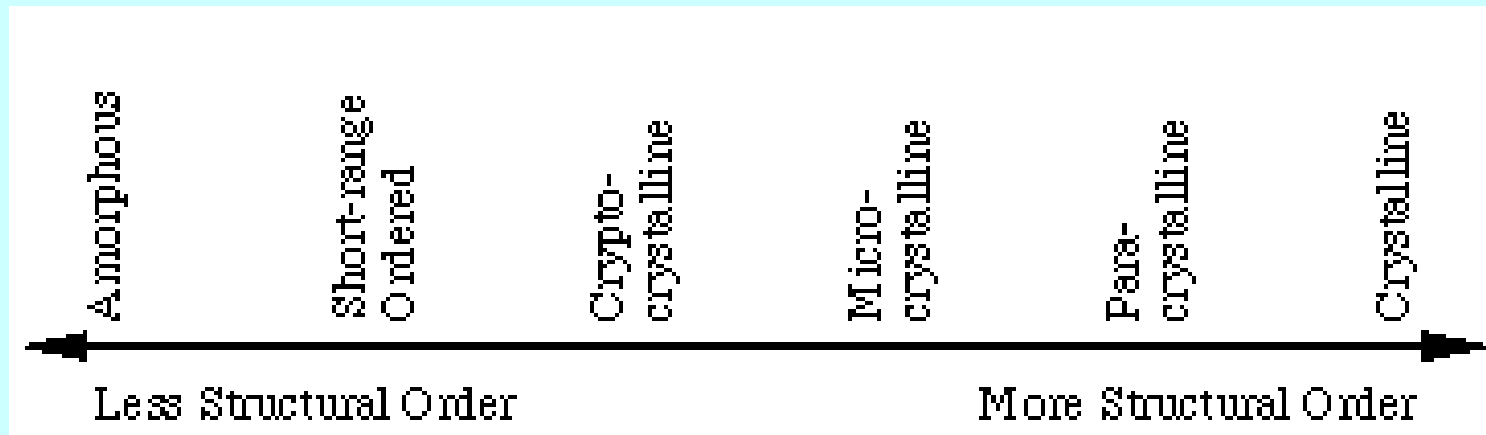


Basic Structural Chemistry

Crystalline state

Structure types

Degree of Crystallinity



Crystalline – 3D long range order

Single-crystalline

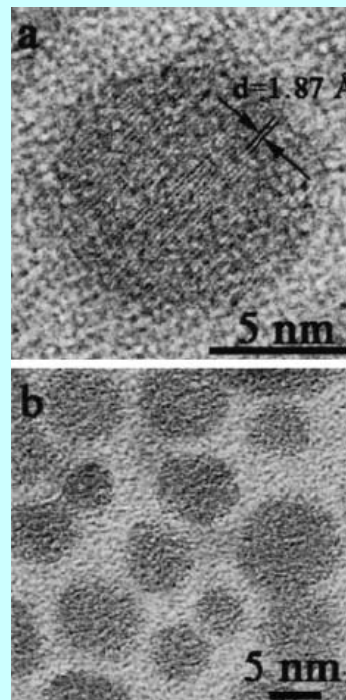
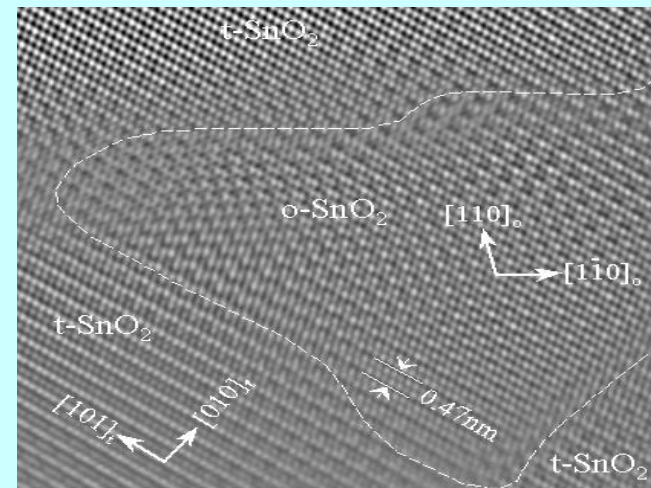
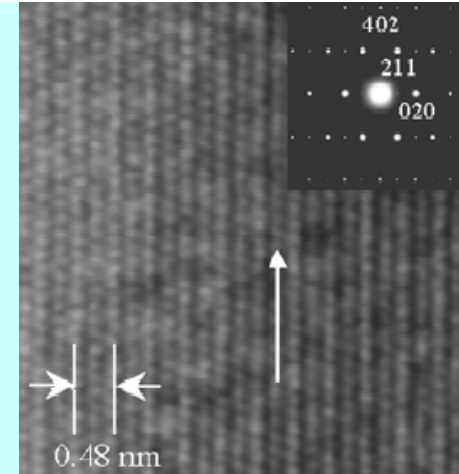
**Polycrystalline - many crystallites of different sizes and orientations
(random, oriented)**

