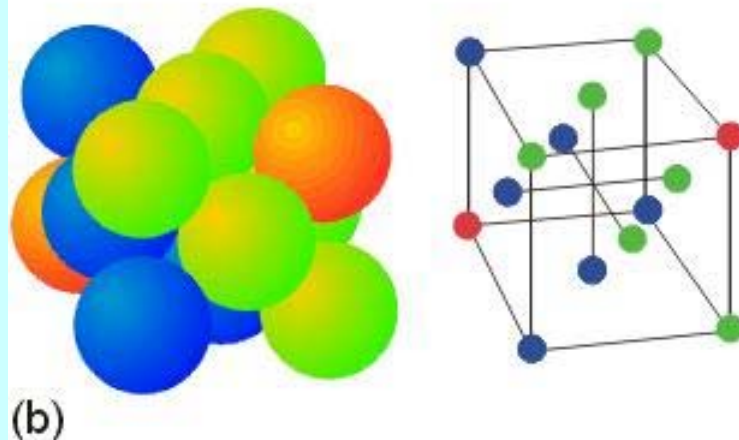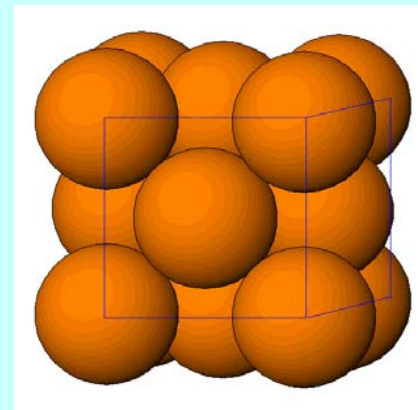
hexagonal

cubic

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

Structures with Larger Motifs

BUCKMINSTERFULLERENE

FOOT & MOUTH VIRUS

FCC

BCC

HEXAGONAL CLOSE-PACKING

Unit Cell

$a = b$ $c = 1.63$ $\gamma = 120°$

A

B

A

Anti-Cuboctahedron
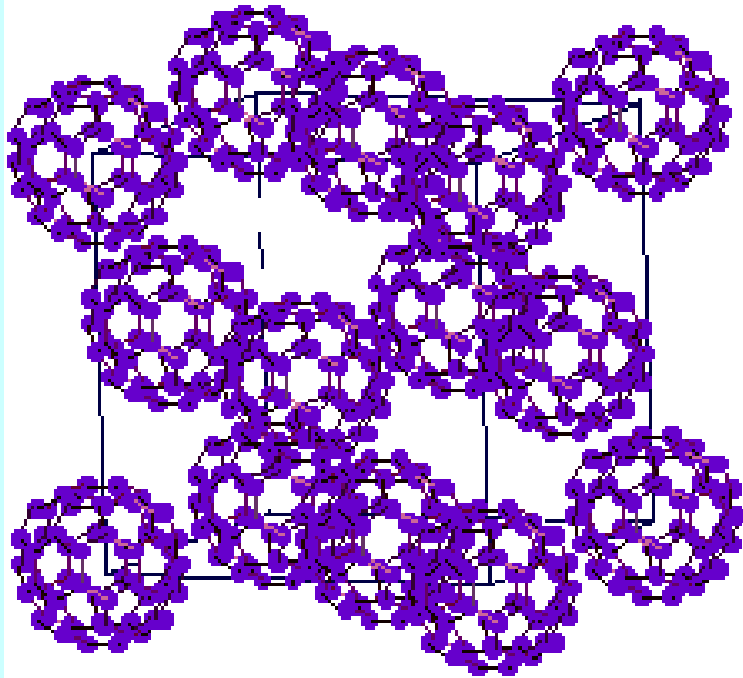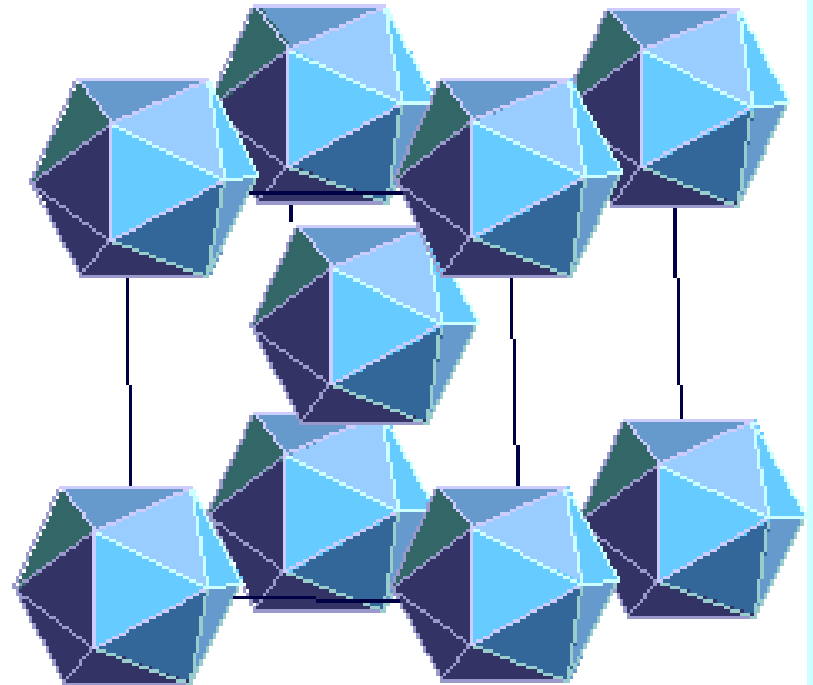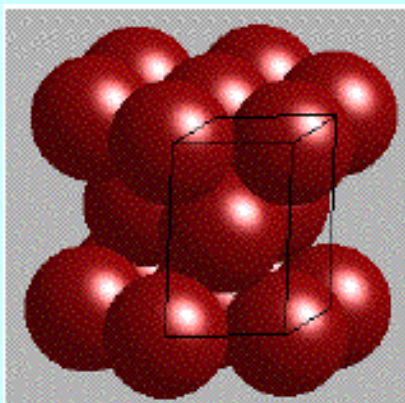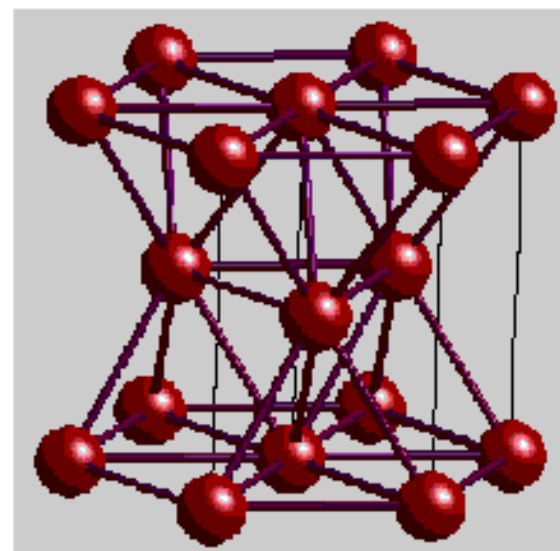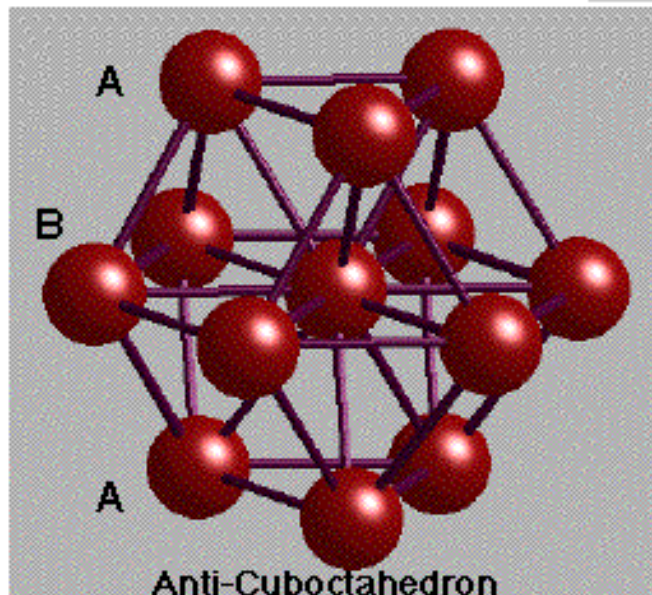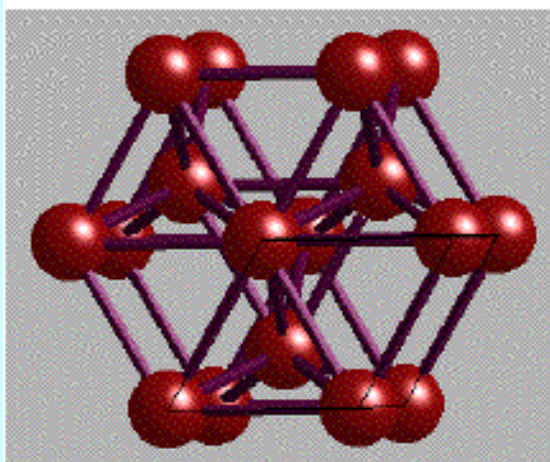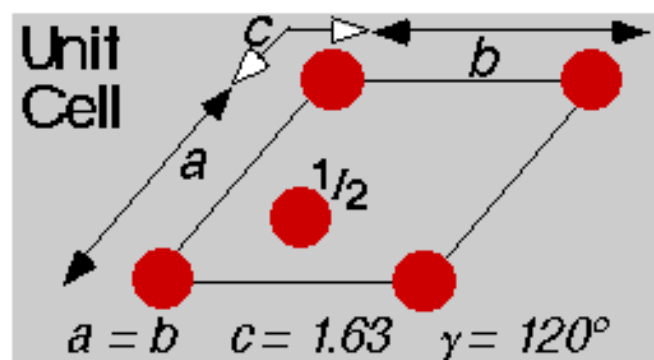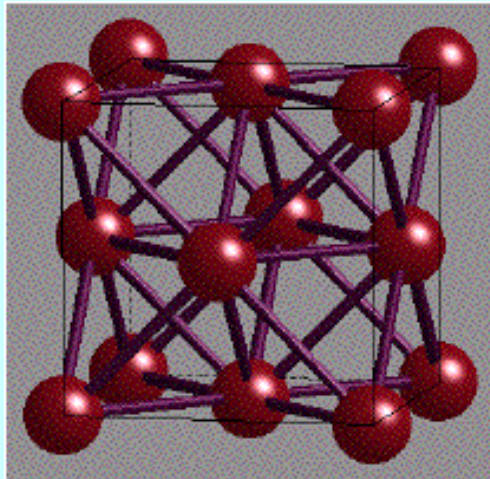
CUBIC CLOSE-PACKING

Face-Centred Cubic (FCC) Unit Cell

Unit Cell

$a = b = c$

$\alpha = \beta = \gamma = 90°$

$1/2$

Cuboctahedron

C
B
A

A
B
C
A
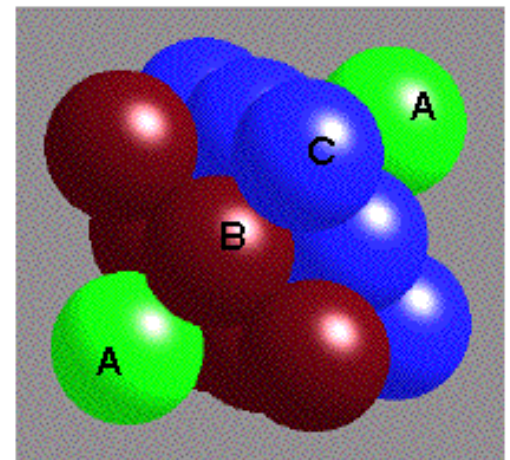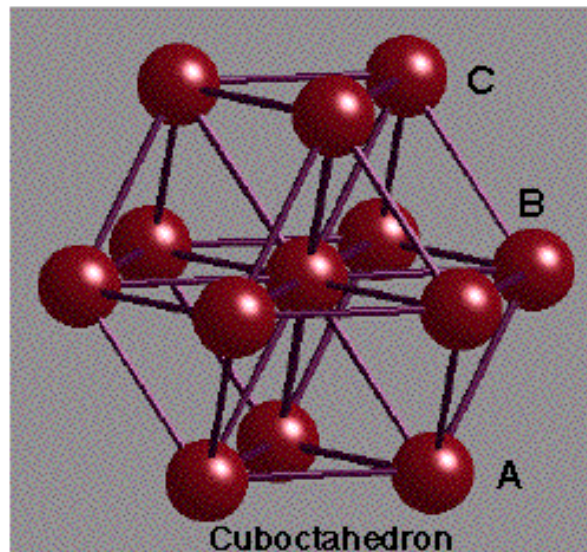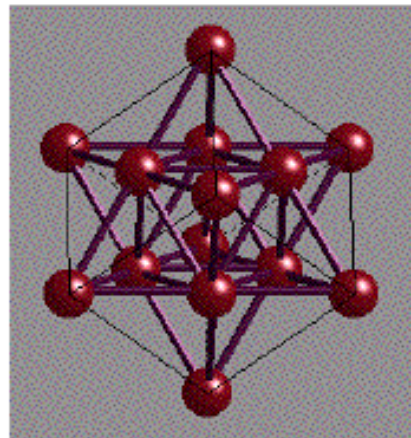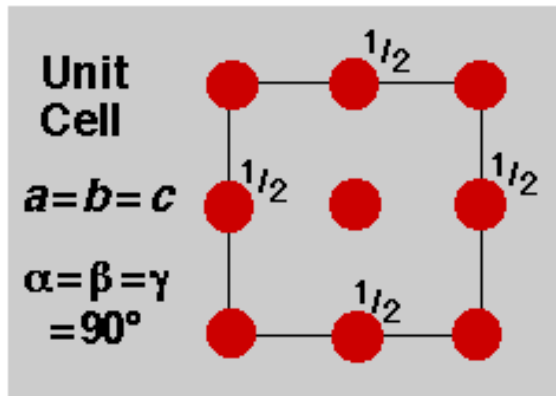
Coordination Polyhedrons
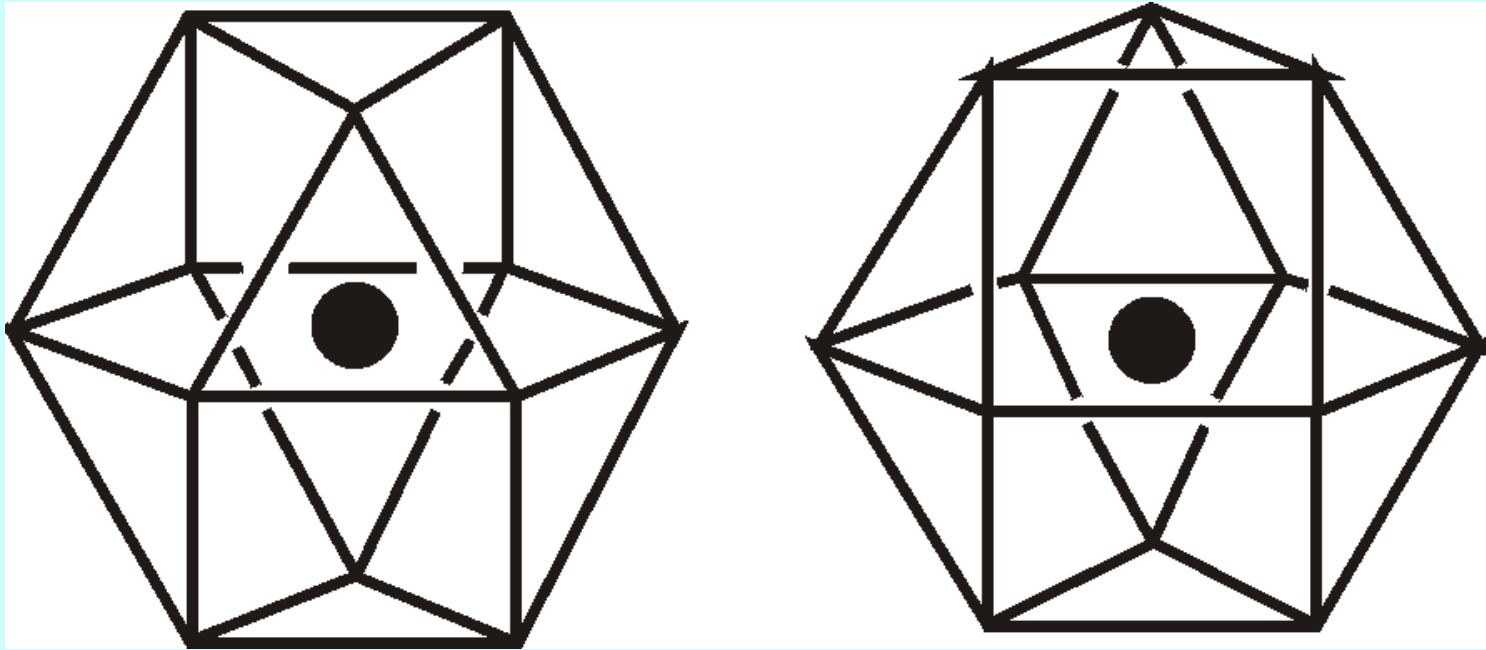
Coordination Polyhedrons
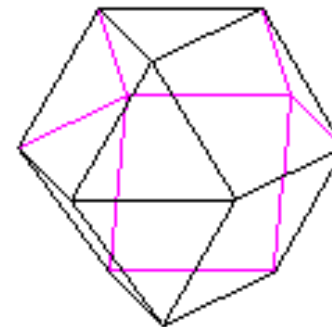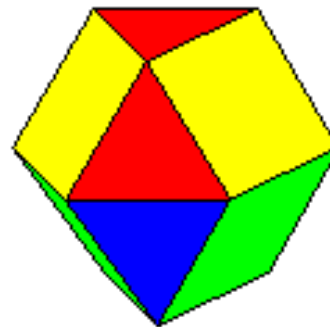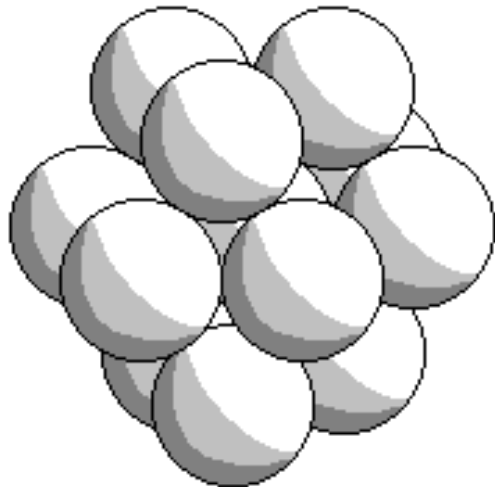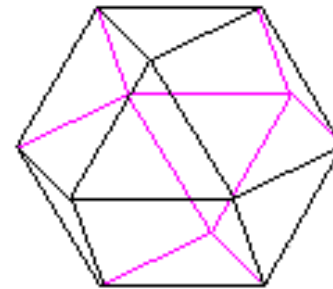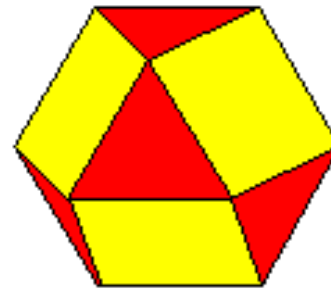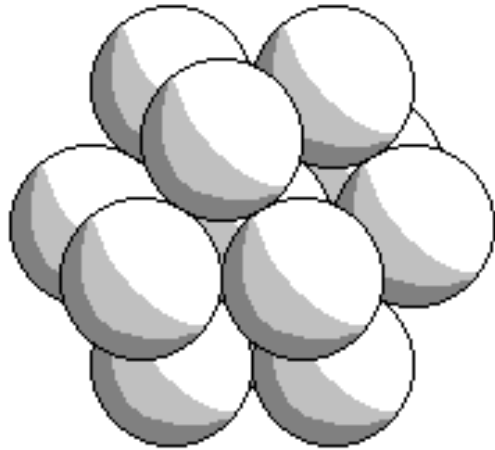
Space Filling

a = lattice parameter	Atom Radius, r	Number of Atoms (lattice points), Z	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
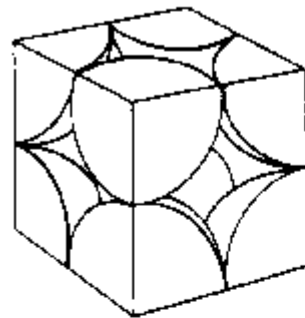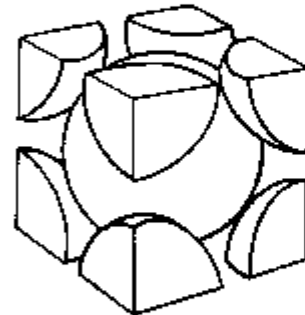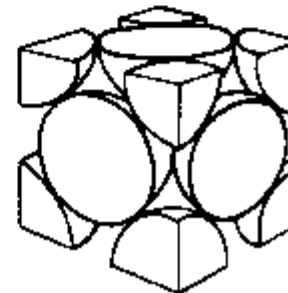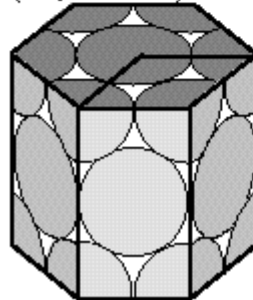
CCP = FCC

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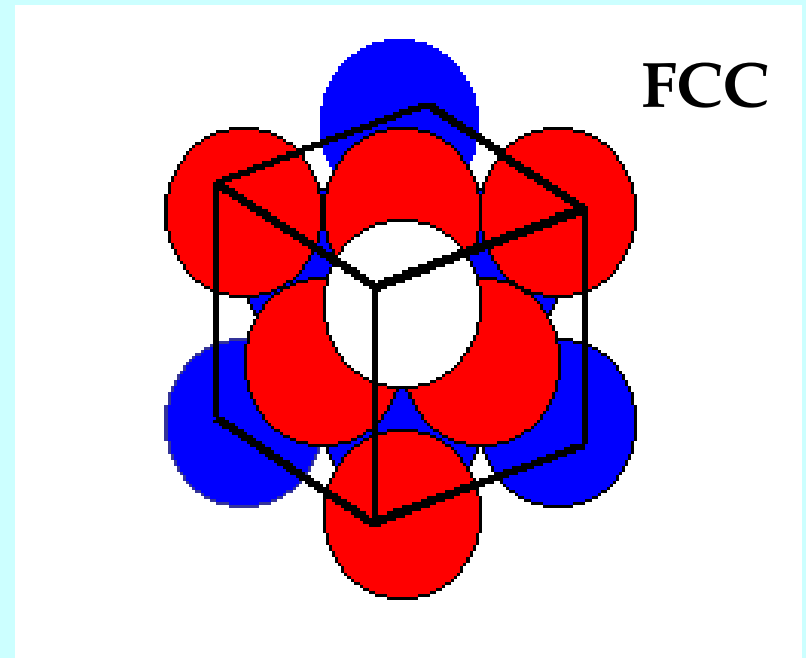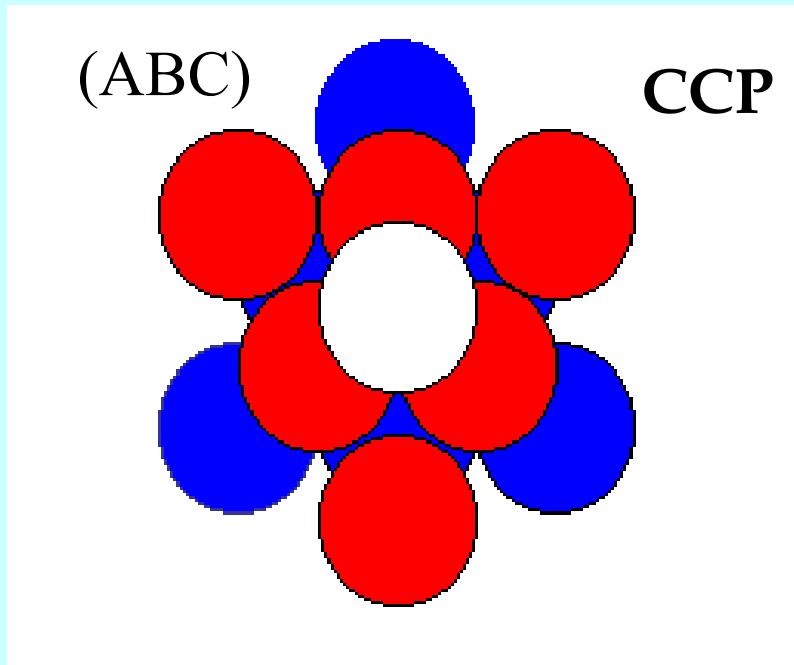
Close packed layers of CCP are oriented perpendicularly to the body diagonal of the cubic cell of FCC

Two Types of Voids (Holes)

