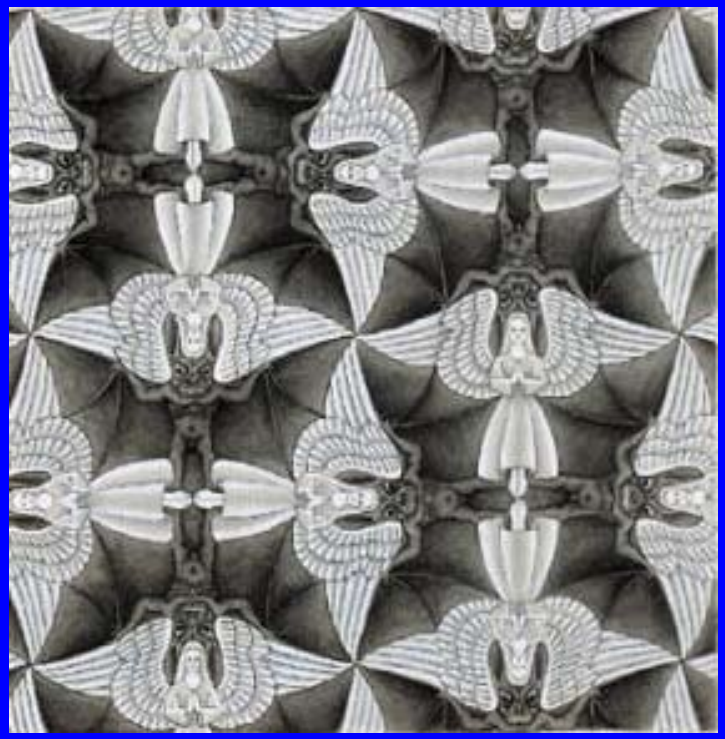
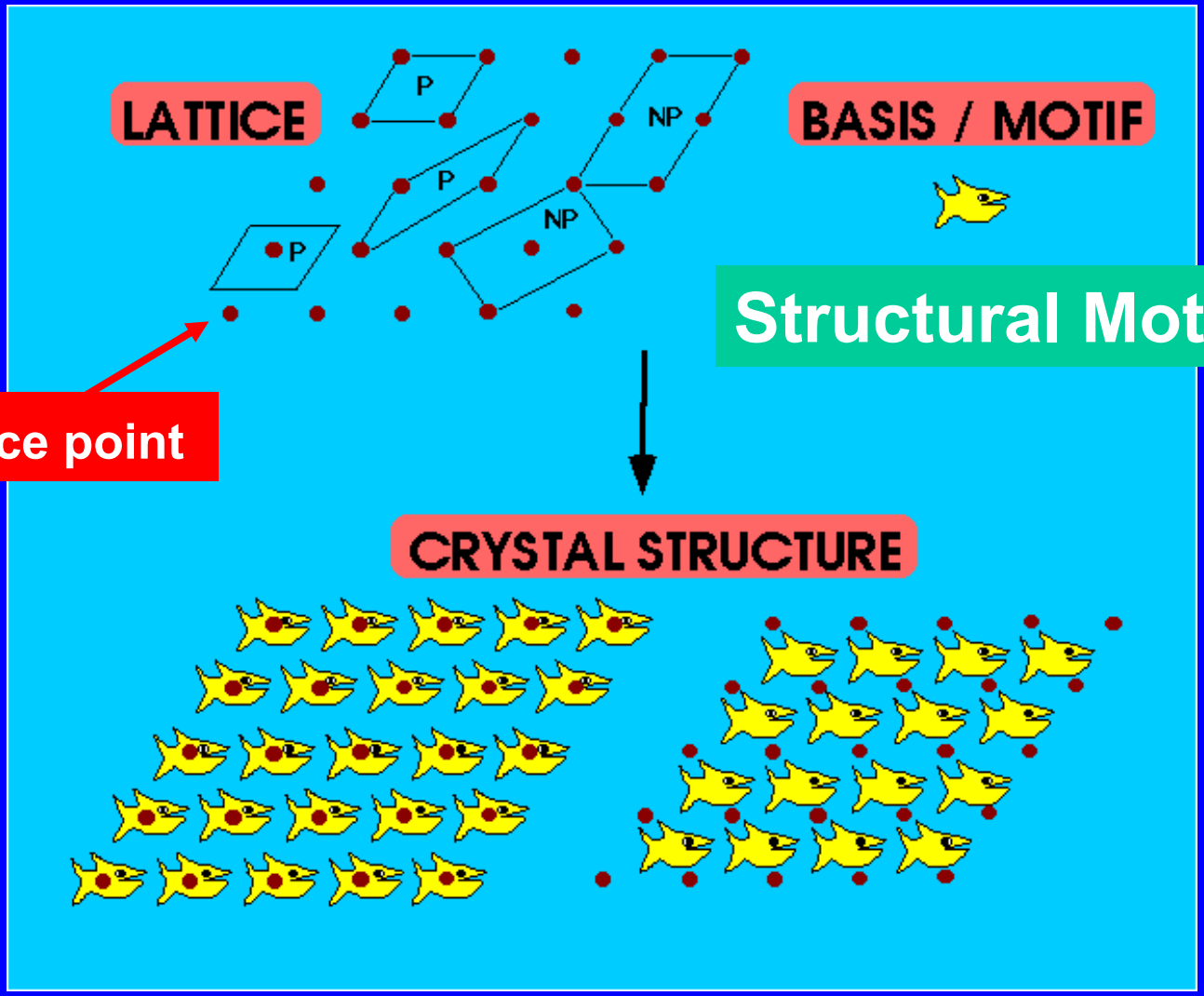
Structure of Crystalline Compounds



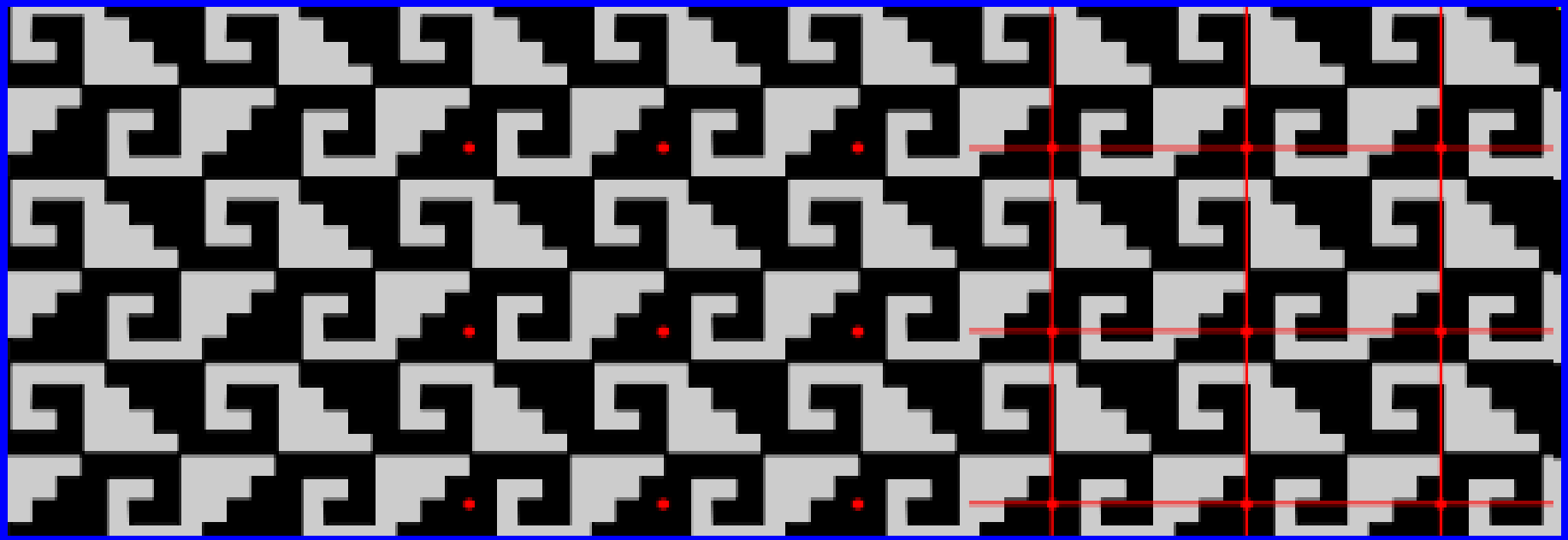
Periodical repeat of the same building units

Lattice and Structure

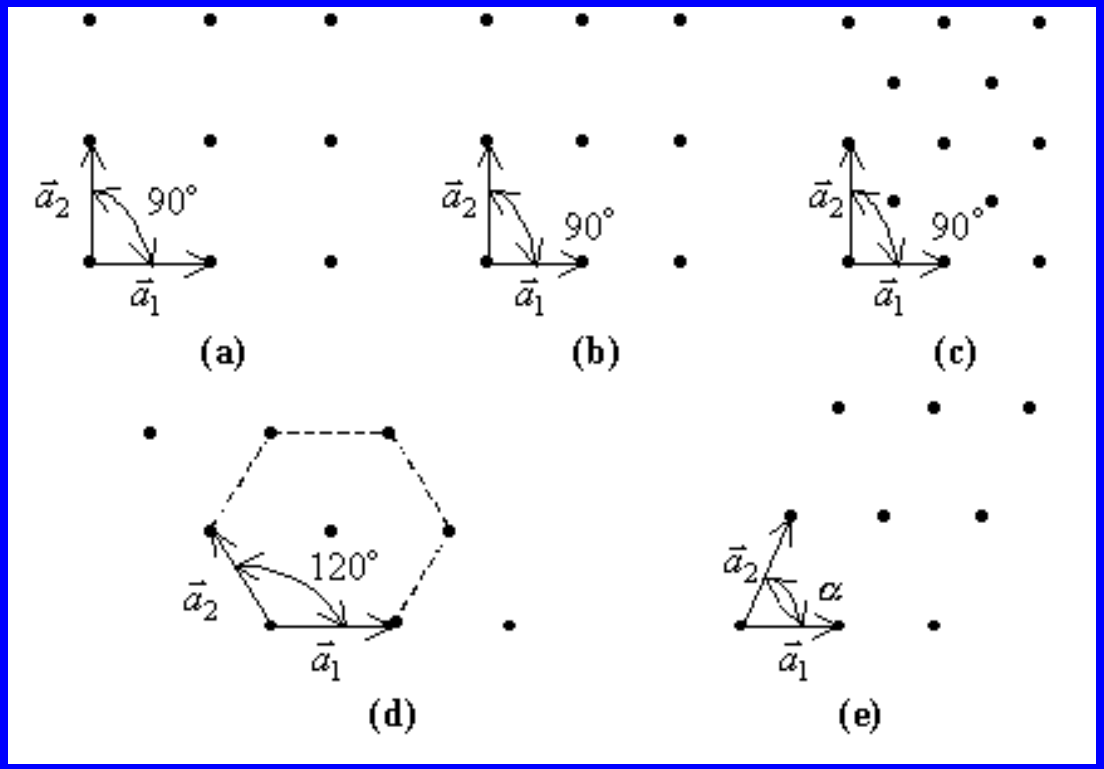


Unit Cell

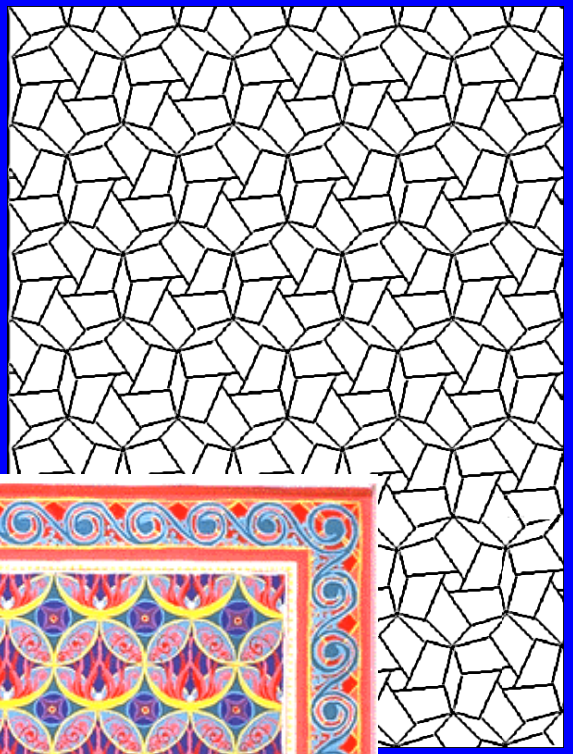
Periodical repeat of unit cells = crystal

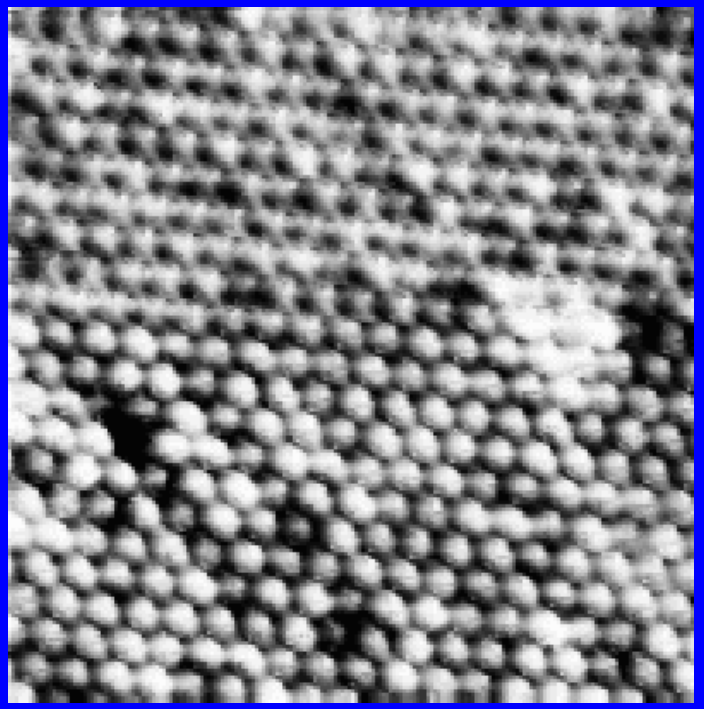


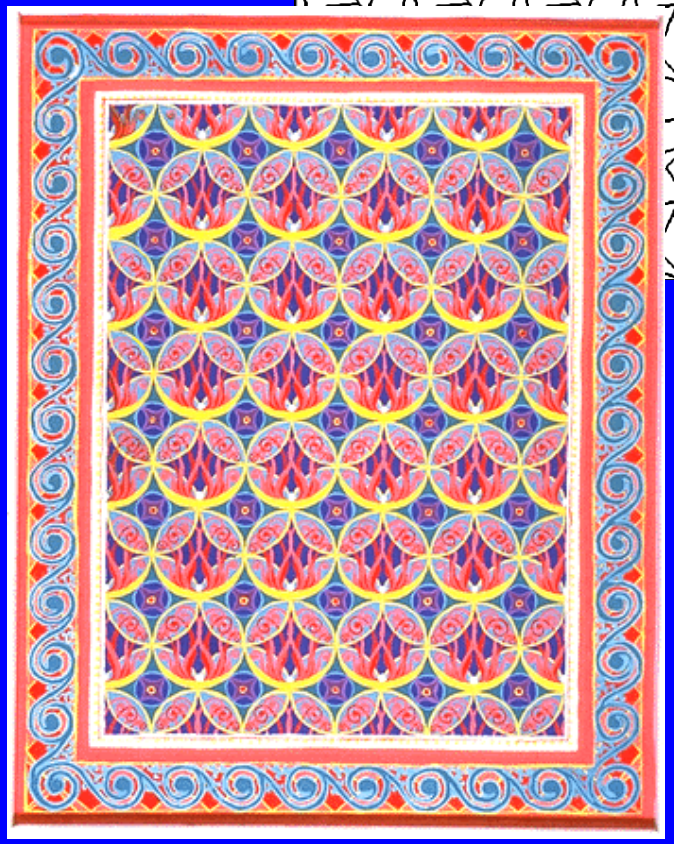
Five Planar Lattices



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







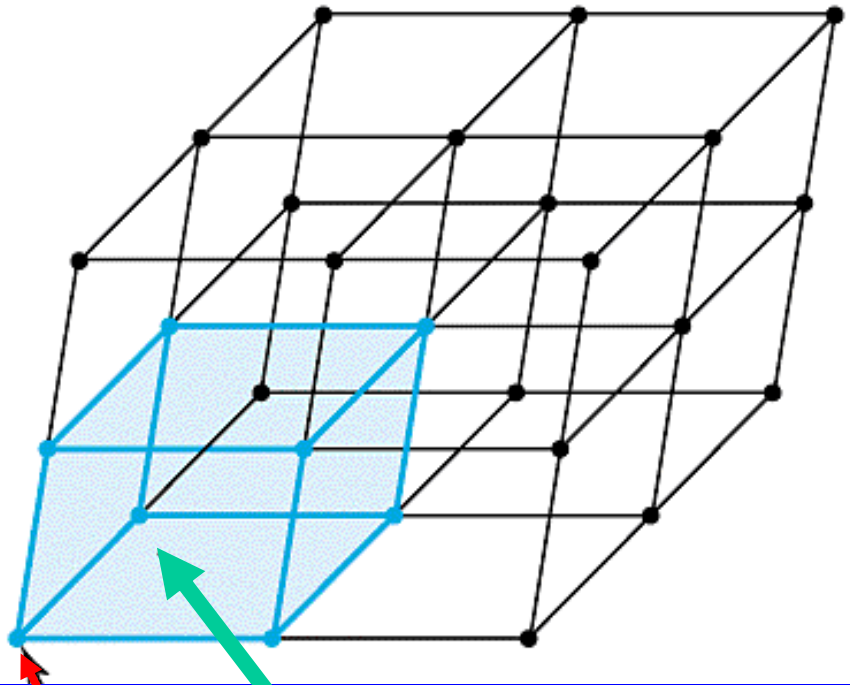
STM Nb/Se

Lattice and Unit Cell

Unit Cell Parameters

a, b, c – edge lengths

α, β, γ – angles

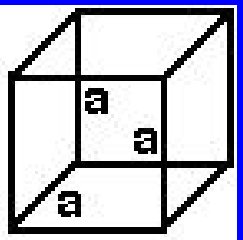


Seven Crystal Systems

Cubic

$a = b = c$

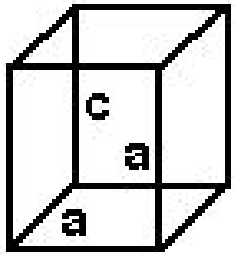
$\alpha = \beta = \gamma = 90^\circ$



Tetragonal

$a = b \neq c$

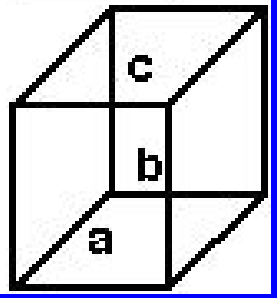
$\alpha = \beta = \gamma = 90^\circ$



Orthorhombic

$a \neq b \neq c$

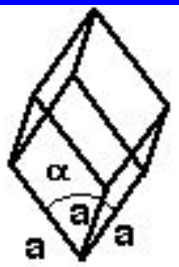
$\alpha = \beta = \gamma = 90^\circ$



Rhombohedral

$a = b = c$

$\alpha = \beta = \gamma \neq 90^\circ$

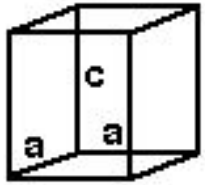


Hexagonal

$a = b \neq c$

$\alpha = \beta = 90^\circ$

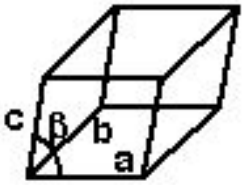
$\gamma = 120^\circ$



Monoclinic

$a \neq b \neq c$

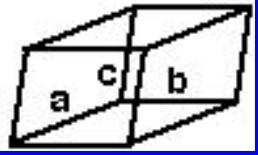
$\alpha = \gamma = 90^\circ \neq \beta$



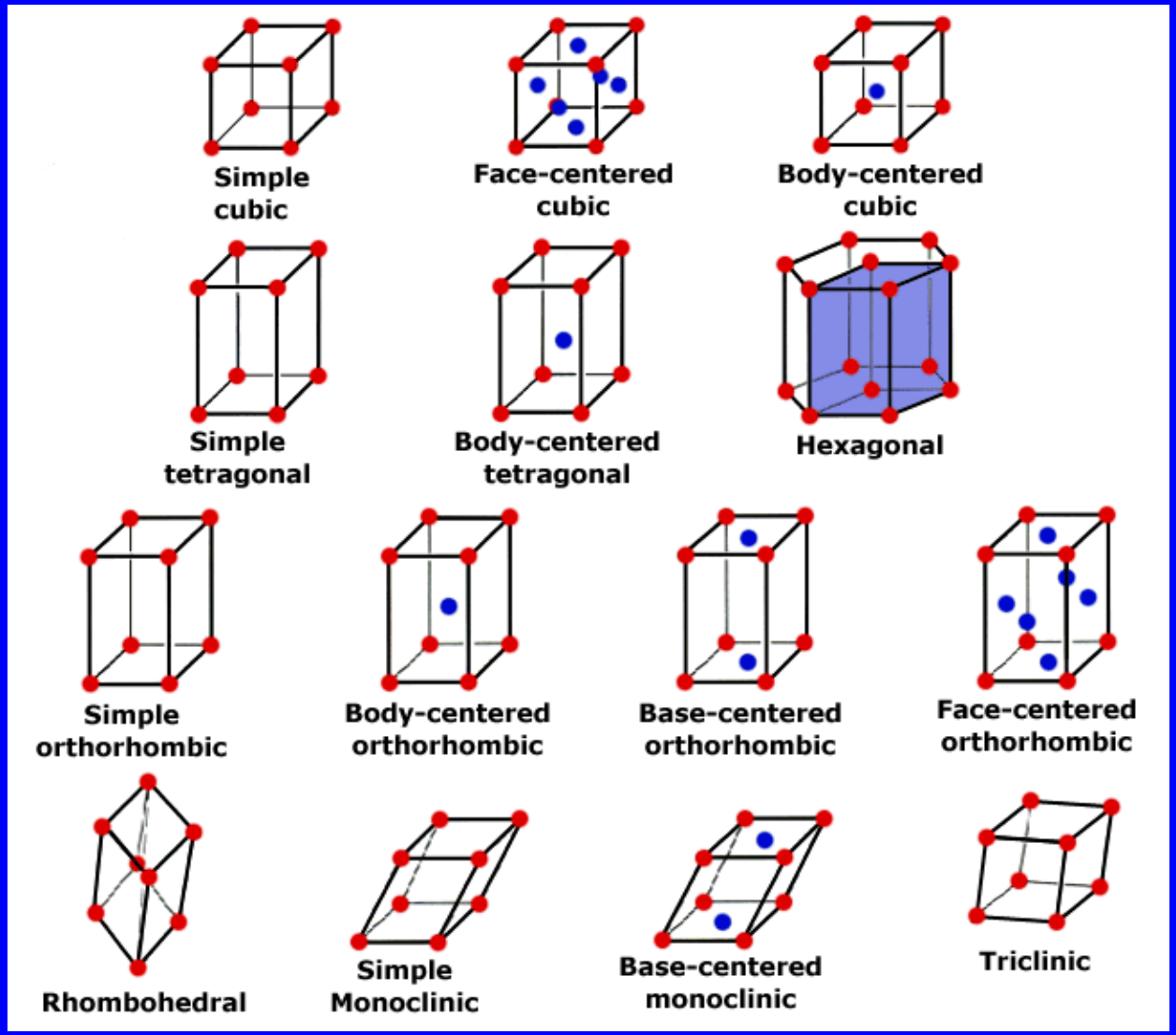
Triclinic

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90^\circ$



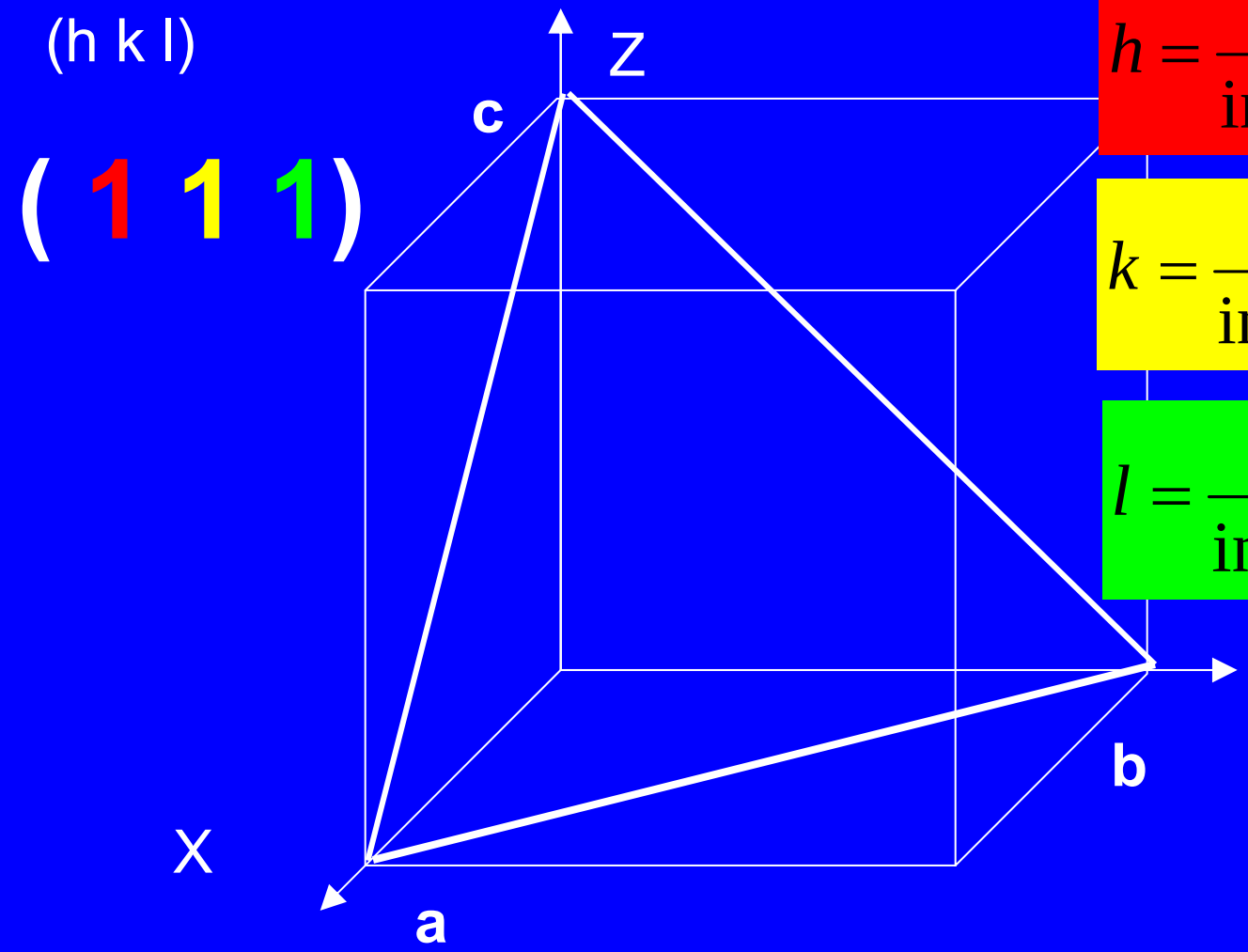
14 Bravais Lattices



Miller Indices

(h k l)