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

Amorphous – no order, random

Degree of Crystallinity

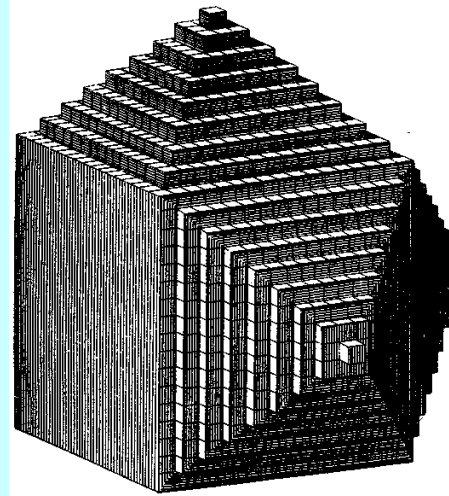
- Single Crystalline
- Polycrystalline
- Semicrystalline
- Amorphous



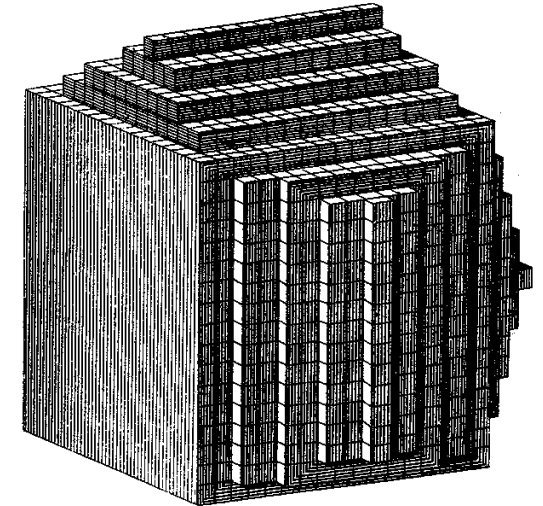
Grain boundaries

Crystal Structure

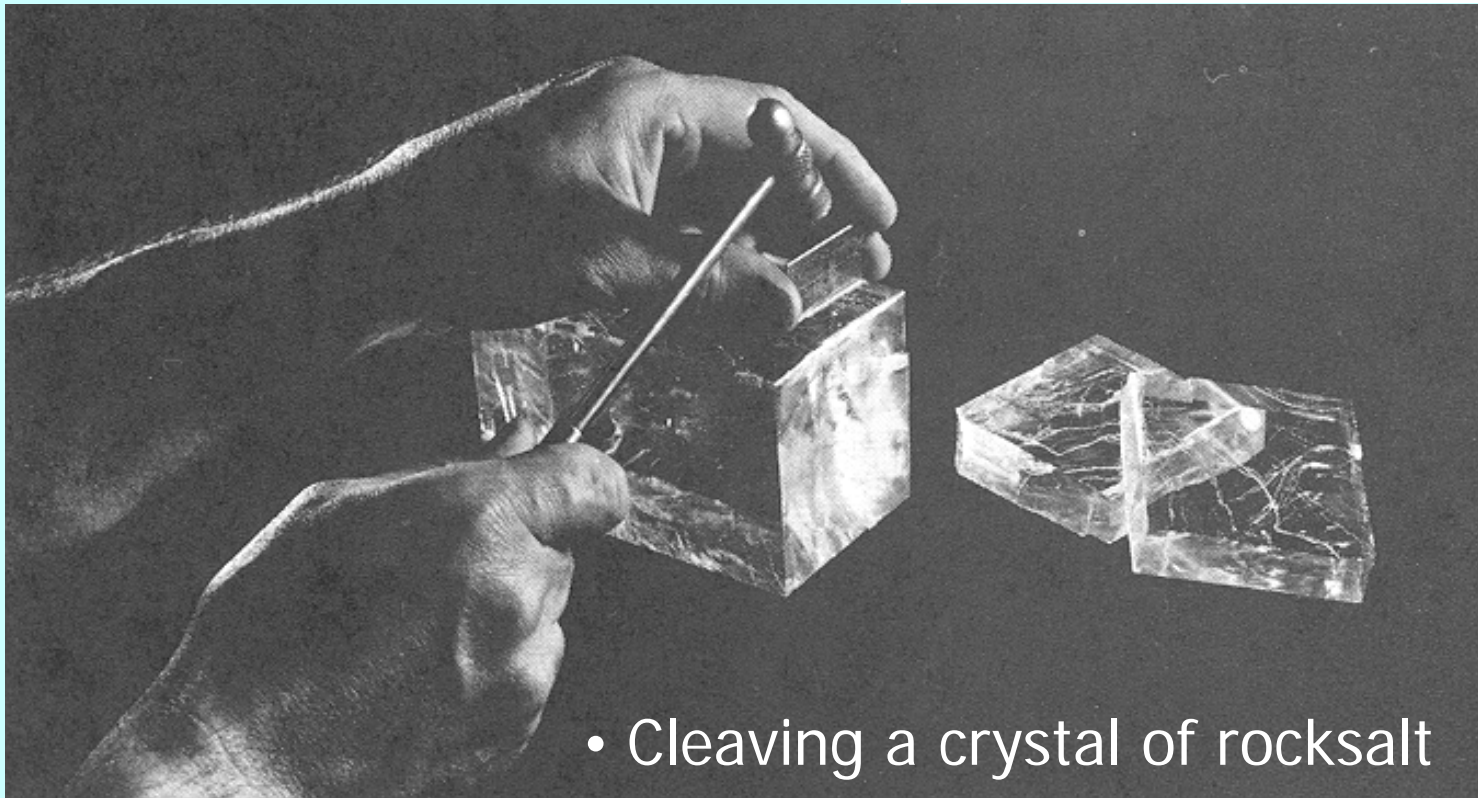
- The building blocks of these two are identical, but different crystal faces are developed



(a)



(b)