5 Tetrahedral hole

2 Octahedral hole

3
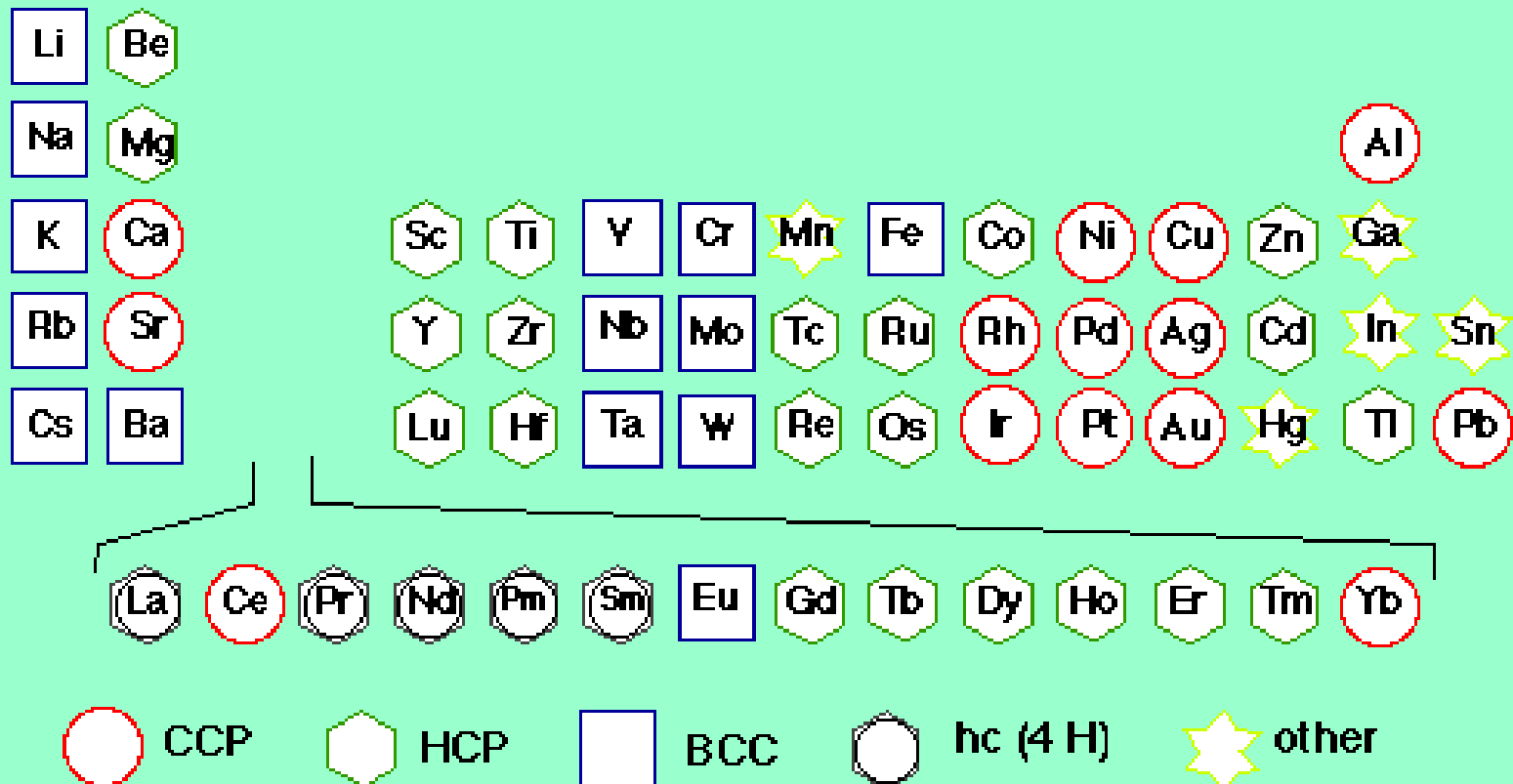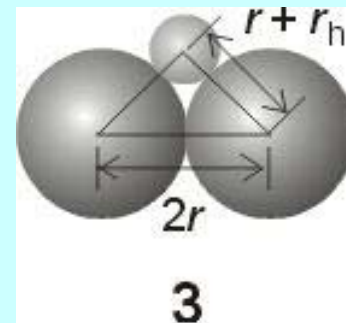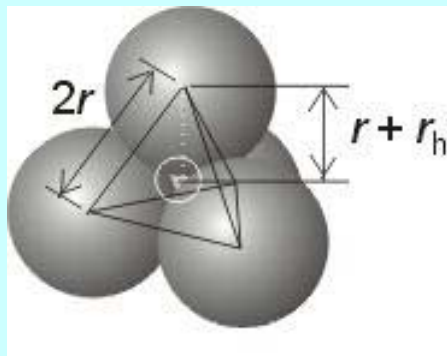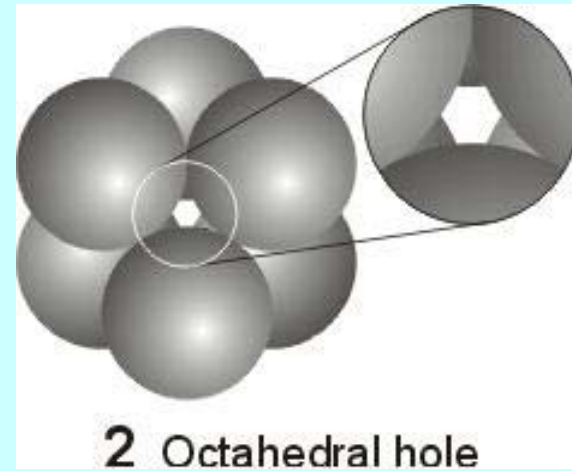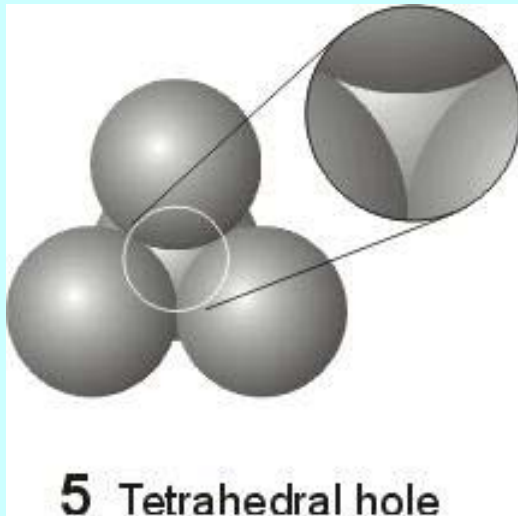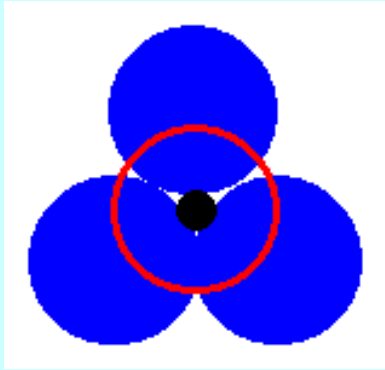
Tetrahedral Holes T+
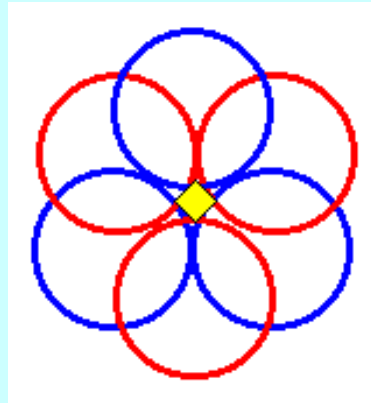
Octahedral Holes
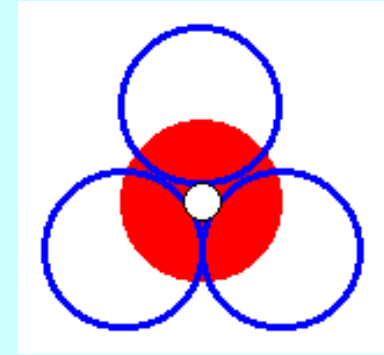
Tetrahedral Holes T-

N cp atoms in lattice cell

N Octahedral Holes
2N Tetrahedral Holes
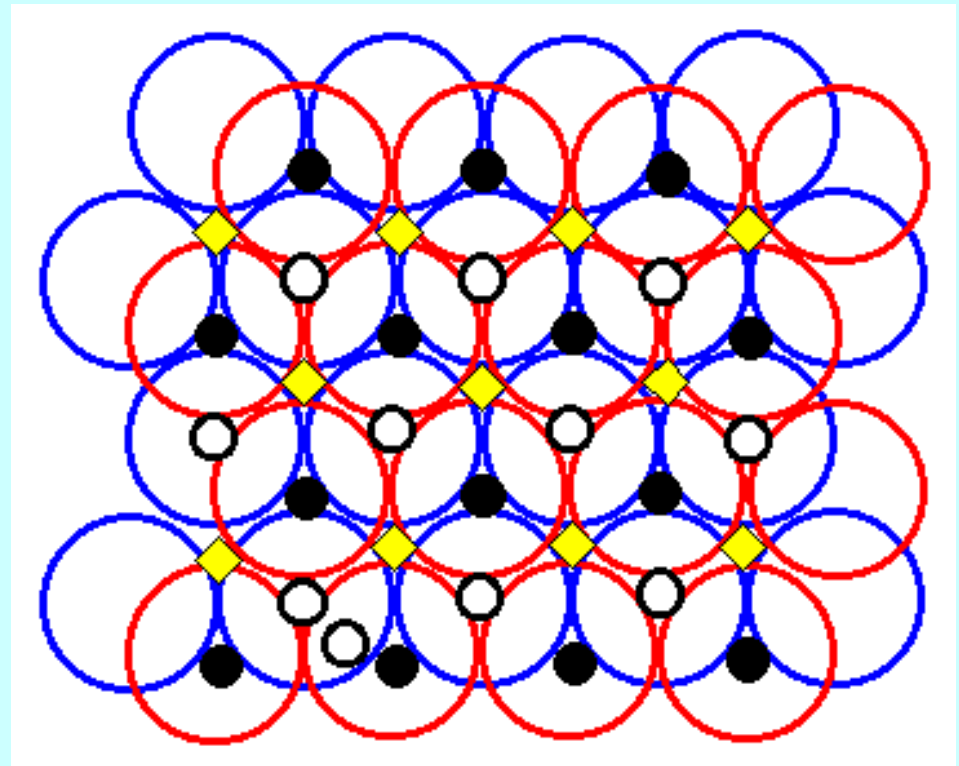
Two Types of Voids (Holes)
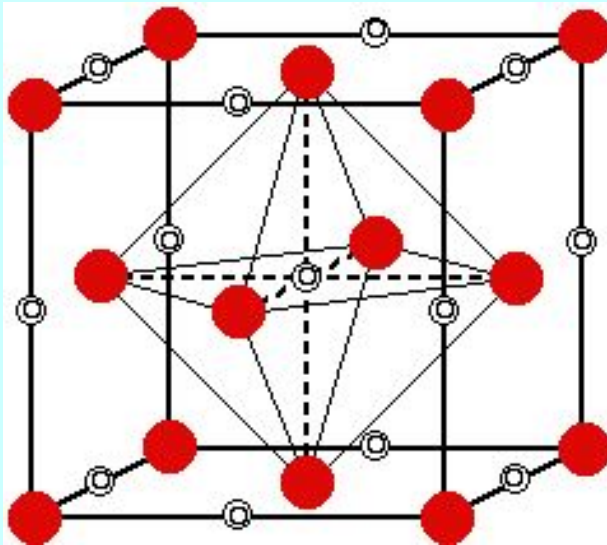
Octahedral Holes
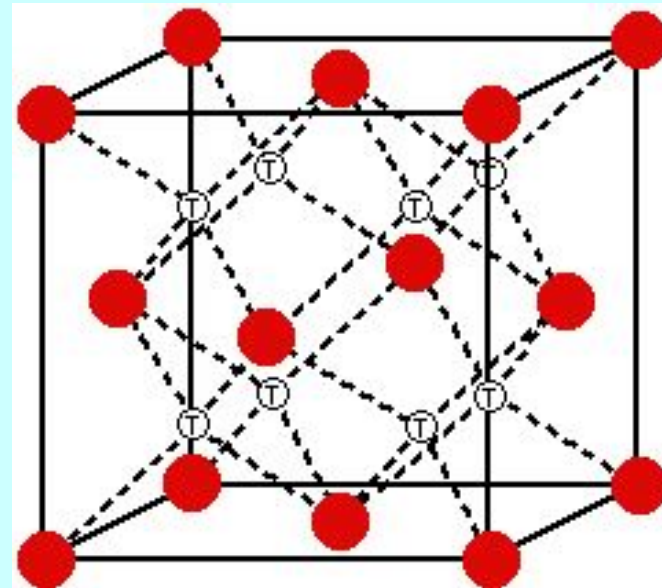
Tetrahedral Holes

Tetrahedral Holes (2N)
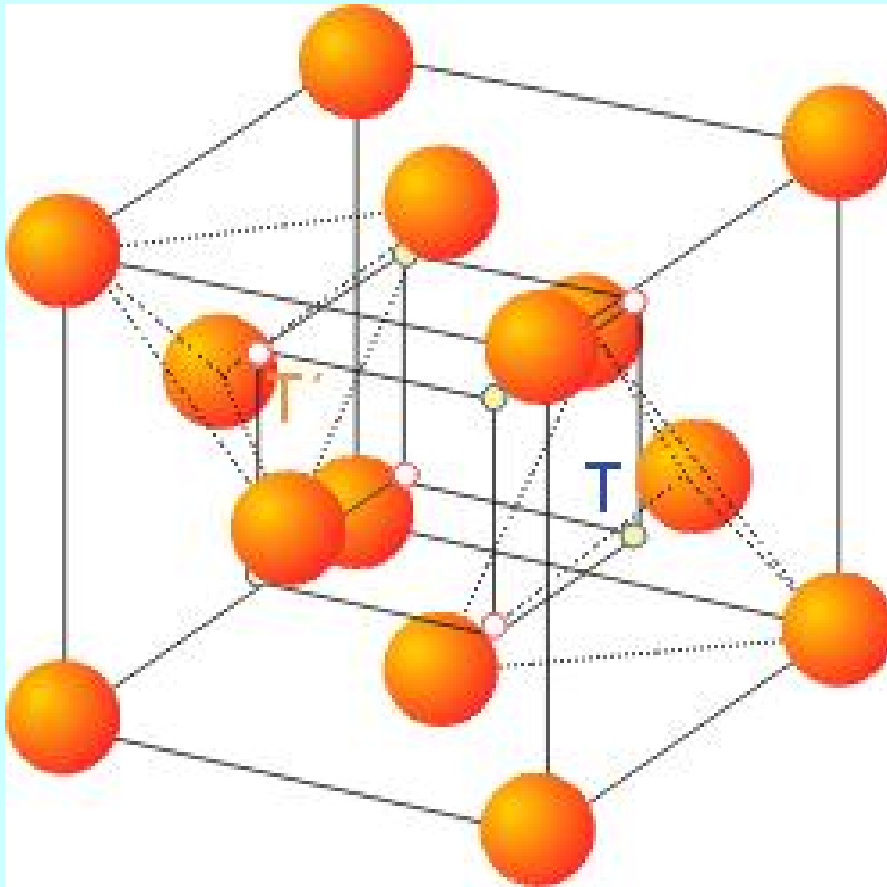
Z = 4
number of atoms in the cell (N)

N = 8
number of tetrahedral holes (2N)

Octahedral Holes (N)
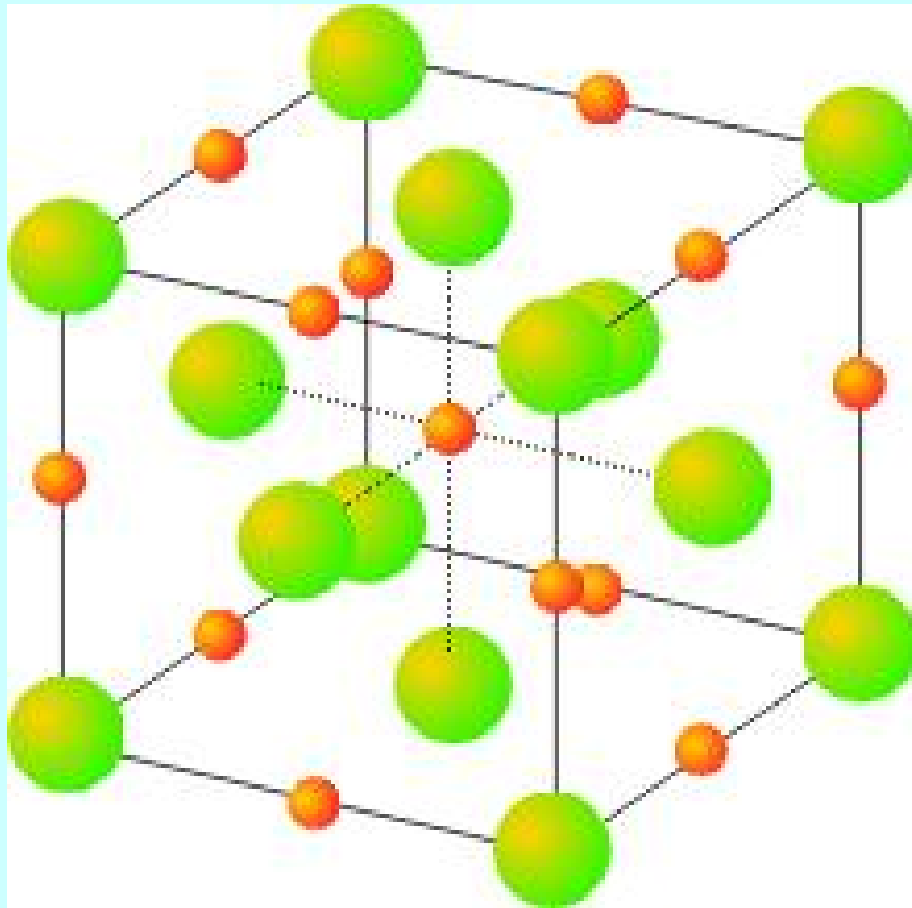
$Z = \underline{4}$
number of atoms in the cell (N)

$N = \underline{4}$
number of octahedral holes (N)

Different Types of Radii

1 Metallic radius

$2r_M$

2 Covalent radius

r

3 Ionic radius

$r_+ + r_-$
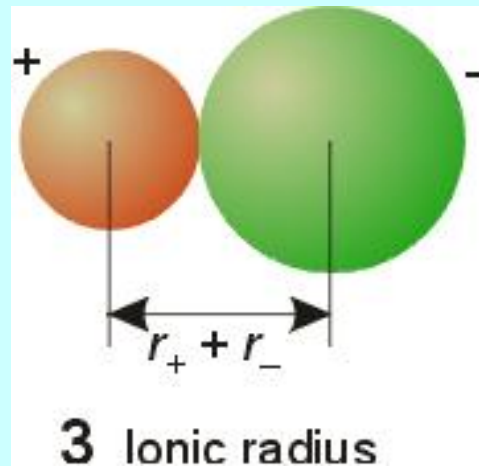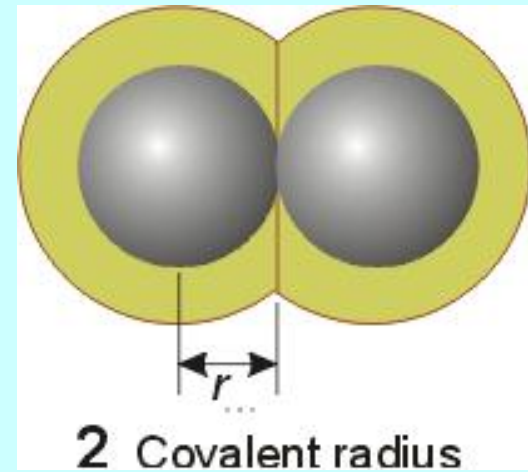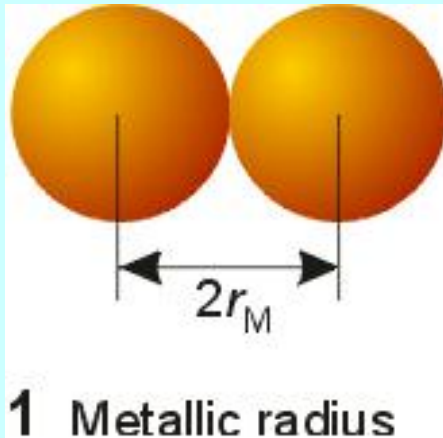
Variation of the electron density along the Li – F axis in LiF

P – Pauling radius
G – Goldschmidt radius
S – Shannon radius.
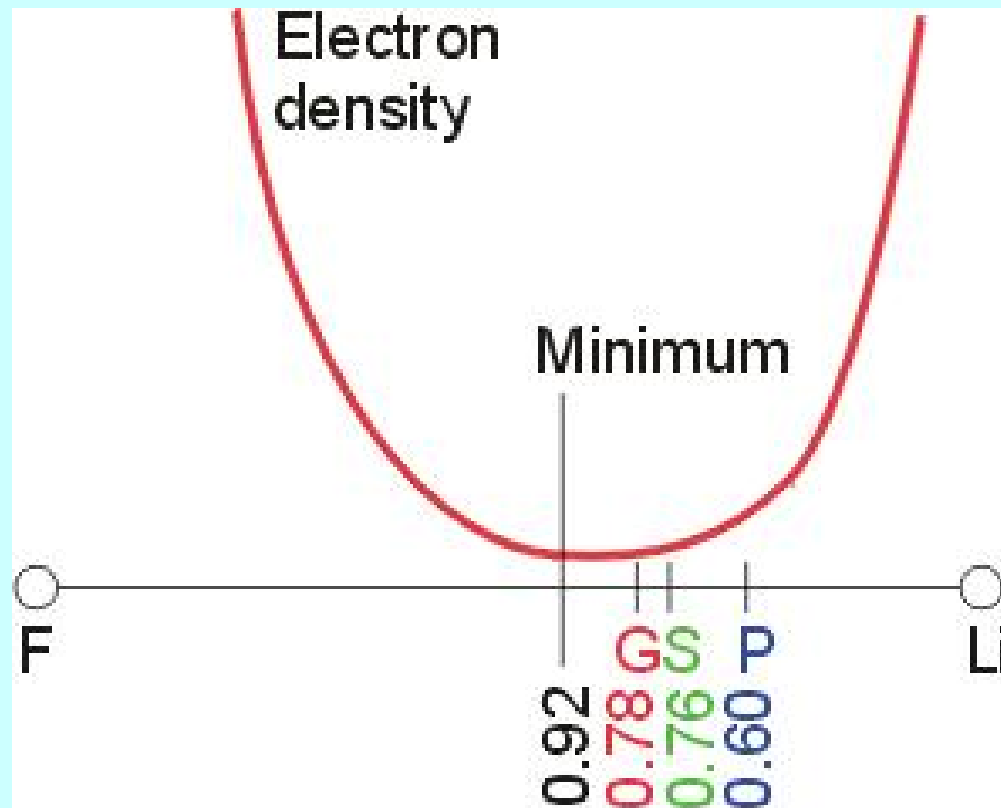
Variation of ionic radii with coordination number
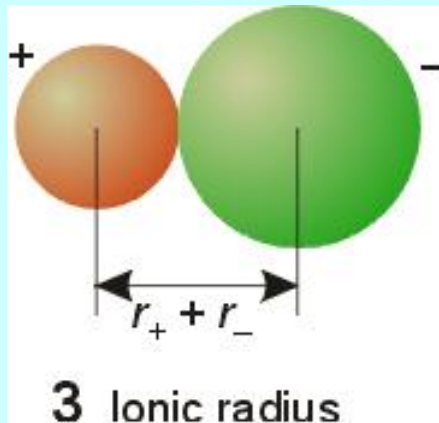
3 Ionic radius

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.
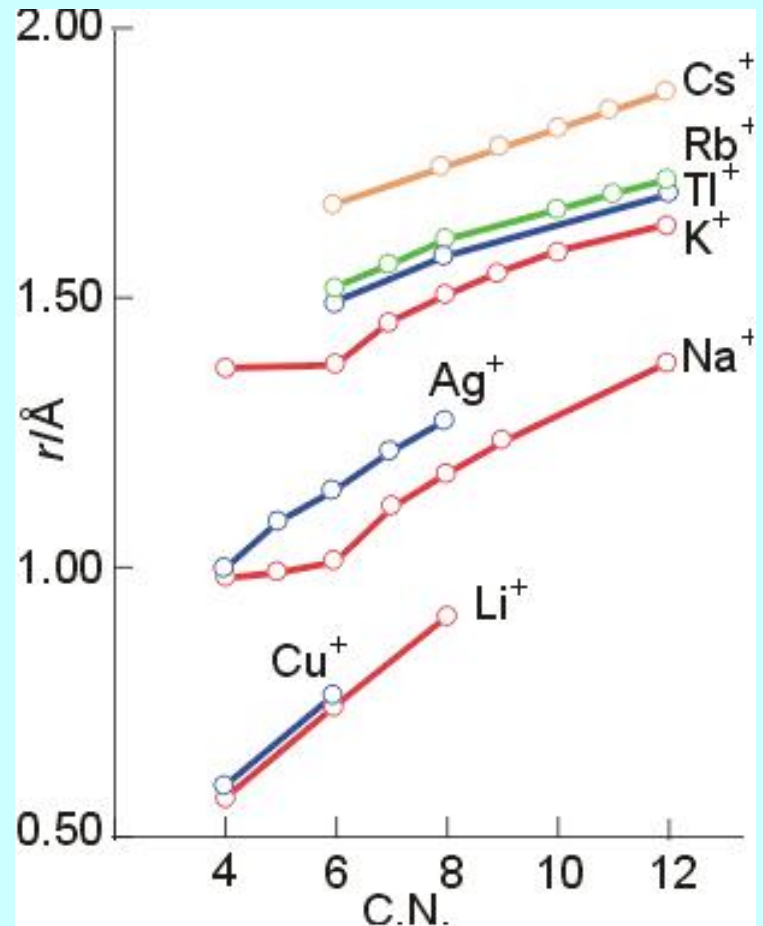
Variation of atomic radii
through the Periodic table
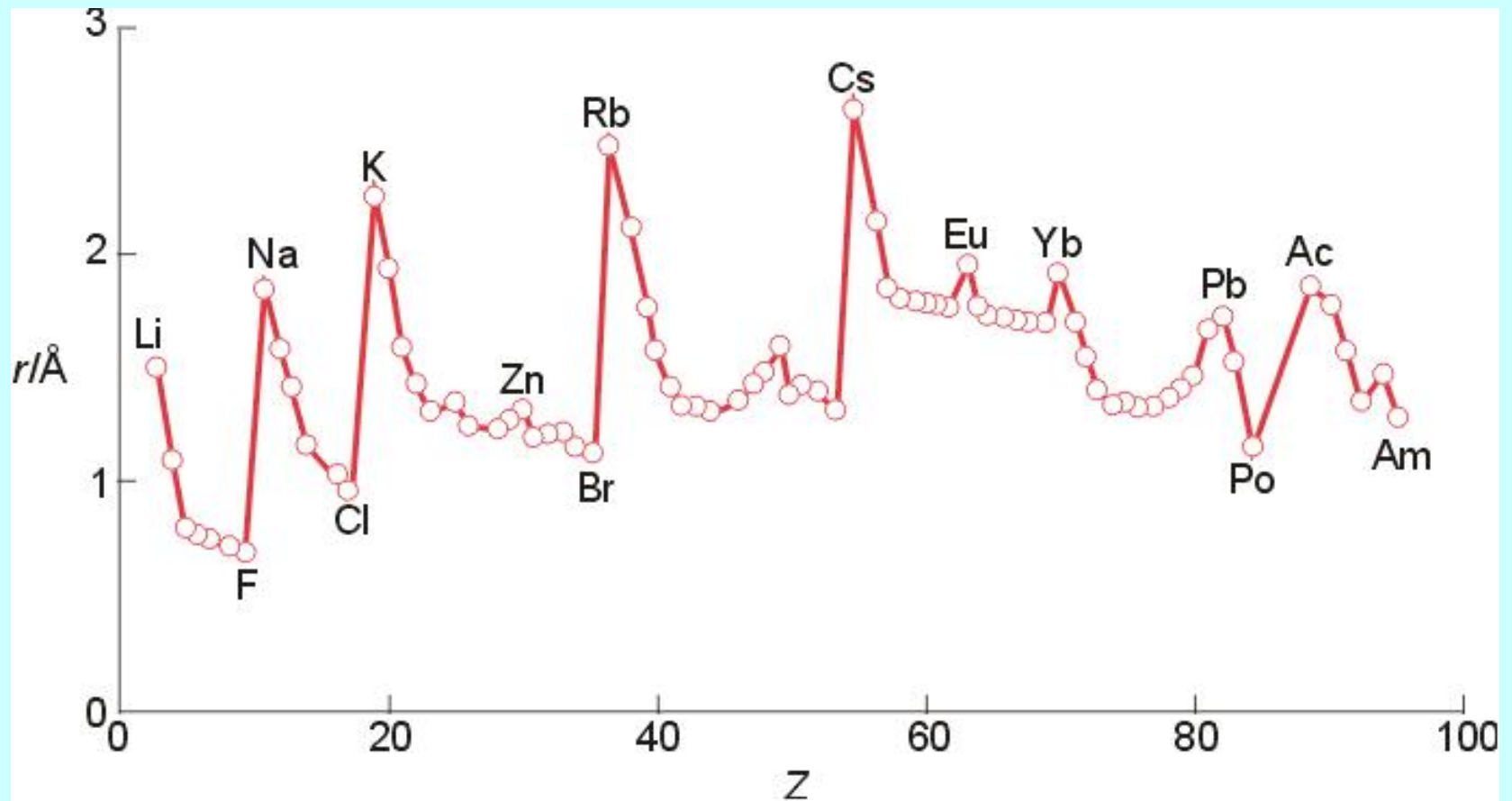
General trends for ionic radii

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)