(1 1 1)

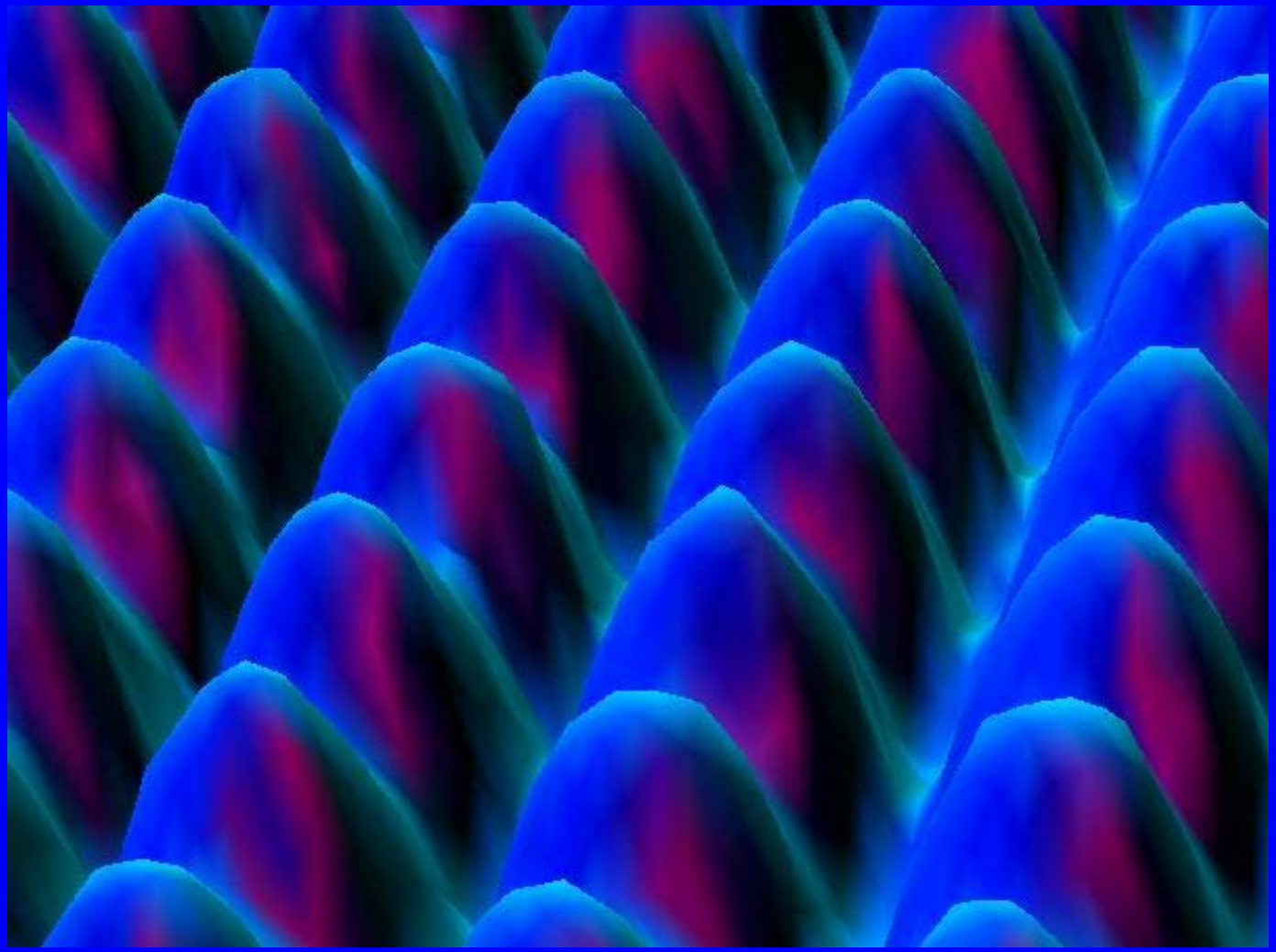


$$h = \frac{1}{\text{intercept} * x}$$

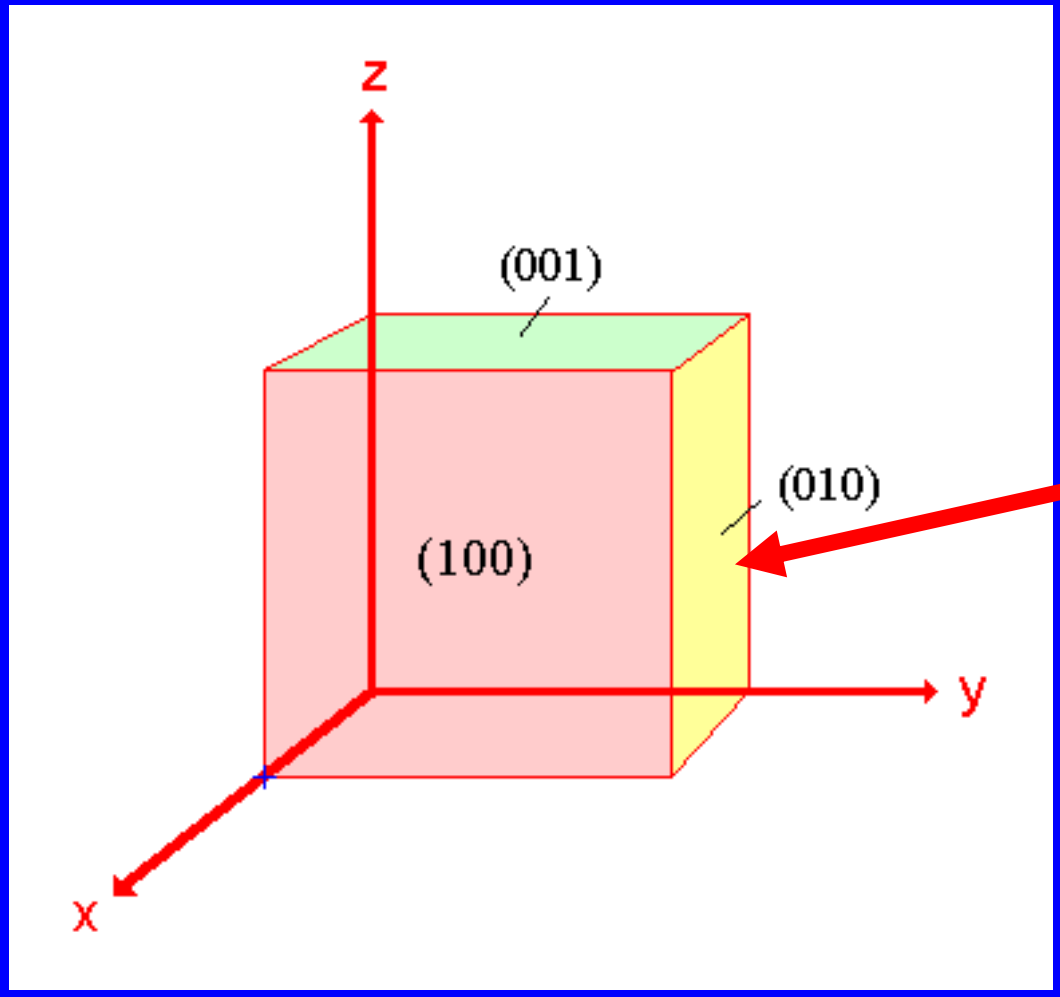
$$k = \frac{1}{\text{intercept} * y}$$

$$l = \frac{1}{\text{intercept} * z}$$

STM Picture of Fe in (110) Plane



Miller Indices



$$h = \frac{1}{\text{intercept} * x}$$

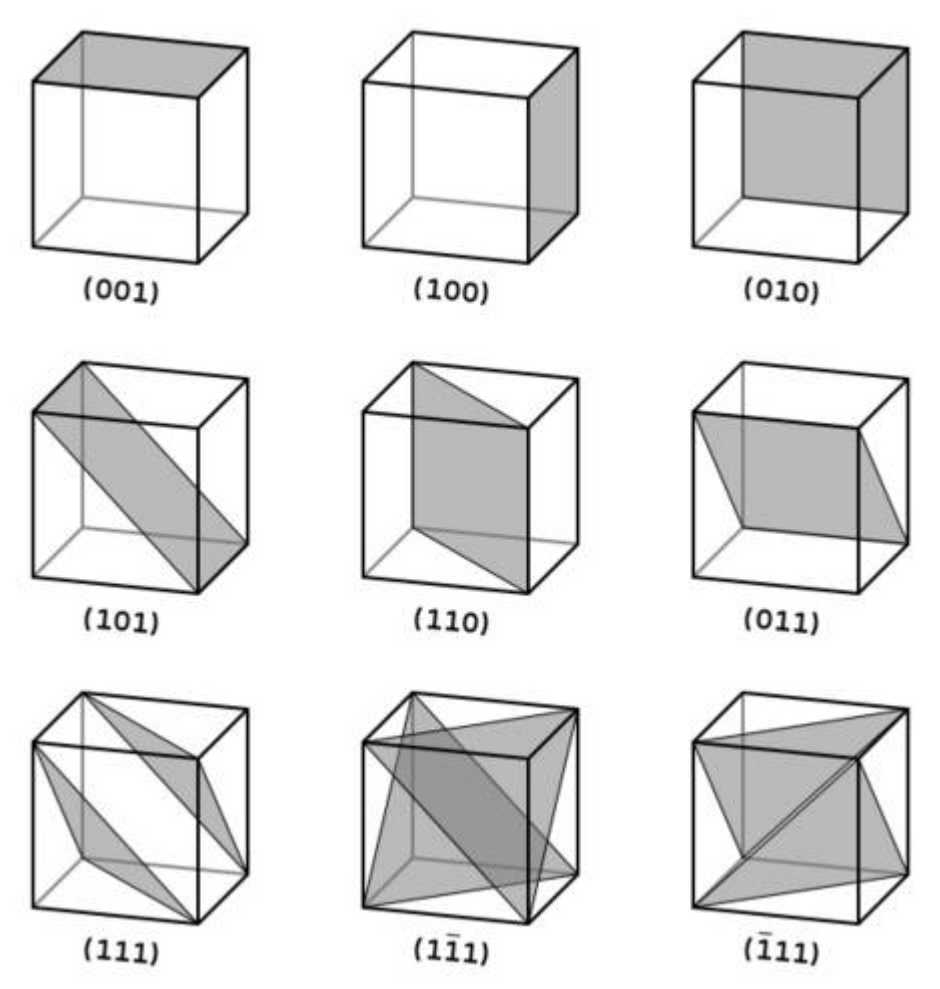
$$k = \frac{1}{\text{intercept} * y}$$

$$l = \frac{1}{\text{intercept} * z}$$

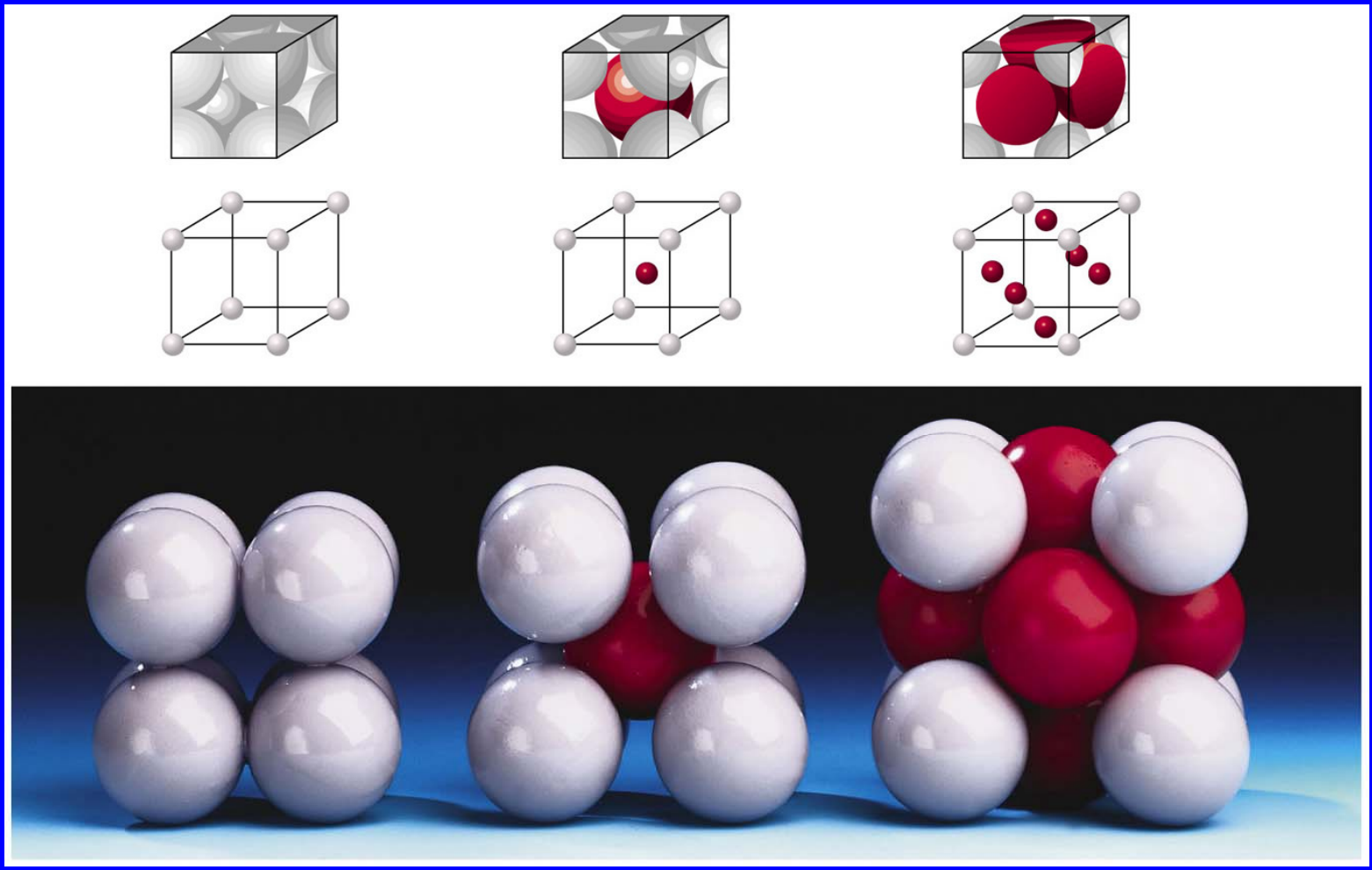
(0 1 0)

h = 1 / ∞ = 0
k = 1 / 1 = 1
l = 1 / ∞ = 0

Miller Indices

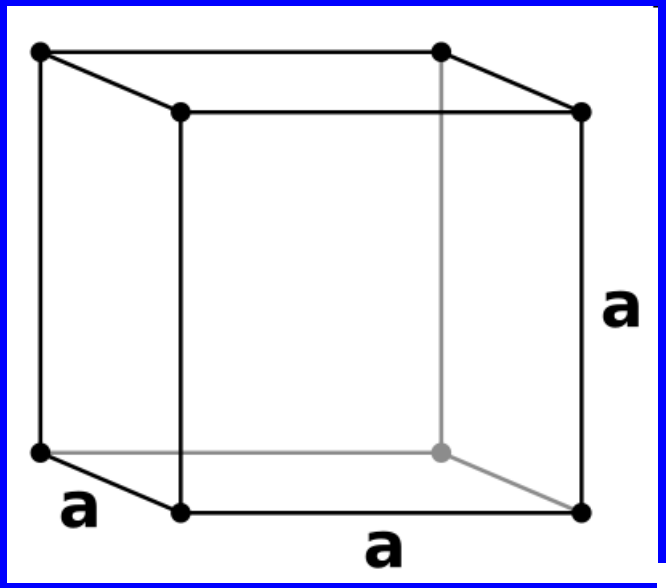


Three Cubic Cells

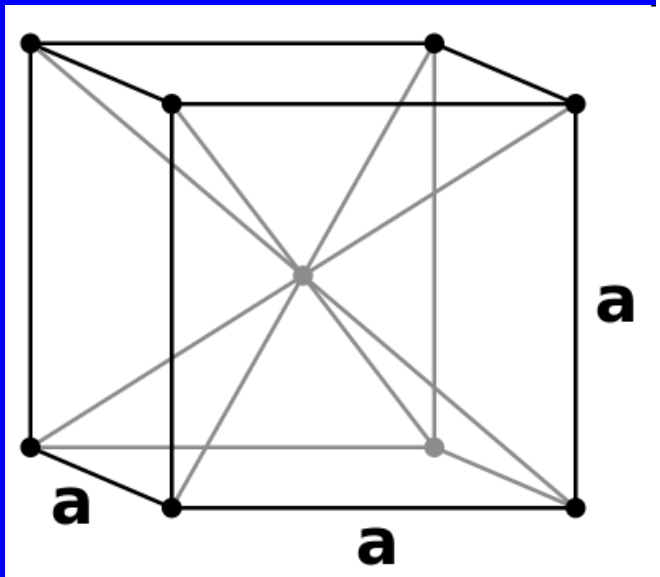


Primitive (P) Body centered (I) Face centered (F)

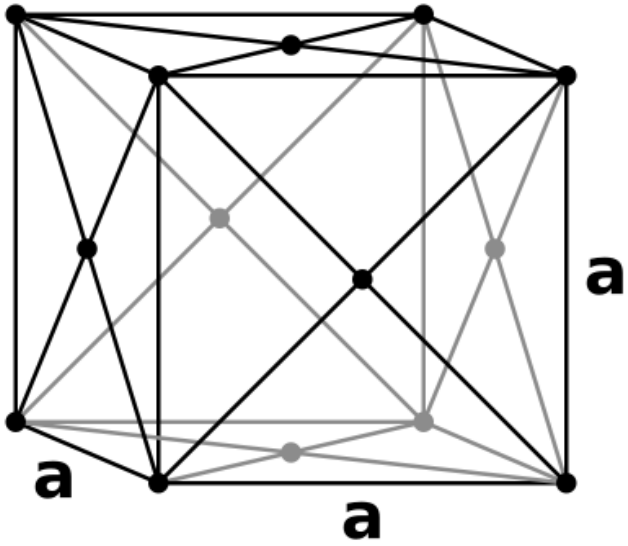
Primitive (P)



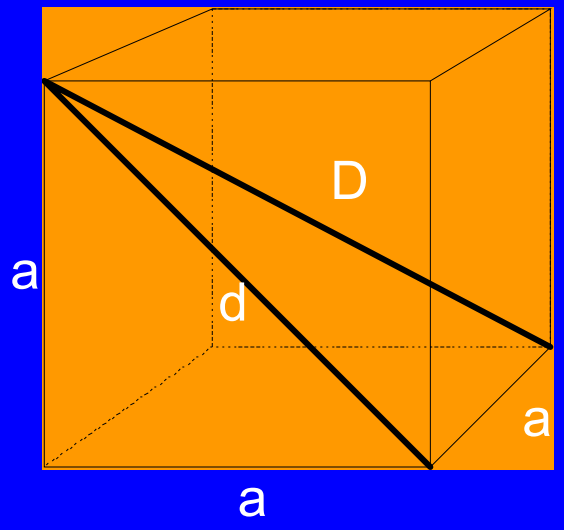
Body centered (I)



Face centered (F)



Cube



a = edge

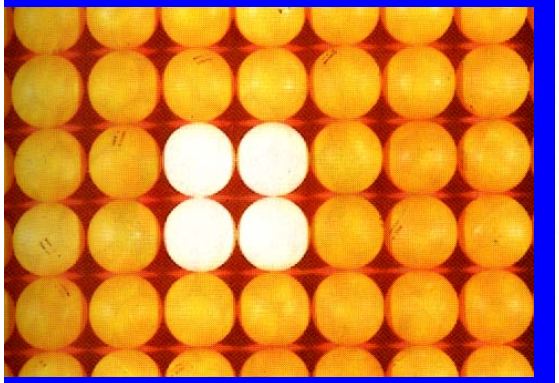
d = face diagonal
($d^2 = a^2 + a^2 = 2a^2$)

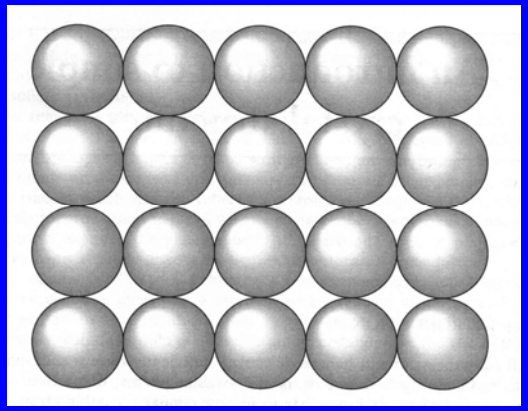
D = body diagonal
($D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2$)