- Cleaving a crystal of rock salt

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:**

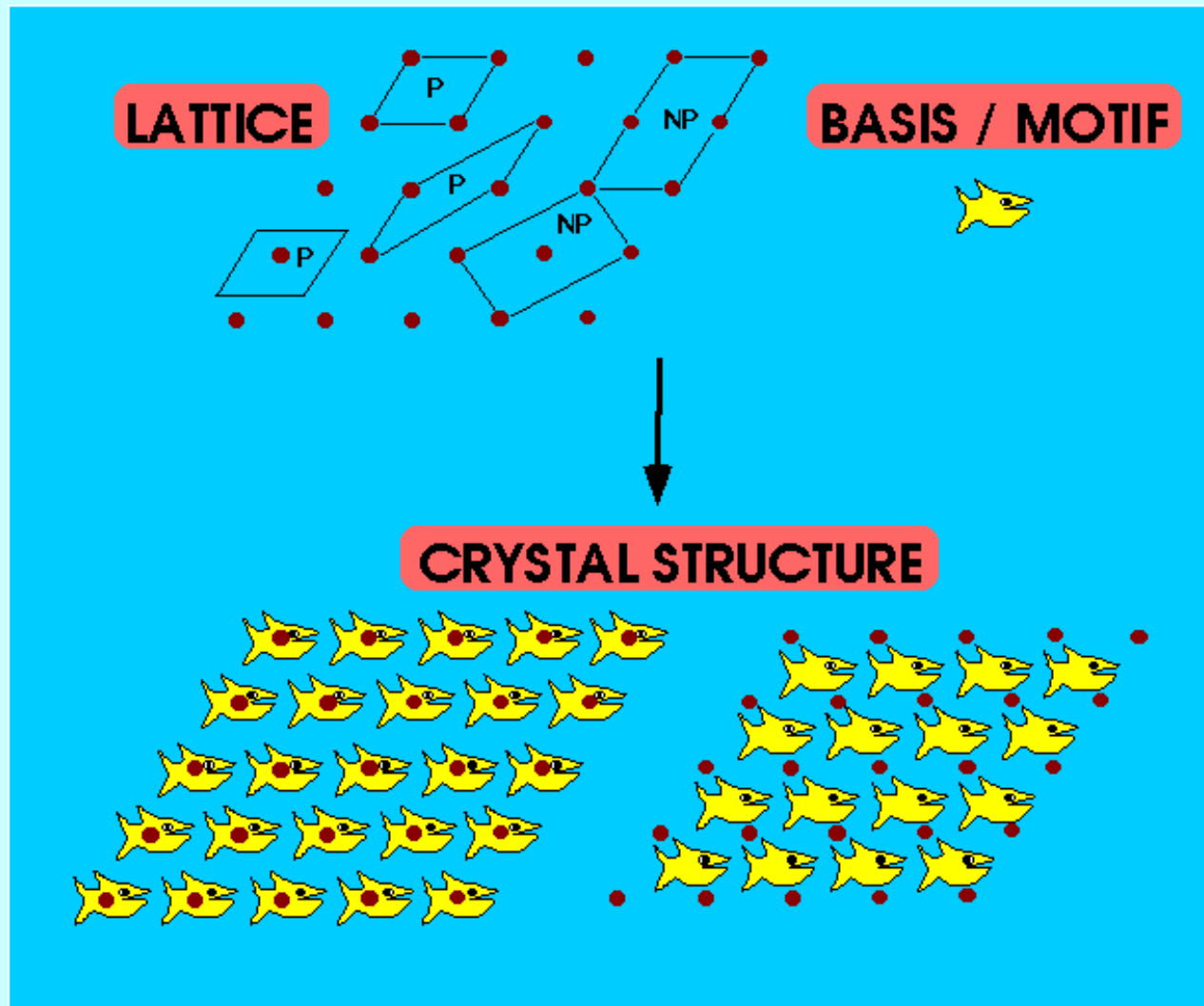
$$\bar{T} = n_1\bar{a} + n_2\bar{b} + n_3\bar{c}$$