Cation/anion Radius Ratio
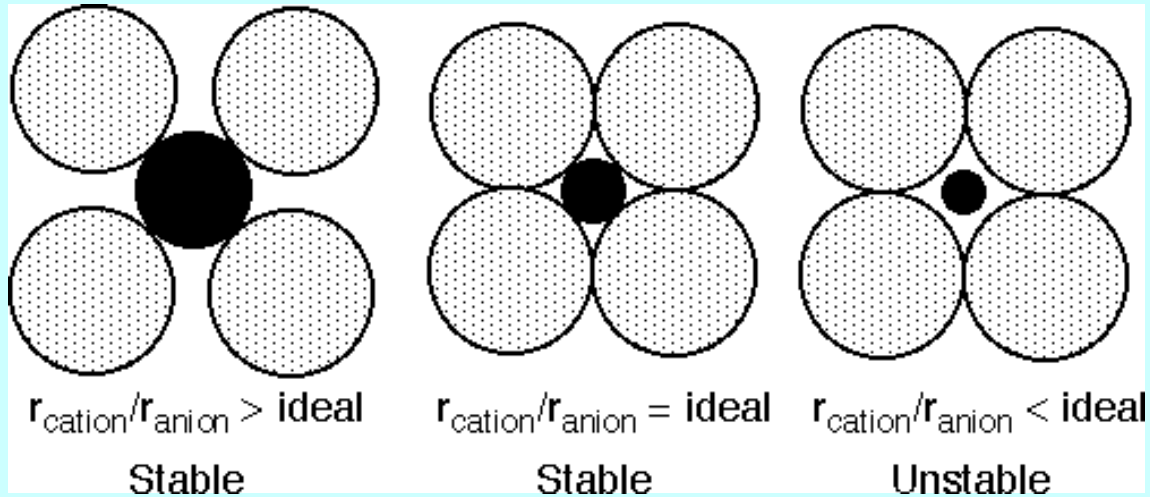
r_{cation}/r_{anion} > ideal — Stable

r_{cation}/r_{anion} = ideal — Stable

r_{cation}/r_{anion} < ideal — Unstable

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   **NaCl 6:6**   **ZnS 4:4**
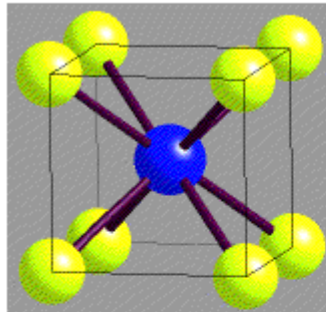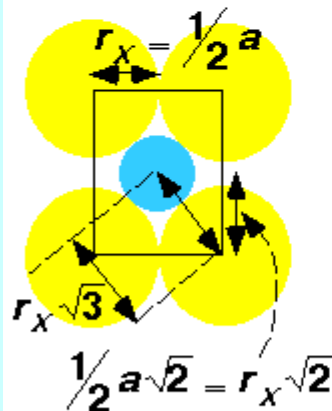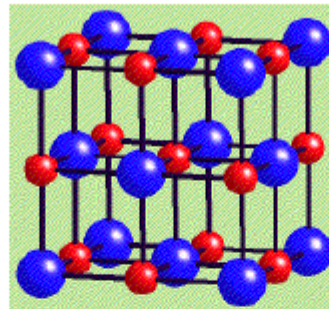
unit cell   *unit cell*   *1/8th unit cell*

cell side a face diagonal $a\sqrt{2}$ body diagonal $a\sqrt{3}$

$r_X = \frac{1}{2}a$ $2r_X$ $\frac{1}{2}r_X\sqrt{6}$

$r_X\sqrt{3}$ $\frac{1}{2}a = r_X\sqrt{2}$ $\frac{1}{4}a$

$\frac{1}{2}a\sqrt{2} = r_X\sqrt{2}$ $\frac{1}{4}a\sqrt{2} = r_X$

$r_M + r_X = r_X\sqrt{3}$ $r_M + r_X = r_X\sqrt{2}$ $r_M + r_X = \frac{1}{2}r_X\sqrt{6}$

$r_M / r_X = \sqrt{3} - 1$ $r_M / r_X = \sqrt{2} - 1$ $r_M / r_X = \frac{1}{2}\sqrt{6} - 1$
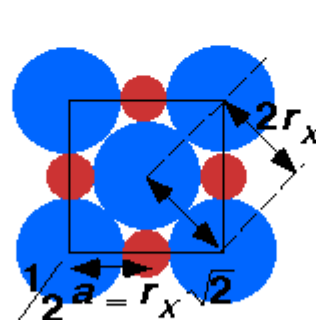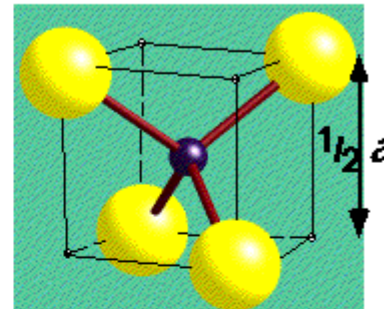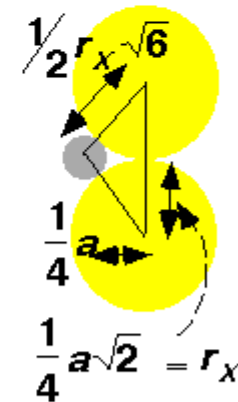
$= 0.732$ $= 0.414$ $= 0.225$
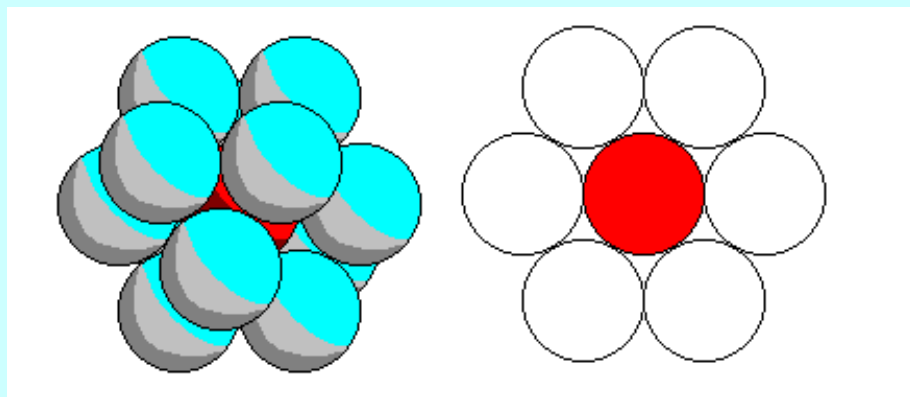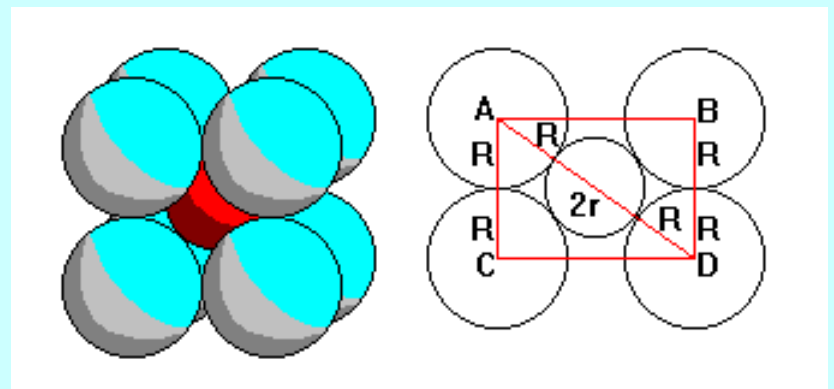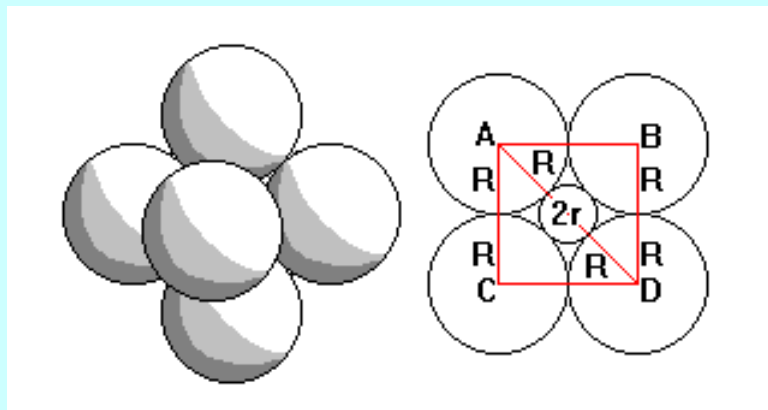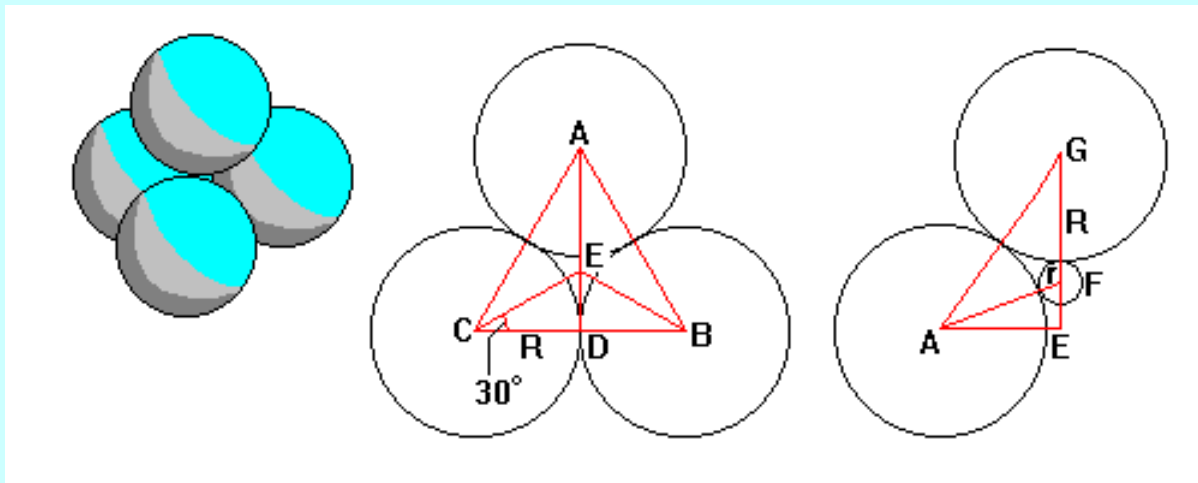
Structure Map

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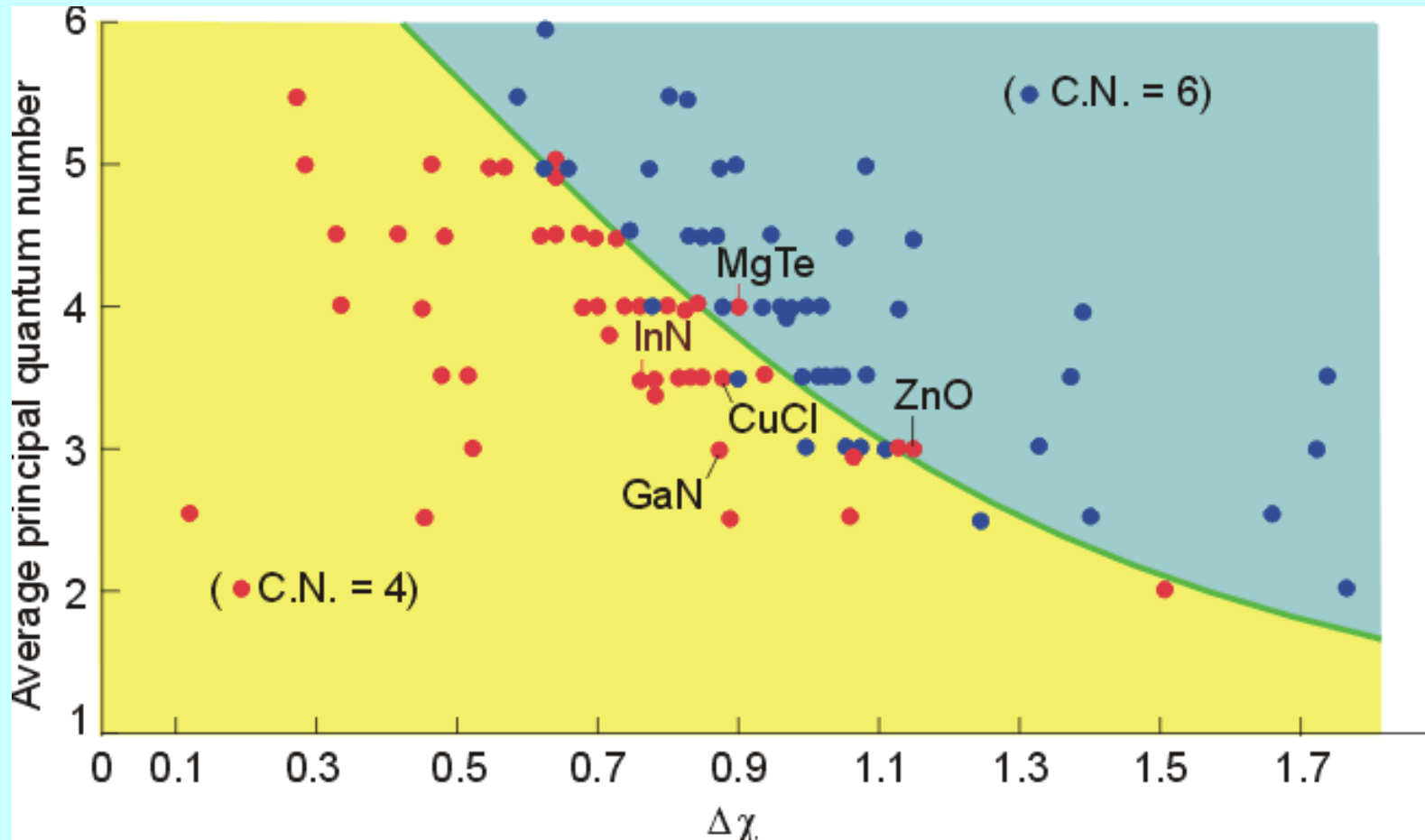
Lattice Enthalpy

The <u>lattice enthalpy</u> change ΔH_L^0 is the standard molar enthalpy change for the following process:

$$\text{M}^+_{(gas)} + \text{X}^-_{(gas)} \rightarrow \text{MX}_{(solid)} \qquad\qquad \Delta H_L^0$$
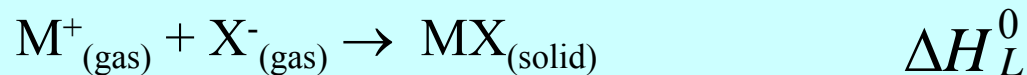
Because the formation of a solid from a „gas of ions" is always <u>exothermic</u> lattice enthalpies (defined in this way) are usually negative.
If entropy considerations are neglected the <u>most stable crystal structure</u> of a given compound is the one with the <u>highest lattice enthalpy.</u>

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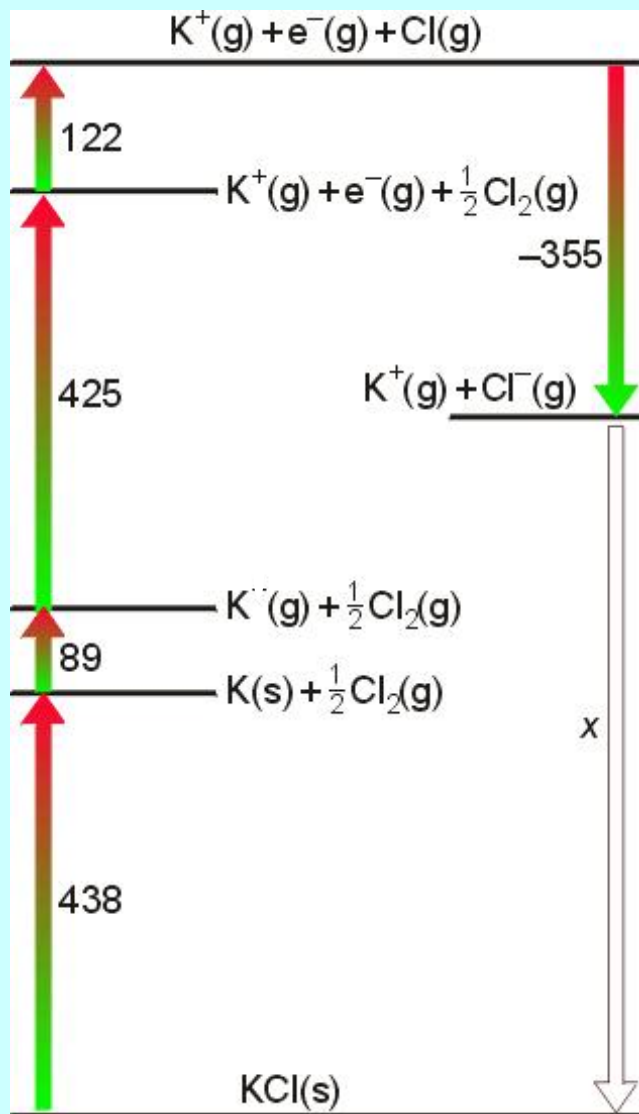
A Born-Haber cycle for KCl

(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

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

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

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

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

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

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

$$1/2\ D = 121\ kJ\ mol^{-1}$$

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

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

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

$$L = ?$$

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

$$NaCl_{(s)}$$
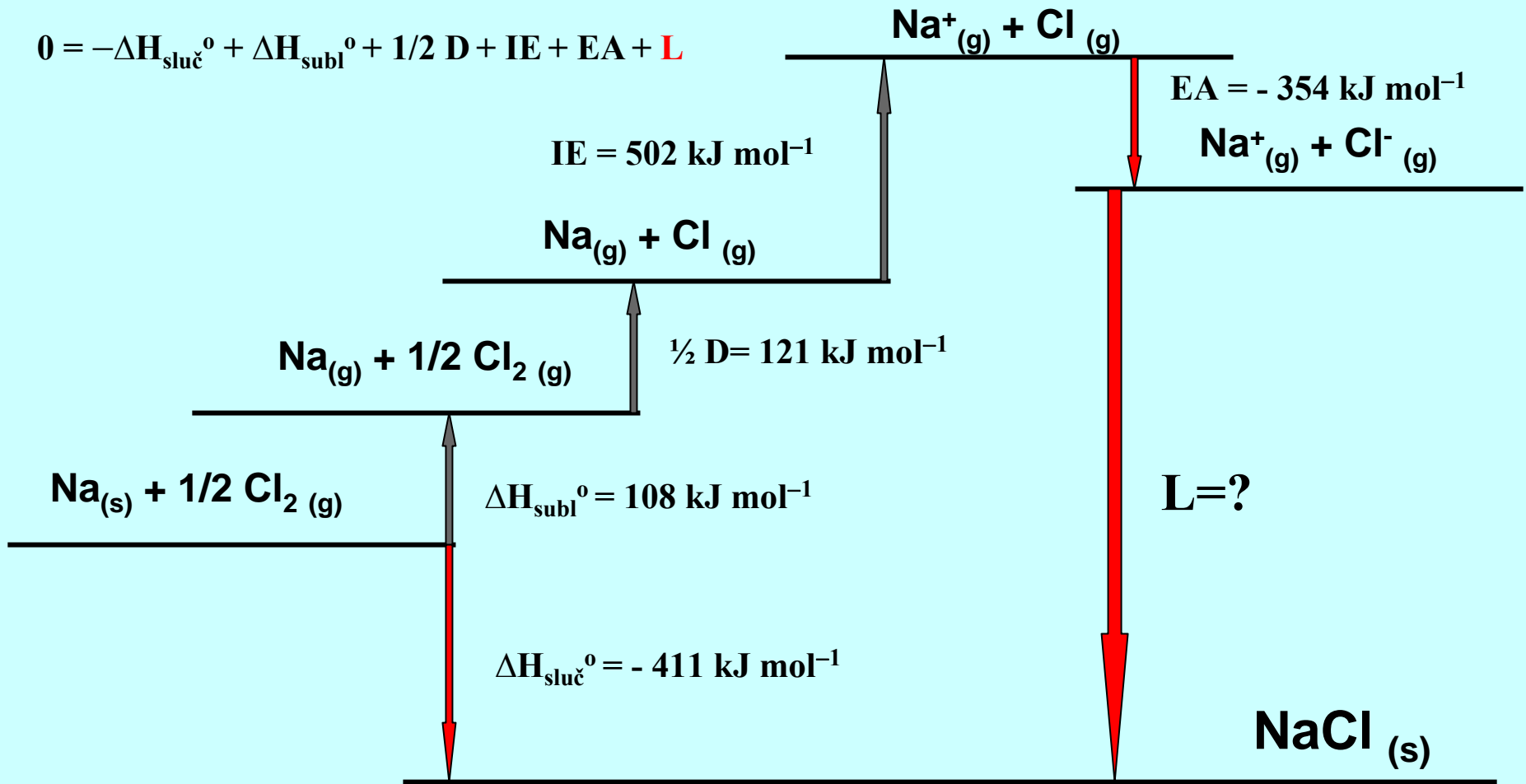
$$0 = 411 + 108 + 121 + 502 + (-354) + L$$

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

all enthalpies: kJ mol^{-1} for normal conditions $\rightarrow$ standard enthalpies

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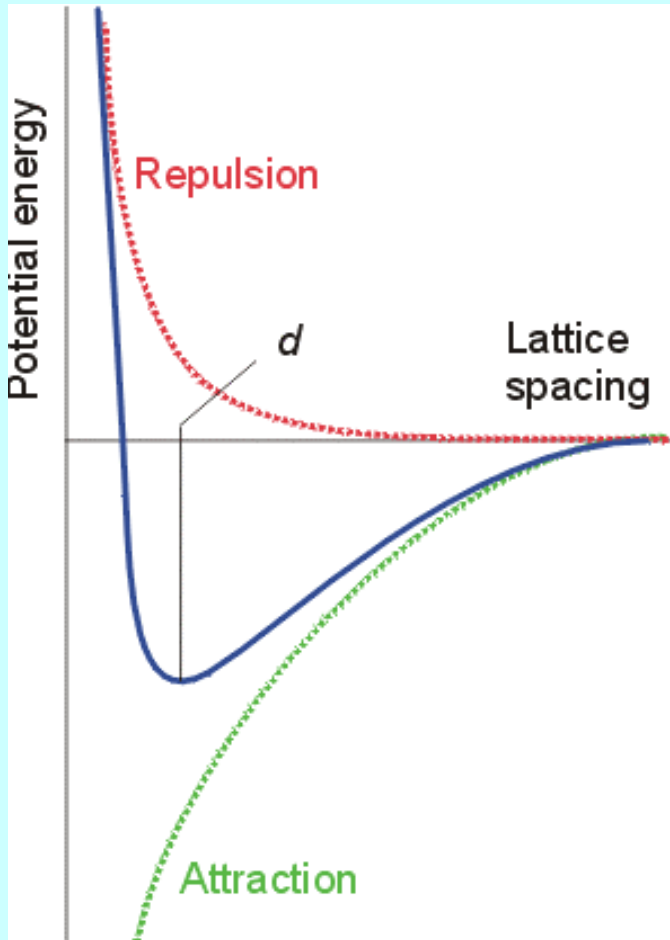
$$L = E_{coul} + E_{rep}$$

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

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

← Coulomb potential of an ion pair

V_{AB}: Coulomb potential (electrostatic potential)
A: Madelung constant (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
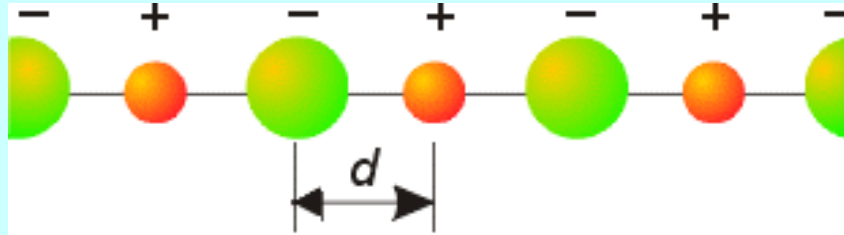
$E_{coul} = (e^2 / 4 \pi \varepsilon_0)*(z_A z_B / d)*[+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + ...]$

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

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

Calculation of the Madelung constant
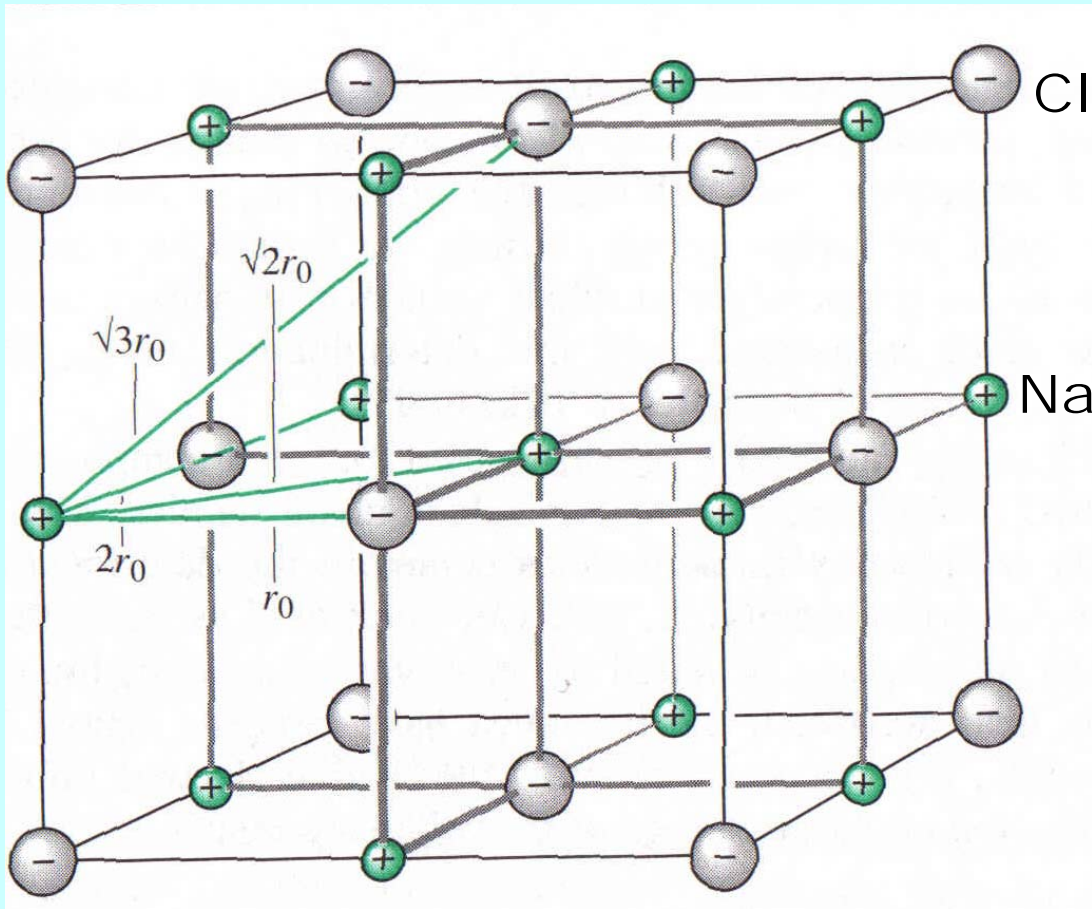
3D ionic solids:
Coulomb attraction and
repulsion

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

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

= 1.748… (NaCl)
(infinite summation)

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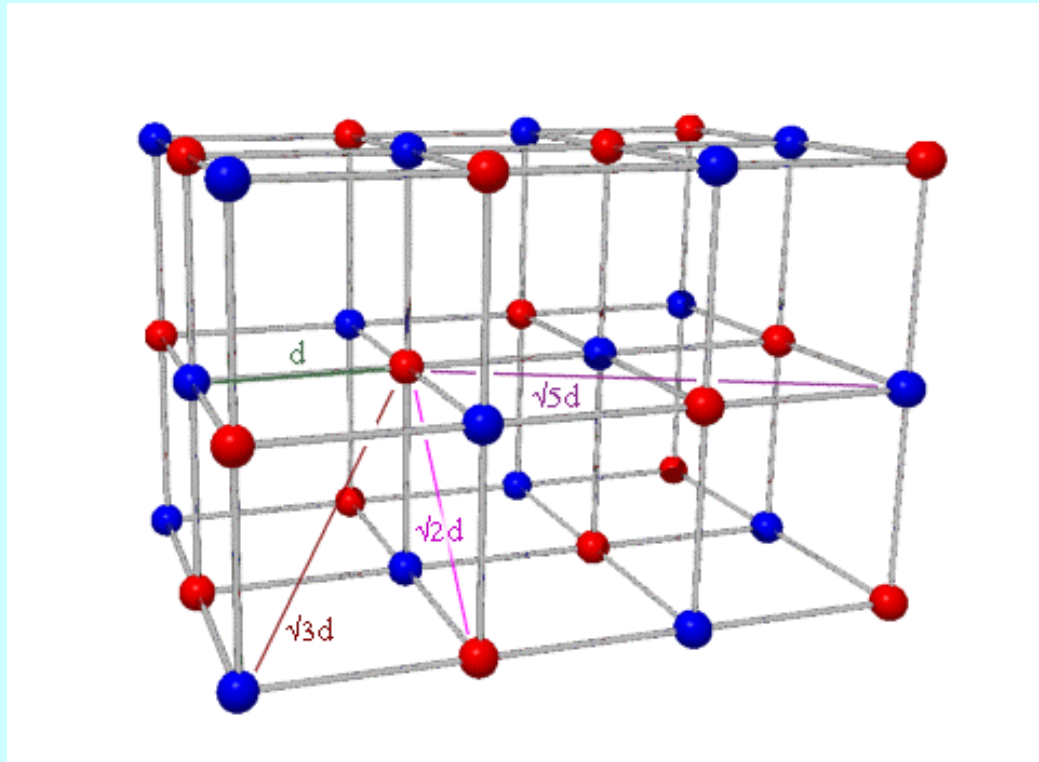
$E_{coul} = (e^2 / 4 \pi \varepsilon_0) * (z_A z_B / d) * [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) ....]$