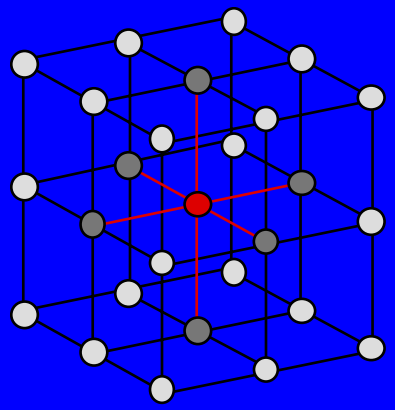
$$d = \sqrt{2} \cdot \mathrm{a}$$

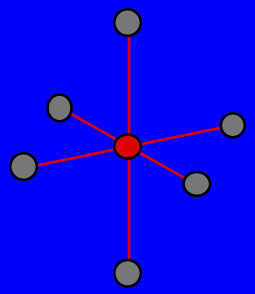
$$D = \sqrt{3} \cdot \mathrm{a}$$

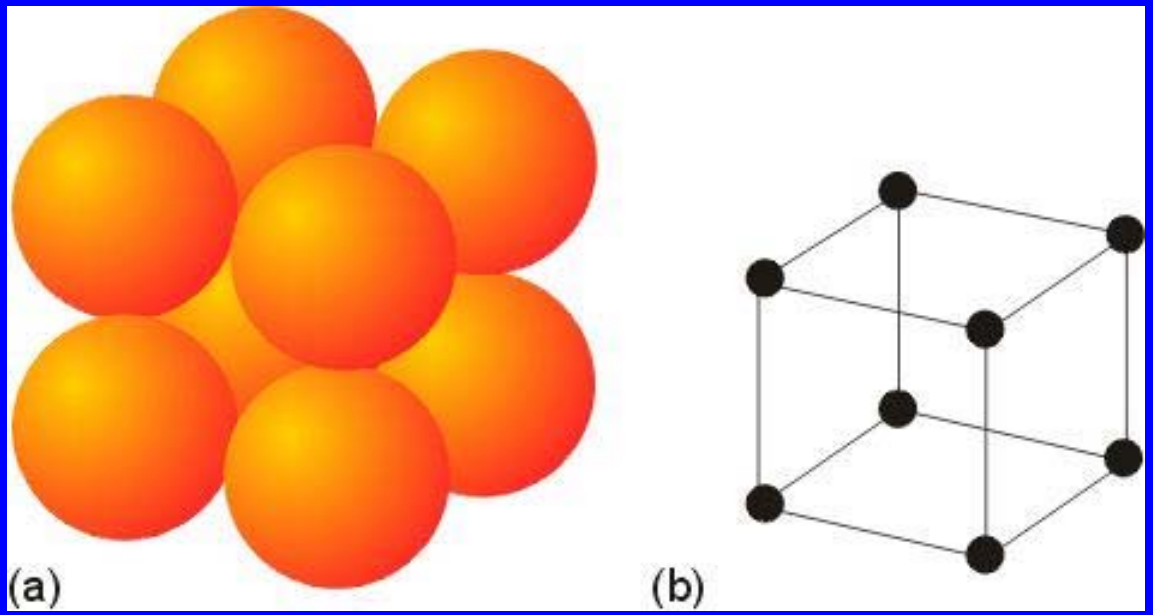
Primitive Cubic Cell, Po - Litviněnko









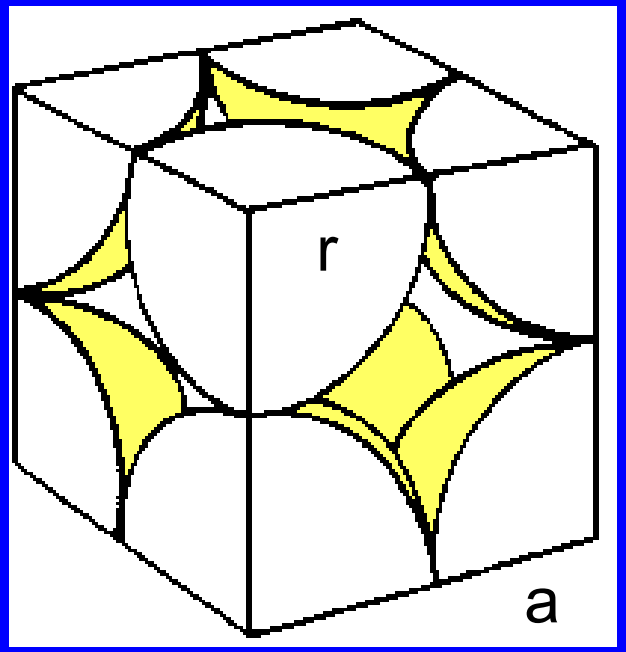


Space filling 52%

Coord. No. 6

Primitive Cubic Cell

Number of lattice points in the cell



$$\frac{1/8 \text{ atom}}{\text{vertes}} \times 8 \text{ vertices} = \frac{\mathbf{1 \text{ atom}}}{\mathbf{cell}}$$

Space filling

atoms touch along edge (a)

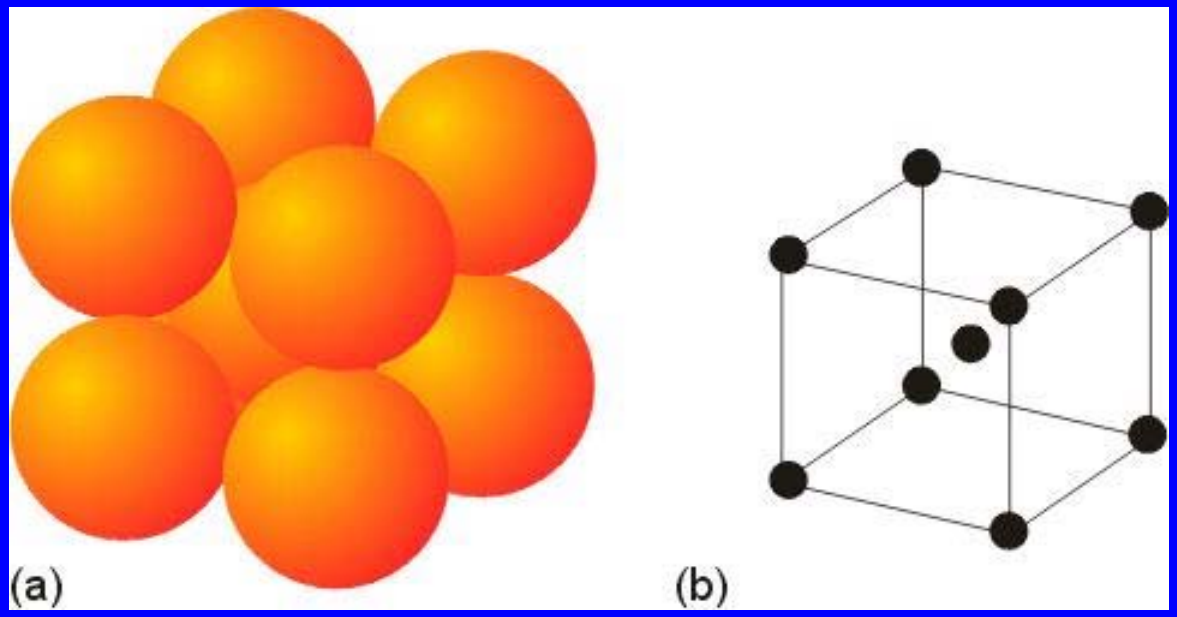
a = 2r then $r = \frac{a}{2}$

Cell volume $V = a^3 = 8r^3$

Volume of atoms in the cell
$V_A = 4/3\ \pi\ r^3$

Space filling = $V_a/V\ 100 = 52\%$

Body Centered Cell, W

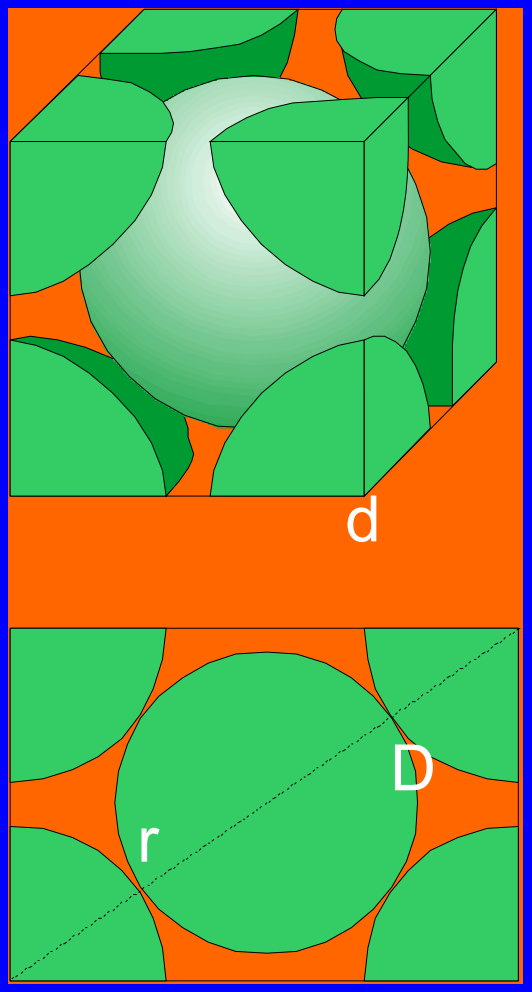


Space filling 68%

Coord. no 8

Body Centered Cell, W

Number of lattice points in the cell



$\frac{1/8 \text{ atom}}{\text{vertex}}$ x 8 vertices = 1 atom

+ center = 1 atom

2 atoms/cell

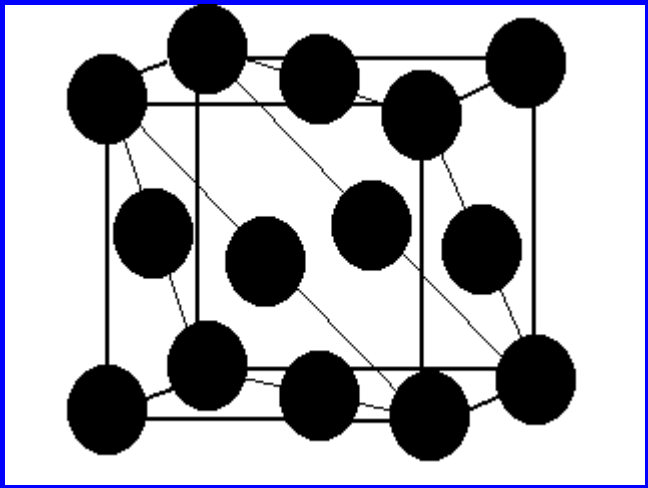
Atoms touch along body diagonal (D)

D = 4r = $\sqrt{3} \cdot a$

$a = \frac{4r}{\sqrt{3}}$ then $r = \frac{\sqrt{3} \cdot a}{4}$

$V = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$

Face Centered Cell, Cu
(= Close Cubic Packing)



Space filling 74%

Coord. no 12

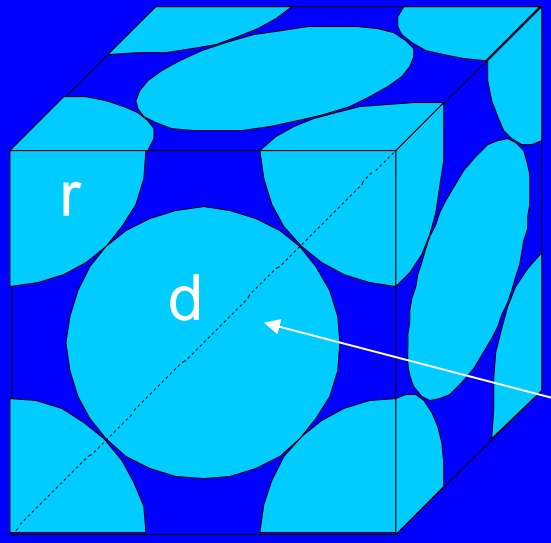
Face Centered Cell

Number of lattice points in the cell

$\frac{1/8 \text{ atom}}{\text{vertex}}$ x 8 vertices = 1 atom

$\frac{1/2 \text{ atom}}{\text{face}}$ x 6 faces = 3 atoms

4 atoms/cell



a

Atoms touch along face diagonal (d)

d = 4r = $\sqrt{2} \cdot a$

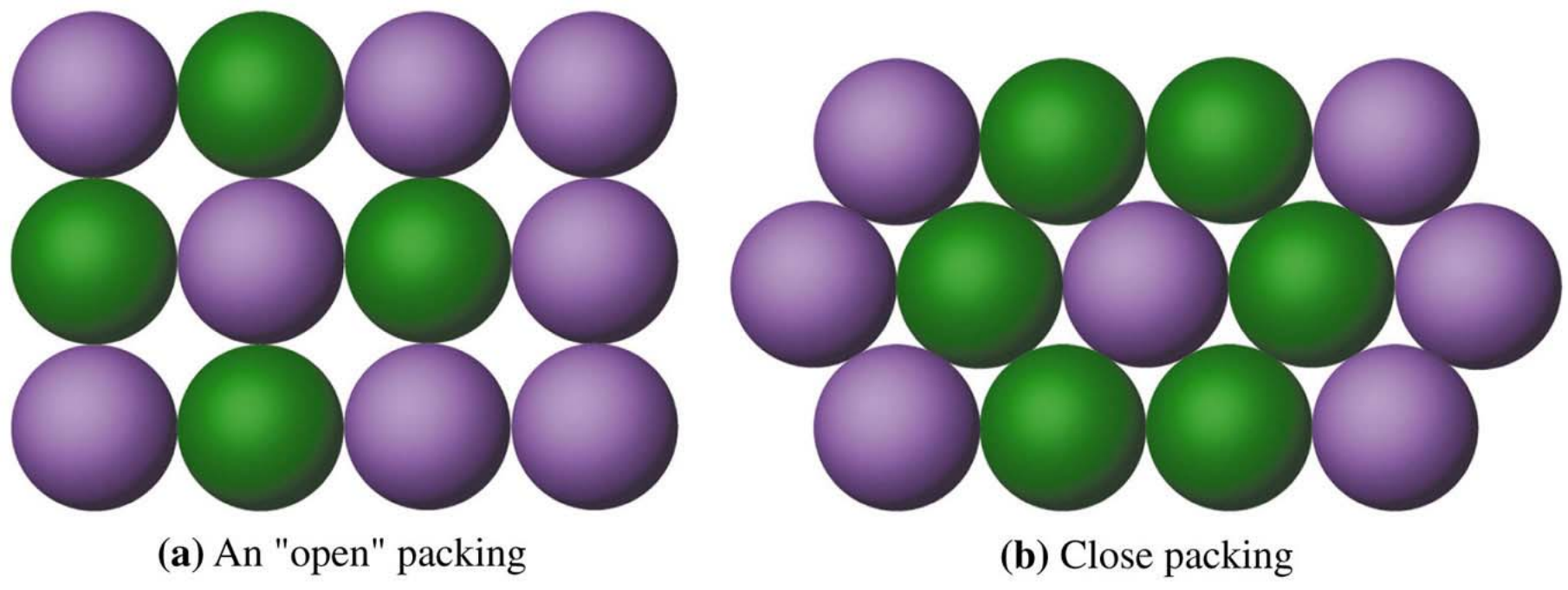
$a = \frac{4r}{\sqrt{2}}$ or $r = \frac{\sqrt{2} \cdot a}{4}$

$V = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$

Space Filling

	Radius	No. of atoms	Space Filling
Primitive cubic	a/2	1	52%
Body centered	$\sqrt{3}a/4$	2	68%
Face centered	$\sqrt{2}a/4$	4	74%
Diamond	$\sqrt{3}a/8$	8	34%