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

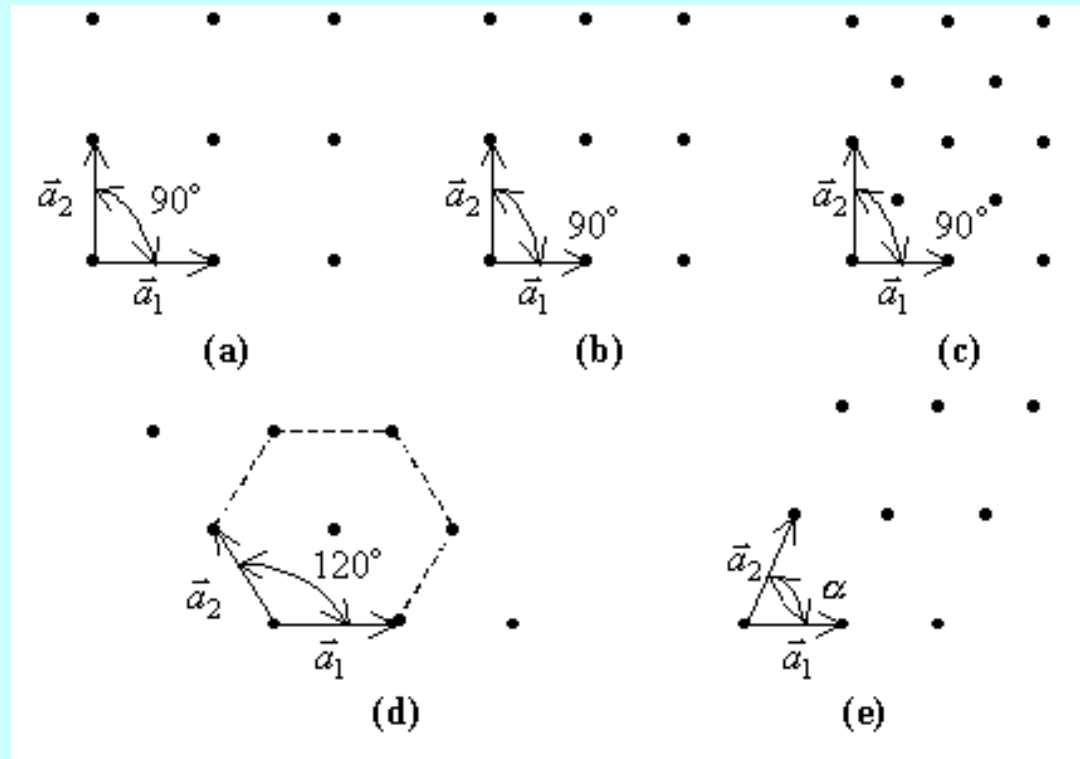
then it falls on another identical building block with the same orientation.