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}
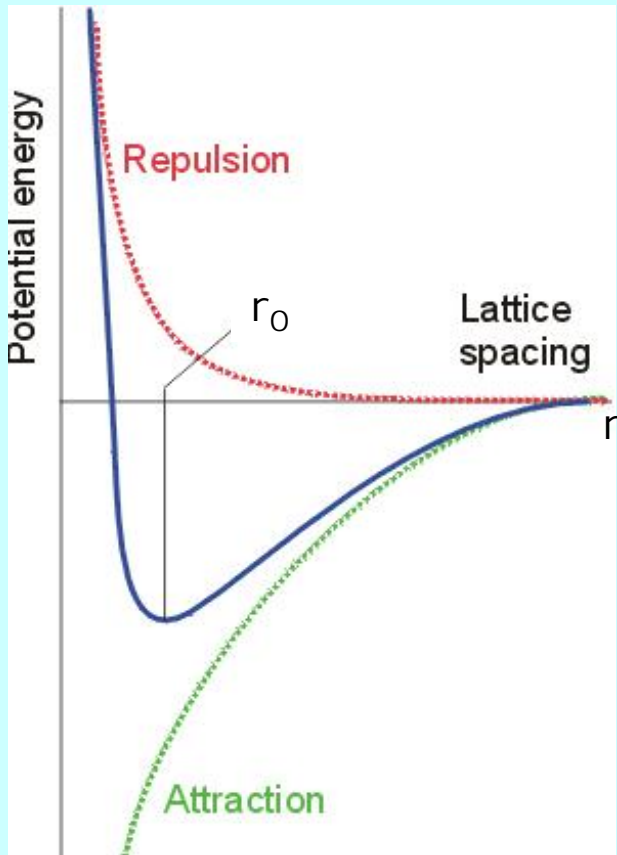
Repulsion arising from overlap of electron clouds

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

approximation:

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

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)

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

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$_2$O$_3$	4.172	0.83	6:4

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

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

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

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

Born – Mayer

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

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

$d^* = 0.345$ Å

Lattice Enthalpy

Kapustinski

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

M je nahrazena 0.87 v, není nutno znát strukturu

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

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:

$\rightarrow$ thermal stabilities of ionic solids

$\rightarrow$ stabilities of oxidation states of cations

$\rightarrow$ Solubility of salts in water

$\rightarrow$ calculations of electron affinity data

$\rightarrow$ lattice enthalpies and stabilities of „non existent"
compounds

Cation/anion Radius Ratio
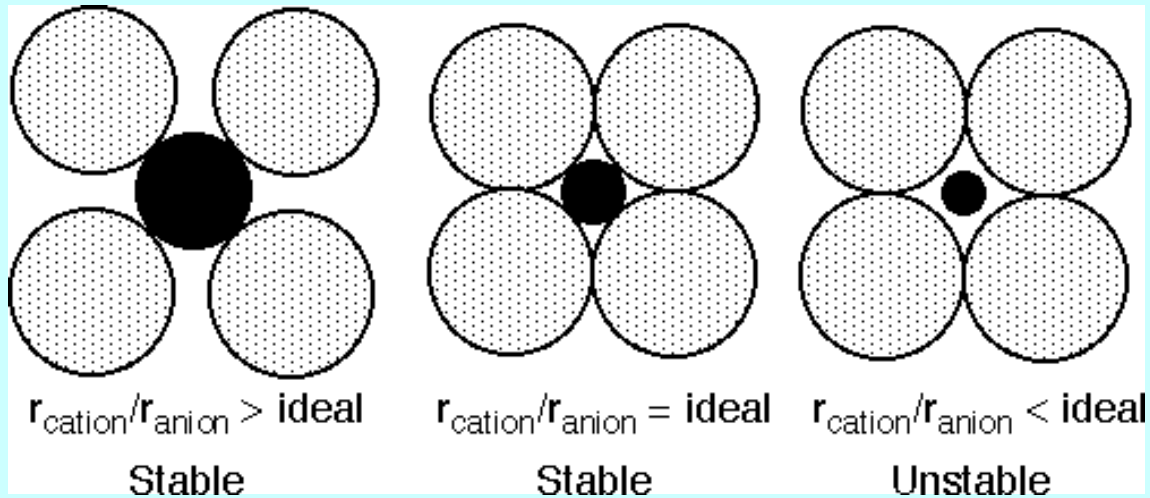
$r_{cation}/r_{anion} >$ ideal — Stable

$r_{cation}/r_{anion} =$ ideal — Stable

$r_{cation}/r_{anion} <$ ideal — Unstable

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

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.

Characteristic Structures of Solids = Structure Types

Rock salt $\underline{NaCl}$ 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) $\underline{ZnS}$ CuCl, HgS, GaAs ...

Nickel arsenide $\underline{NiAs}$ FeS, PtSn, CoS ...
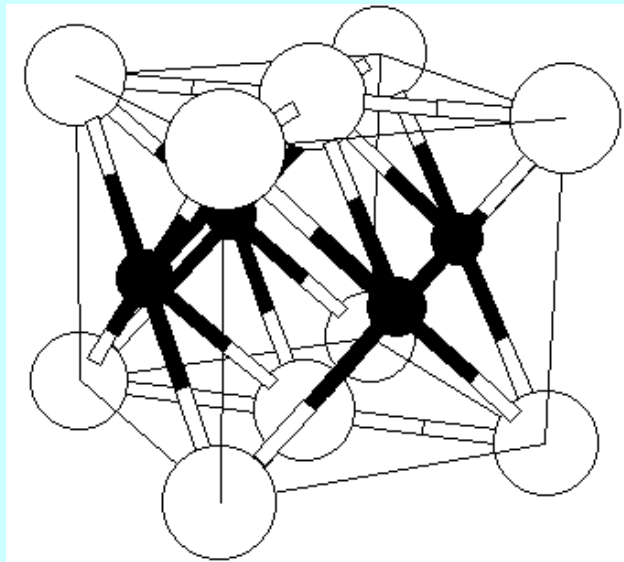
Wurtzite $\underline{ZnS}$ ZnO, MnS, SiC

Rhenium diboride ReB_2

Structure Types Derived from CCP = FCC
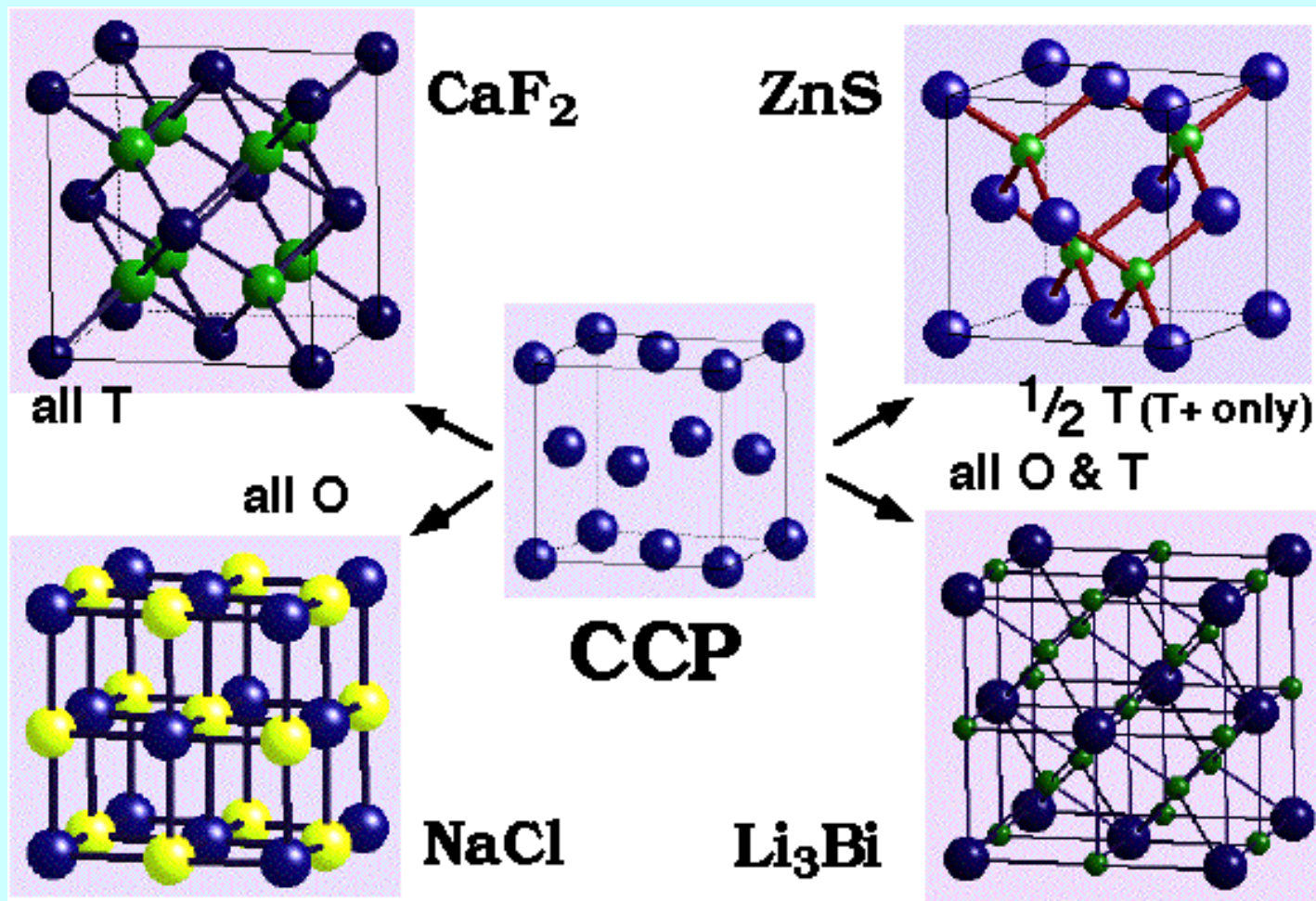
Structure Types Derived from CCP = FCC
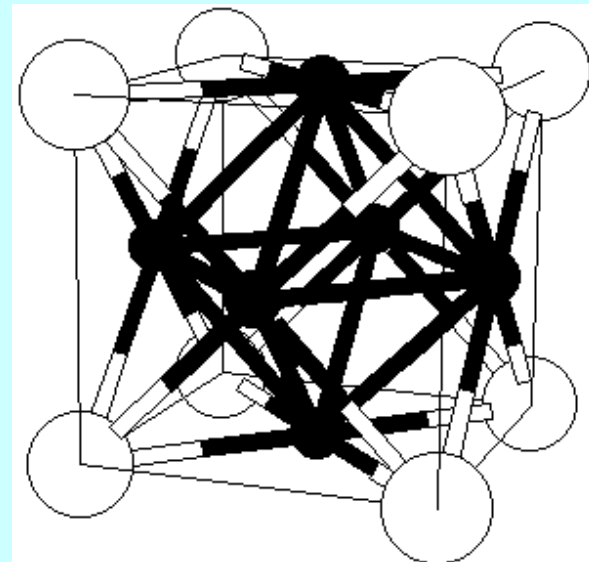
Structure Types Derived from CCP = FCC

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 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$_2$, antifluorite Li$_2$O)
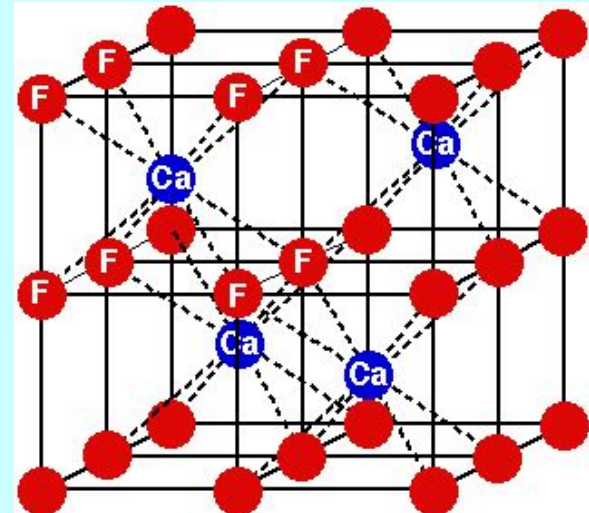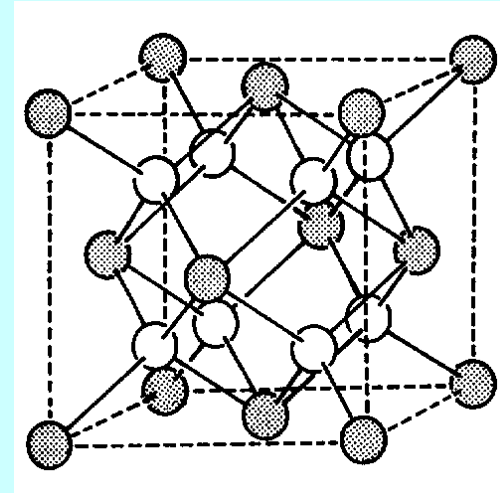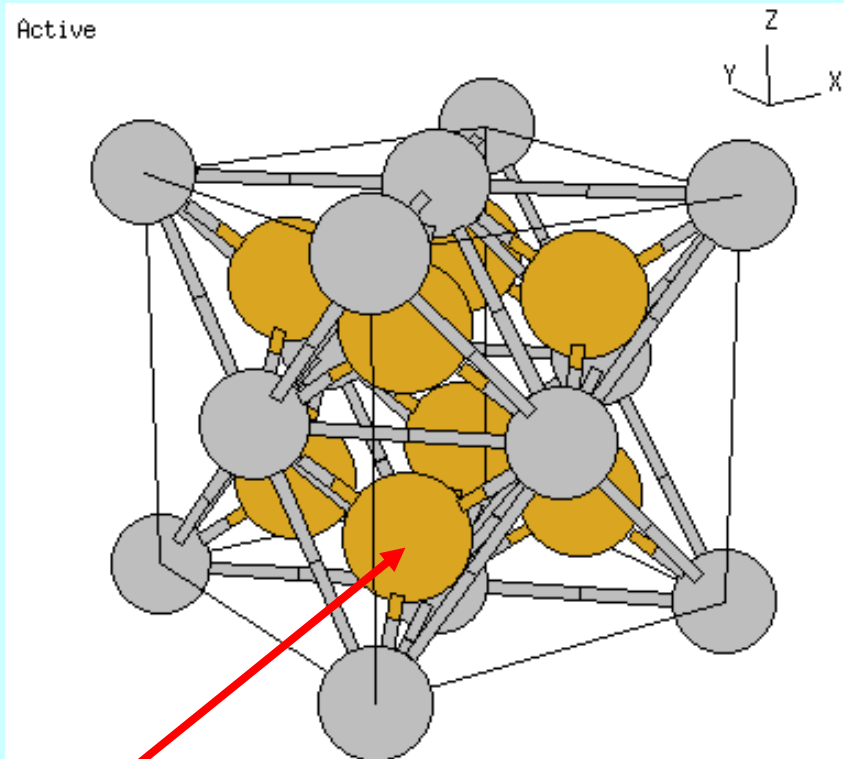
F / Li

K$_2$[PtCl$_6$], Cs$_2$[SiF$_6$], [Fe(NH$_3$)$_6$][TaF$_6$]$_2$

Fluorite structures (CaF_2, antifluorite Li_2O)
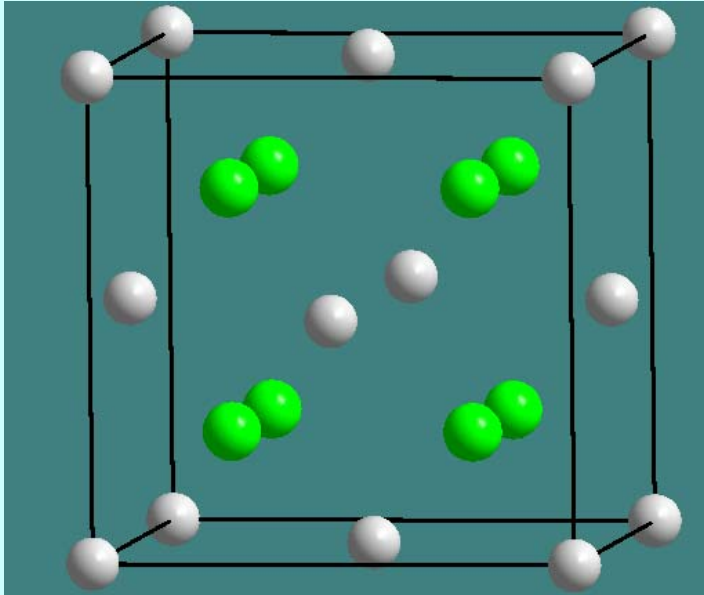
Oxides: Na_2O, K_2O, UO_2, ZrO_2, ThO_2

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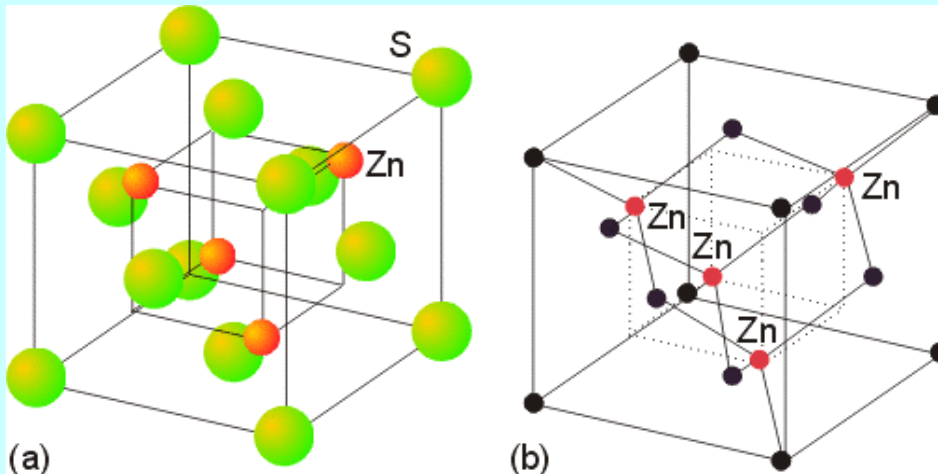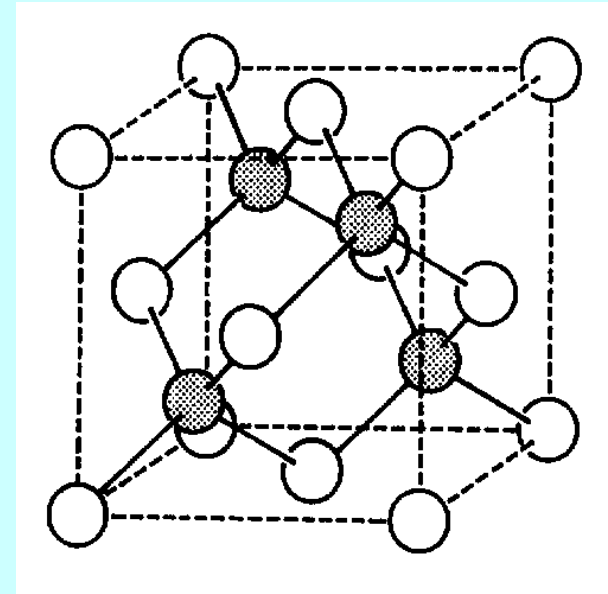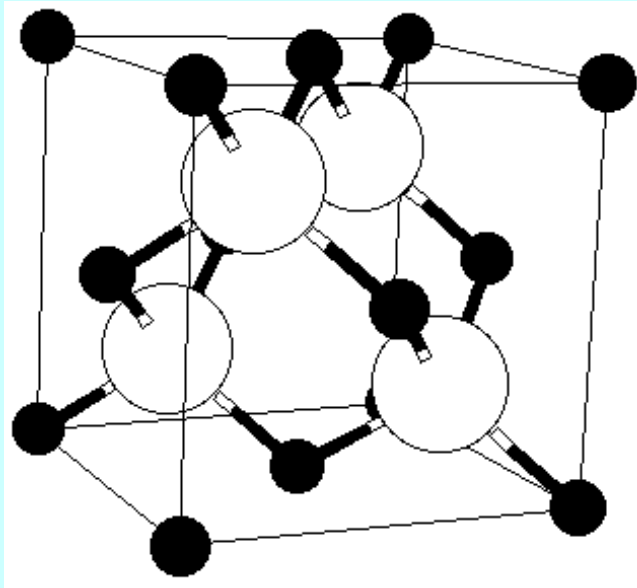
Cubic close packing of anions
with 1/2 tetrahedral holes
filled by cations

Sphalerite (zincblende, ZnS)
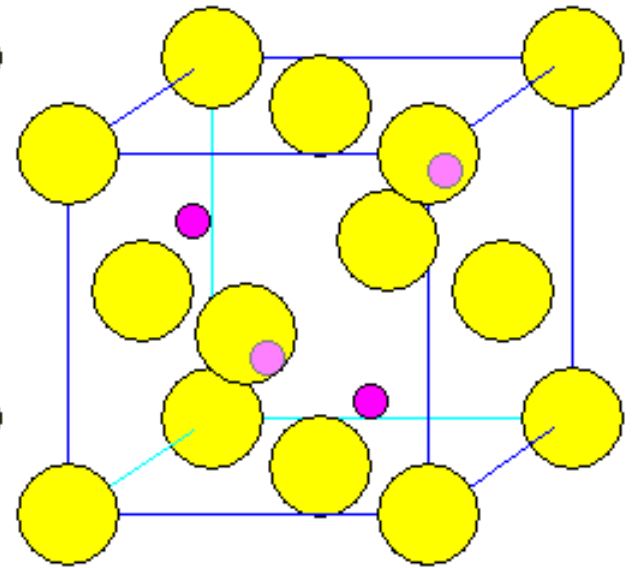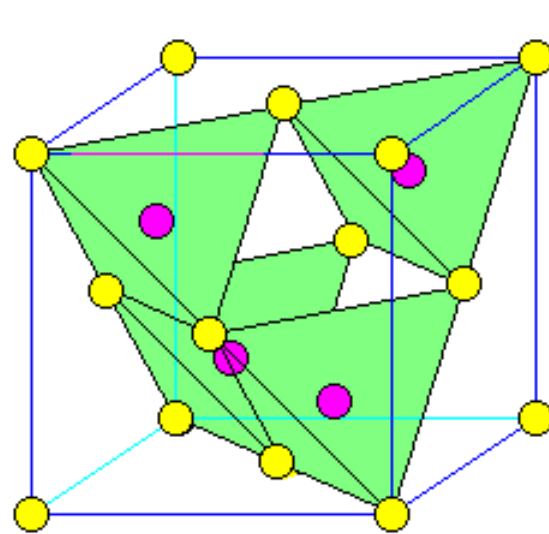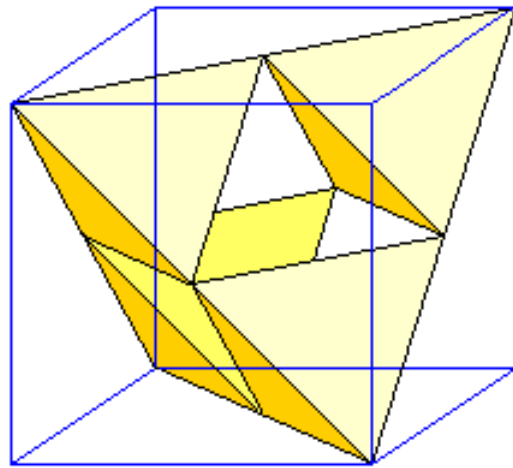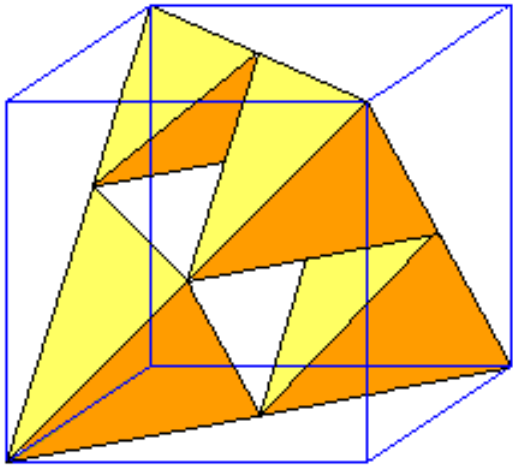
Sphalerite   ZnS

Sphalerite (zincblende, ZnS)
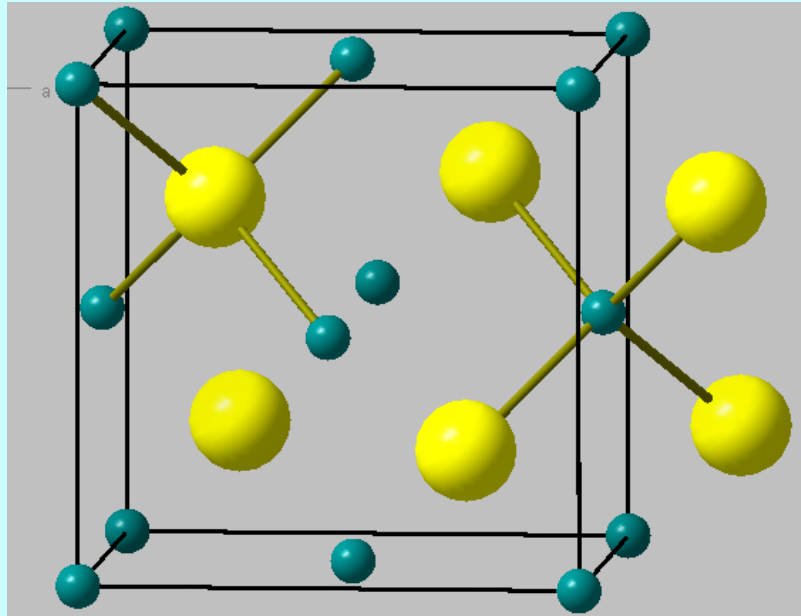
13-15 compounds: BP, BAs, AlP, AlAs, GaAs, GaP, GaSb, AlSb, InP, InAs, InSb