Close Packing on a Plane

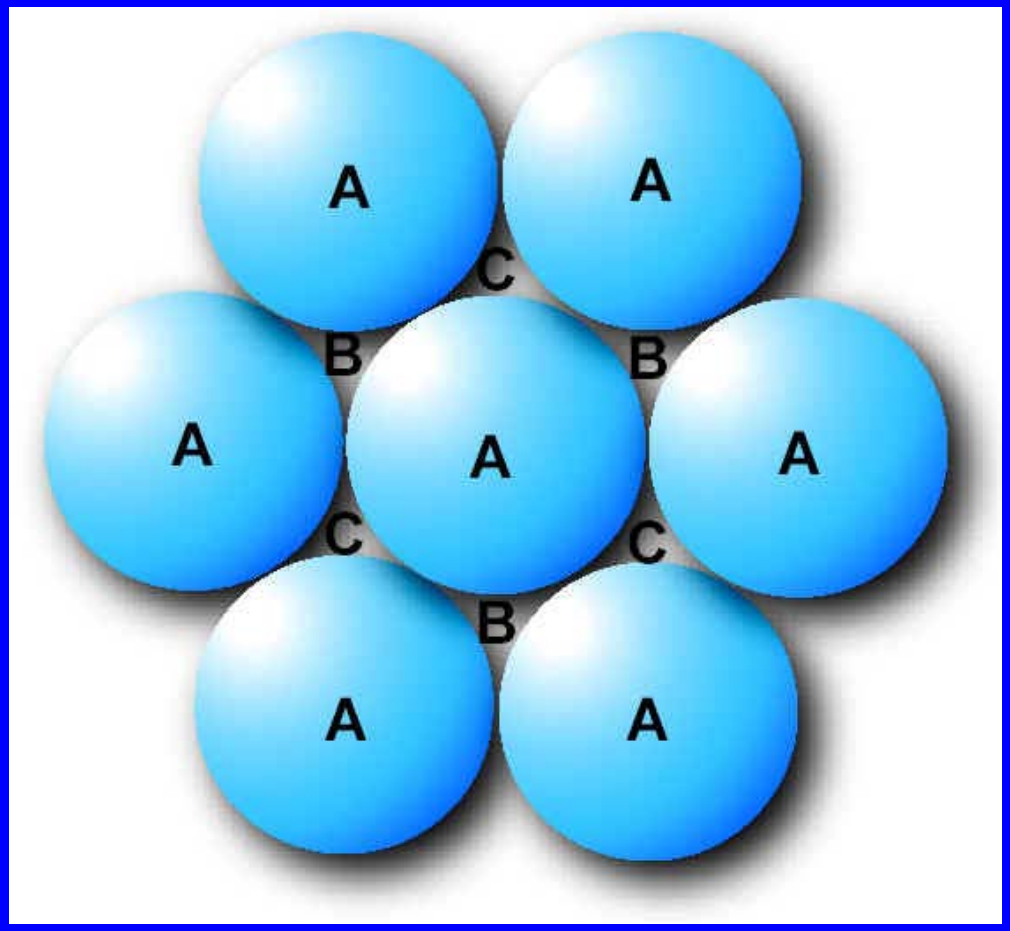


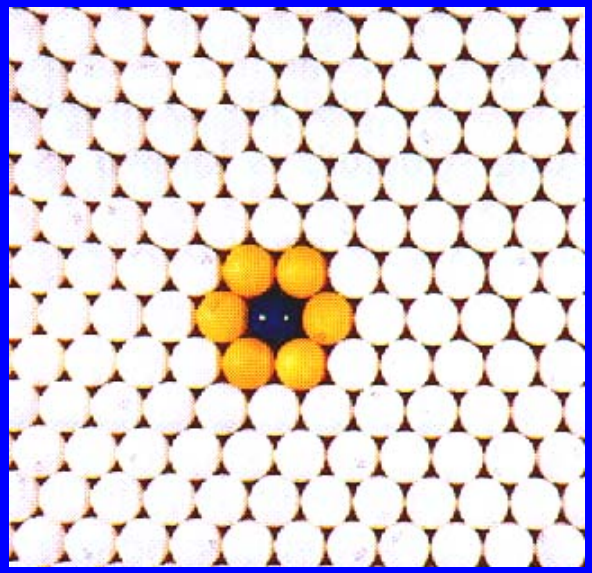
(a) An "open" packing

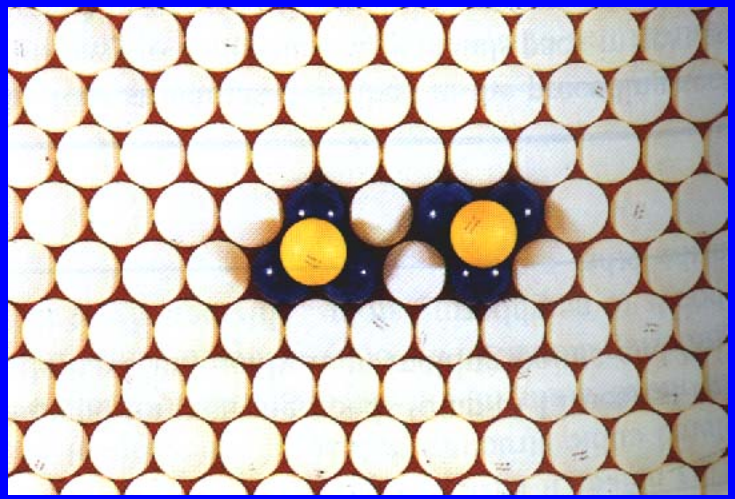
(b) Close packing

Square packing
Lots of free space
4 neighboring atoms

Hexagonal packing
The best use of space
6 neighboring atoms



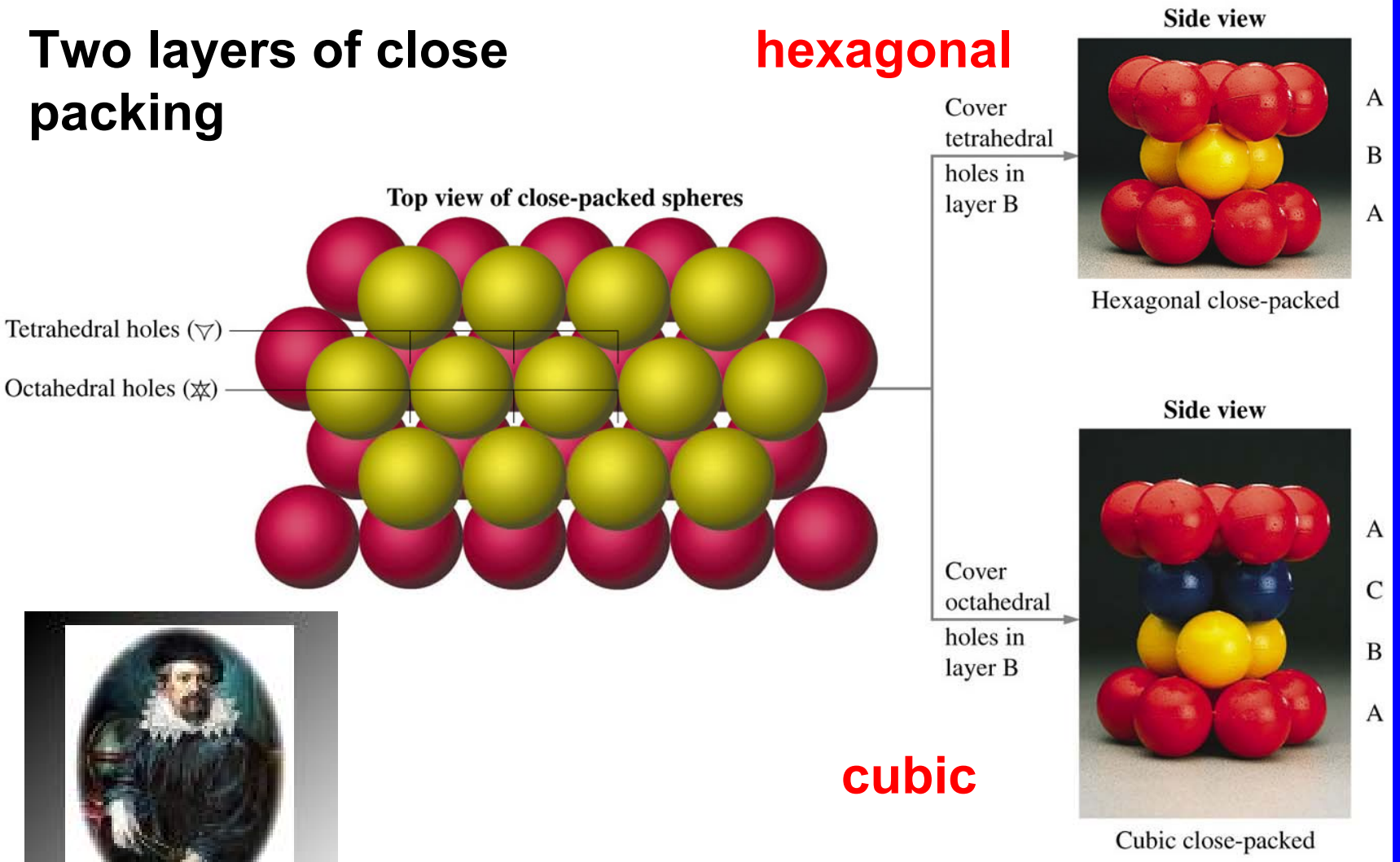




Holes B and C cannot be filled at the same time by atoms in the second layer

Two layers of close packing

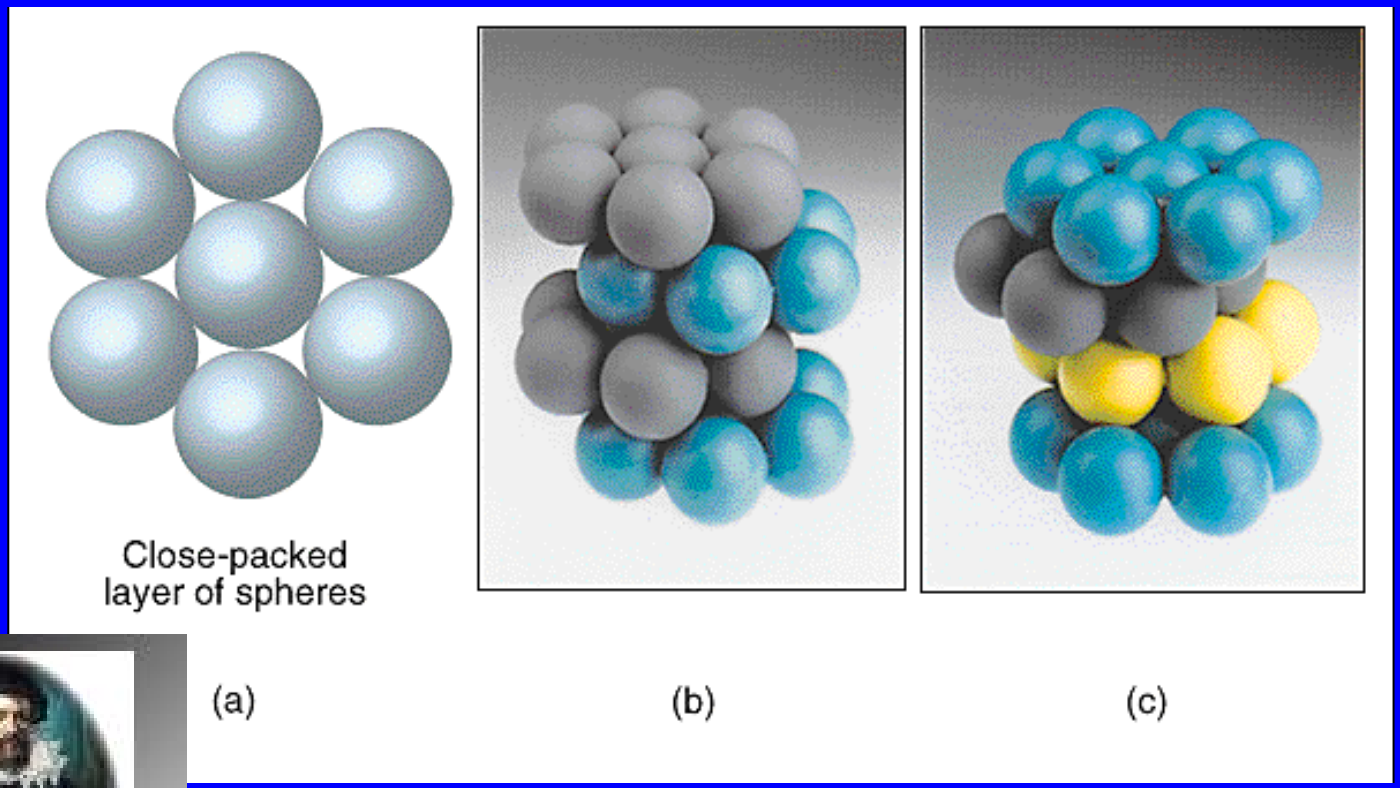
hexagonal



cubic

Johannes Kepler 1611

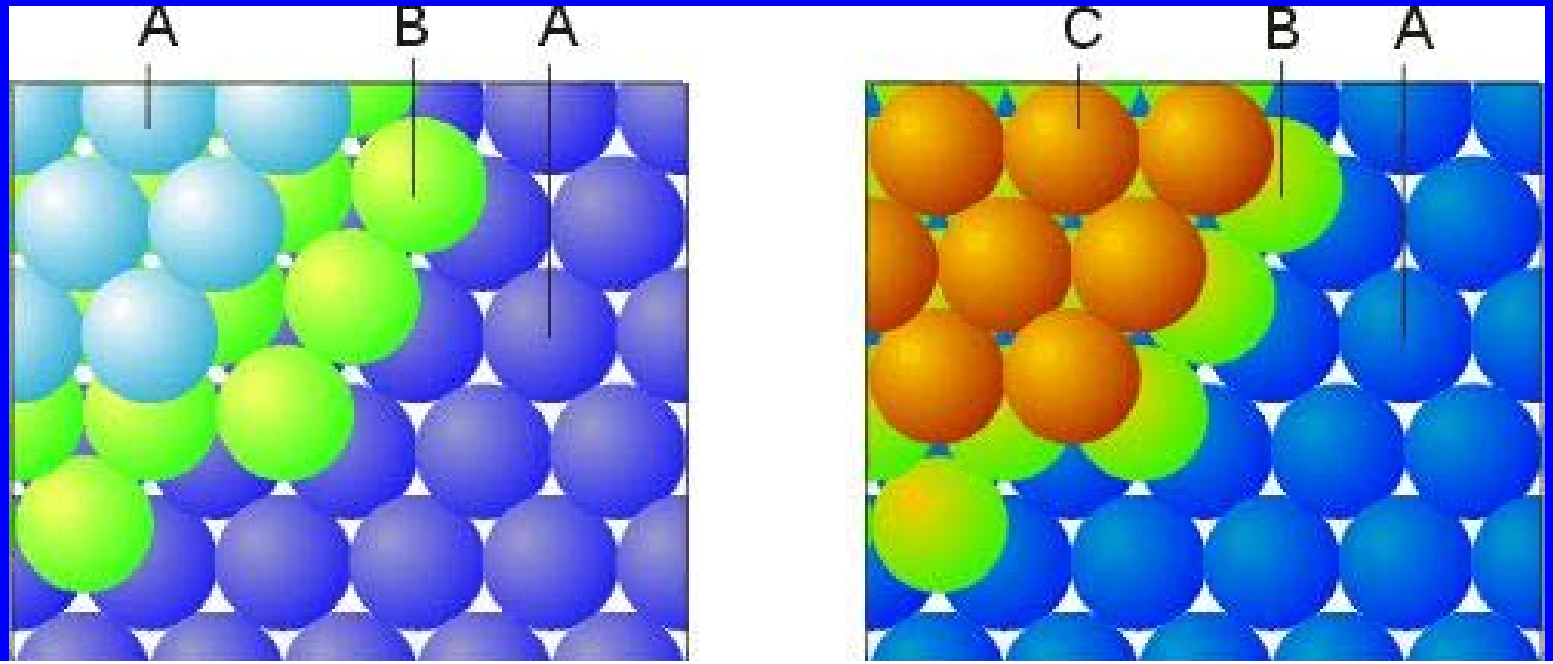
Close Packing in Space

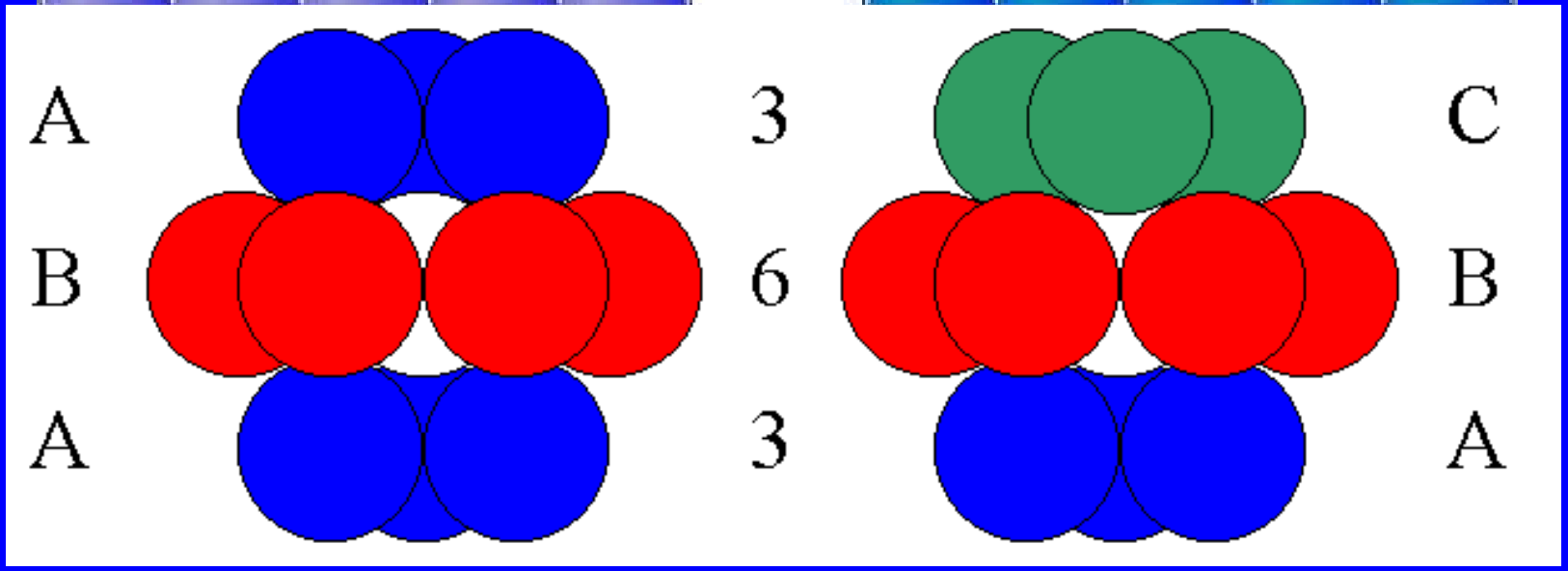


Johannes Kepler 1611

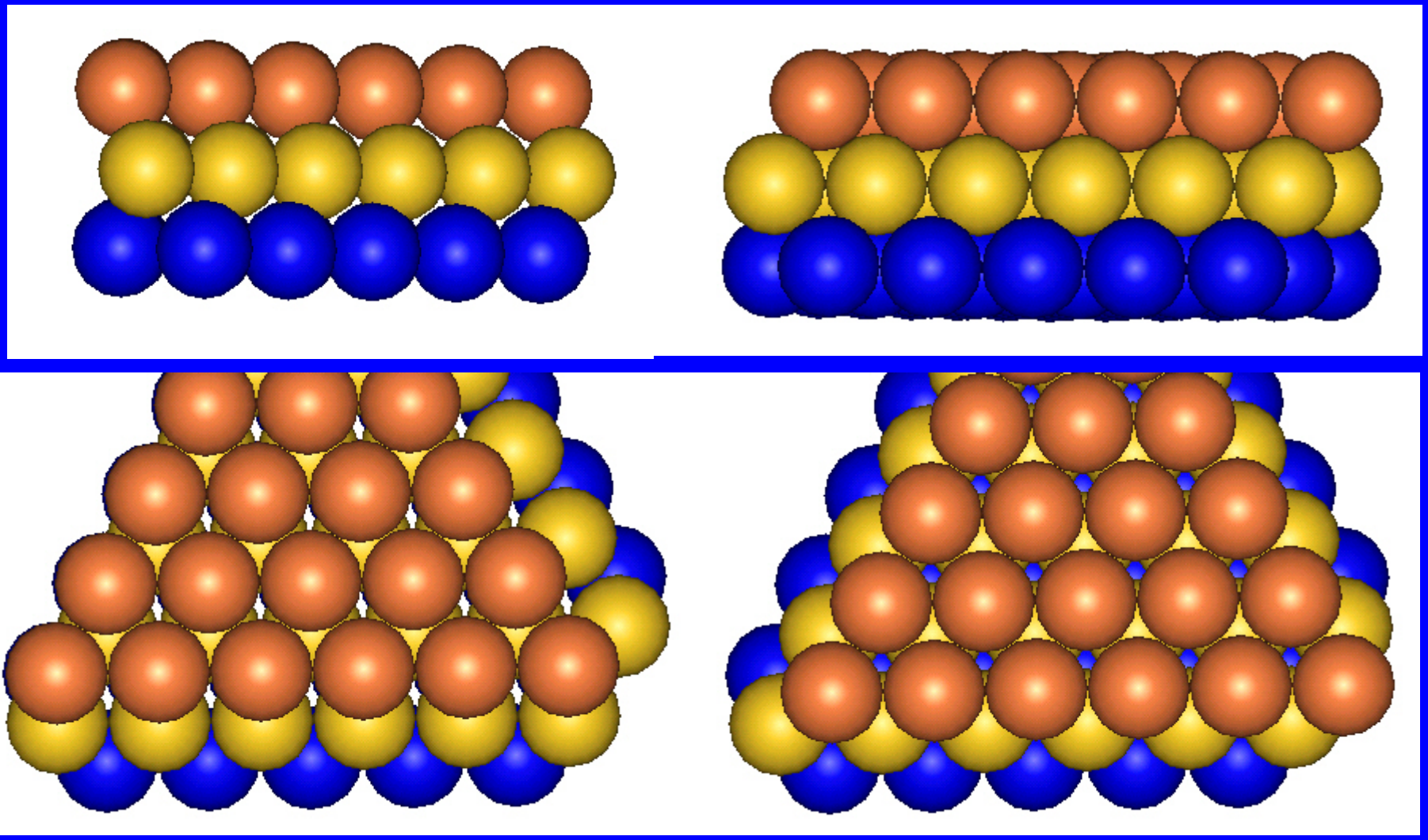
hexagonal cubic

hexagonal **Close Packing** cubic



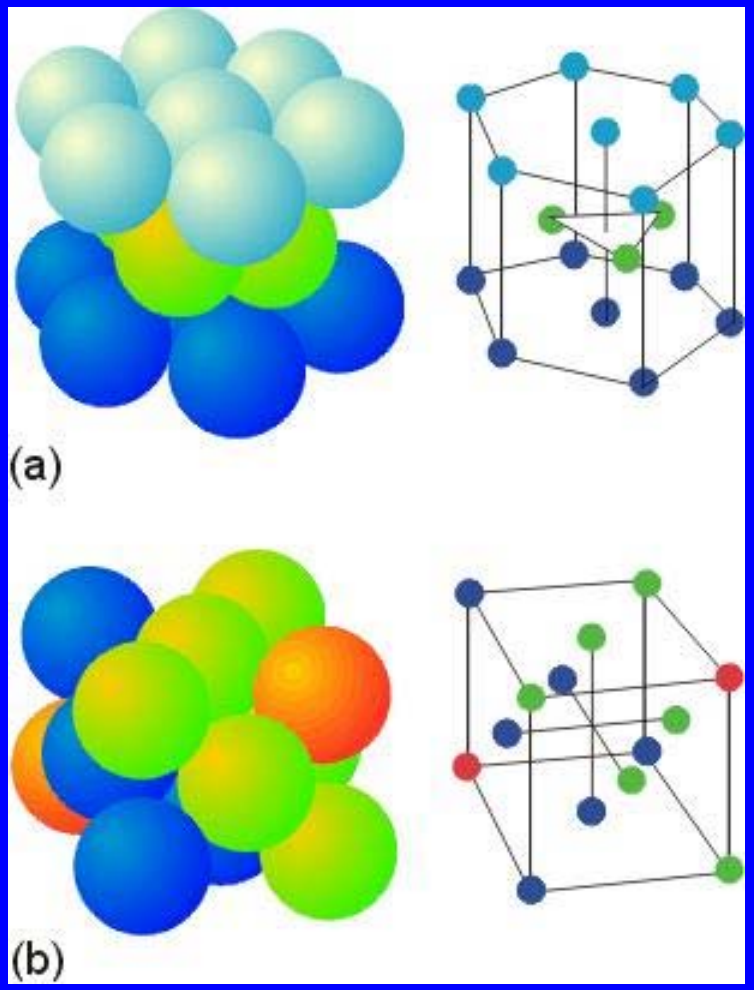


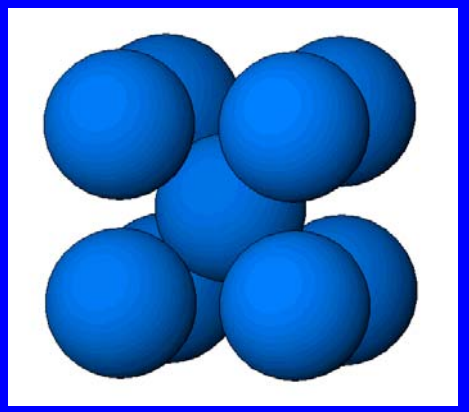
hexagonal **Close Packing** cubic



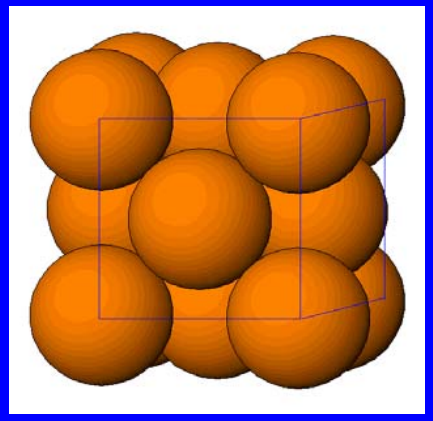
Close Packing

Mg, Be, Zn, Ni, Li, Be, Os, He





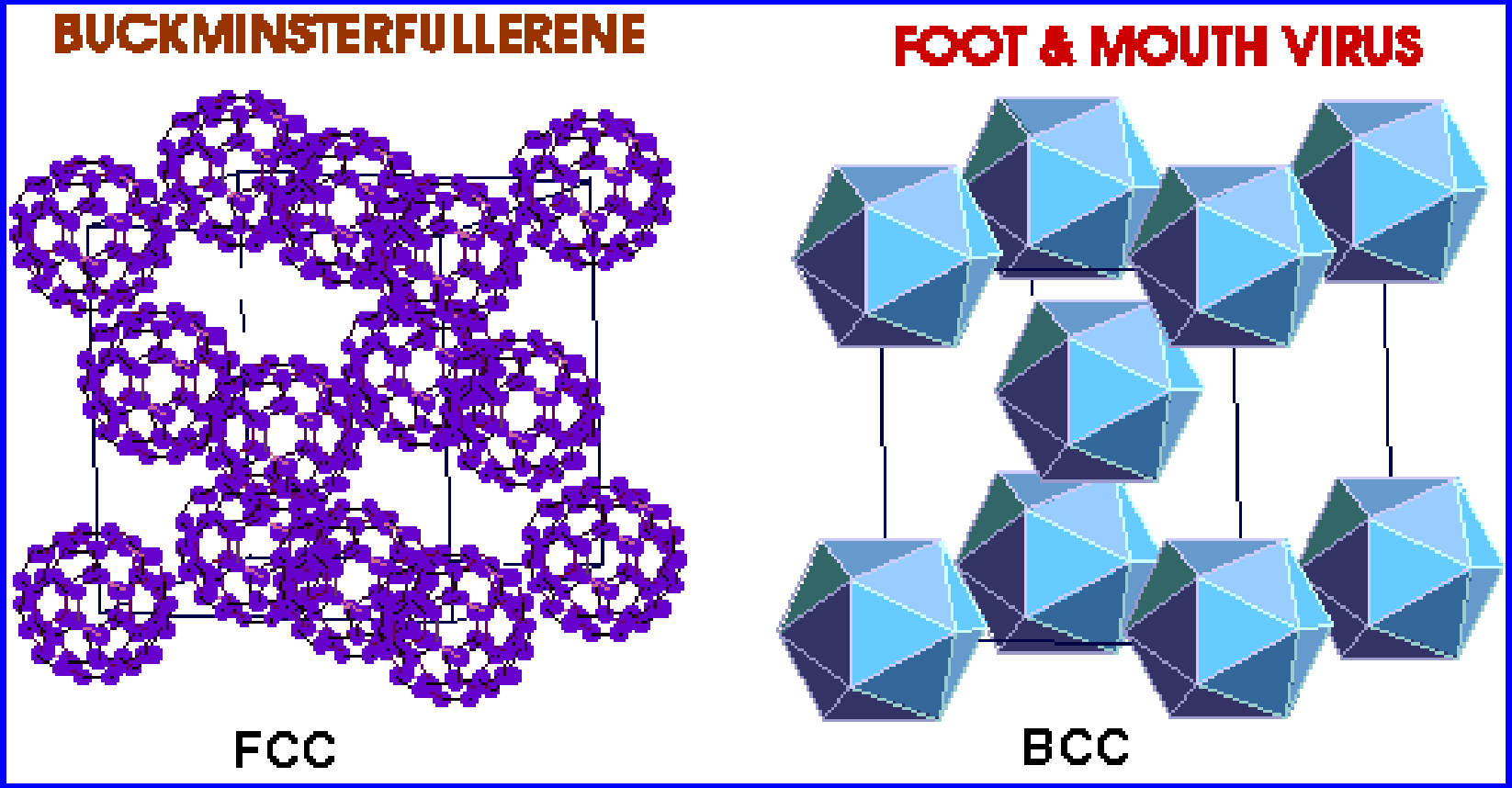
hexagonal

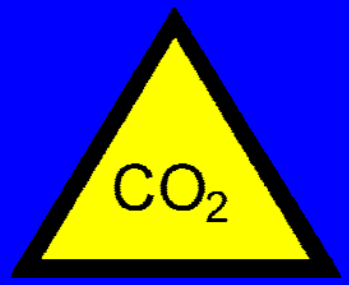


cubic

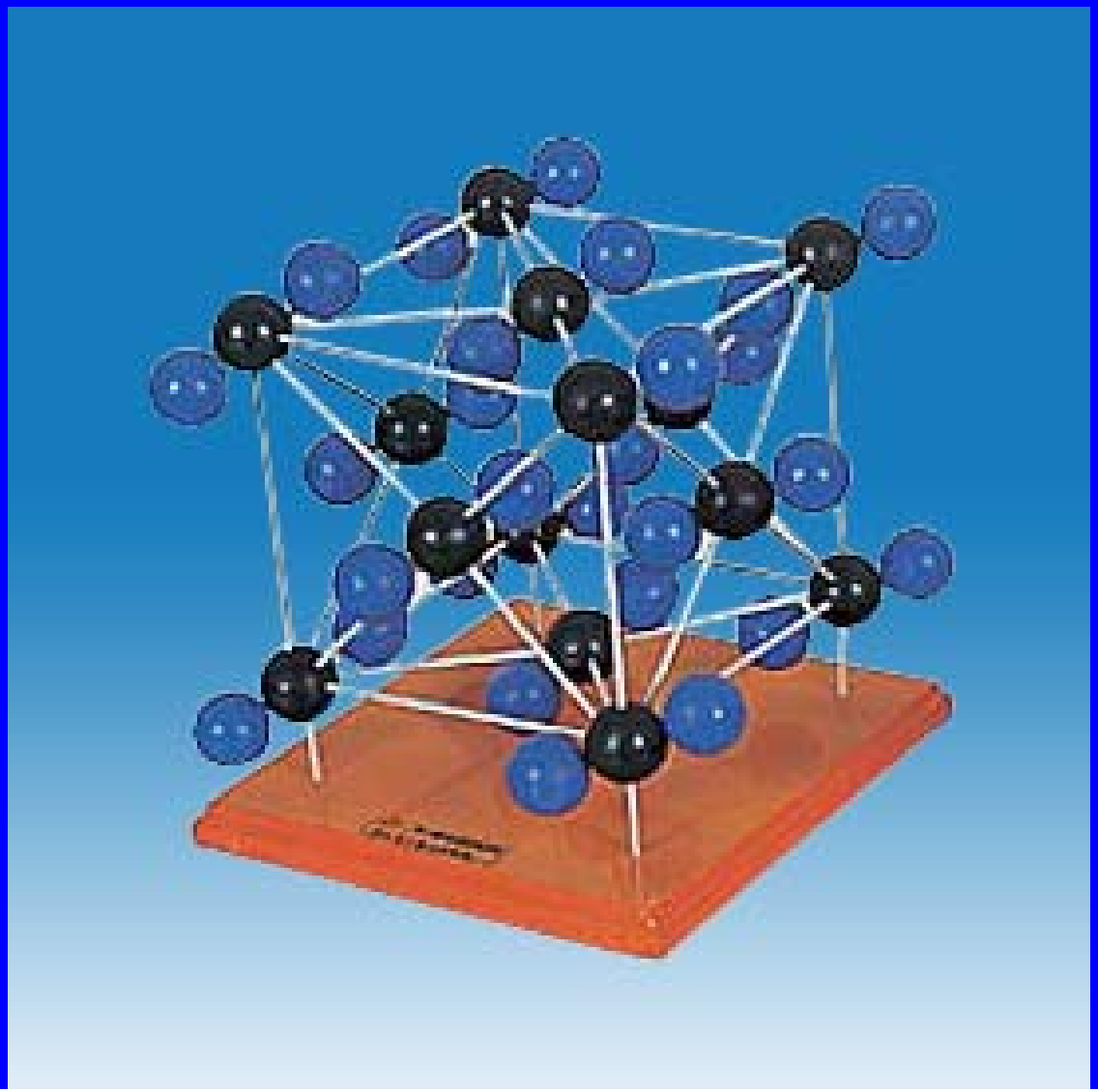
Cu, Ca, Sr, Ag, Au, Ar, F_2, C_{60}, opal (300 nm)