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

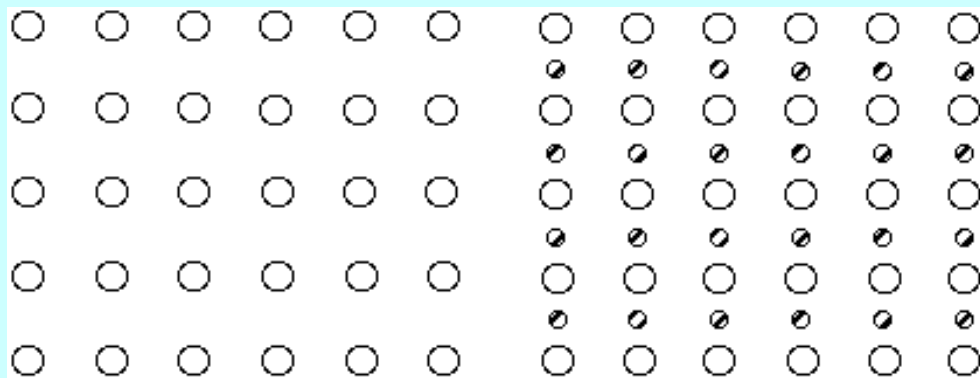
Planar Lattice 2D



Five Planar Lattices

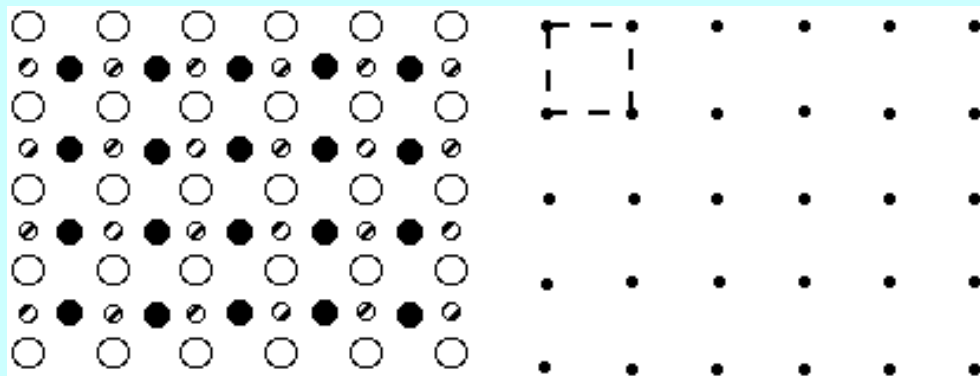


Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2, \alpha = 90^\circ$
Rectangular	2	$a_1 \neq a_2, \alpha = 90^\circ$
Hexagonal	1	$a_1 = a_2, \alpha = 120^\circ$
Oblique	1	$a_1 \neq a_2, \alpha \neq 120^\circ, \alpha \neq 90^\circ$