12-16 compounds: BeS, BeSe, BeTe, β-MnS (red), β-MnSe, β-CdS, CdSe, CdTe, HgS, HgSe, HgTe, ZnSe, ZnTe
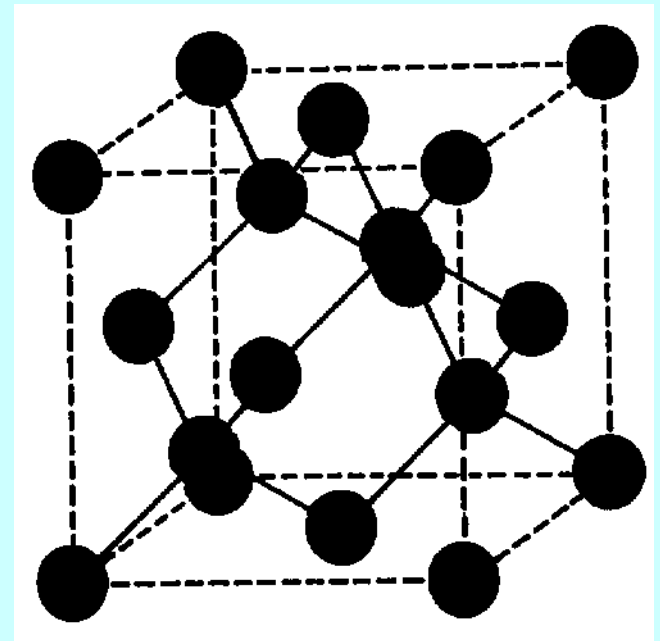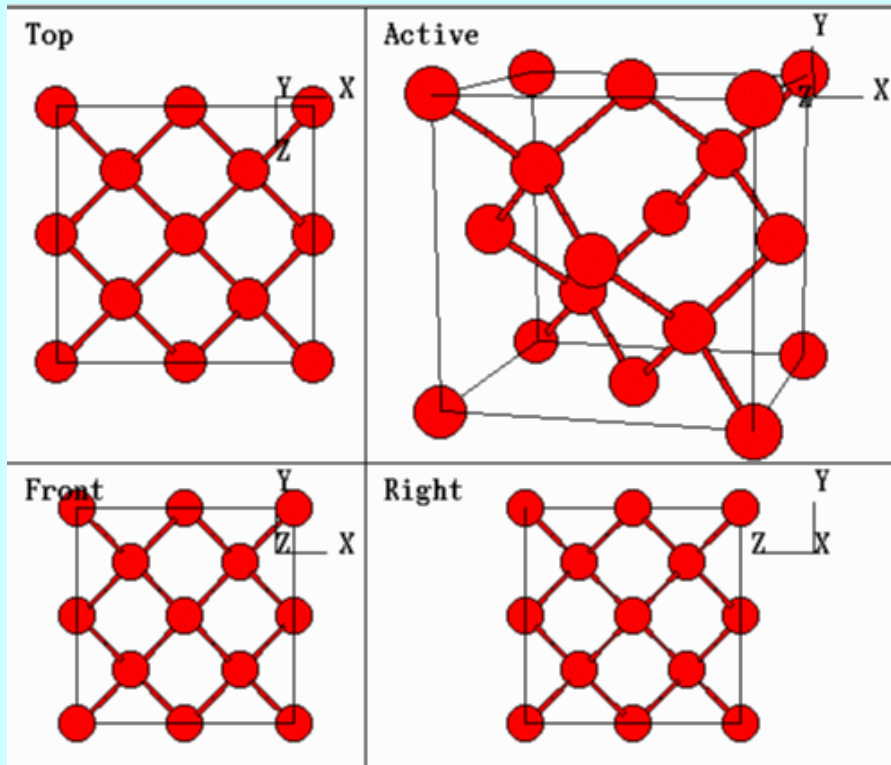
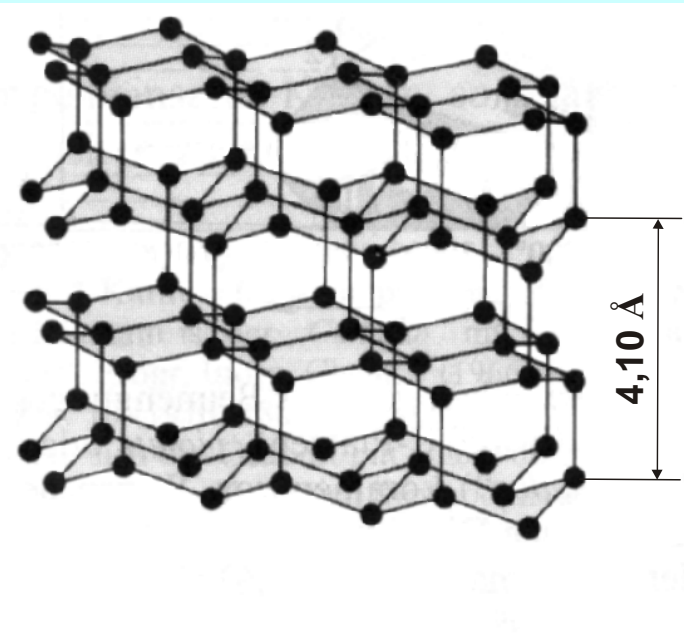**Halogenides: AgI, CuF, CuCl, CuBr, CuI, NH4F**

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

Diamond

Diamond

cubic   hexagonal
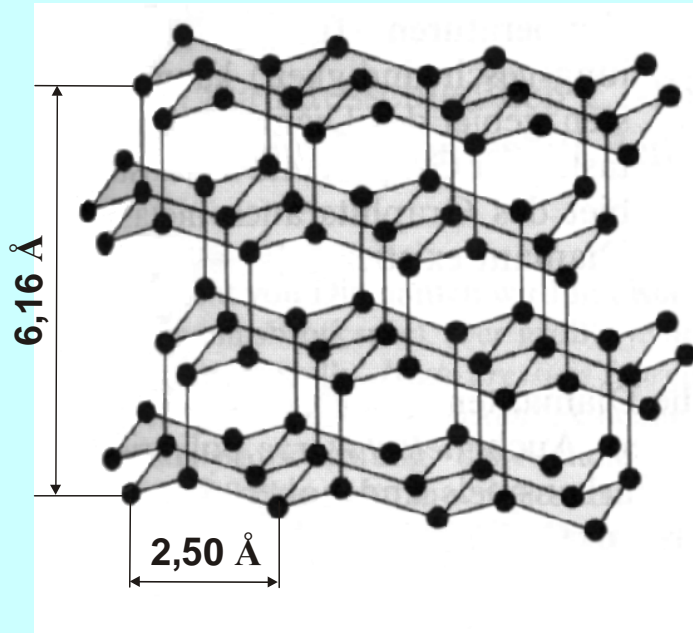
SiO$_2$ cristobalite   SiO$_2$ tridymite
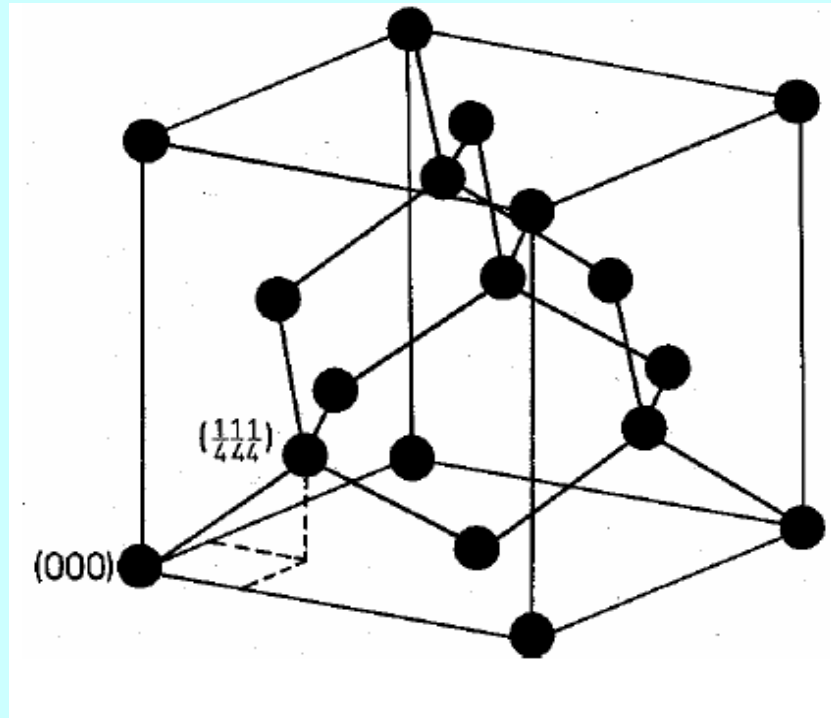   ice

Cubic Diamond
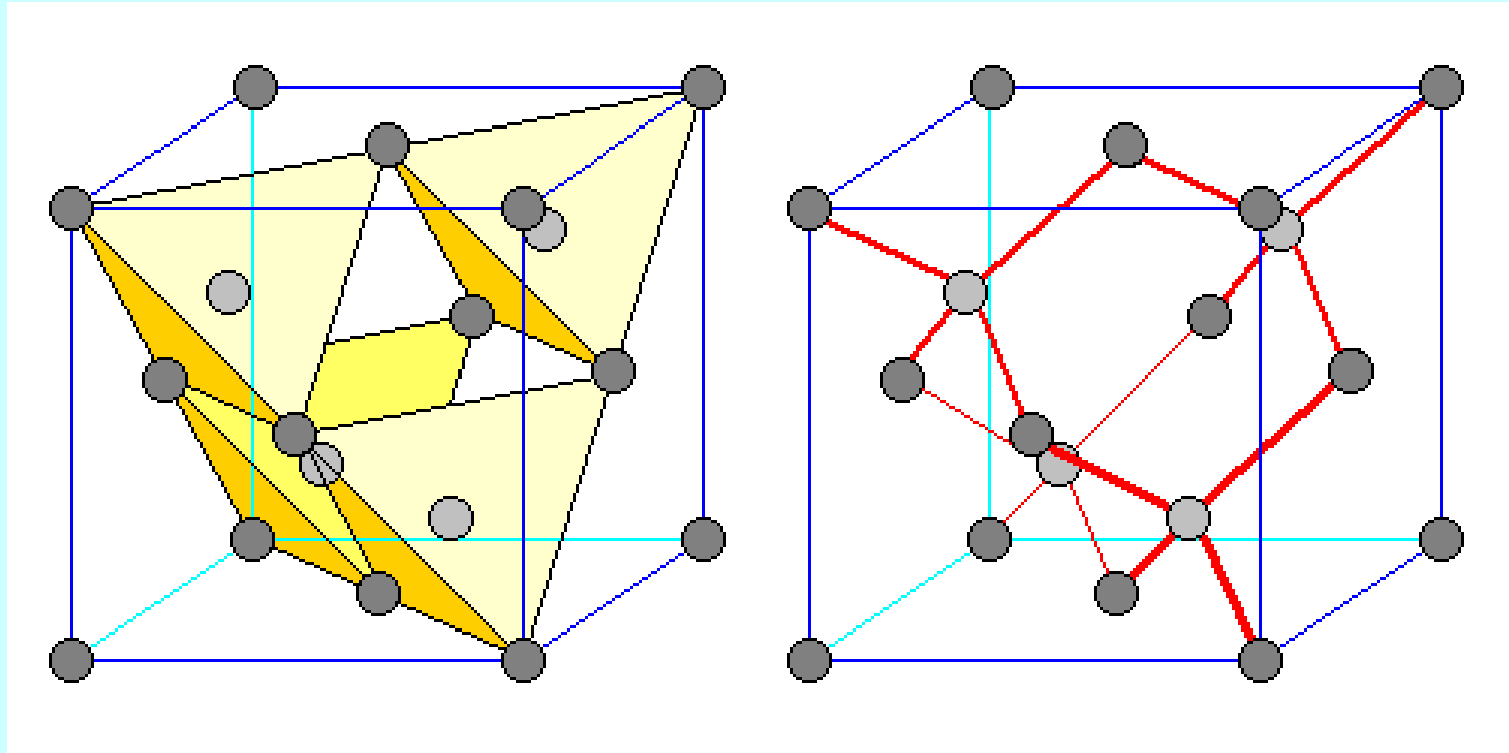
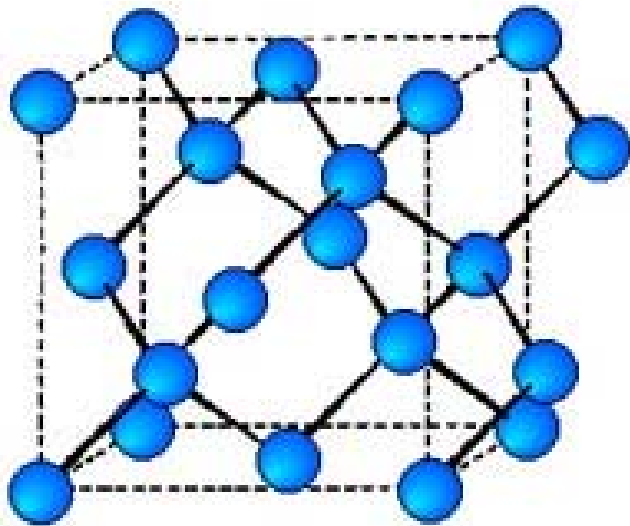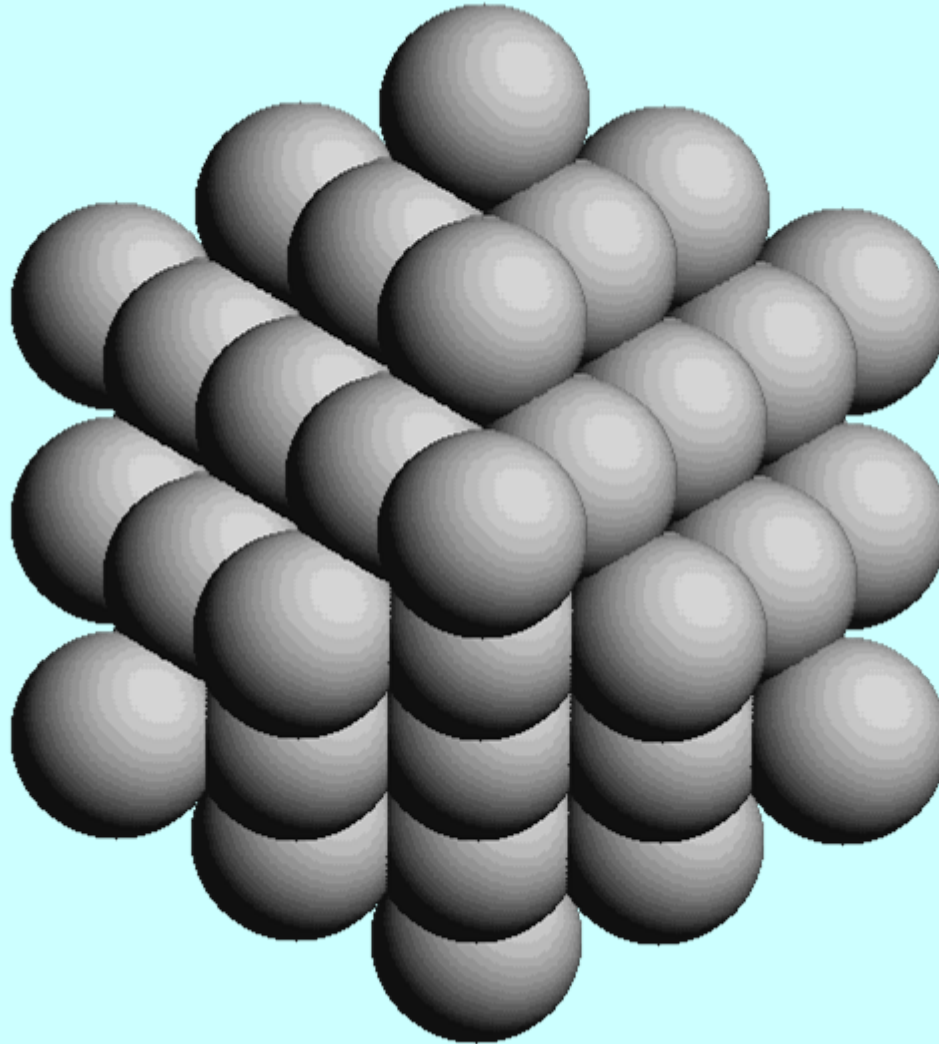# Diamond Structure

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
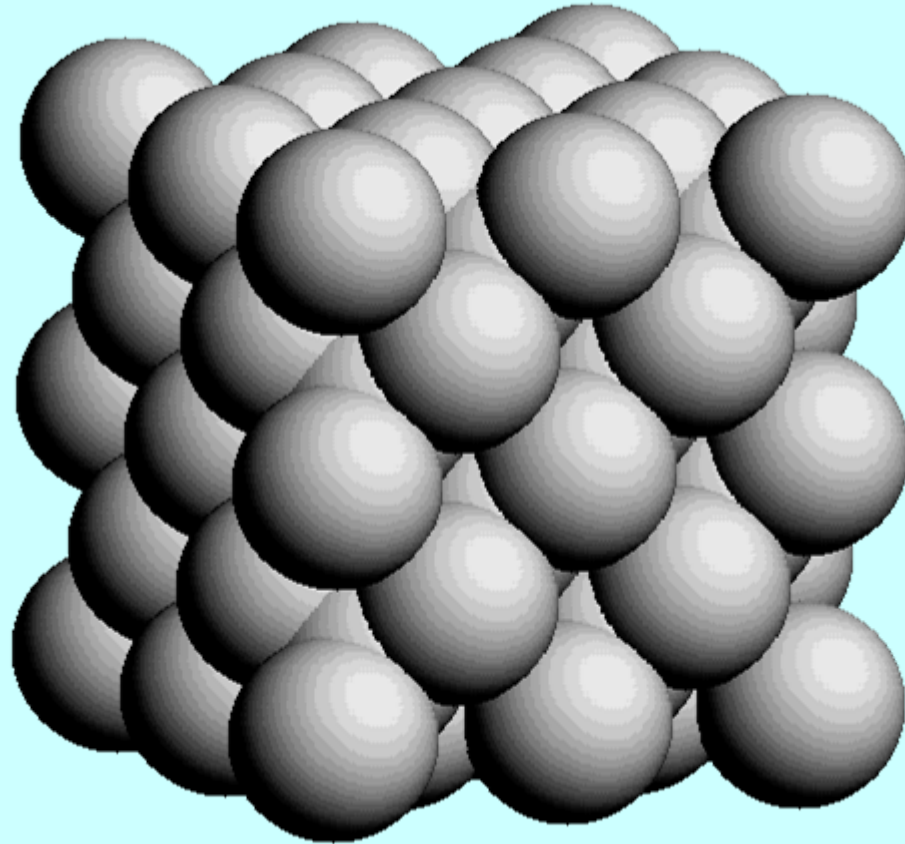
Elements of the 14th Group

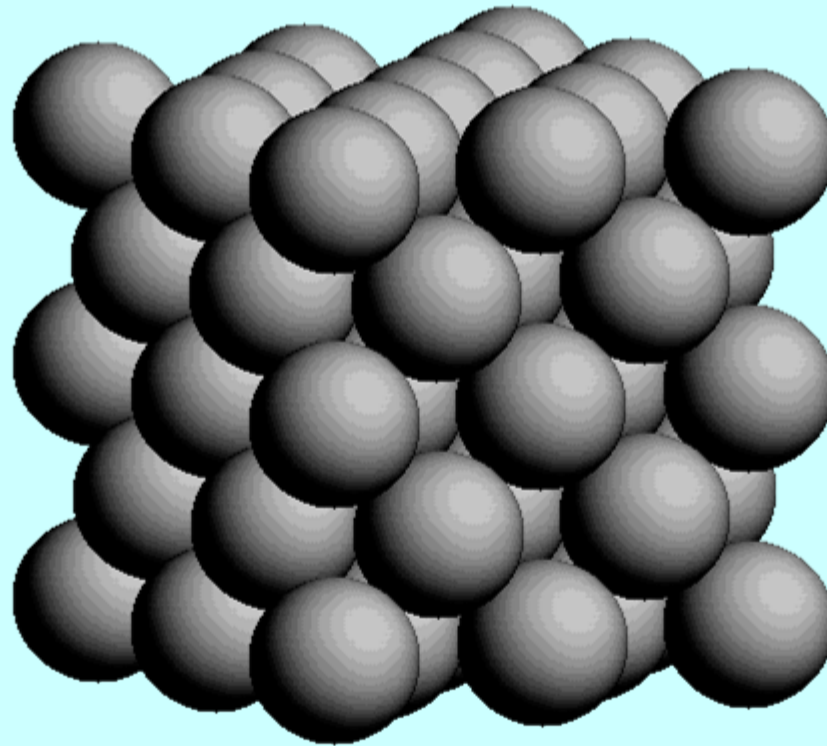|	a (Å)	d (g.cm^{-3})
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
a-Sn	6.489	7.285

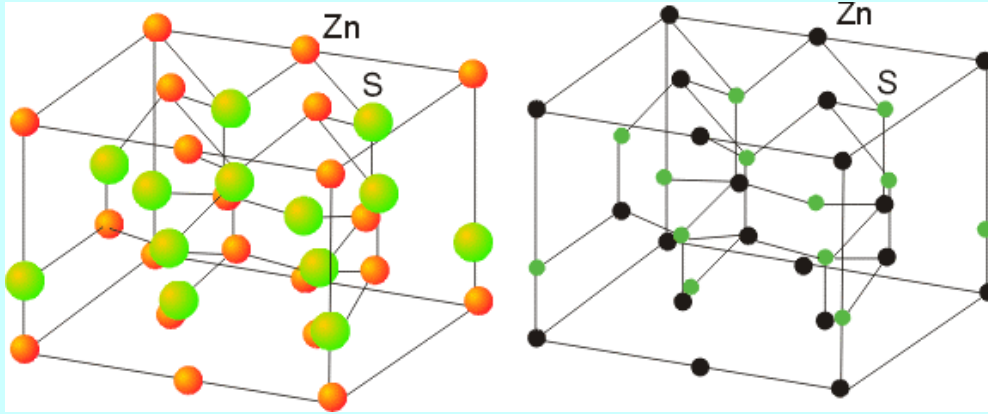# Diamond Lattice (111) Hard Sphere Model

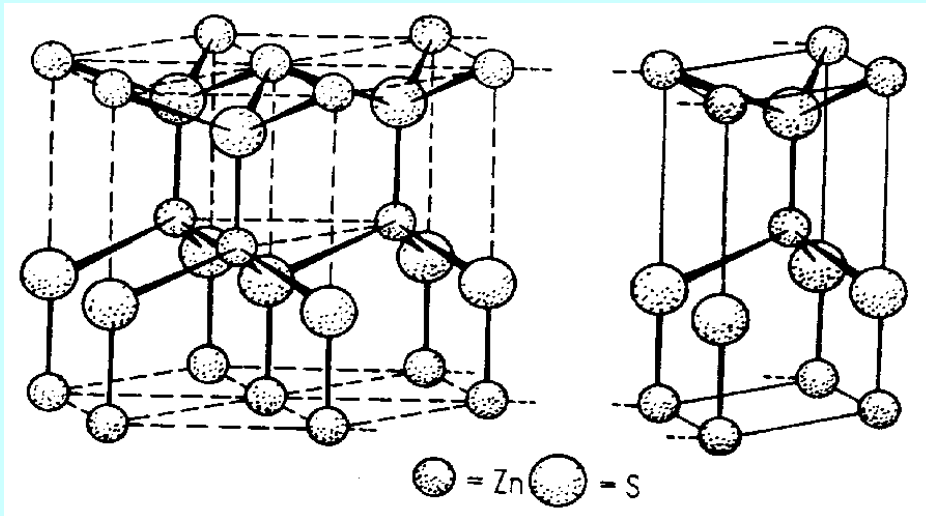# Diamond Lattice (111) Hard Sphere Model

Face Centered Cubic Lattice (111) Hard Sphere Model
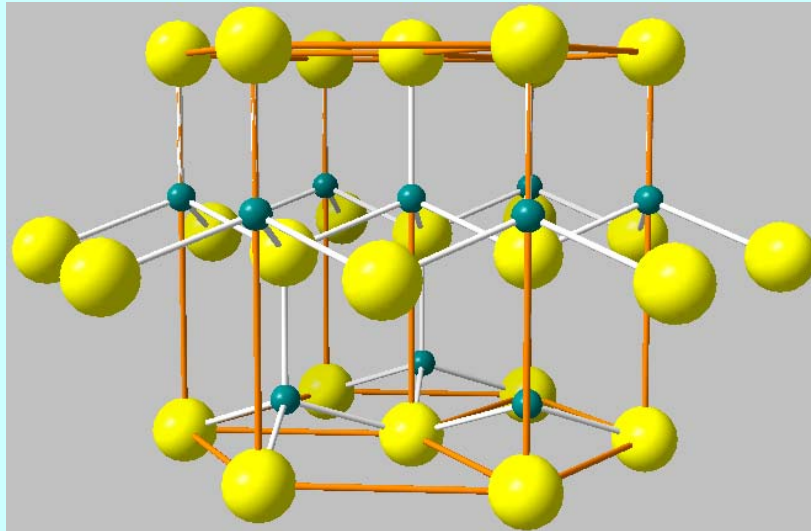
Wurzite, ZnS

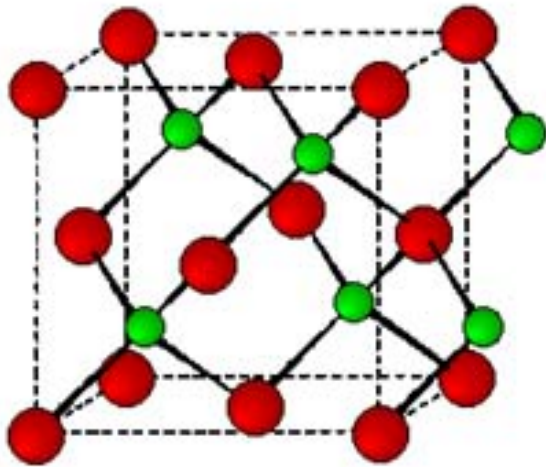**Hexagonal close packing of anions with 1/2 tetrahedral holes filled by cations**
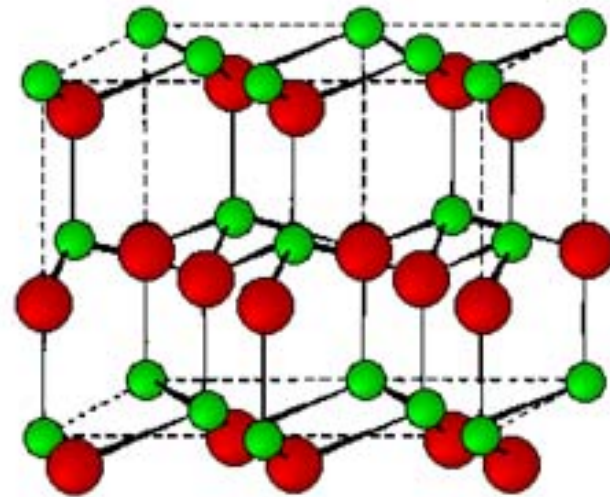
Wurzite, ZnS

ZnO, ZnS, ZnSe, ZnTe, BeO, CdS, CdSe, MnS, AgI, AlN
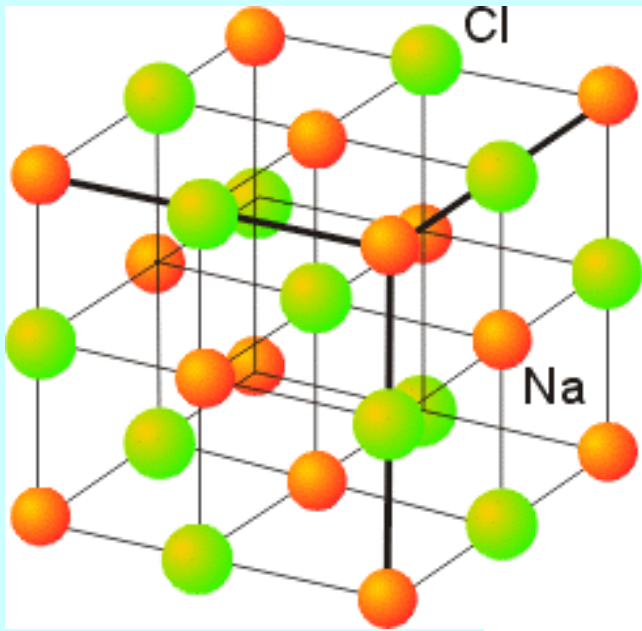
Semiconductors of 13-15 and 12-16 type
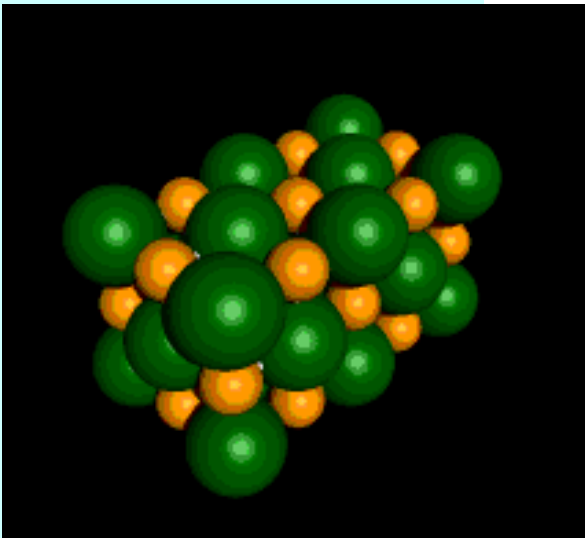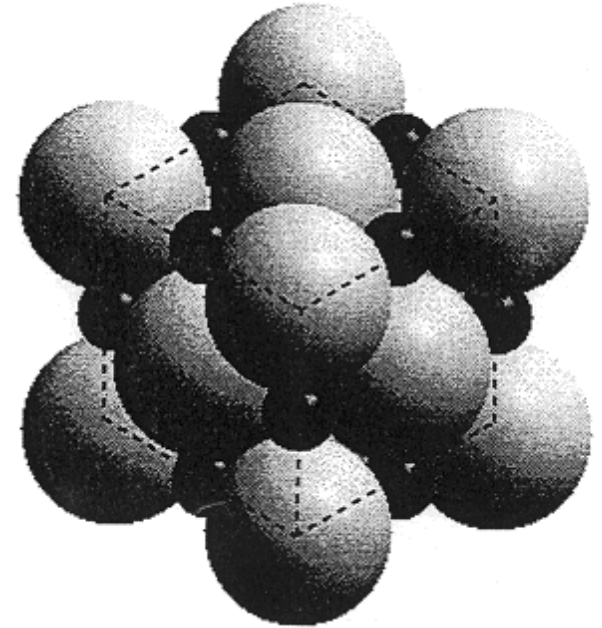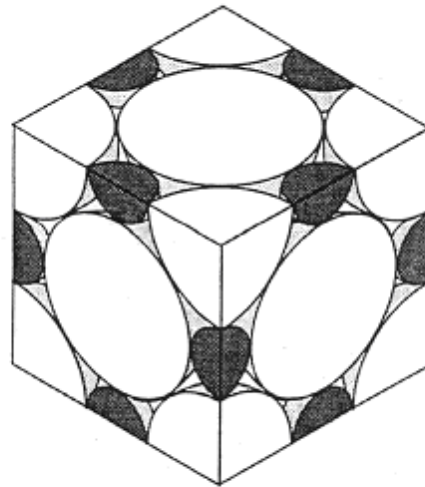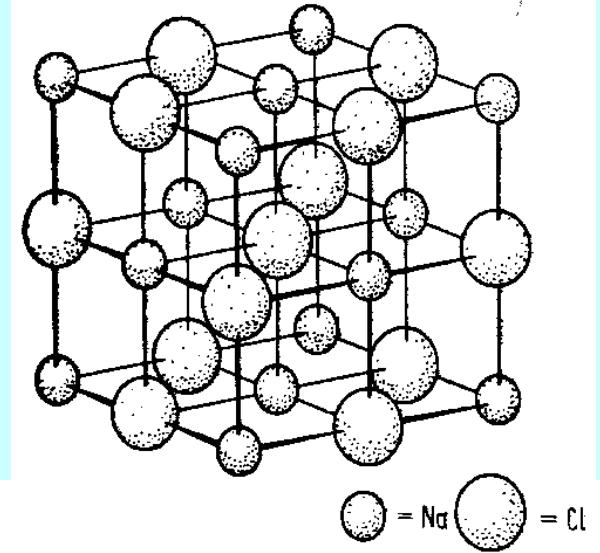