Close Packing of Large Structures

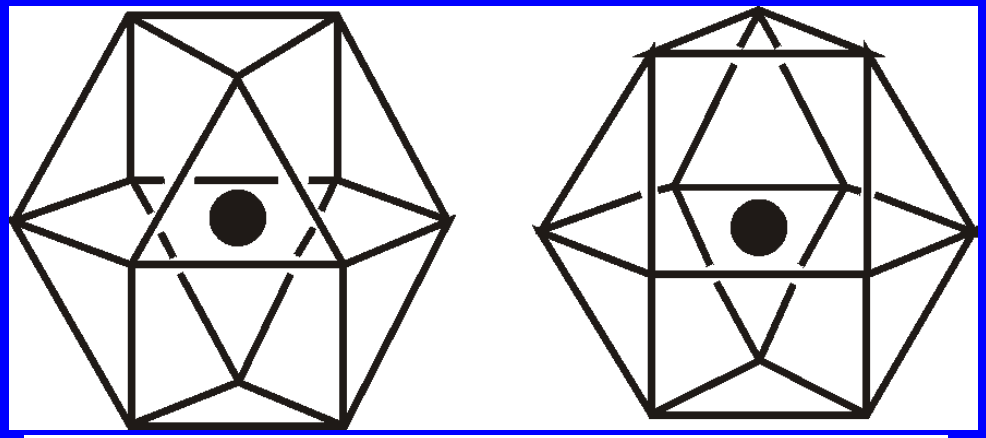


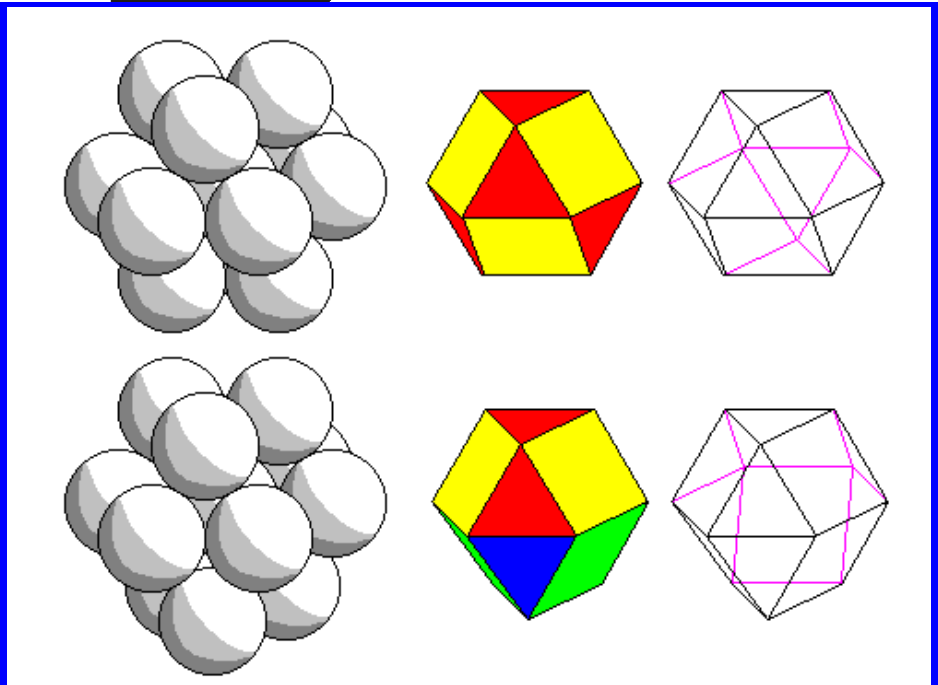


Structure of Dry Ice



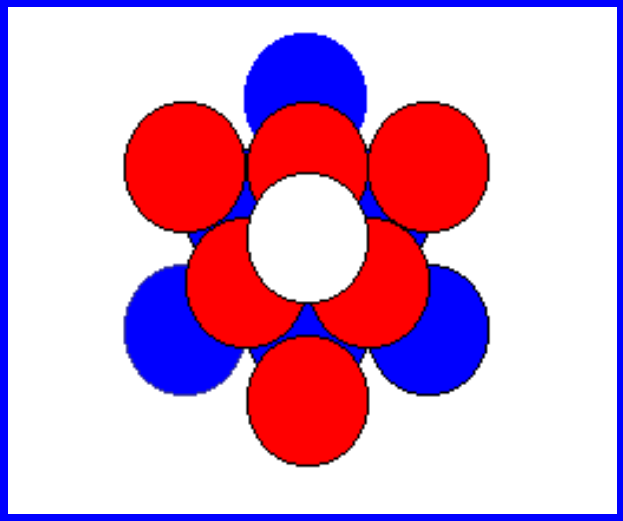
Coordination Polyhedra

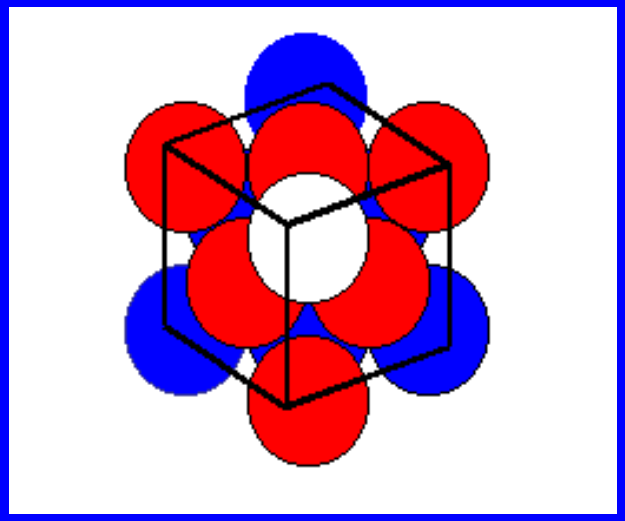




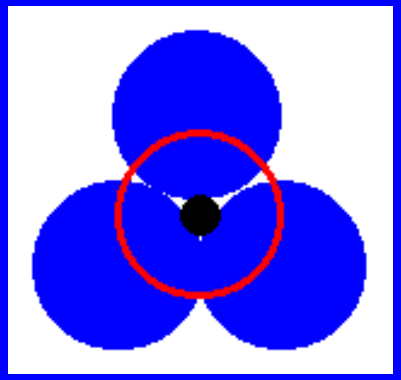
Cubic Close Packing = Face Centered Cell

Layers (ABC)

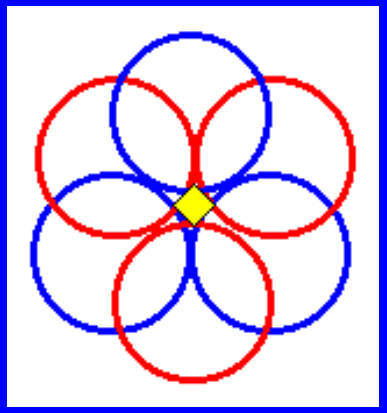




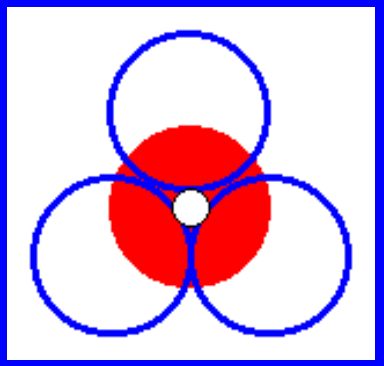
Close packed layers are oriented perpendicular to body diagonal of cubic cell



Tetrahedral T_+

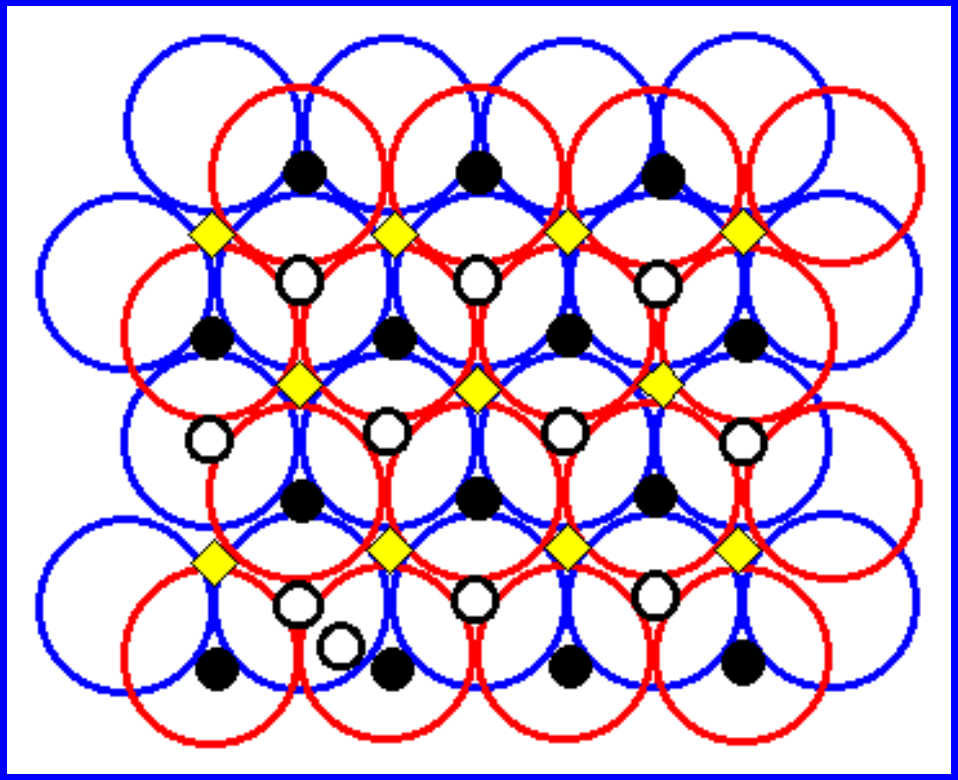


Octahedral O



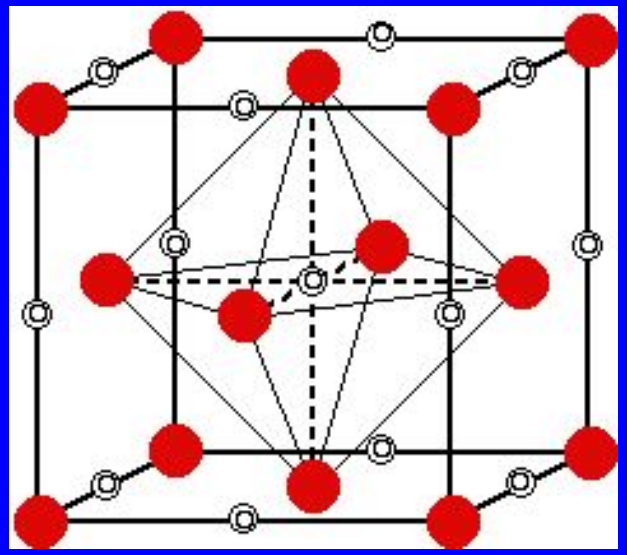
Tetrahedral T_-

For N close packed atoms, there are N octahedral and 2N tetrahedral holes per one cell

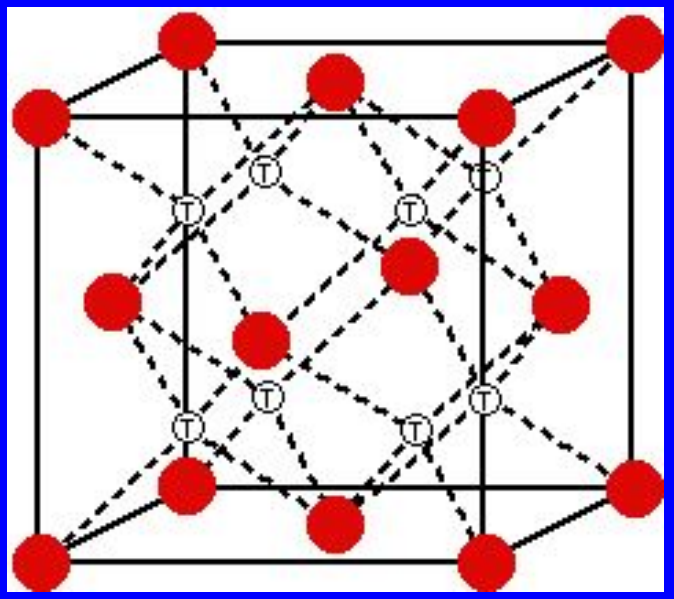


Two Types of Holes

Cubic Close Packing = Face Centered Cell
Number of atoms in a cell N = 4

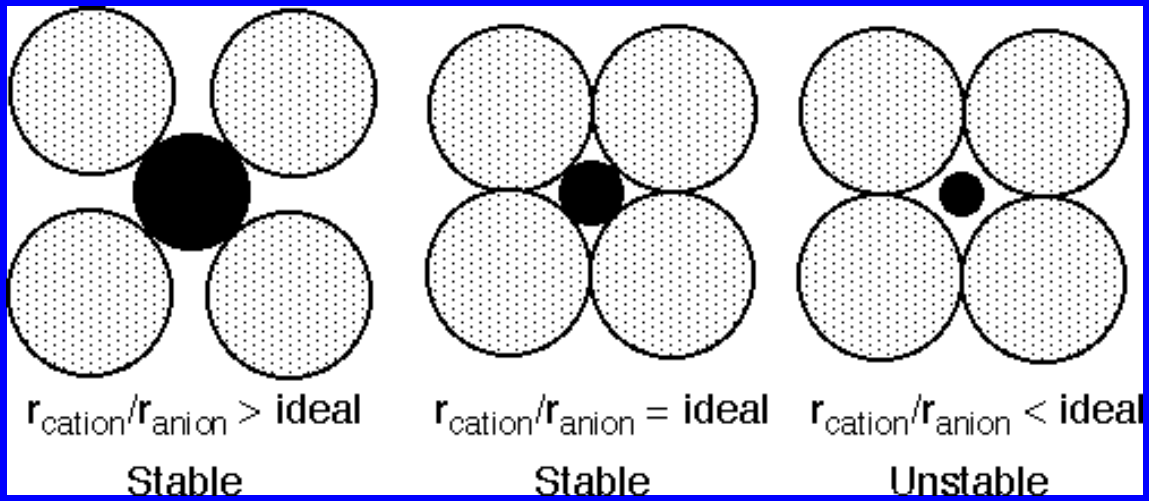


Octahedral (N = 4)



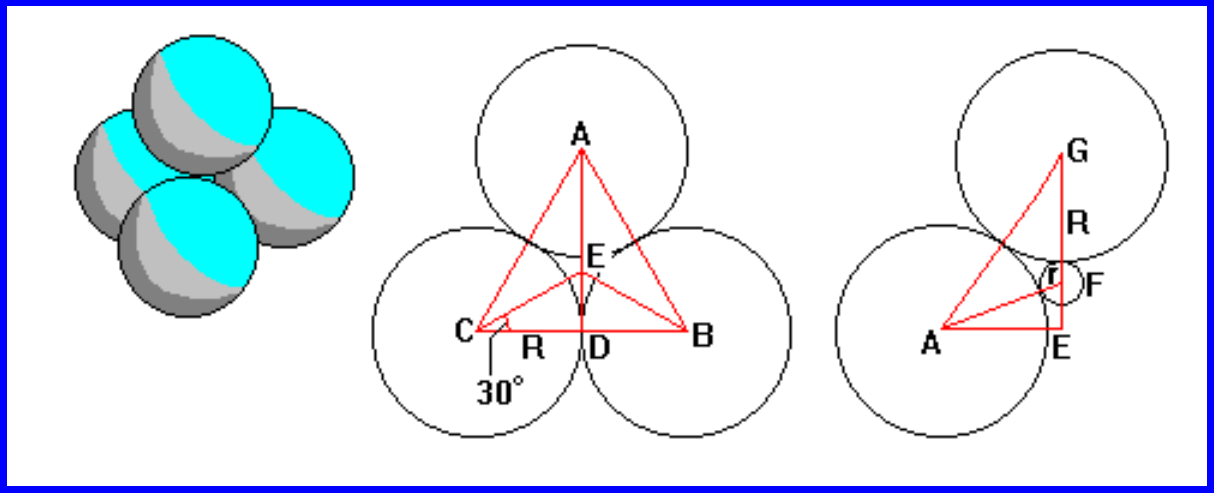
Tetrahedral (2N = 8)

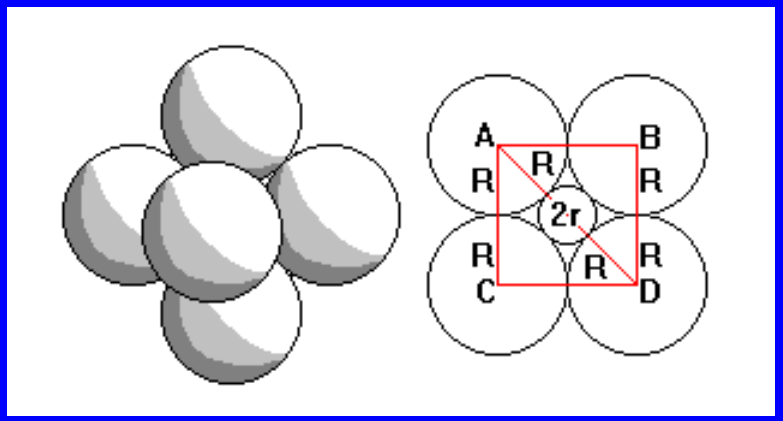
Cation/Anion Radius Ratio

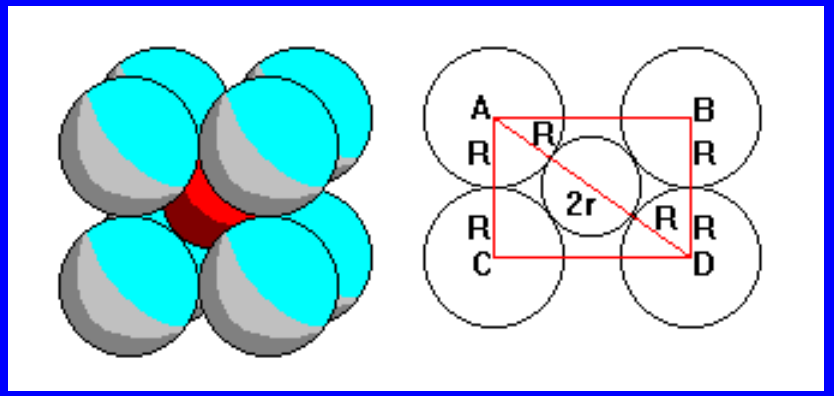


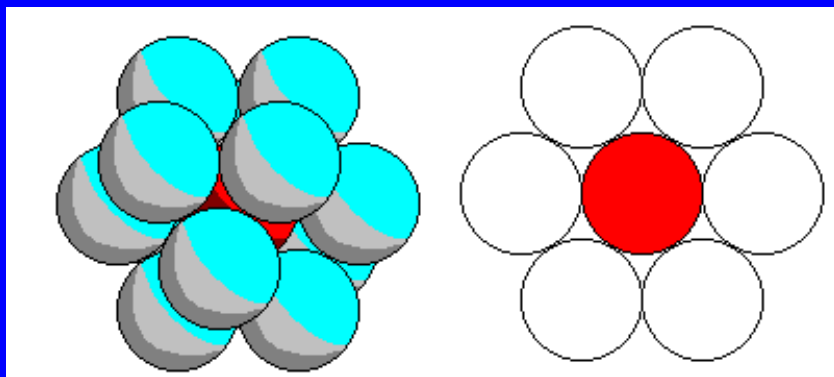
Coord. No.	r/R
12 – Cub. and Hex.	1.00 (substitution)
8 – Cubic	0.732 – 1.00
6 – Octahedral	0.414 – 0.732
4 – Tetrahedral	0.225 – 0.414

Void radius decreases

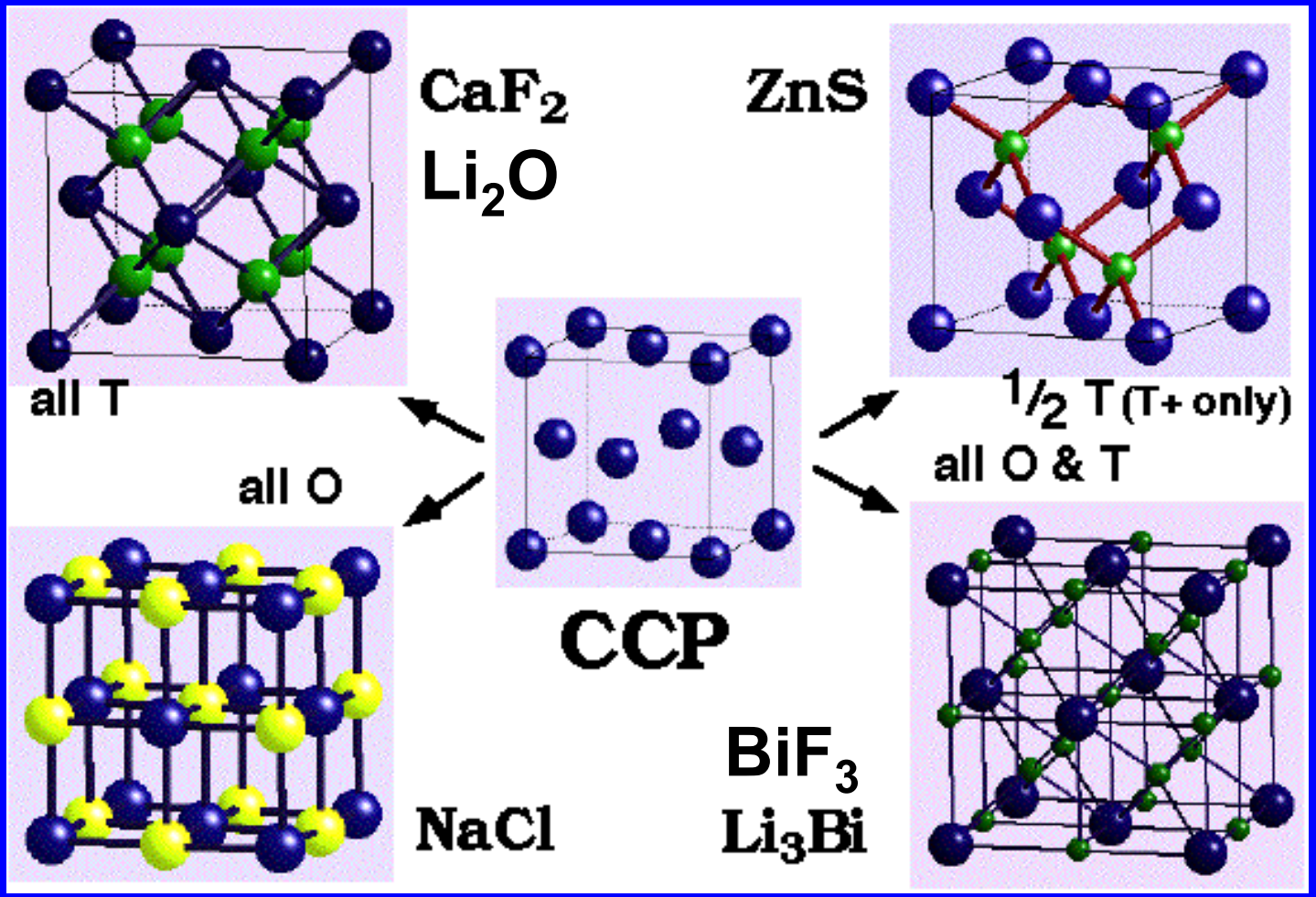

A
E
C
R
D
B
30°
G
R
r
F
A
E


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

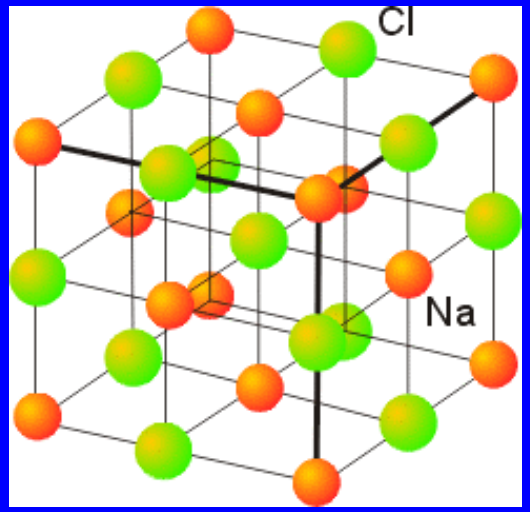

A
B
R
R
R
R
2r
R
R
C
D

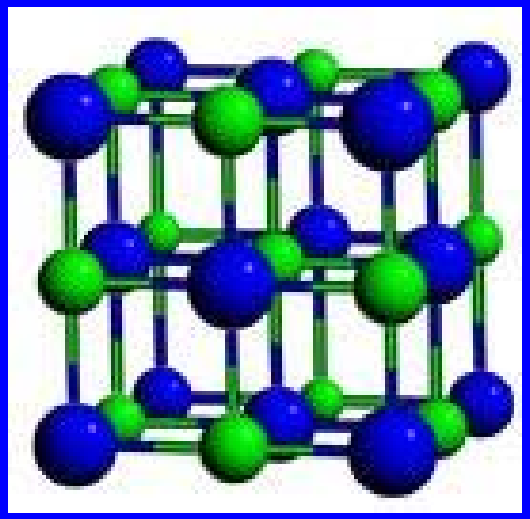


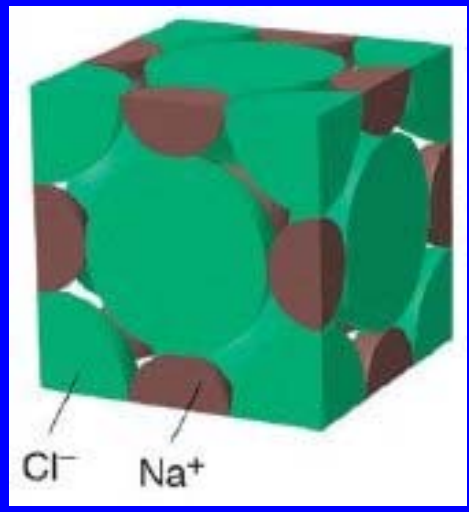
Structures Derived from Cubic Close Packing