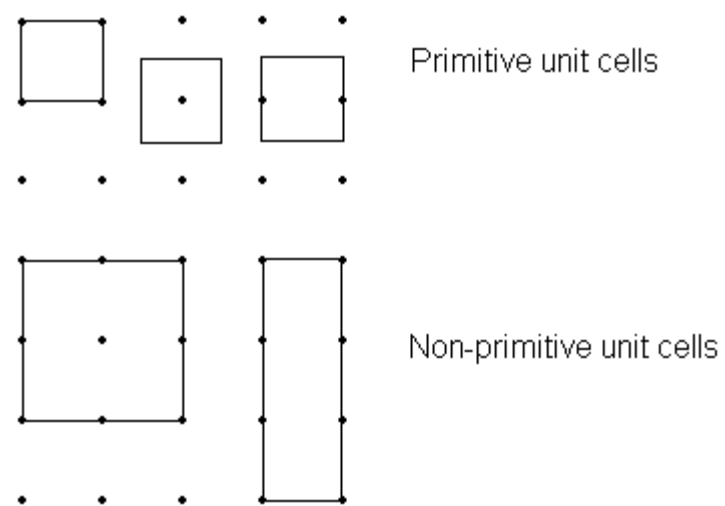
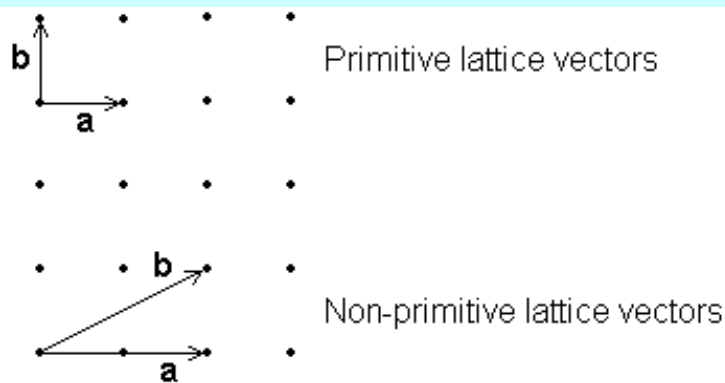
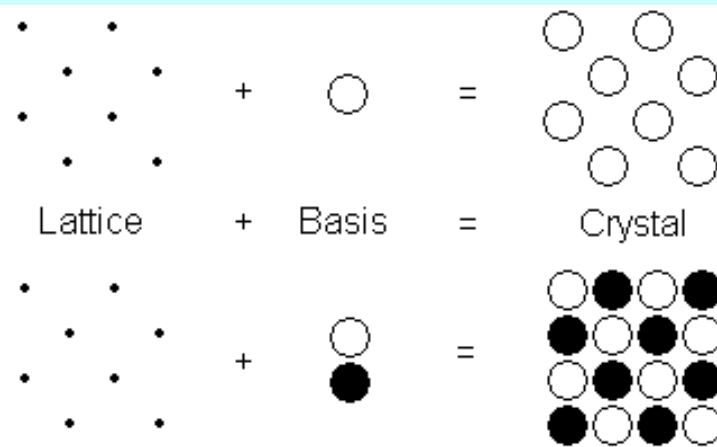
○ = Motif