Structure of III-V and II-VI Compound Semiconductors
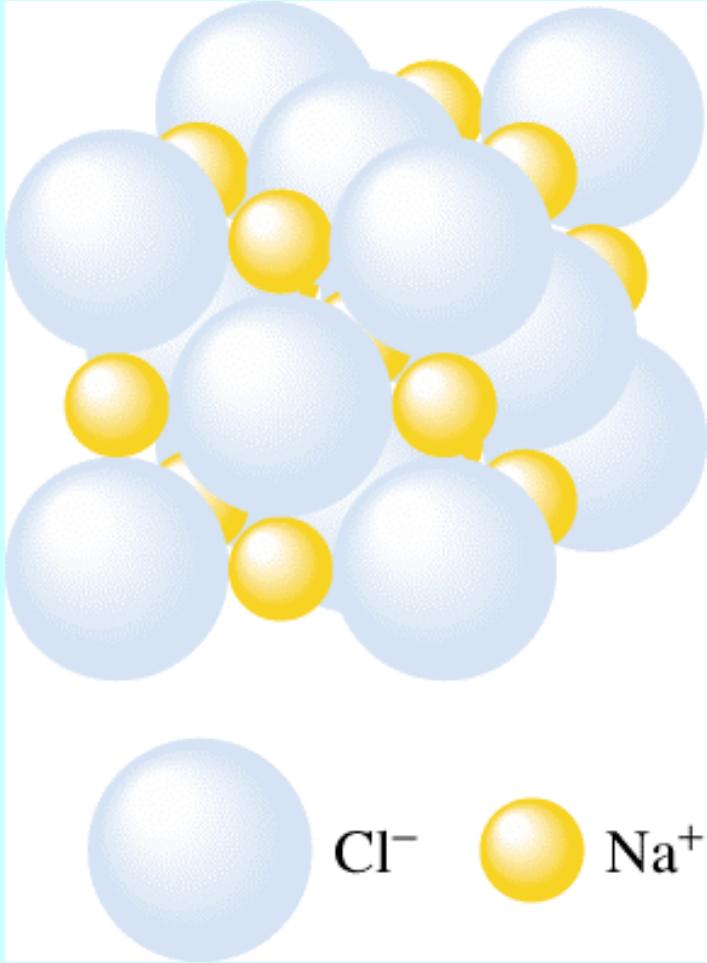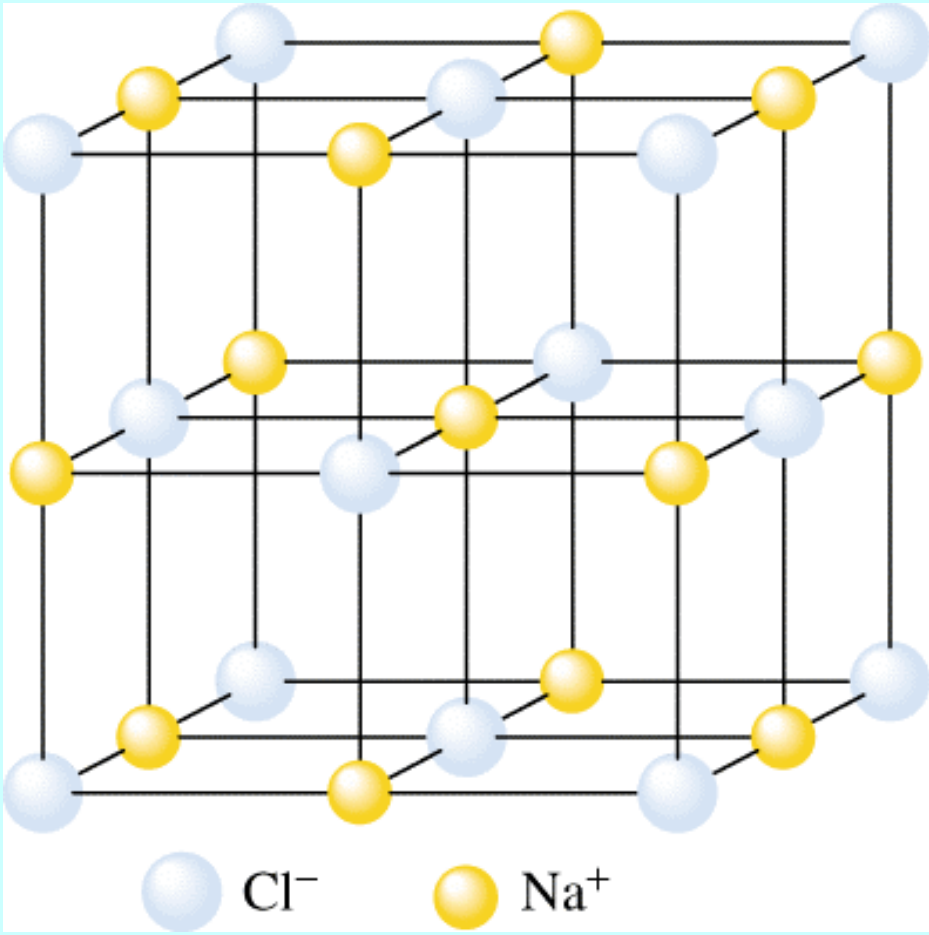
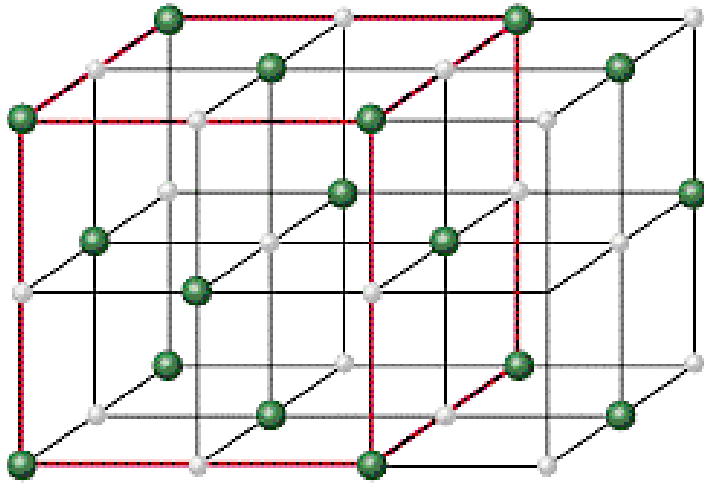Zinc blende

Wurtzite

Rock Salt, NaCl

= Na   = Cl

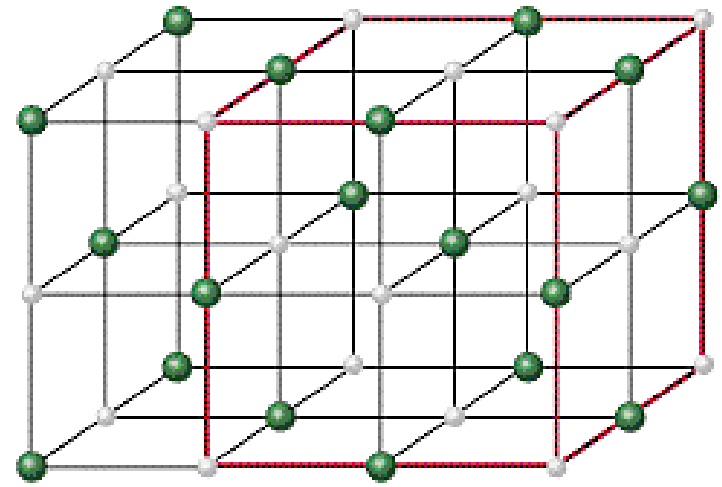Cubic close packing of anions with all
octahedral holes filled by cations
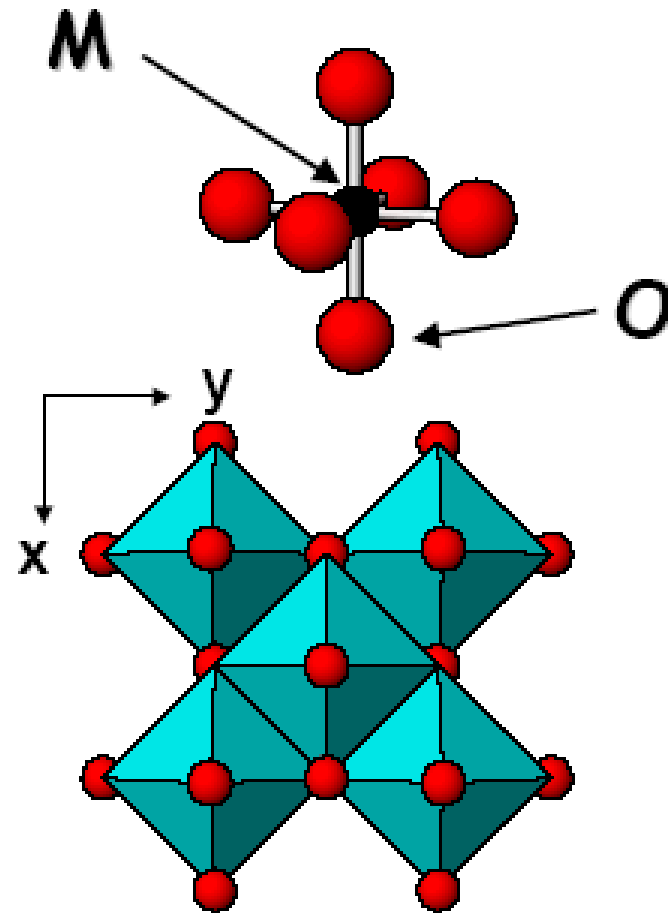
Rock Salt, NaCl

Rock Salt, NaCl

(a)   (b)

Anion and cation sublattices

Rock Salt Crystal Structure
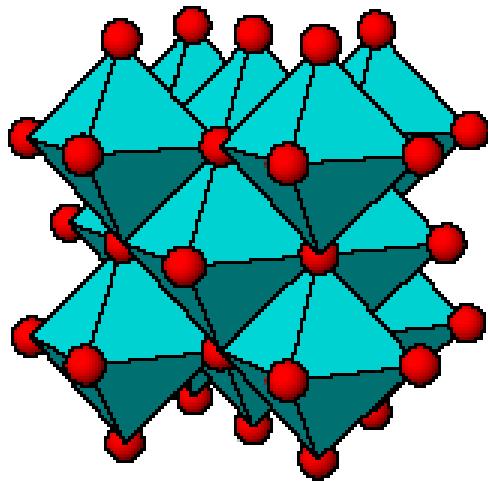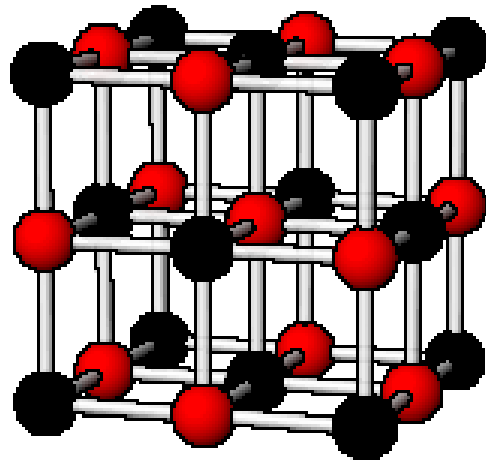
Rock salt structures (NaCl)
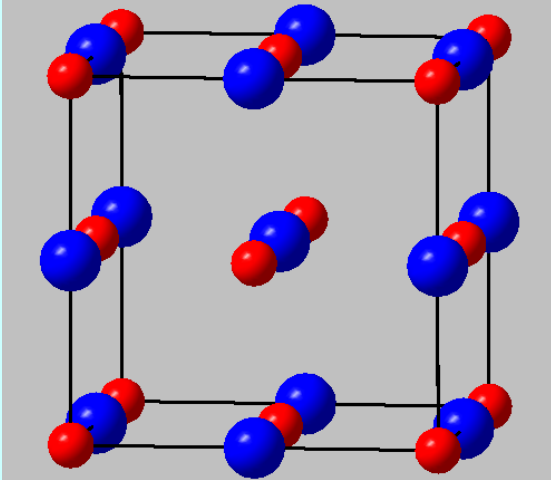
Hydrides: LiH, NaH, KH

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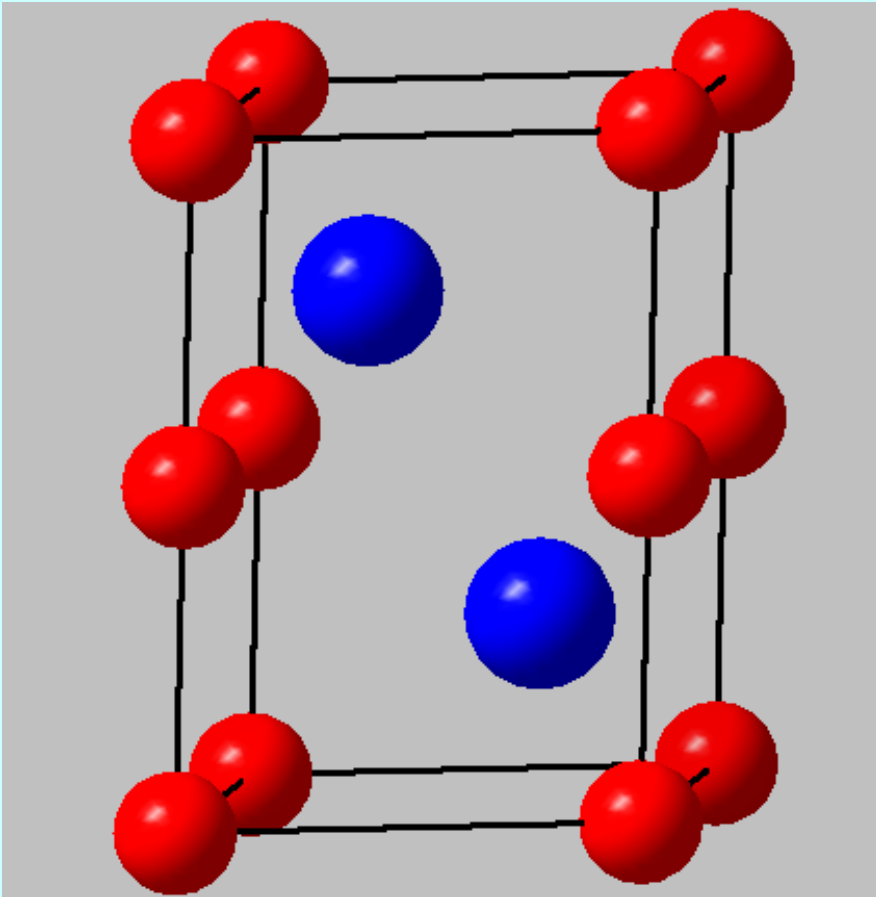
Hexagonal close packing of anions with all octahedral holes filled by cations

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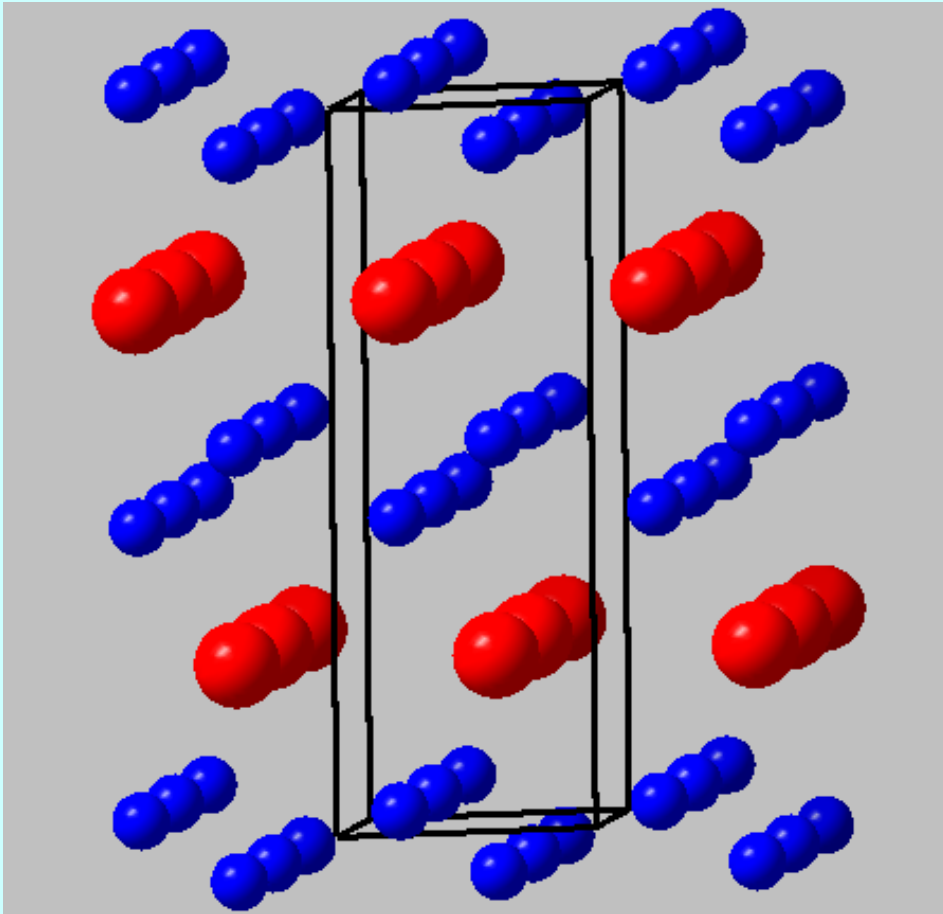
Hexagonal close packing of anions with all tetrahedral holes filled by cations

Li$_3$Bi - type (anti BiF$_3$)
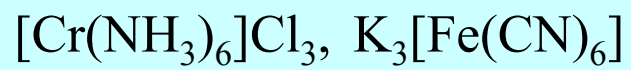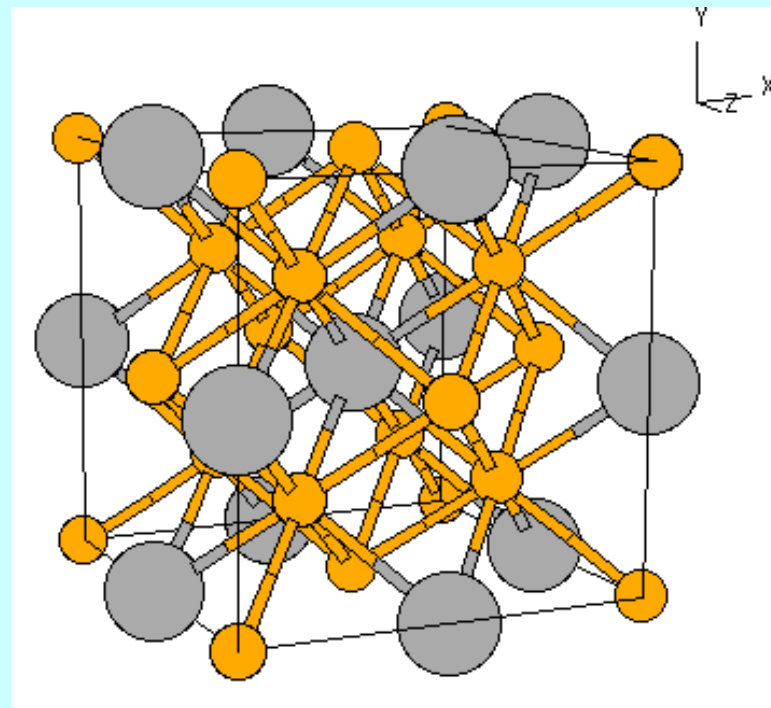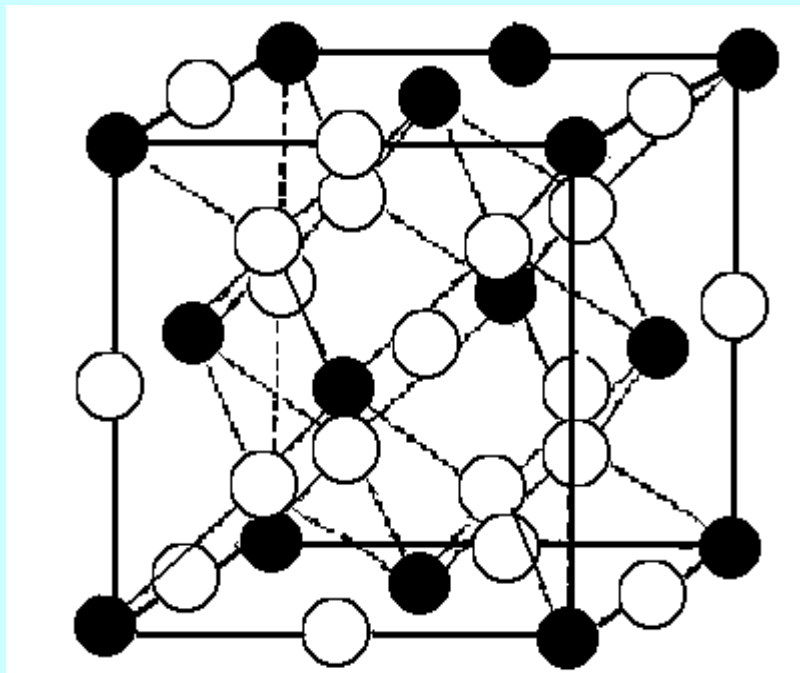
[Cr(NH$_3$)$_6$]Cl$_3$, K$_3$[Fe(CN)$_6$]
bcc