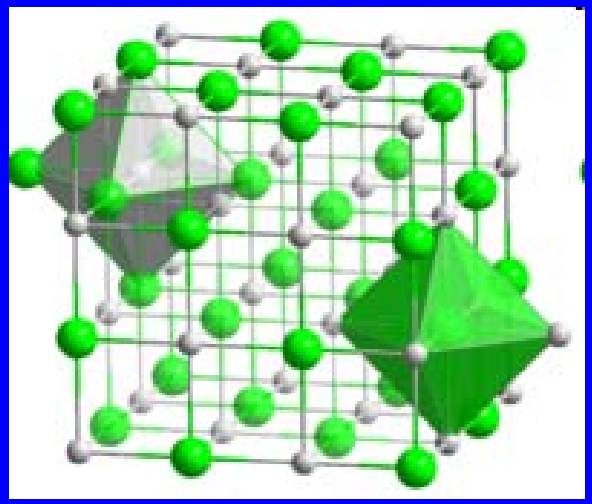
Sodium Chloride, NaCl





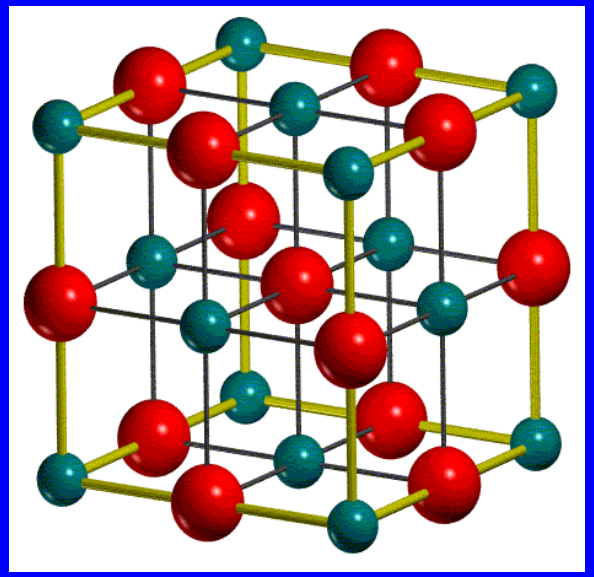


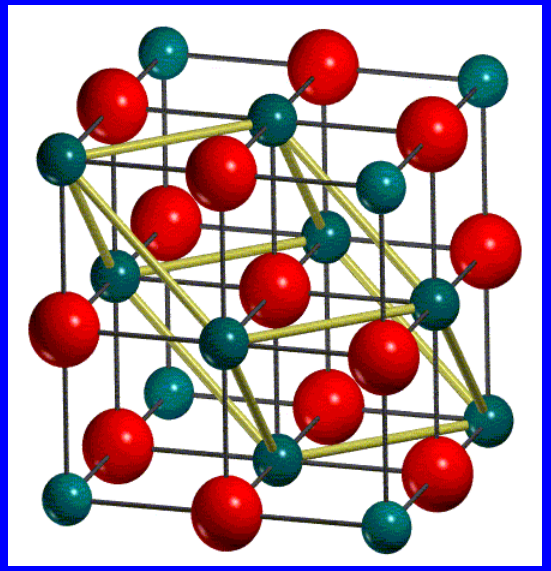
Z = ?

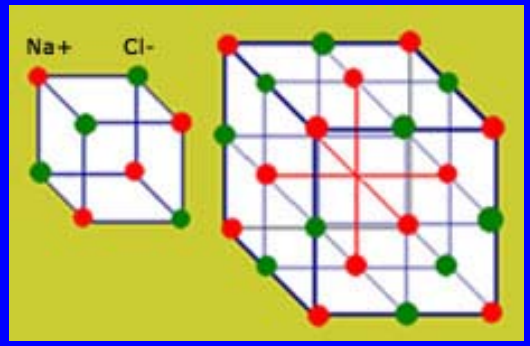


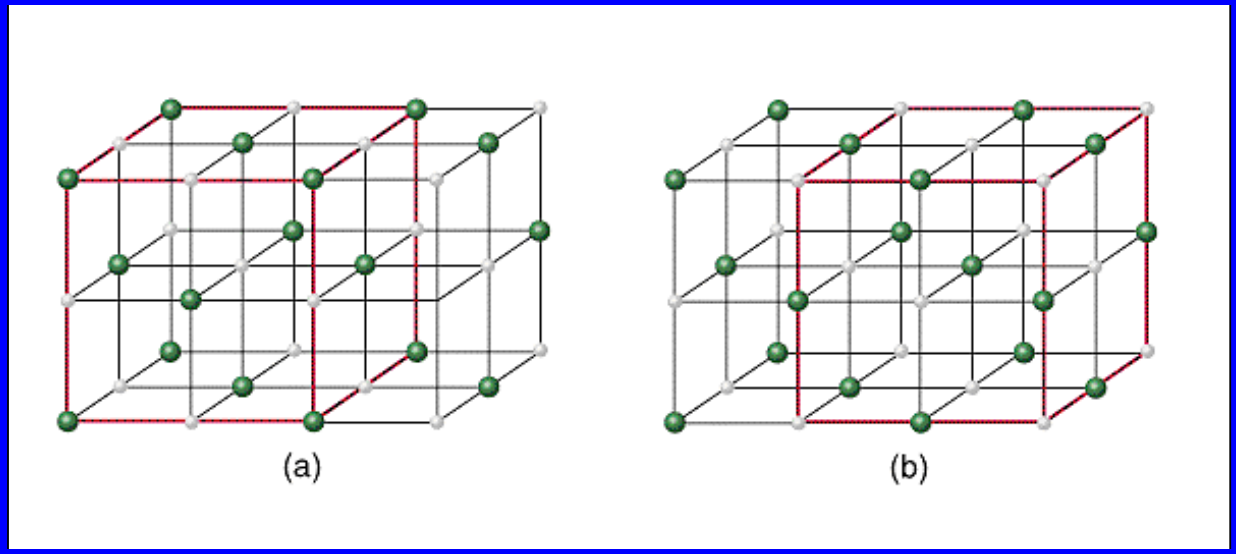
Cubic Close Packing of Cl,
Na occupies octahedral holes

Coord. No.
Na = 6
Cl = 6









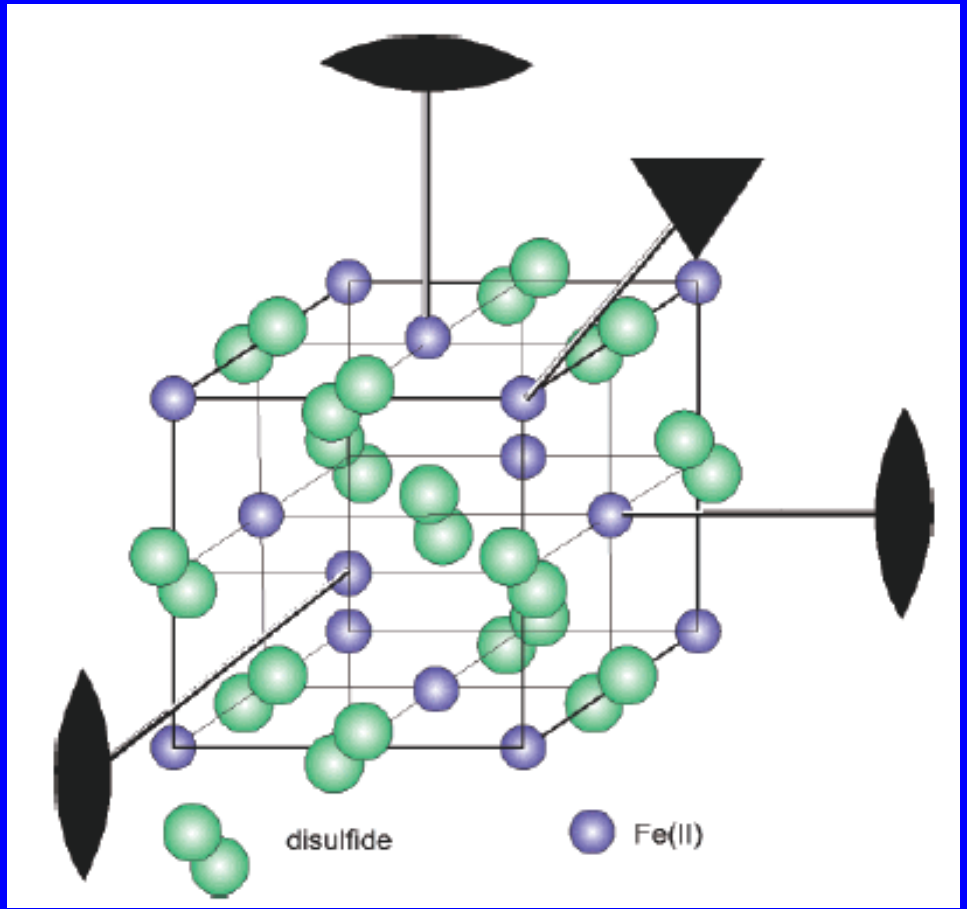
Two close packed lattices of cations and anions

Structure of Pyrite - FeS_2

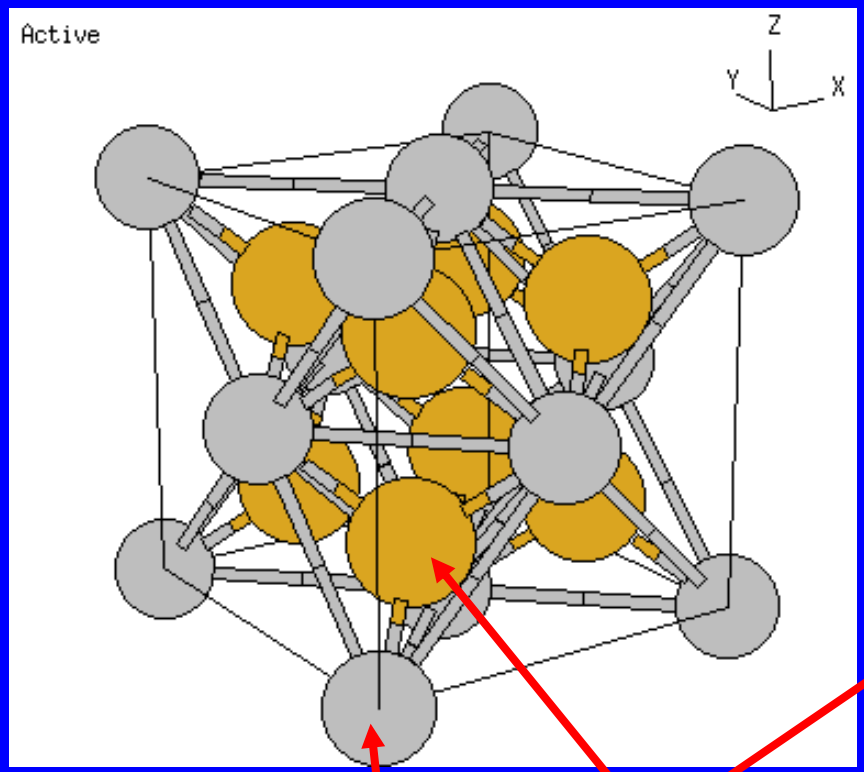
Derive more complex structures from simple structural types

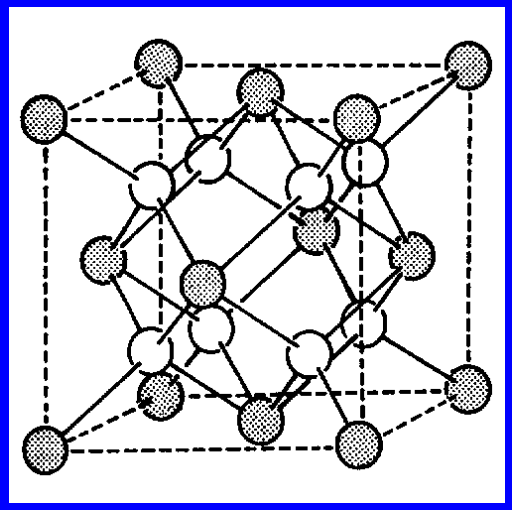
Na^+ Cl^-

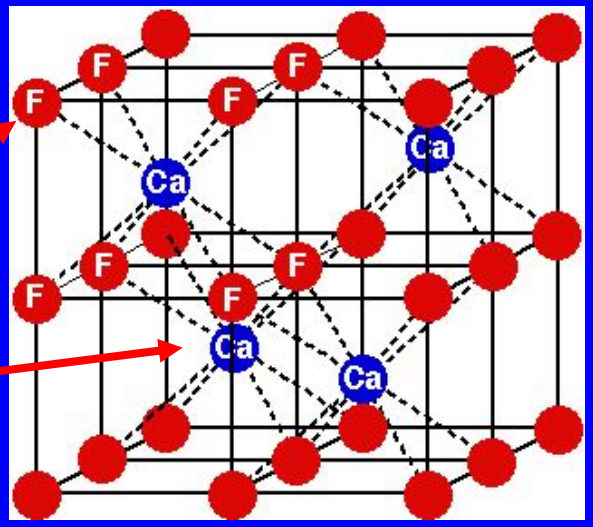
Fe^{2+} S_2^{2-}



Fluorite, CaF_2 (Inverse Type Li_2O)







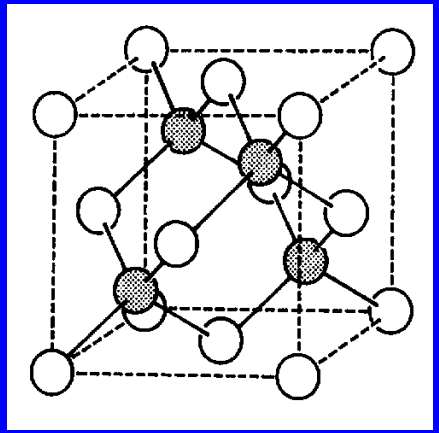
F / Li

Ca / O

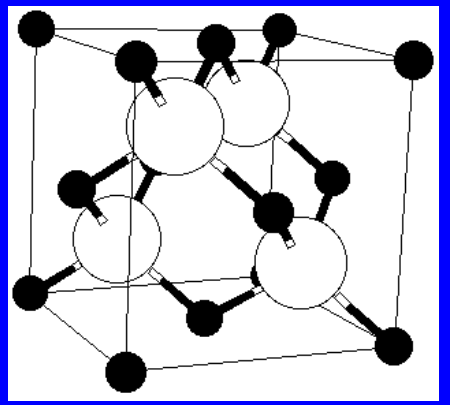
$K_2[PtCl_6]$, $Cs_2[SiF_6]$, $[Fe(NH_3)_6][TaF_6]_2$

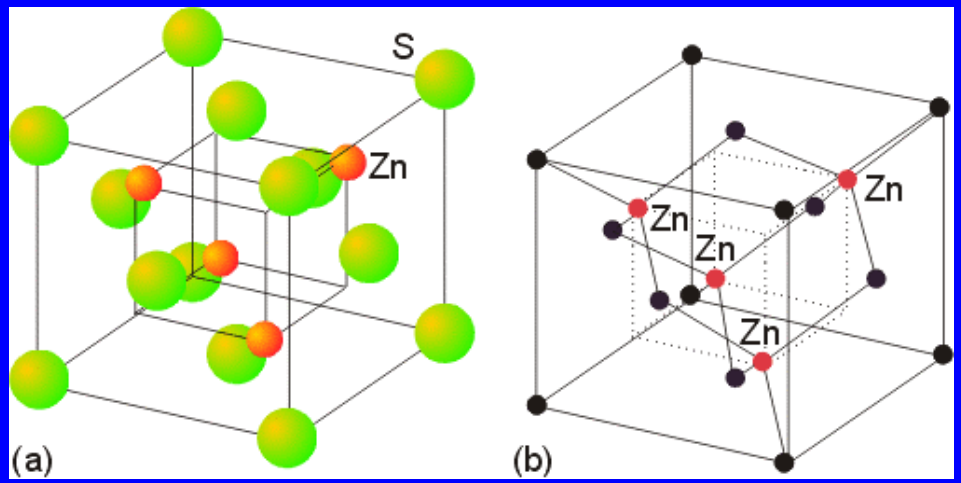
Sfalerite, ZnS

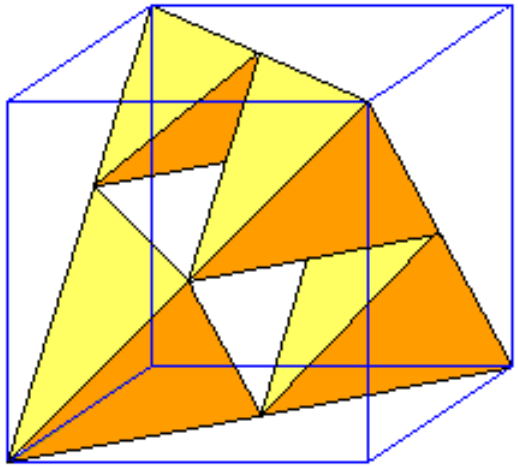
Cubic Close Packing of S
Zn occupies ½ of tetrahedral holes



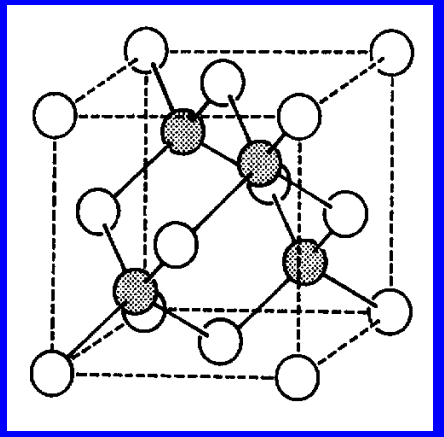
Cubic Close Packing of Zn
S occupies ½ of tetrahedral holes

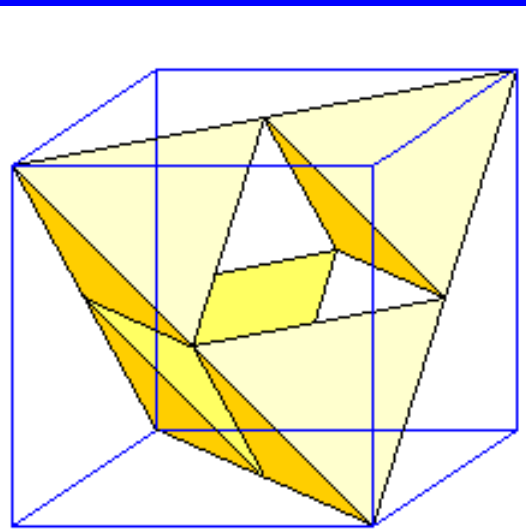


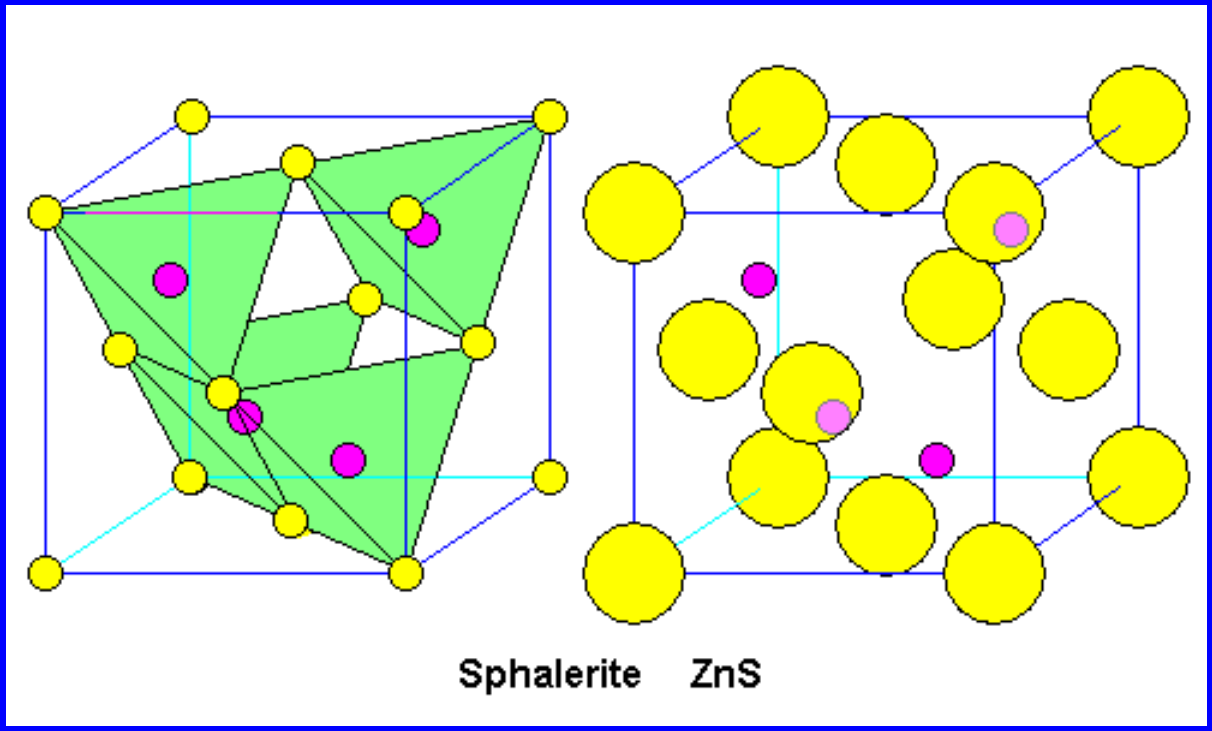




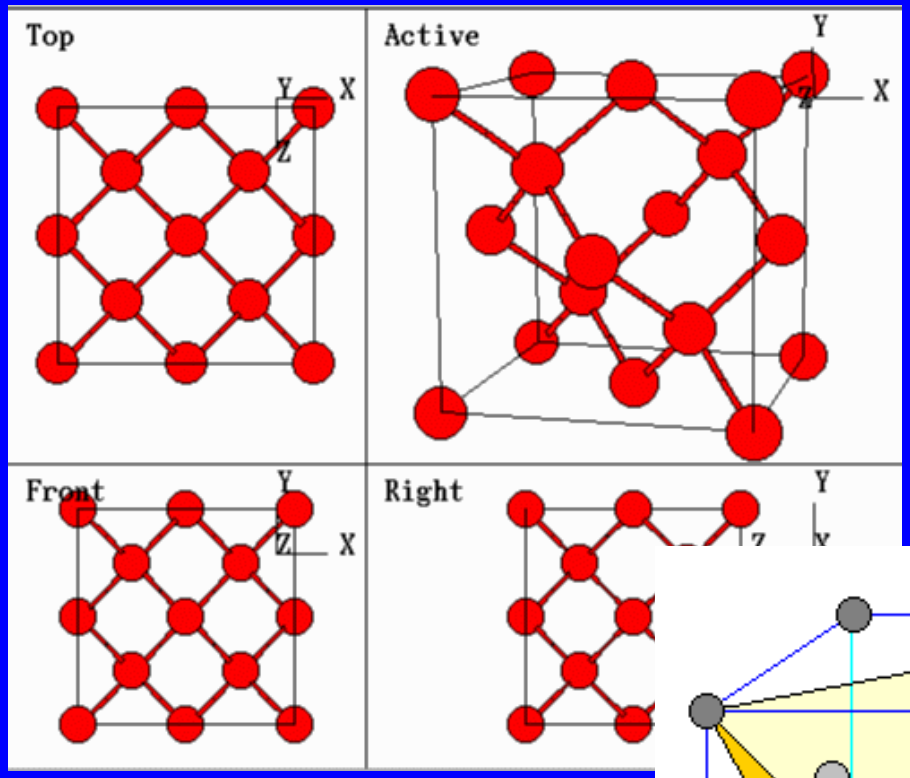
Sfalerite, ZnS

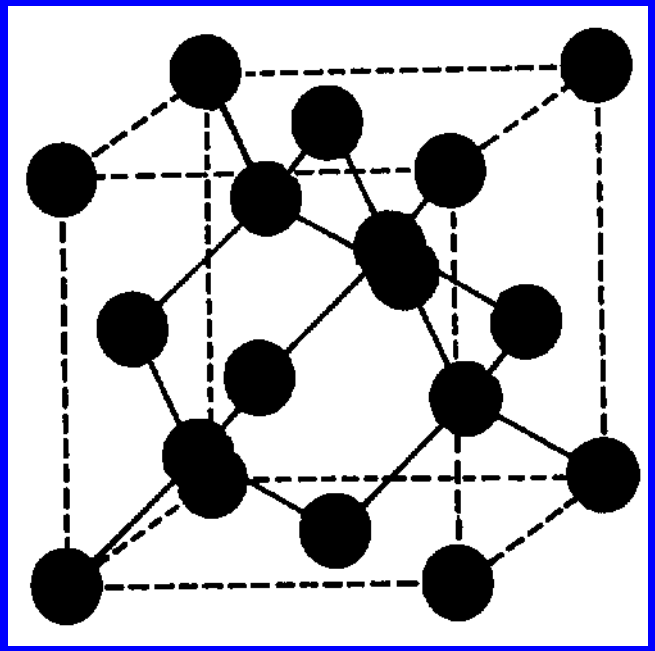


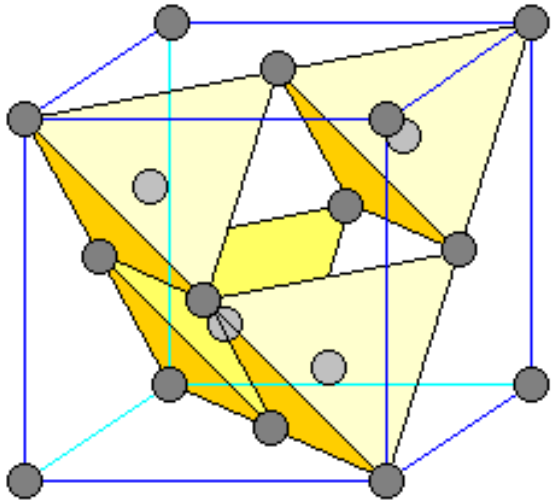


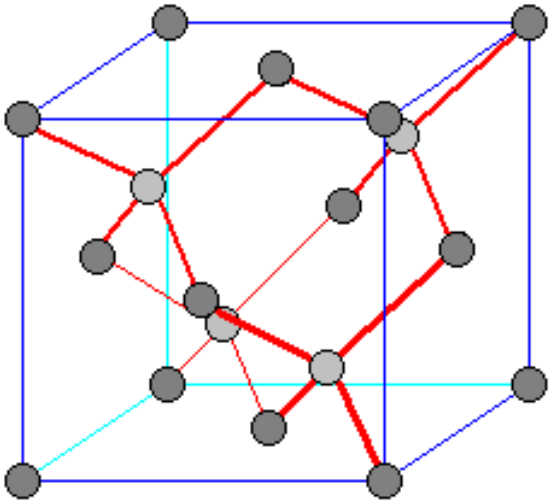


Diamond, C





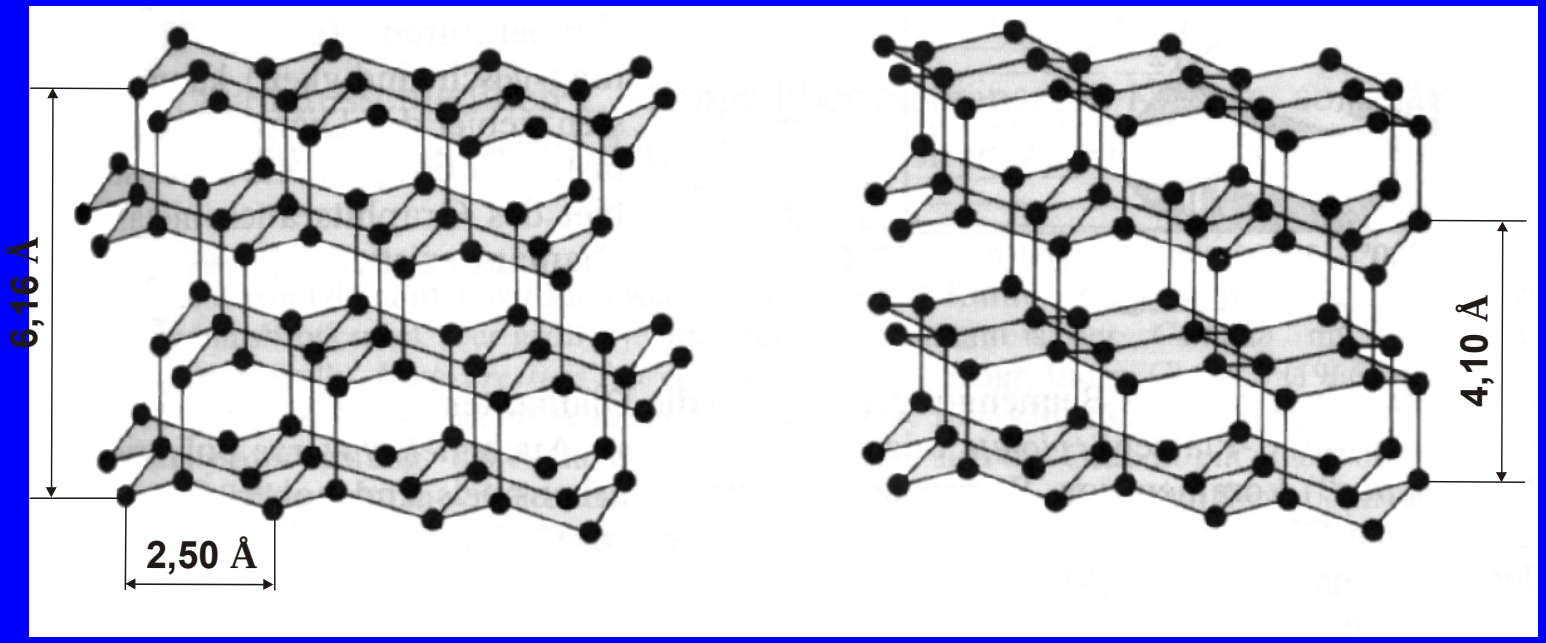




Diamond, C

cubic

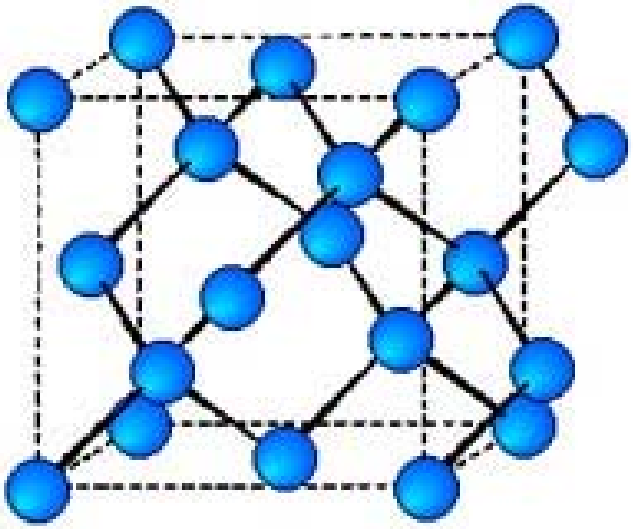
hexagonal
lonsdaleite



SiO_2
cristobalite

SiO_2 tridymite
Ice

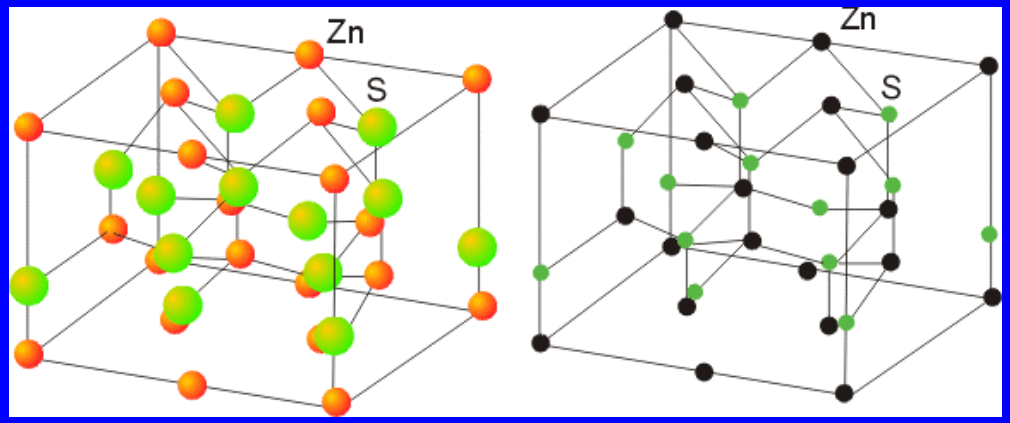
Structure of Group 14 Elements



	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

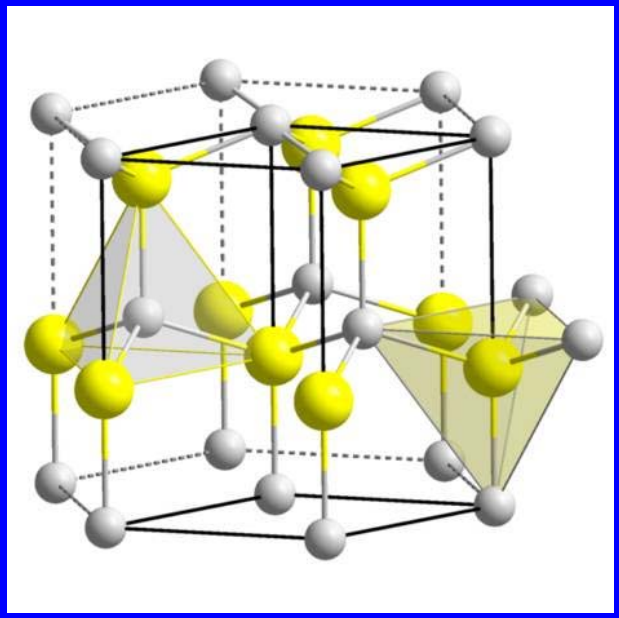
Diamond structure – cell size increases down the group

Wurzite, ZnS

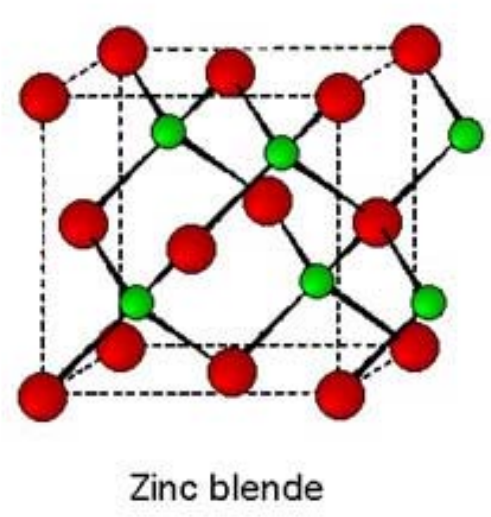


Hexagonal Close Packing of S
Zn occupies ½ of tetrahedral holes

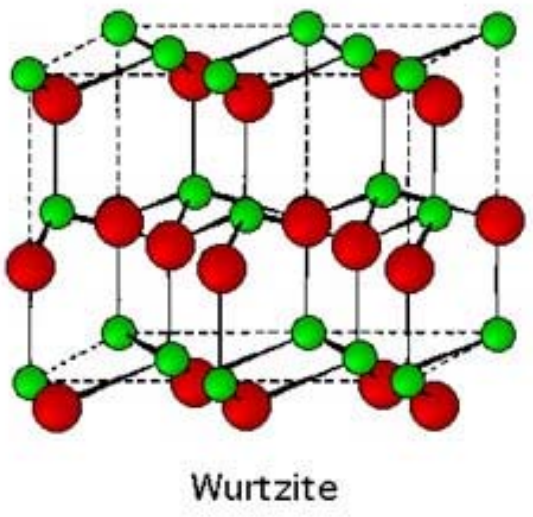
Polymorphs of ZnS



13-15 and 12-16 Semiconductors



Sfalerite



Wurzite

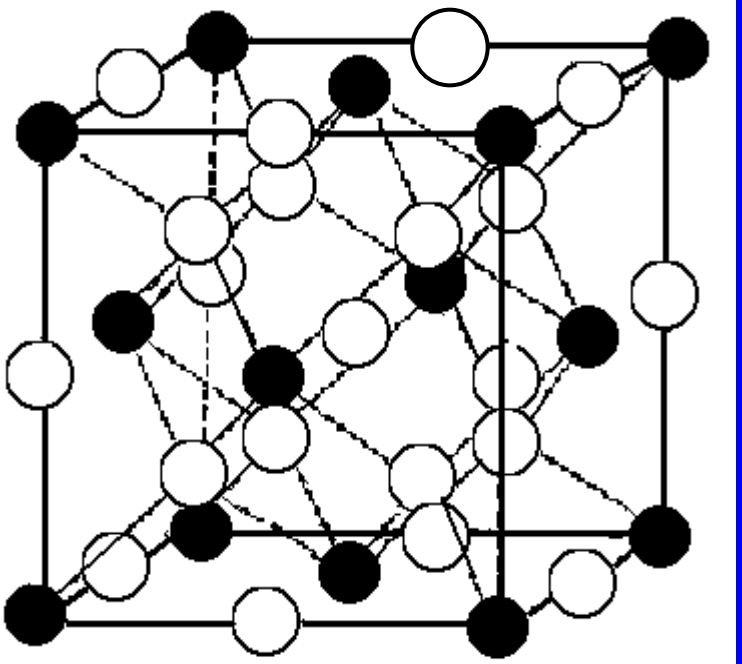
InP, GaAs

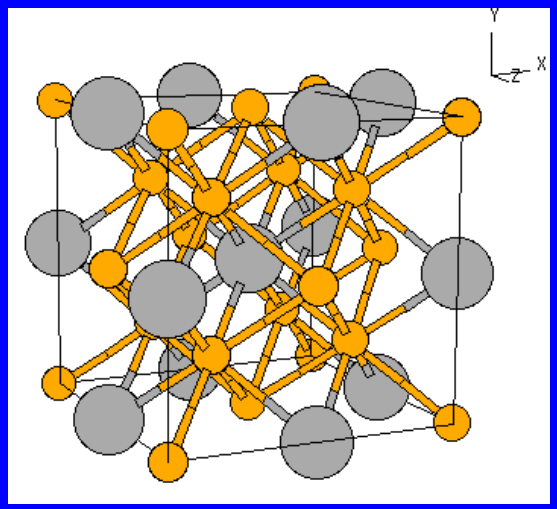
HgTe, CdTe

ZnO, CdSe

AlN, GaN

BiF_3/Li_3Bi



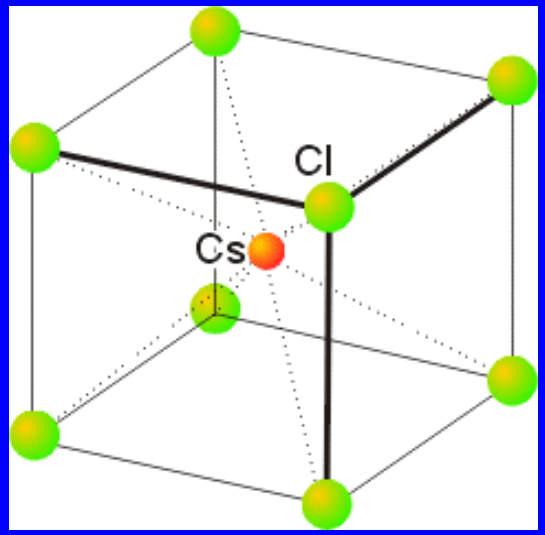


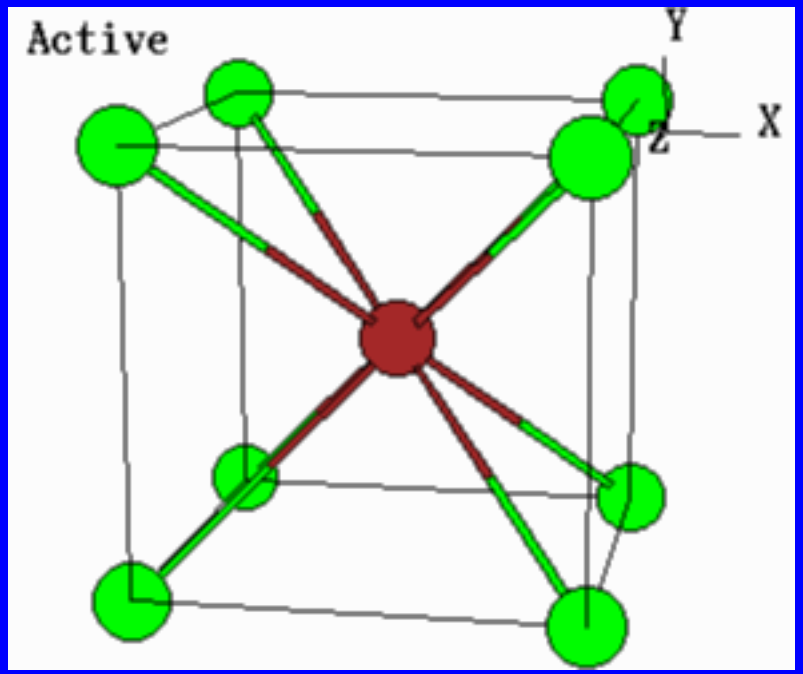
Cubic Close Packing of Bi (4)
F occupies tetrahedral holes (8) and octahedral holes (4)

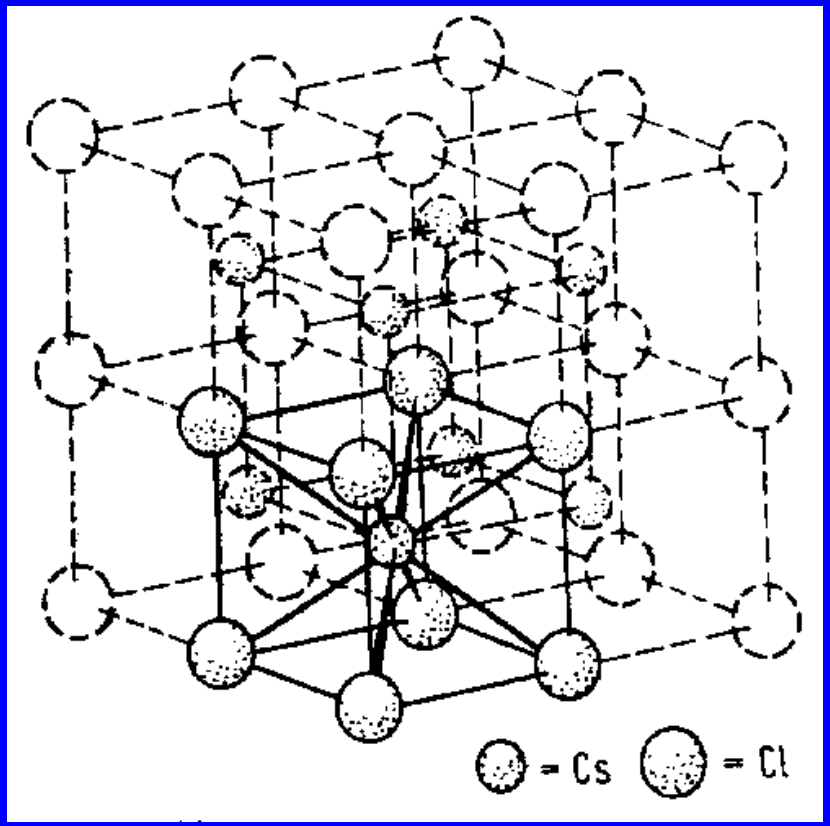
Cubic Close Packing of Bi (4)
Li occupies tetrahedral holes (8) and octahedral holes (4)

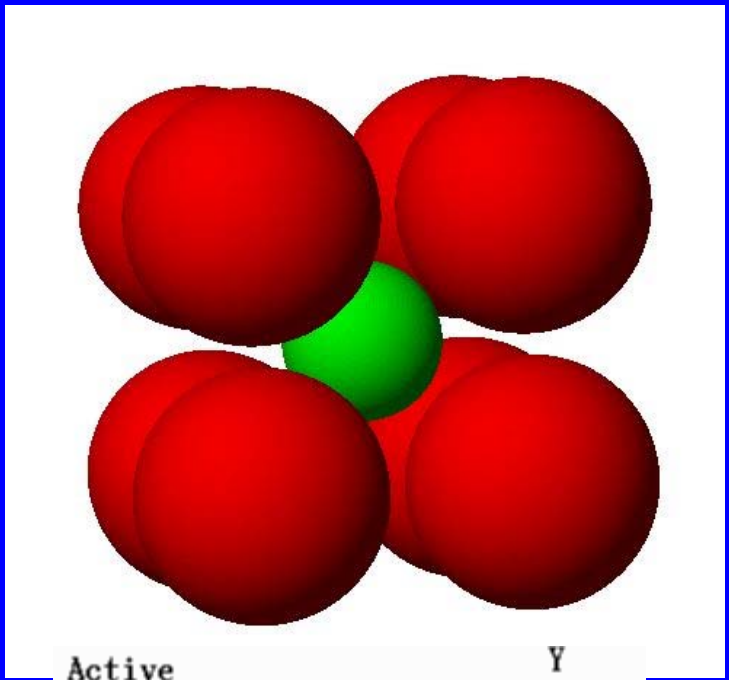
$[Cr(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$