Li$_3$Bi - type (anti BiF$_3$)
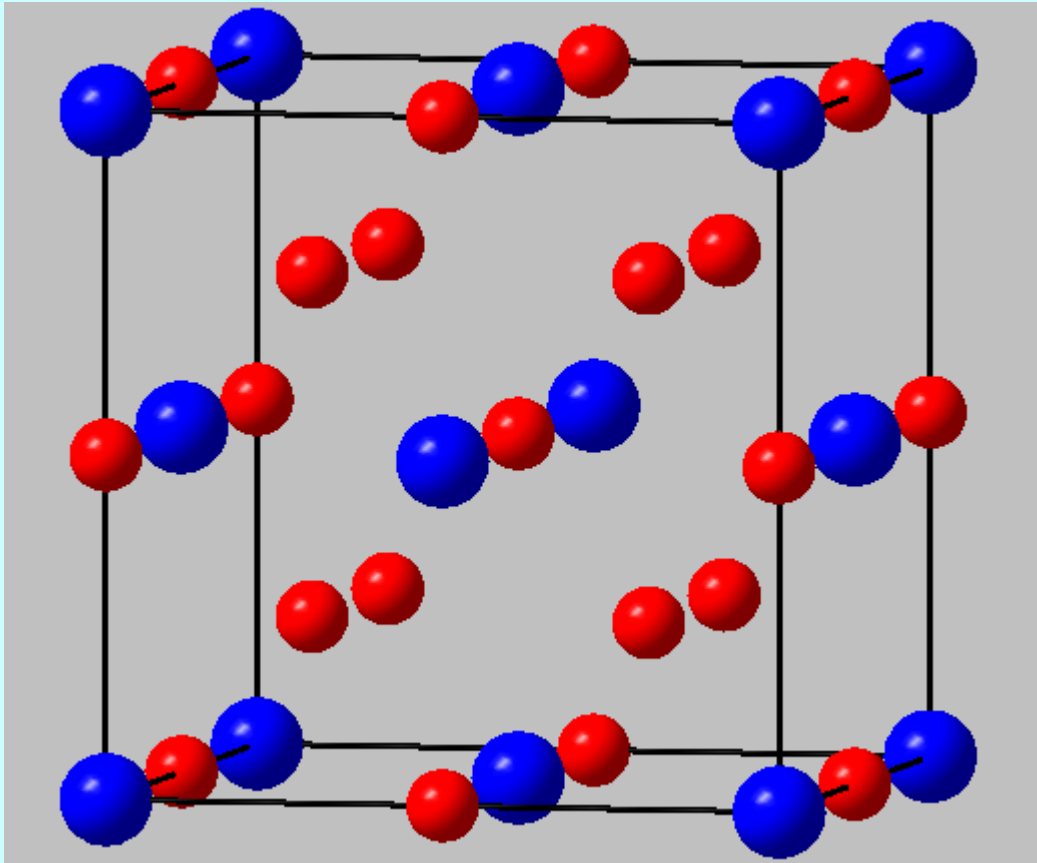
Fe$_3$Al

[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
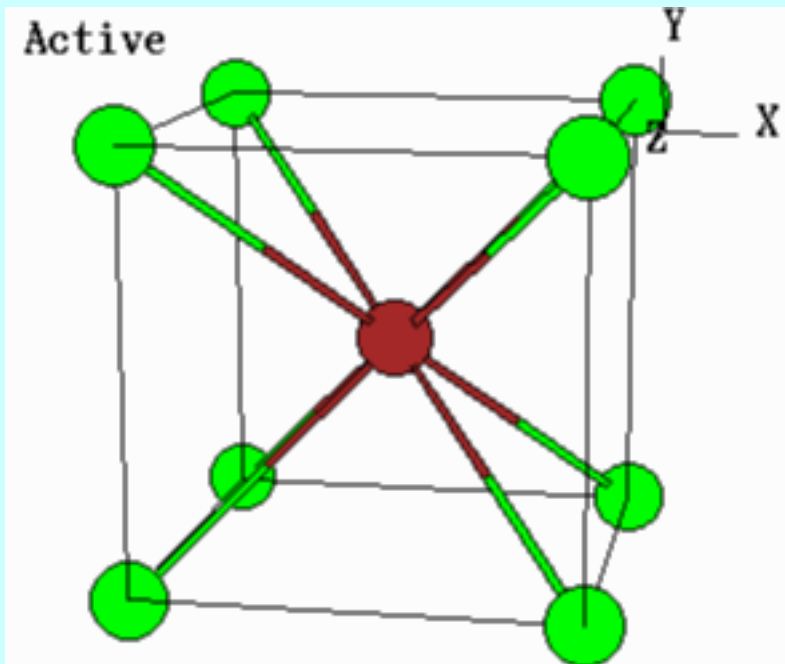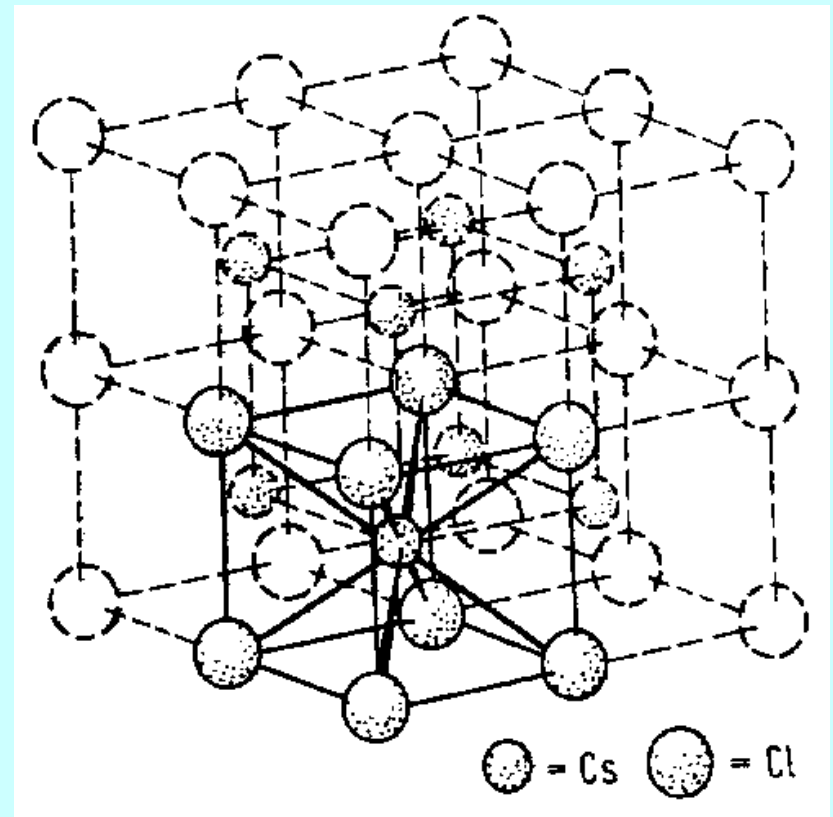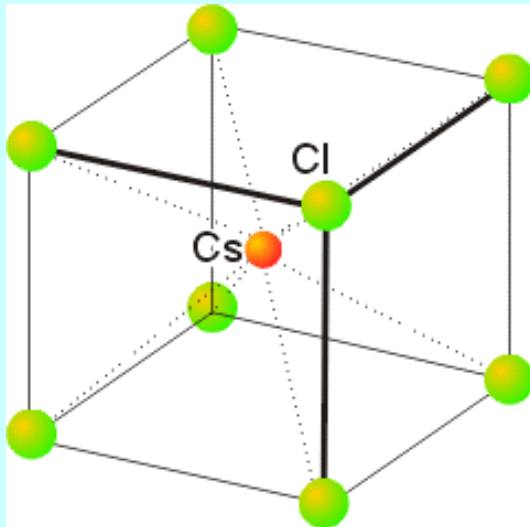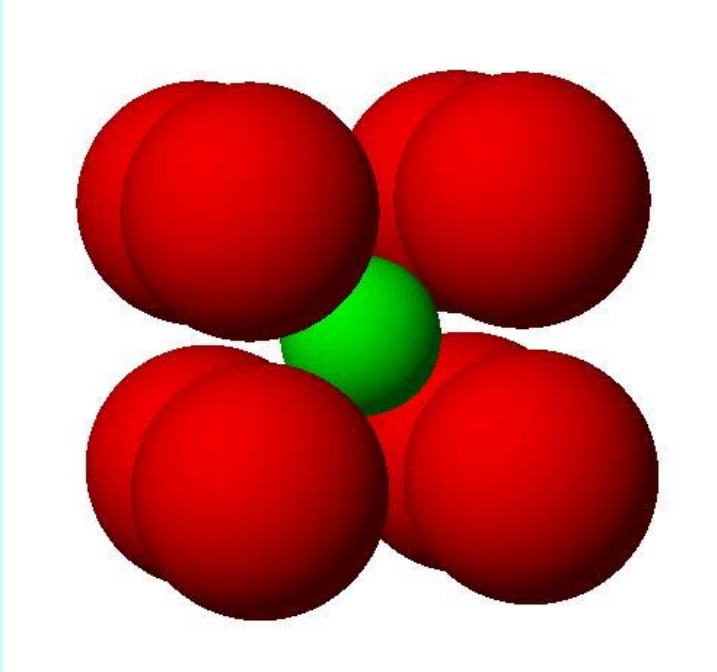
CsCl

CsCl is not BCC
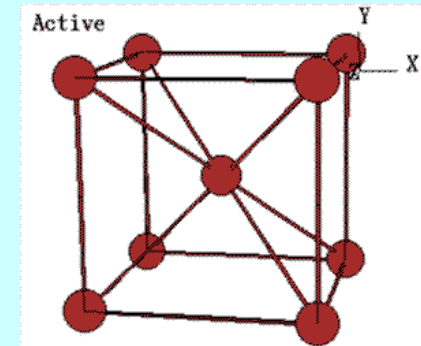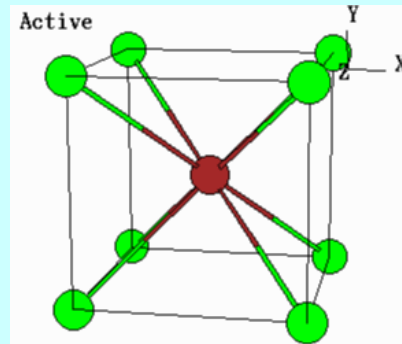
CsBr, CsI, CsCN, NH$_4$Cl, NH$_4$Br, TlCl, TlBr, TlI, CuZn, CuPd, LiHg

ReO$_3$
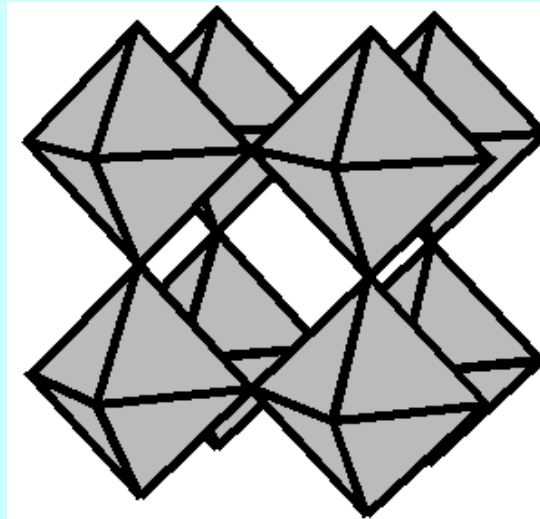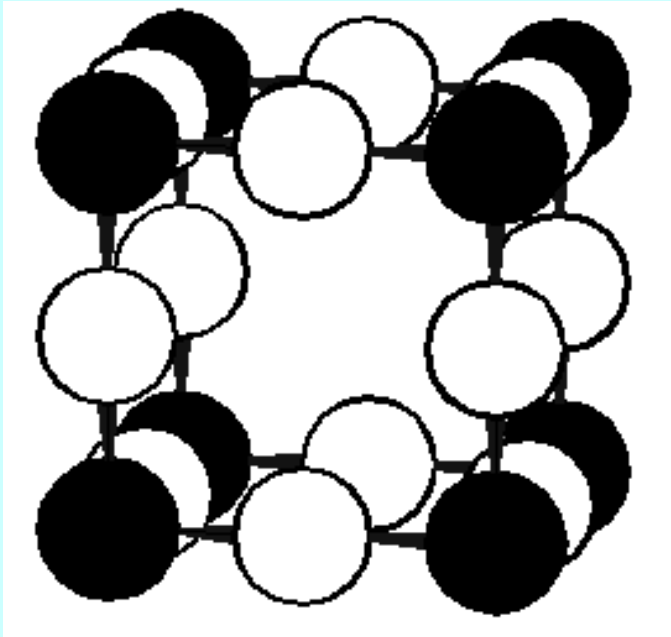
SC of ReO$_6$ octahedra

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

UO$_3$, MoF$_3$, NbF$_3$, TaF$_3$, Cu$_3$N

Perovskite, CaTiO₃

Two equvivalent views of the unit cell of perovskite
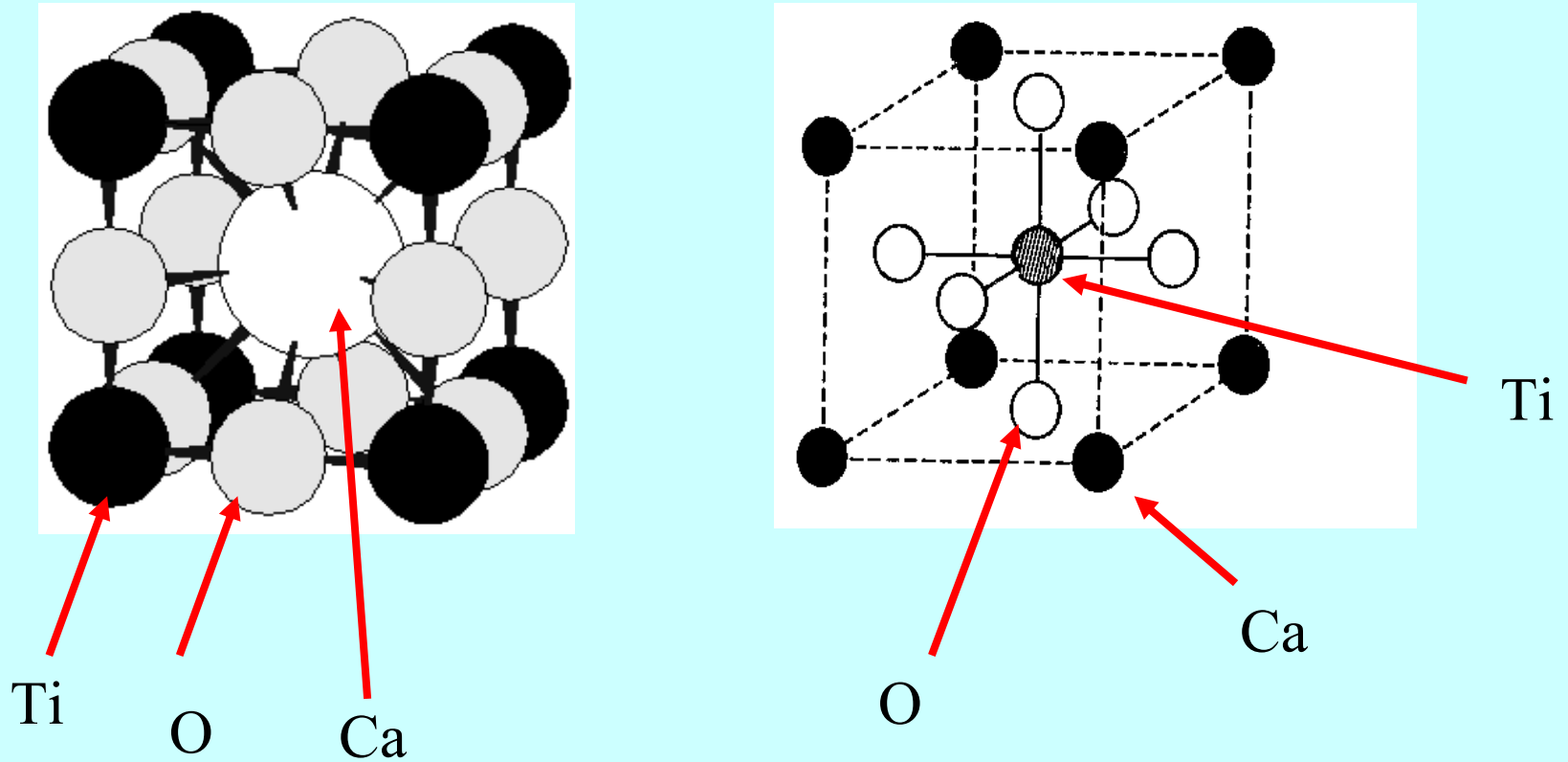
Cubic "close packing" of Ca and O with 1/4 octahedral holes filled by Ti cations

Perovskite structure $CaTiO_3$
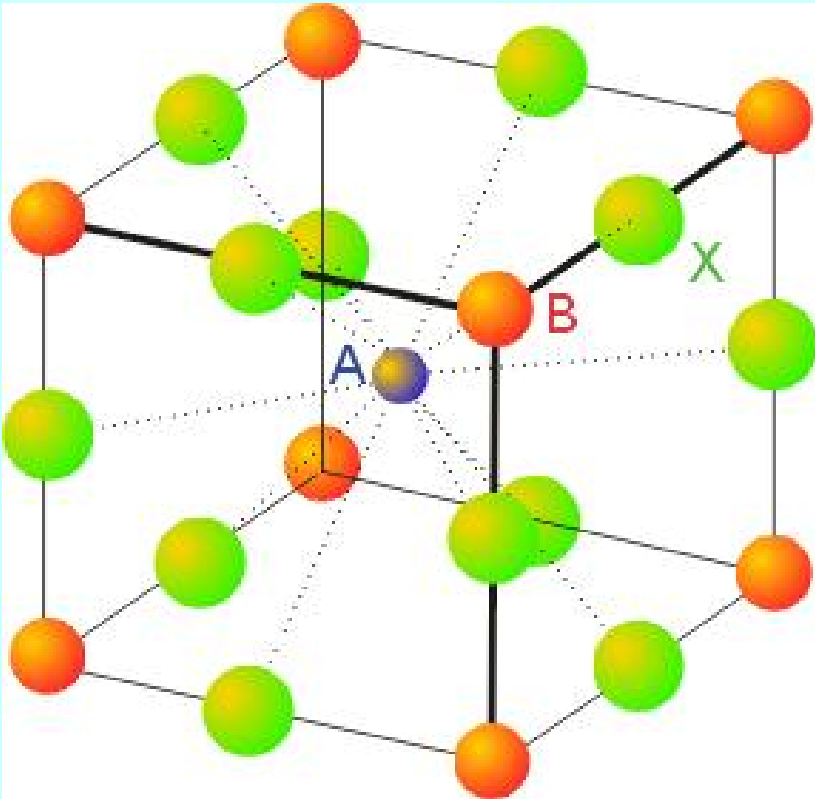
TiO_6 – octahedra

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
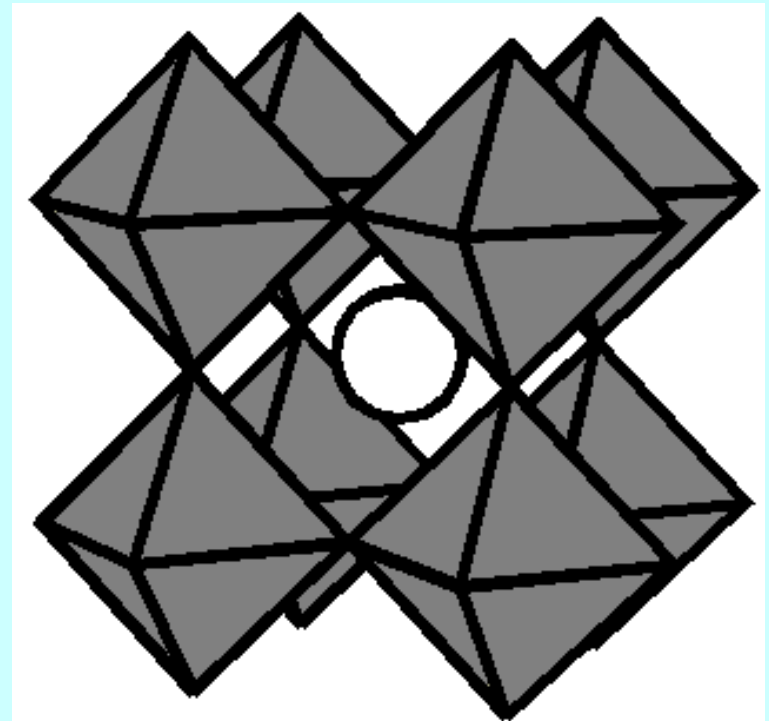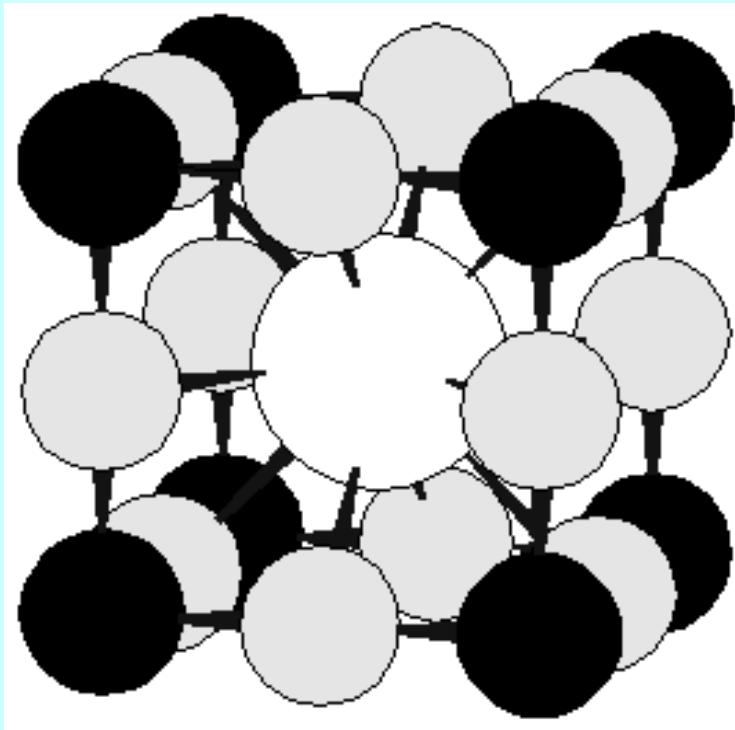
Similarity to CsCl

Perovskite, $CaTiO_3$

Perovskite Crystal Structure

M

O

A
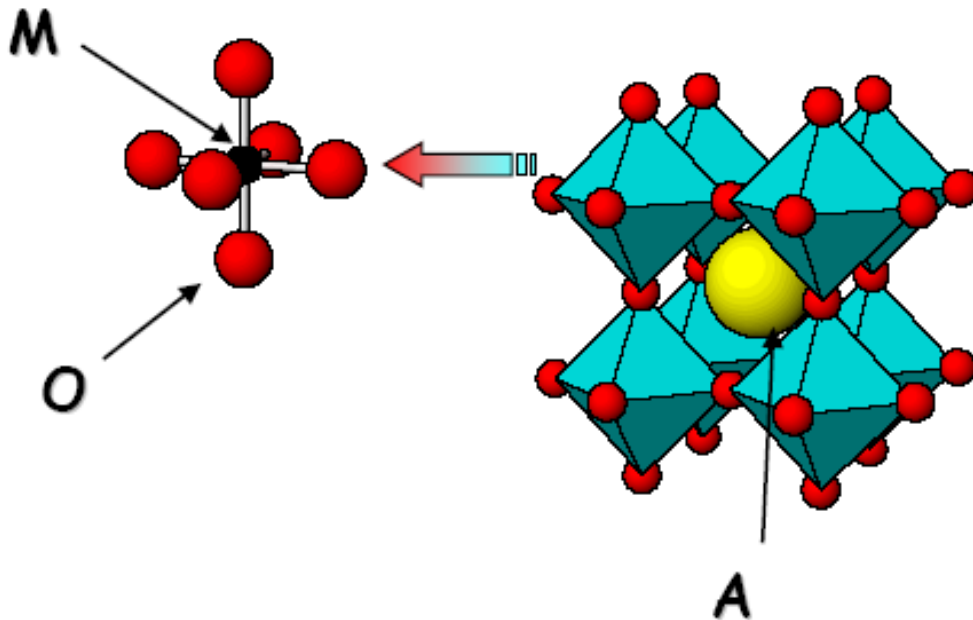
$MgSiO_3$, $CaSiO_3$

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

$ThTaN_3$, $BaTaO_2N$

Rutile, TiO$_2$
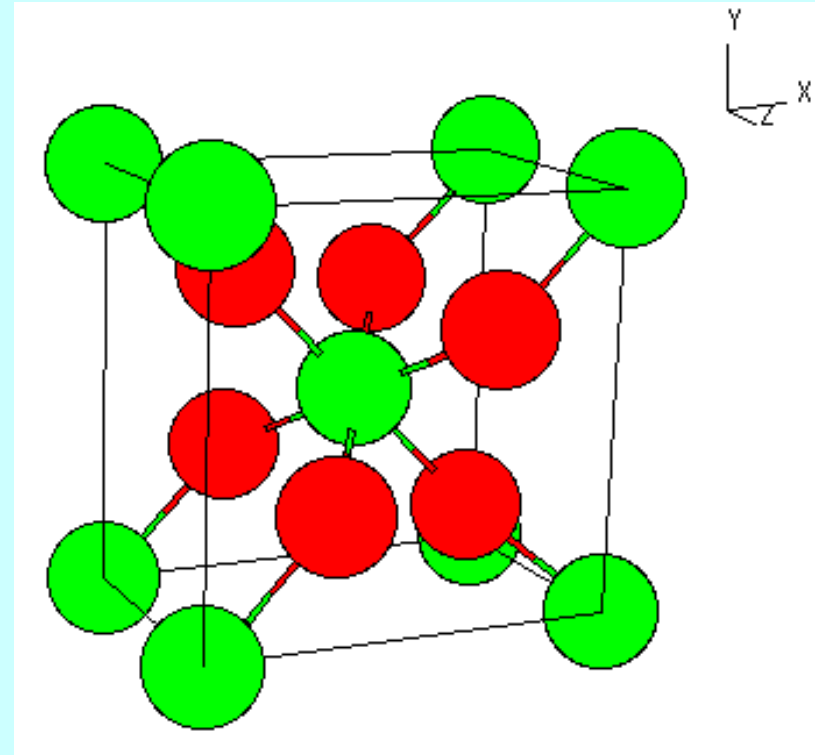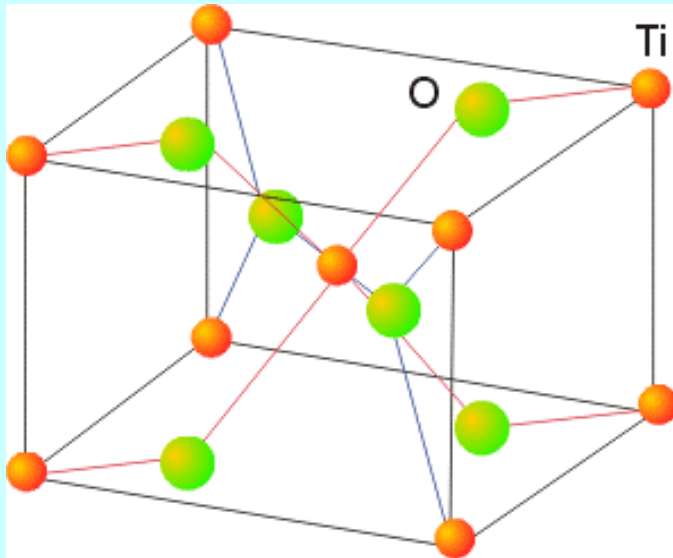
CN – stoichiometry Rule

A$_x$B$_y$

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$_2$

Rutile Crystal Structure
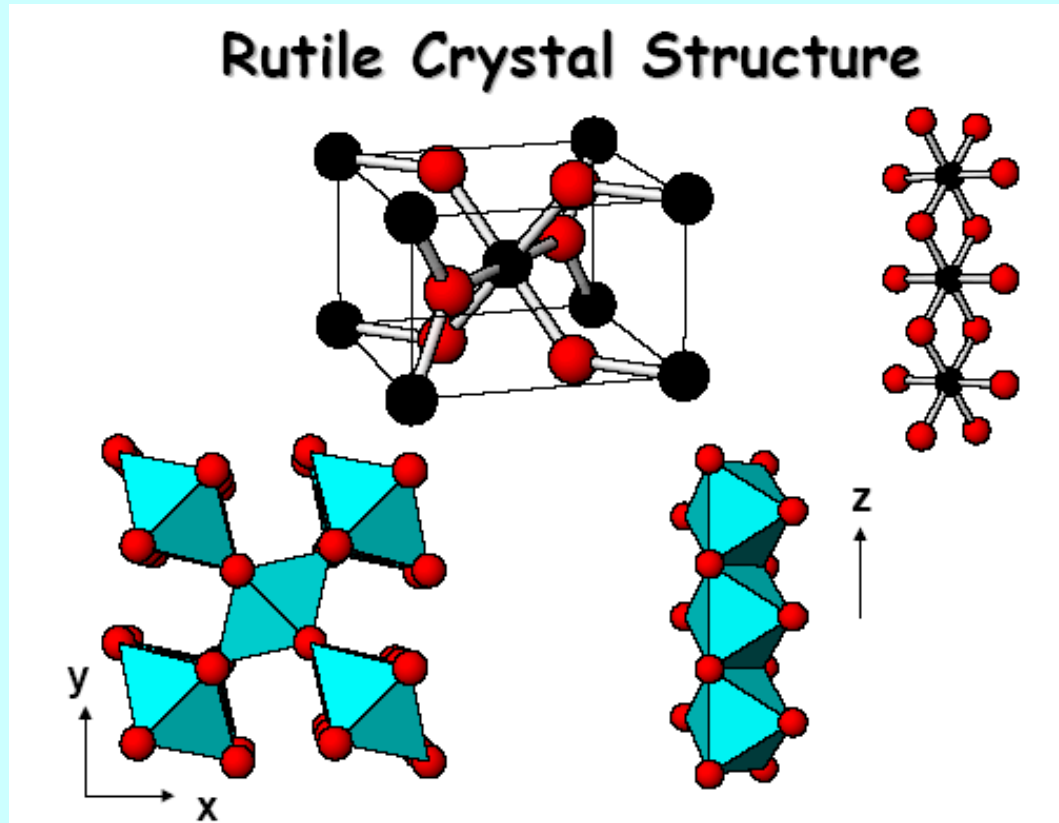
GeO$_2$, CrO$_2$, IrO$_2$, MoO$_2$, NbO$_2$, β-MnO$_2$, OsO$_2$, VO$_2$ (>340K), RuO$_2$, CoF$_2$, FeF$_2$, MgF$_2$, MnF$_2$

The rutile structure: TiO$_2$
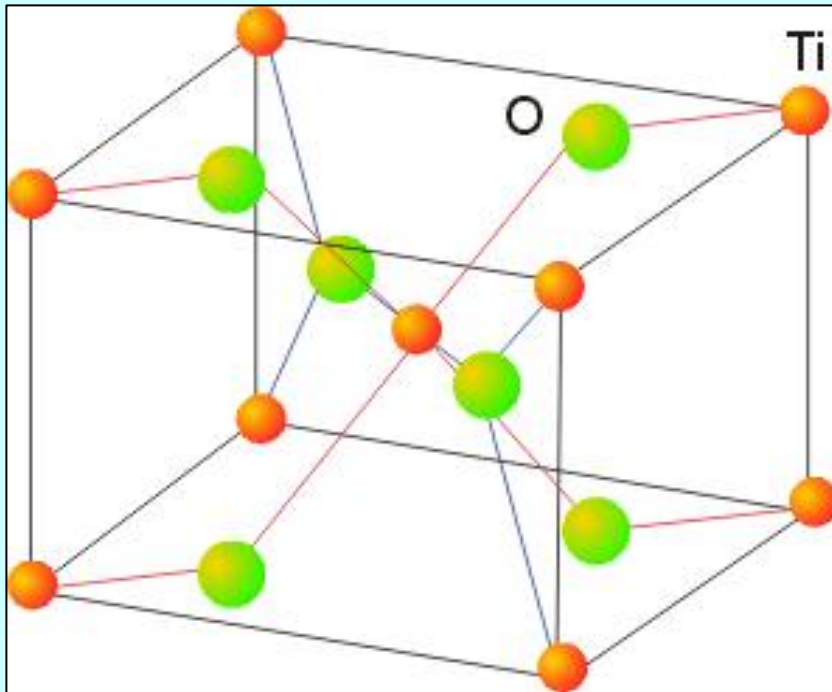
TiO$_6$ – octahedra

OTi$_3$ – trigonal planar

(alternative to CaF$_2$ for highly charged smaller cations)

The spinel structure: $MgAl_2O_4$
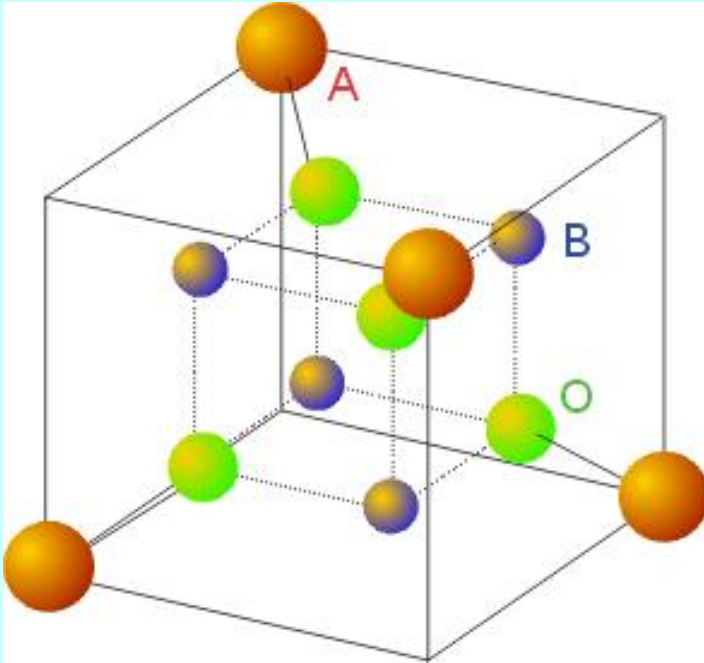
fcc array of O^{2-} ions, A^{2+} occupies 1/8 of the tetrahedral and B^{3+} 1/2 of the octahedral holes

→ <u>normal spinel</u>:
AB_2O_4

→ <u>inverse spinel</u>:
$B[AB]O_4$ (Fe_3O_4):
$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$

→ basis structure for several <u>magnetic materials</u>

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, $FeCo_2O_4$.