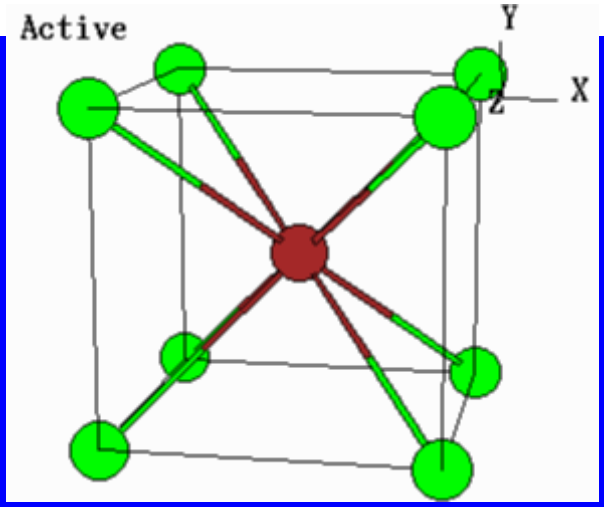
CsCl



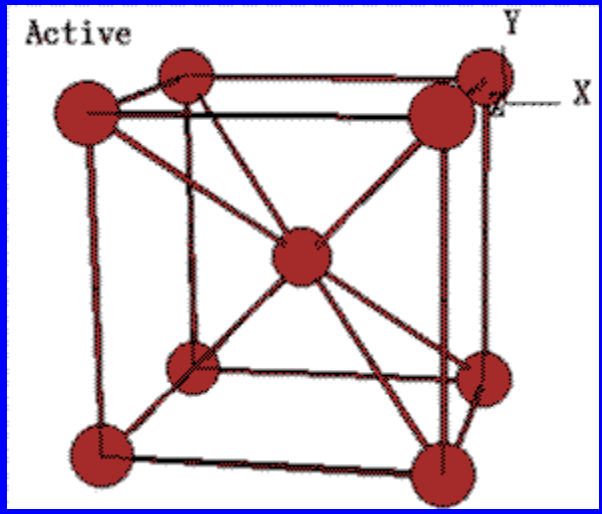




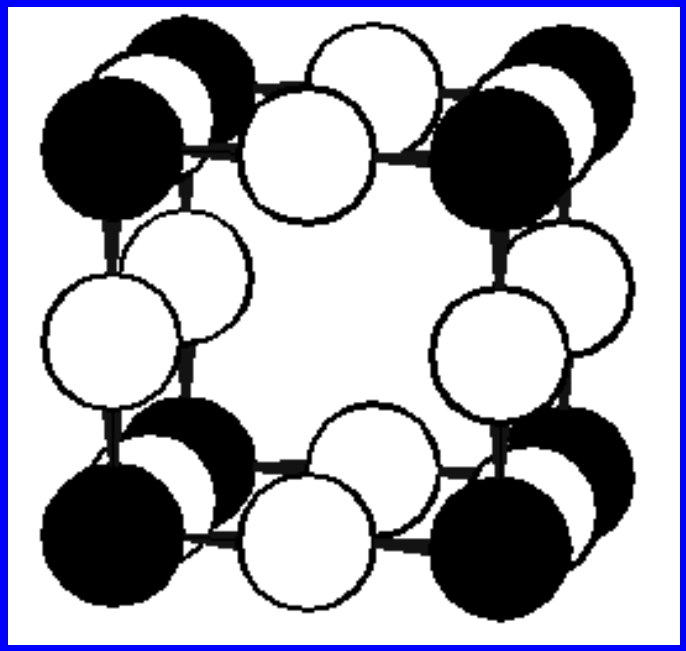


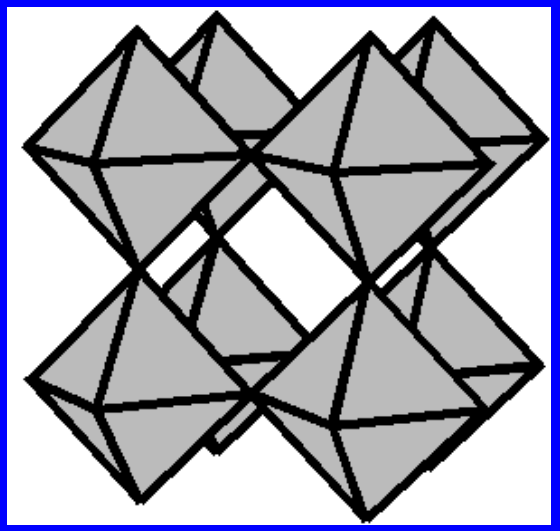


CsCl is not a body centered cubic cell



ReO_3

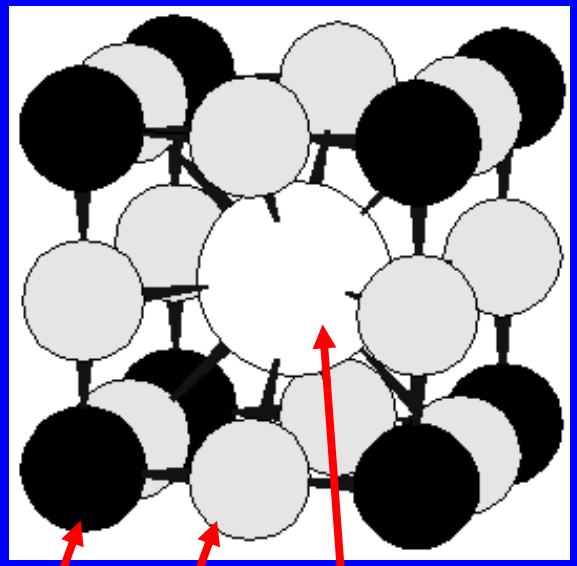


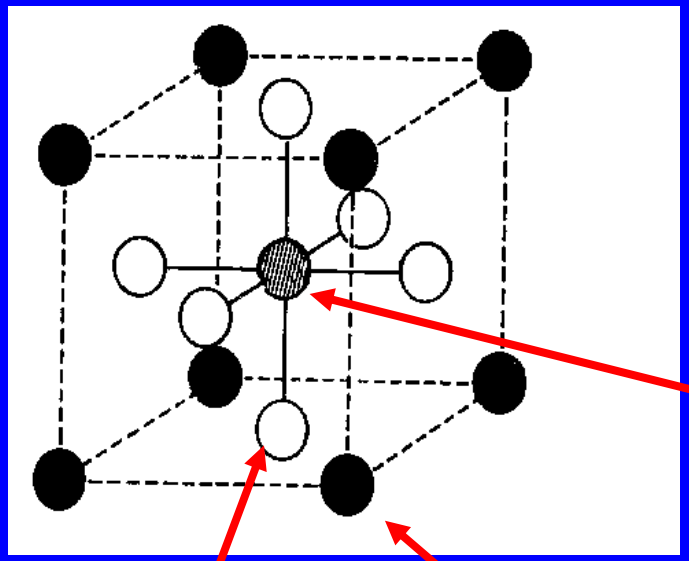


Primitive cubic

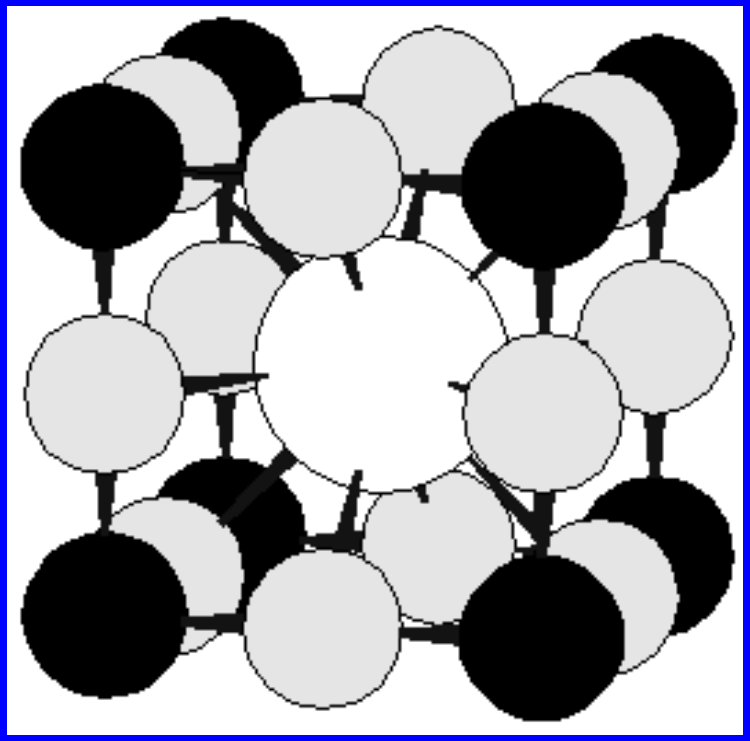
Perovskite, $CaTiO_3$

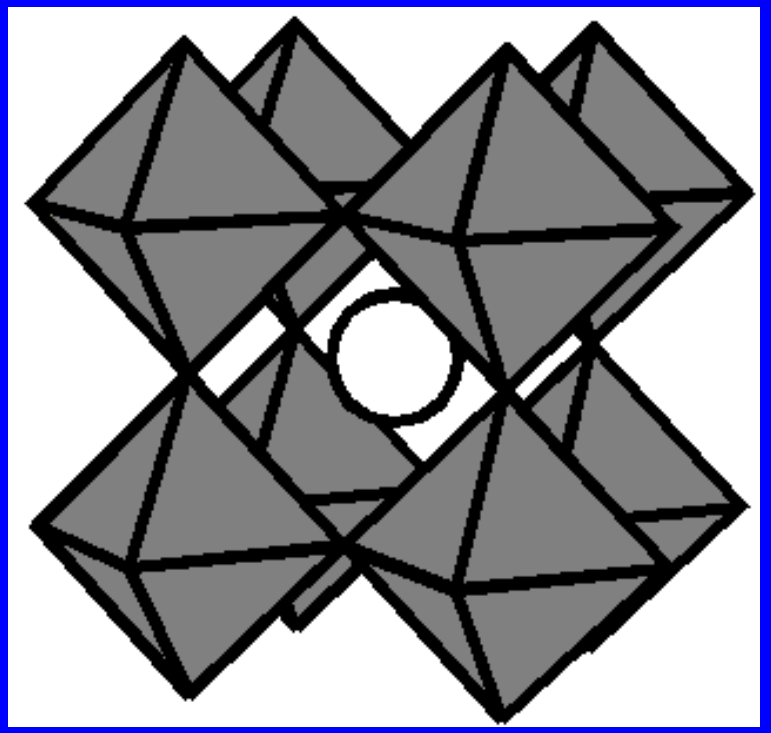
Two equivalent views at perovskite unit cell





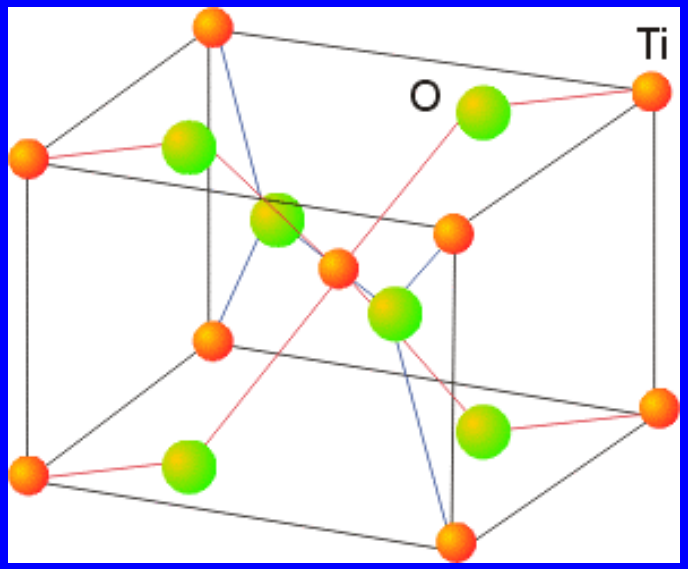
Perovskite, $CaTiO_3$

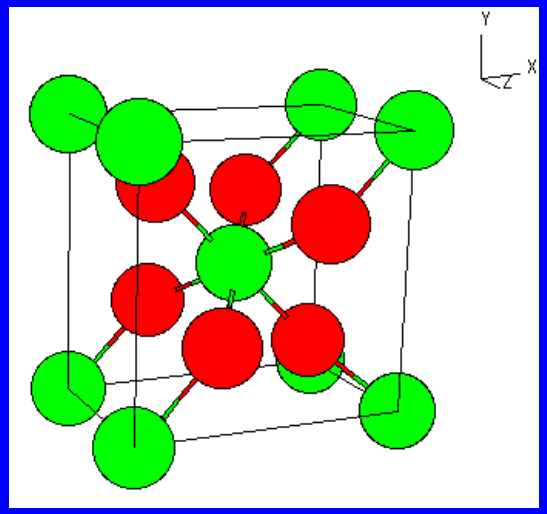




CsCl

Rutile, TiO_2





Coordination Number Rule

A_xB_y

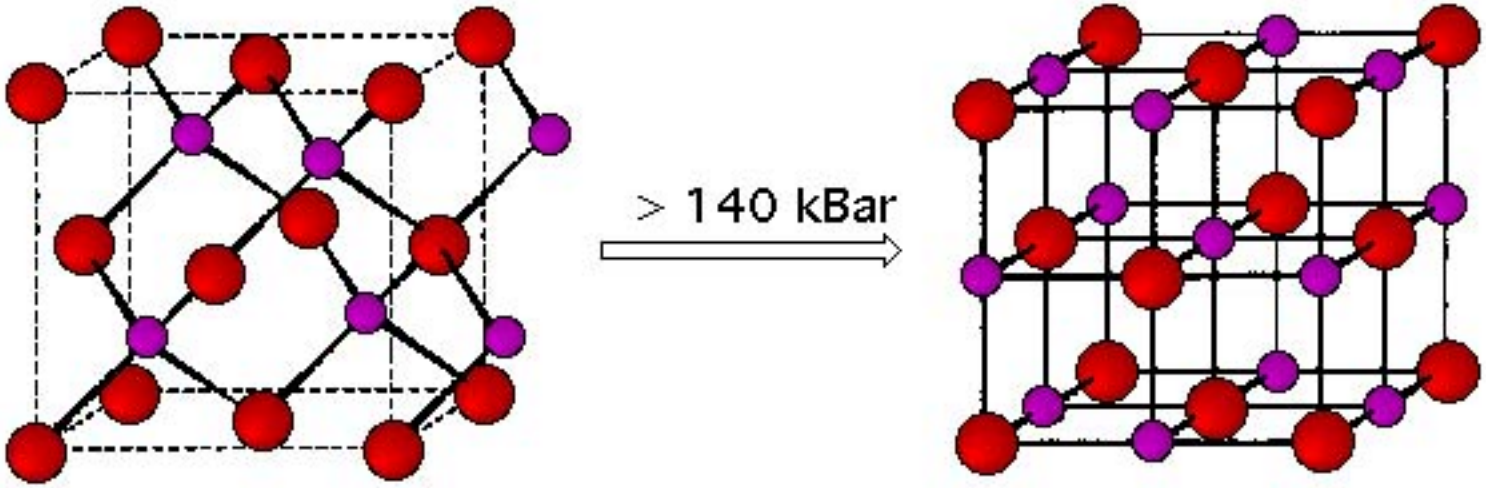
c.n.(A) / c.n.(B) = y / x

Coordination Numbers are in an inverse ratio of stoichiometric coefficients

Phase Transitions at High Pressure

Sfalerite

Sodium Chloride

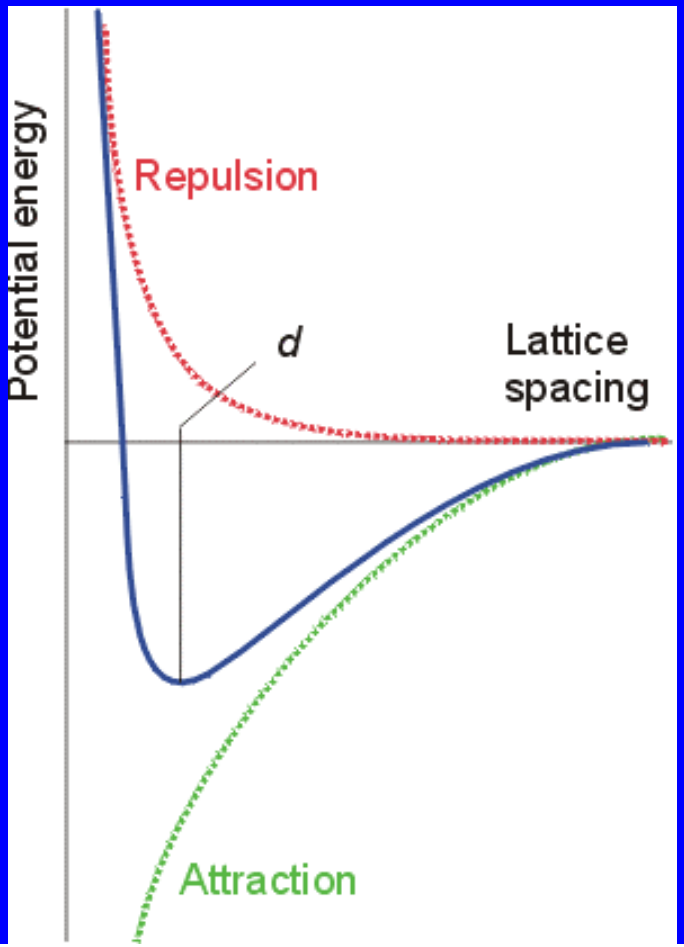


High Pressure Effects

Incr. coordination number
Incr. density
Elongation of bond lengths
Nonmetal-Metal transition

Lattice Energy

Energy released upon the formation of 1 mol of ionic solid from its ions in the gas phase



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

Ion pair

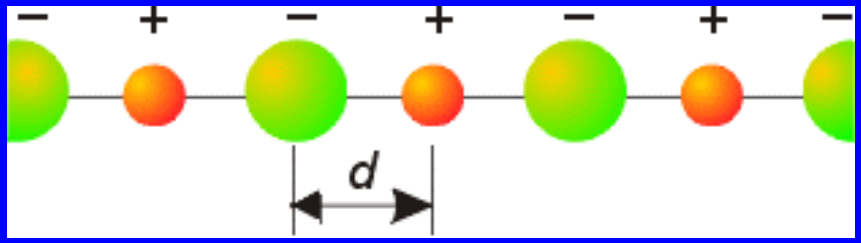
$$E_{coul} = \frac{1}{4\pi\varepsilon_0}\frac{Z_A Z_B e^2}{d}$$

$$E_{rep} = \frac{B}{d^n}$$

n = Born's exponent (experimental data from compressibility measurements)

Madelung's Constant

Counts all interactions in the crystal lattice

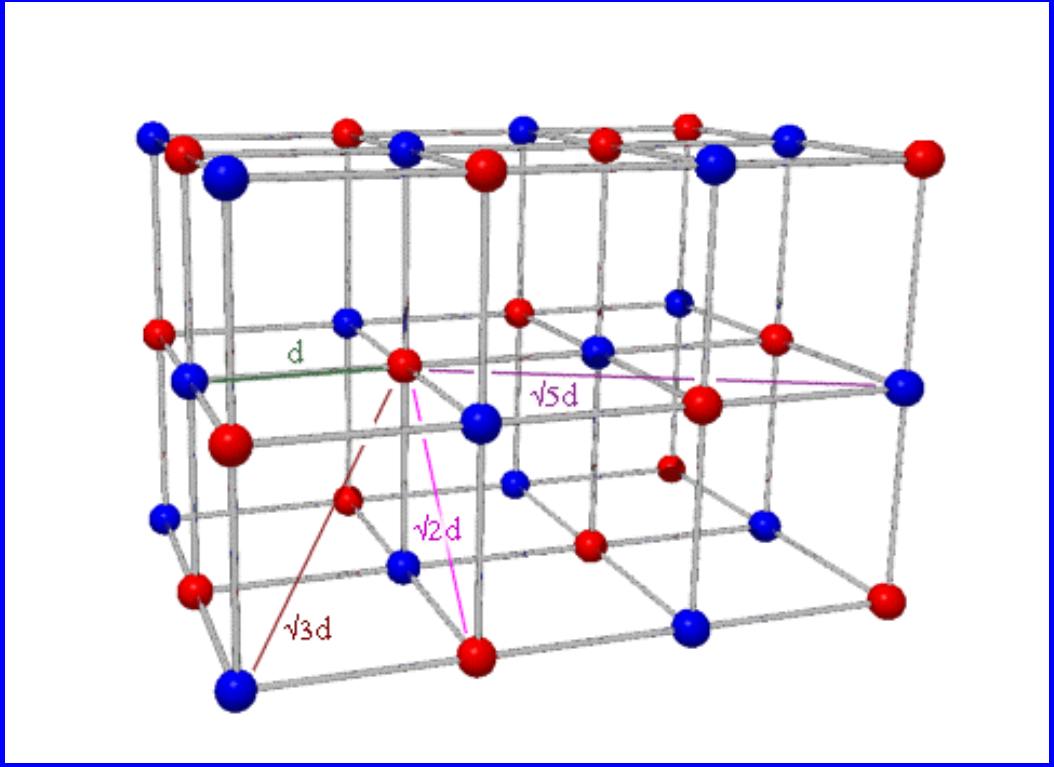


$$E_{coul} = (e^2 / 4 \pi e_0) \times (z_A z_B / d) \times [+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + ...]$$

$$E_{coul} = (e^2 / 4 \pi e_0) \times (z_A z_B / d) \times (2 \ln 2)$$

Madelung's constant M
(for linear arrangement of ions)
= sum of a convergent series

Madelung's Constant for NaCl



$E_{coul} = (e^2 / 4 \pi e_0) * (z_A z_B / d) \times [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) ....]$

Convergent series

$E_{coul} = (e^2 / 4 \pi e_0) \times (z_A z_B / d) \times M$

Madelung's Constants for Different Structures

Structural type	M
NaCl	1.74756
CsCl	1.76267
CaF_2	2.519
ZnS Sfalerite	1.63805
ZnS Wurtzite	1.64132

Lattice Energy

1 mol of ions

Attractive $$E_{Coul} = N_A M \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}$$

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

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

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

Find minimum dL/d(d) = 0

Lattice Energy

Born – Lande equation

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

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

Born – Mayer equation

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

d^* = 0.345 Å

Lattice Energy

Kapustinski

M/*v* is approx. constant for all types of structures
v = number of ions in formula unit

M replaced by 0.87 *v*, no need to know the structure

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

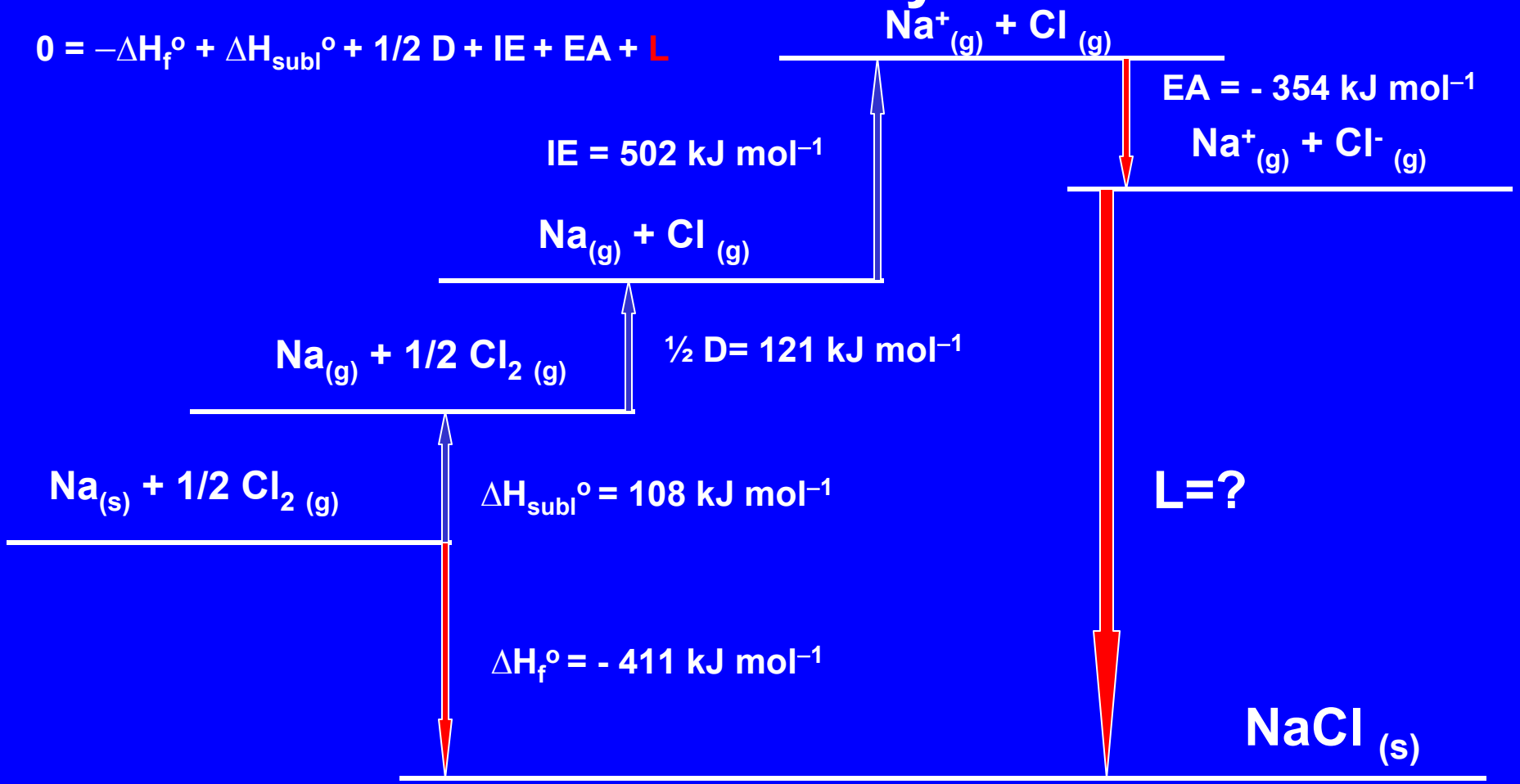
Kapustinski

structure	*M*	CN	stoichio	*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 = number of ions in formula unit

Born-Haber Cycle

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



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

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

Lattice Energy of NaCl

Calculated from Born – Lande eq. $L = -765\ kJ\ mol^{-1}$

Considers only ionic contribution

Measurement from Born–Haber cycle $L = -788\ kJ\ mol^{-1}$

Ionic and covalent contribution