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
$Y_3Al_5O_{12}$
$Y_3Fe_5O_{12}$

Garnets

Pyrope	$Mg_3Al_2(SiO_4)_3$
Almandine	$Fe_3Al_2(SiO_4)_3$
Spessartine	$Mn_3Al_2(SiO_4)_3$
Uvarovite	$Ca_3Cr_2(SiO4)3$
Grossular	$Ca_3Al_2(SiO_4)_3$
Andradite	$Ca_3Fe_2(SiO_4)_3$

Garnets

Garnet $Y_3Al_5O_{12}$

Y_3 = red - dodecahedral trivalent cations, large size

Al_5 = blue
2 octahedral
3 tetrahedral

O_{12}
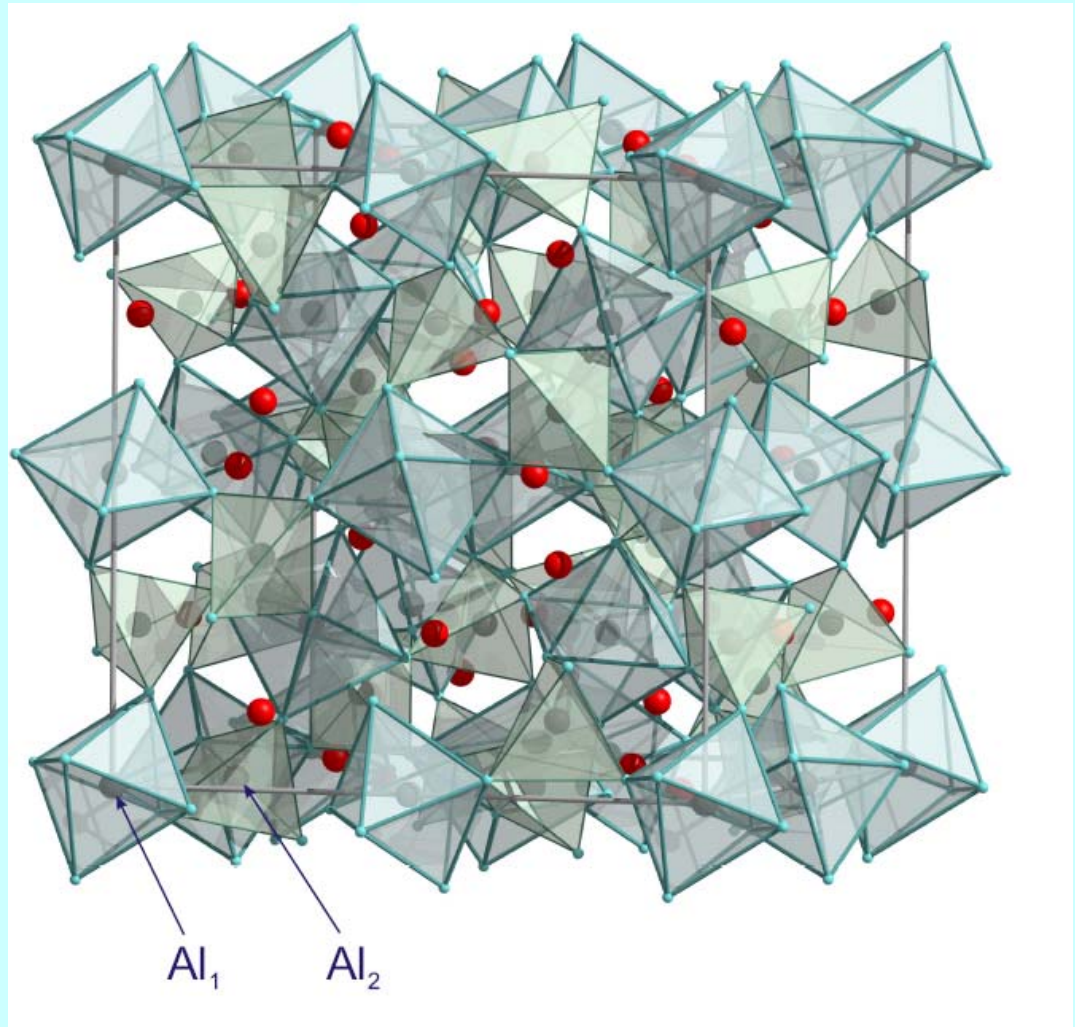
Layered Structures

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)
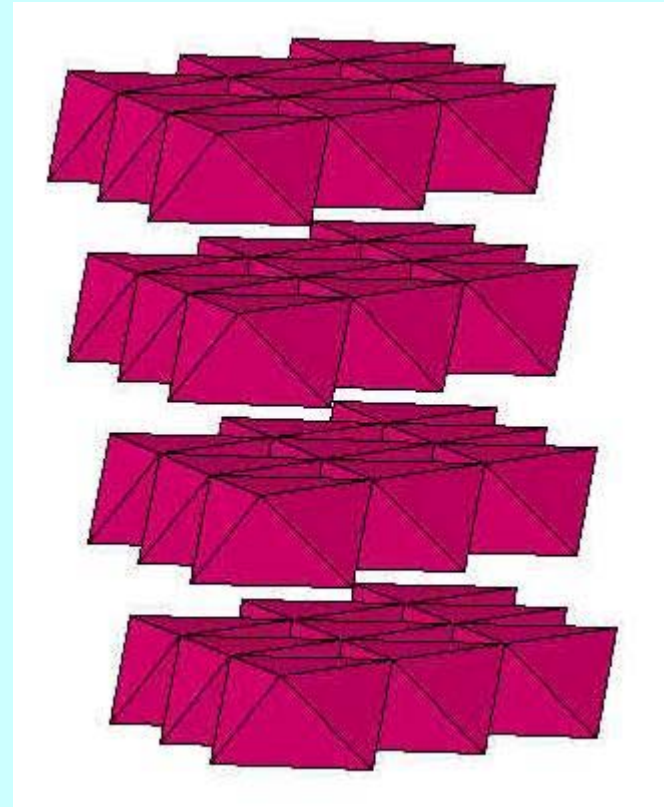
CdI₂ Hexagonal close packing
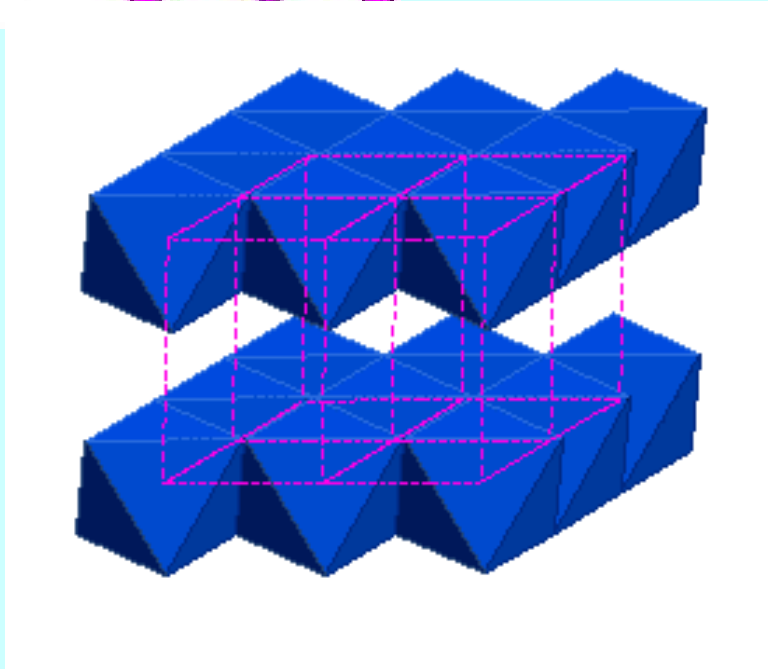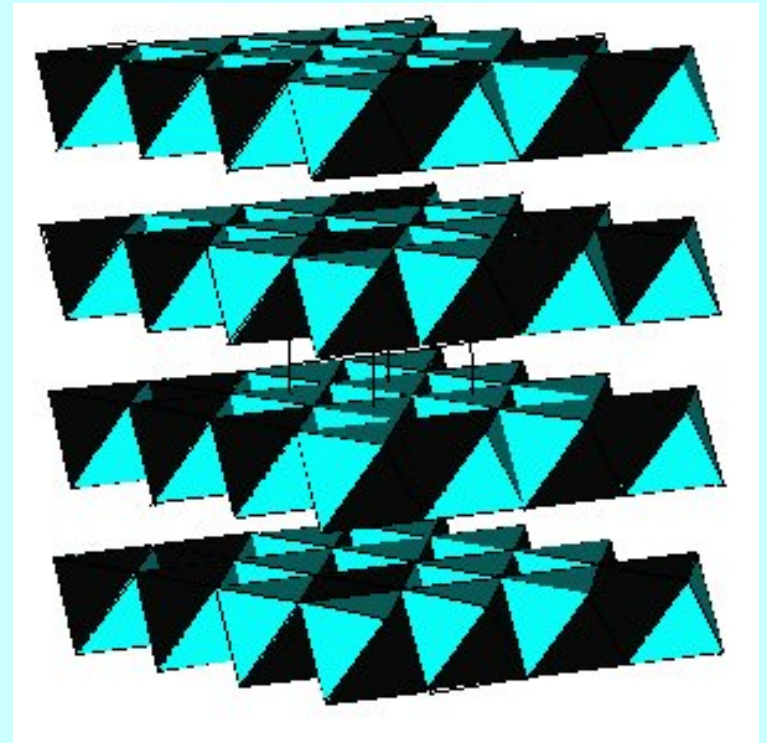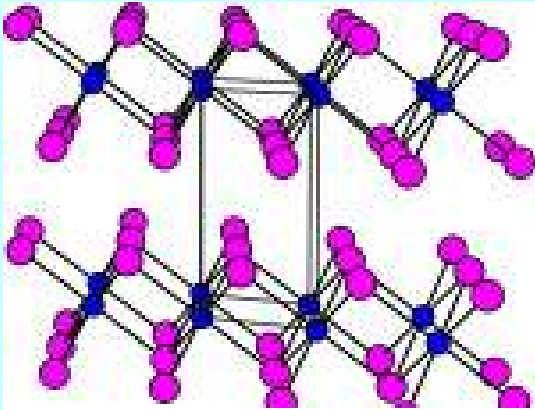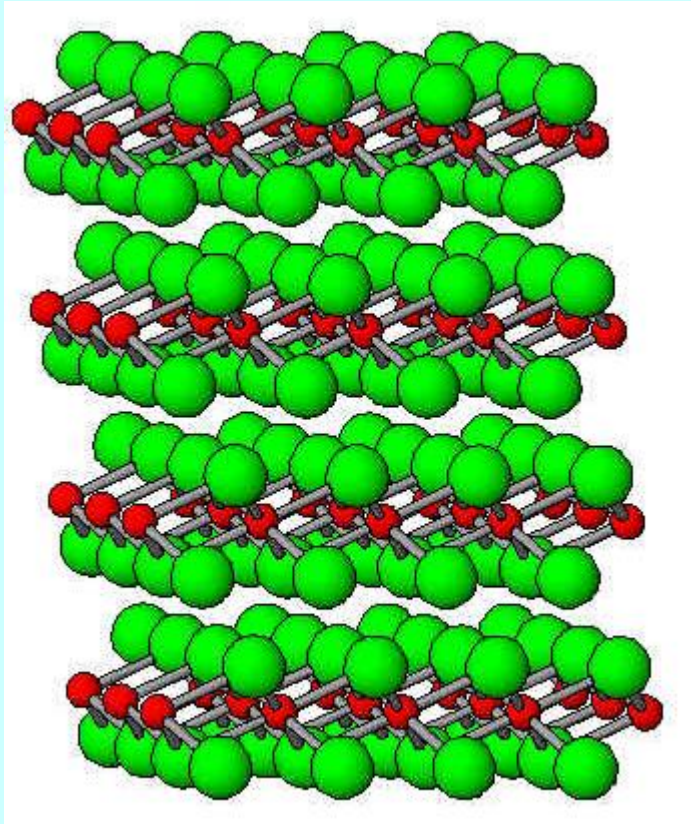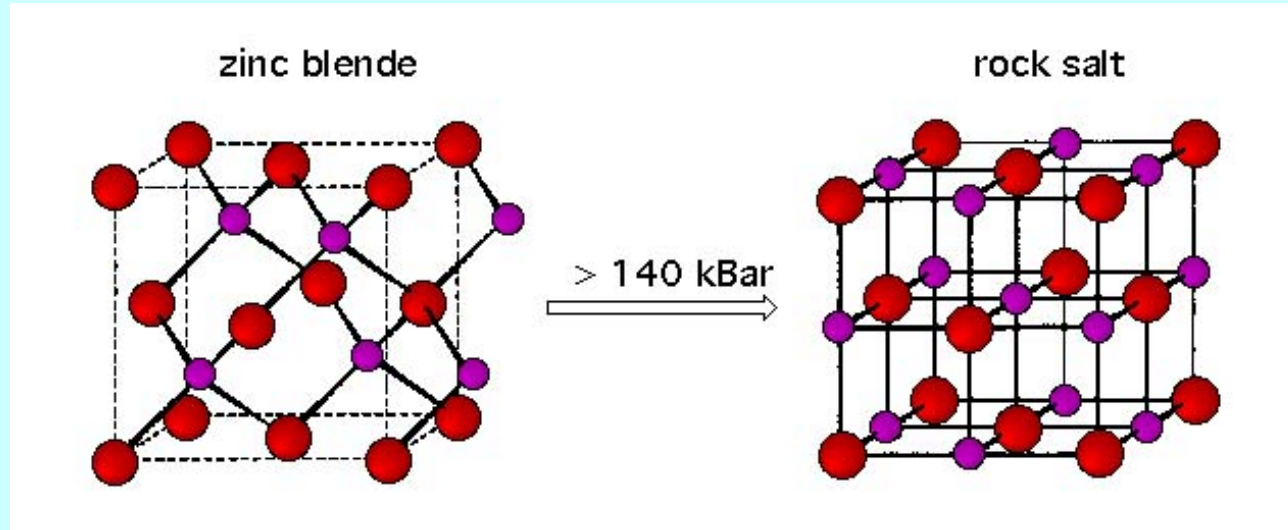
CdCl$_2$ Cubic close packing
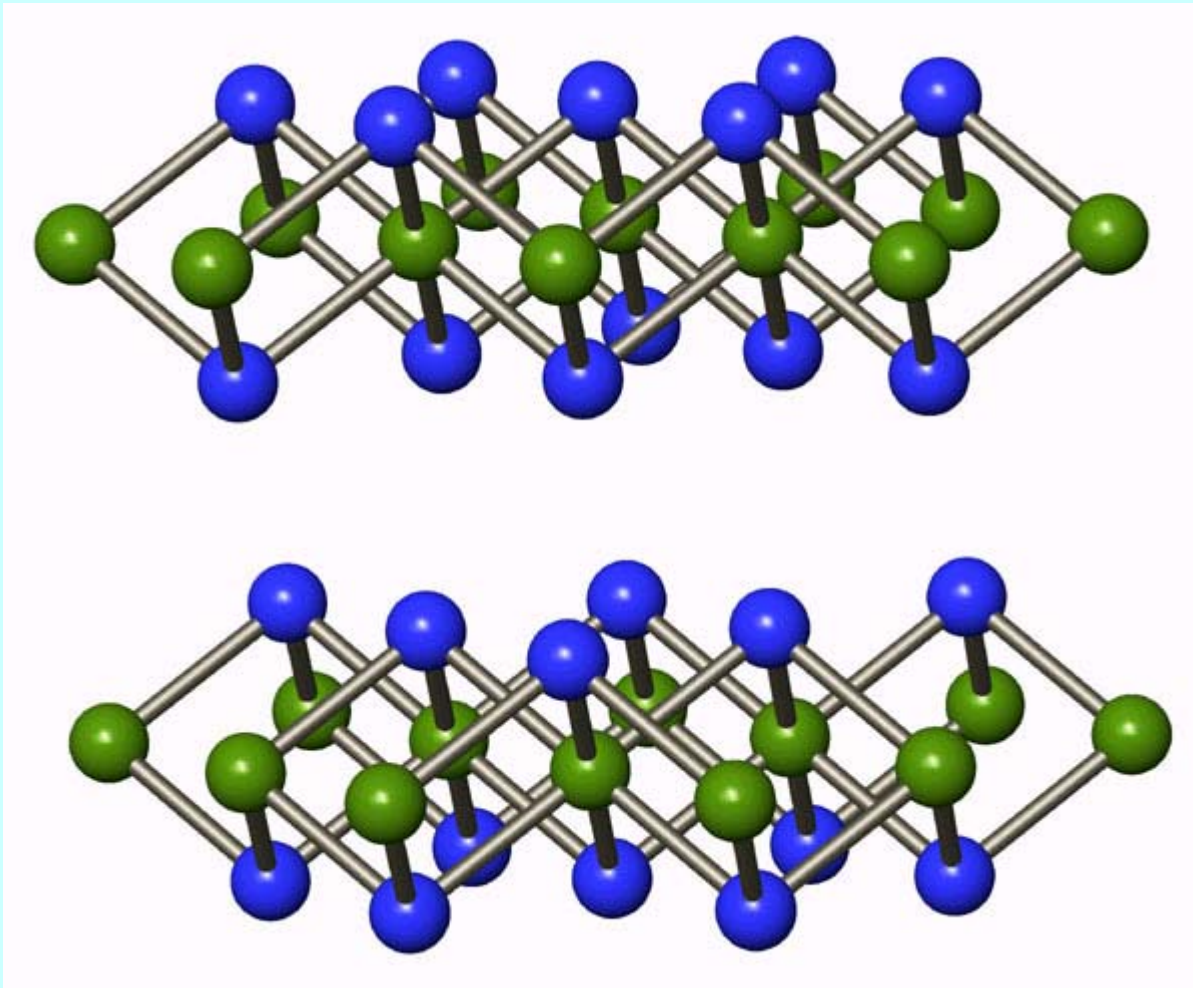
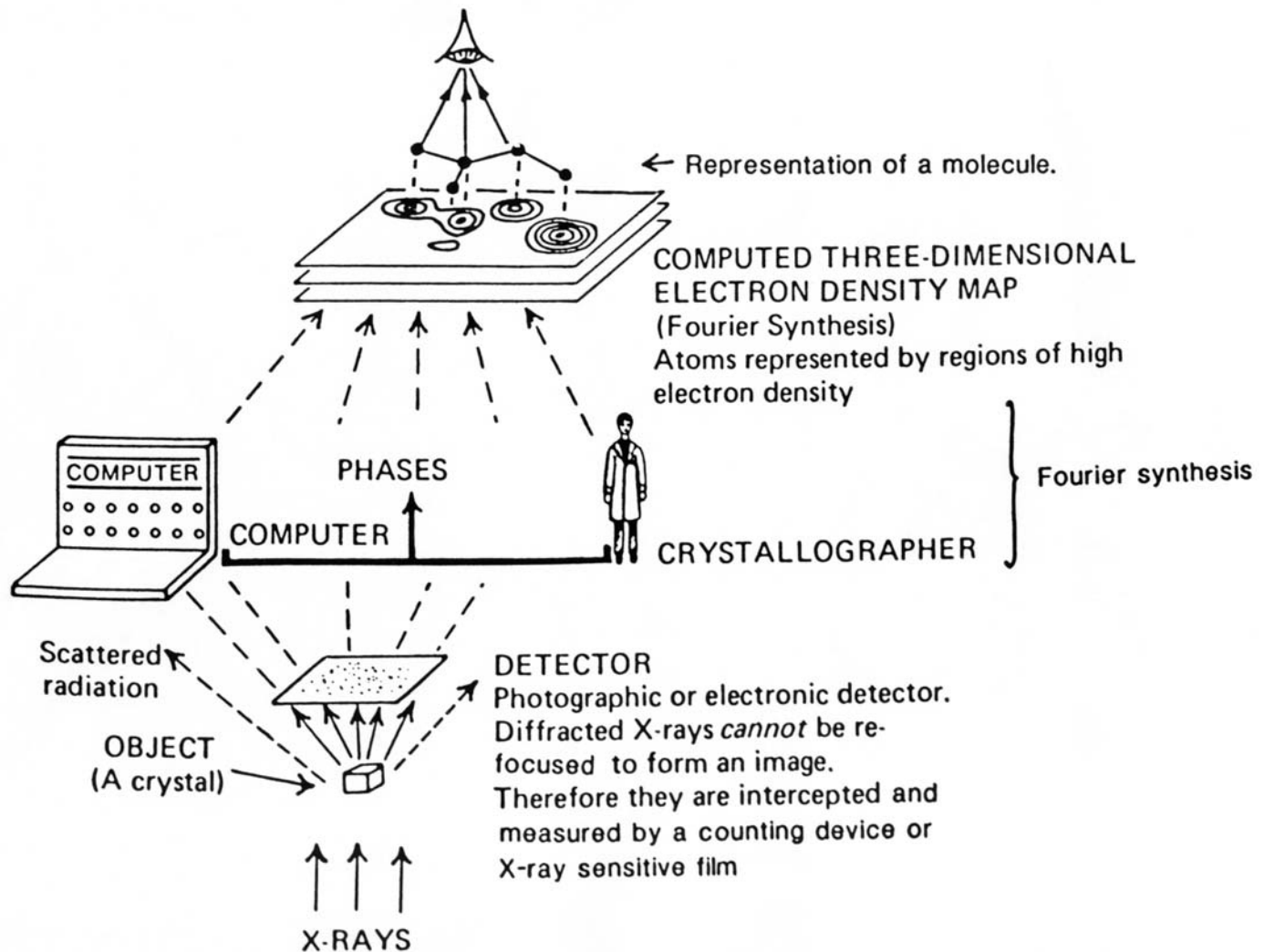# CdCl$_2$ Cubic close packing

High Pressure Transformations

- high pressure phases
- higher density
- higher coodination number
- higher symmetry
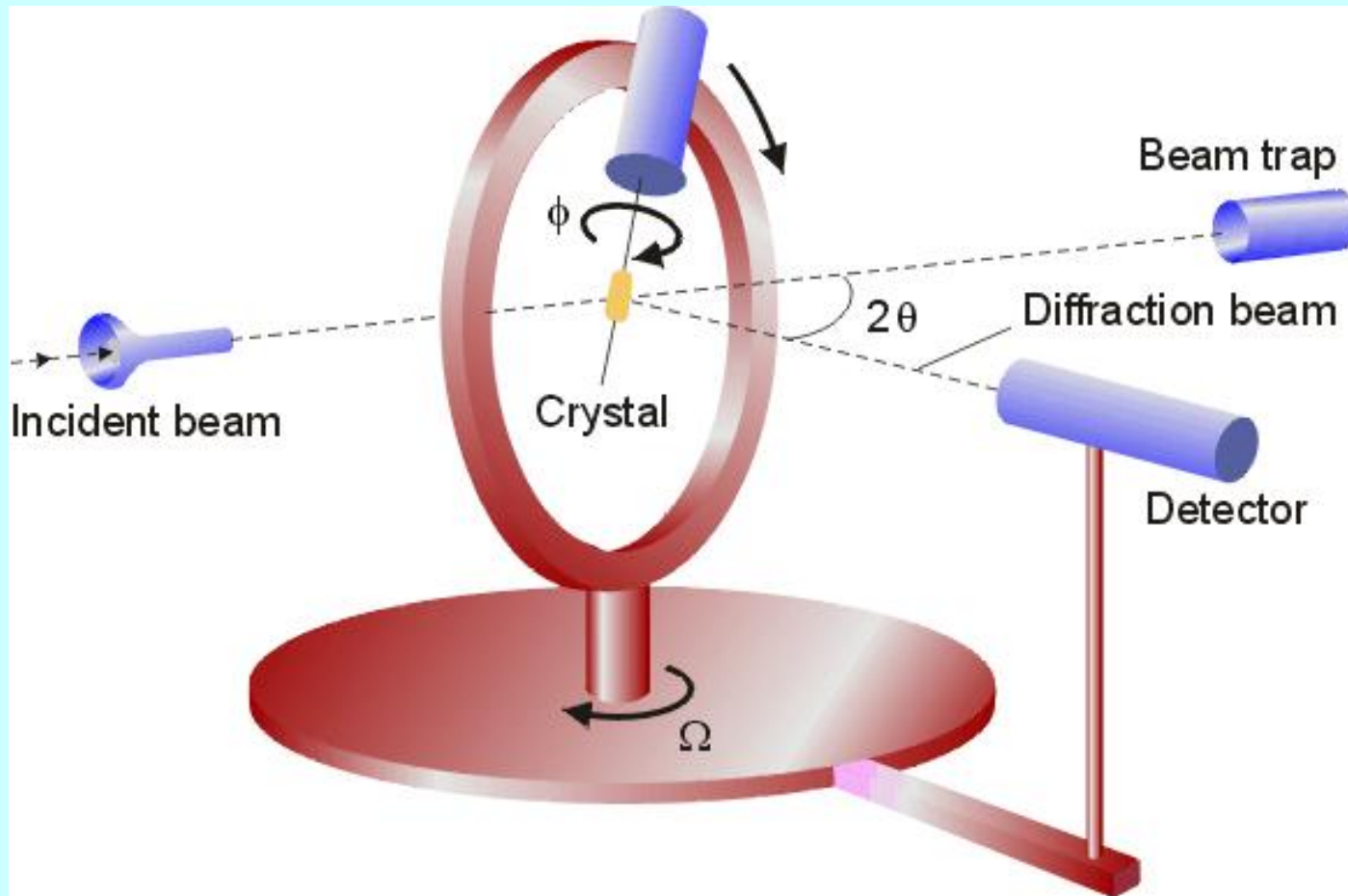- transition to from nonmetal to metal
- band mixing
- longer bonds

Pressure/Coordination Number Rule: increasing pressure – higher CN
Pressure/Distance Paradox: increasing pressure – longer bonds

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

PHASES

COMPUTER

COMPUTER

CRYSTALLOGRAPHER

Fourier synthesis

Scattered radiation

OBJECT (A crystal)

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

X-RAYS

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

CAD4 (Kappa Axis Diffractometer)

IPDS (Imaging Plate Diffraction System)