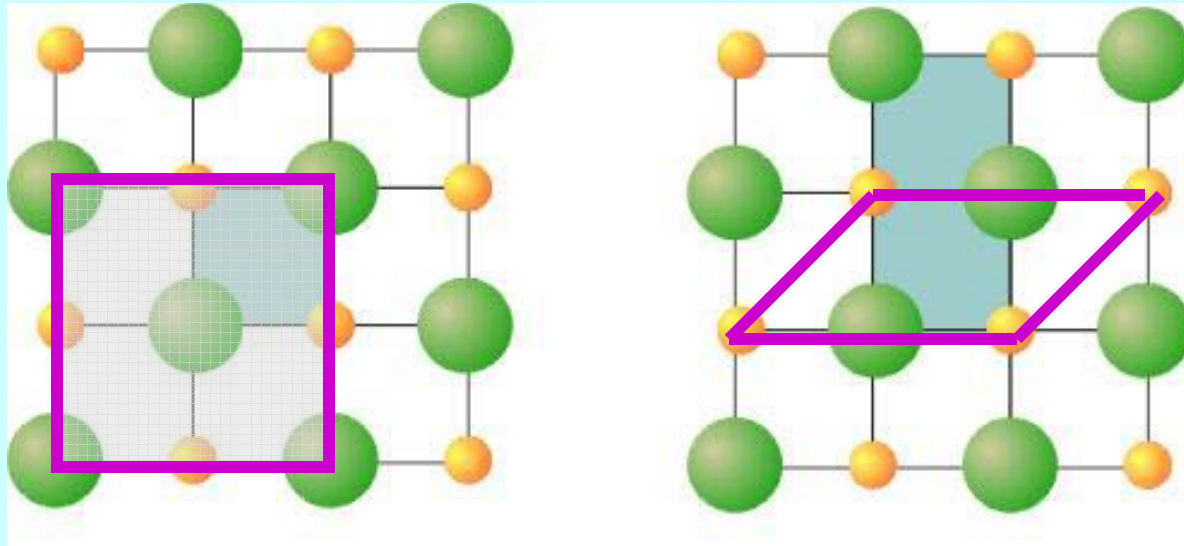
○^o = Motif



○ ● = Motif

Square lattice



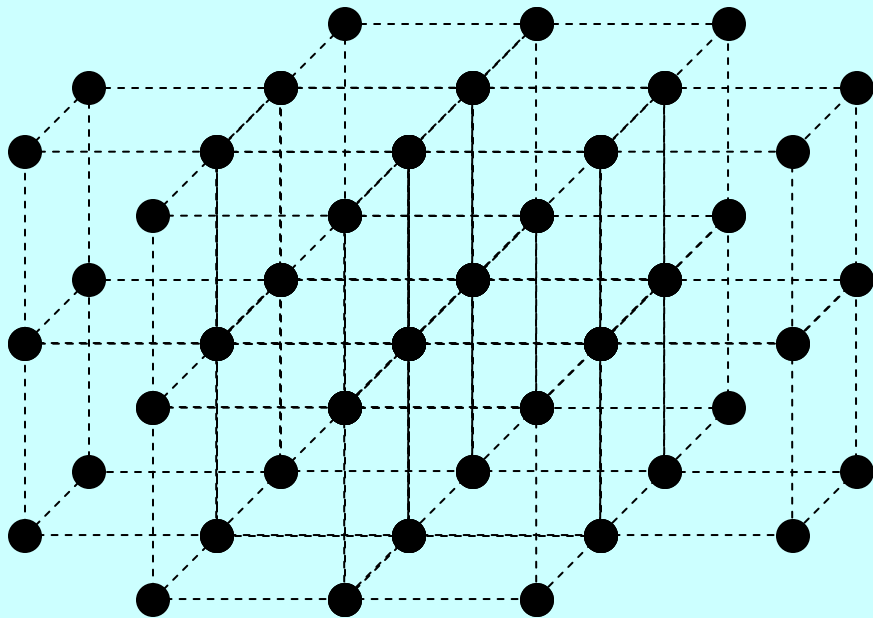
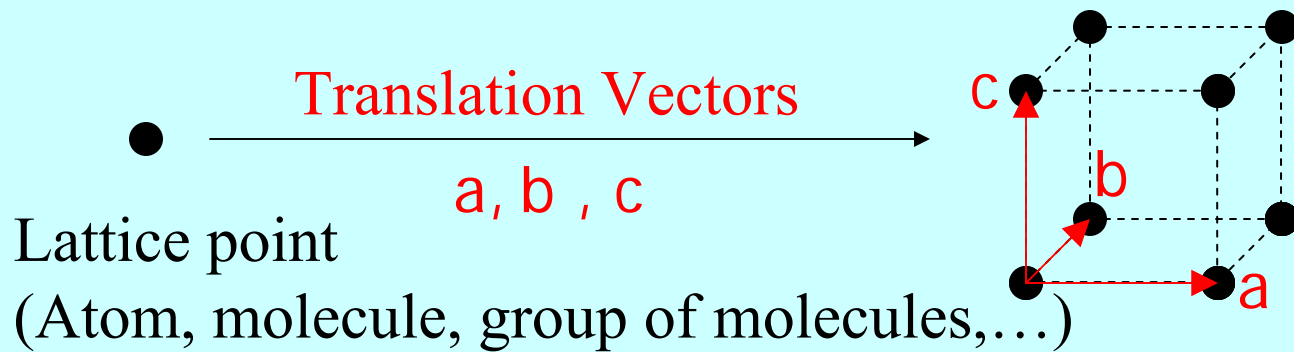


Unit Cell: An „imaginary“ parallel sided region of a structure from which the entire crystal can be constructed by purely translational displacements
Contents of unit cell represents chemical composition

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



Primitive Cell:

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

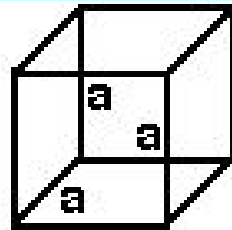
Lattices and Space Groups

	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

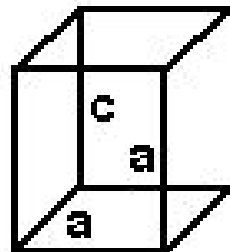
Cubic

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



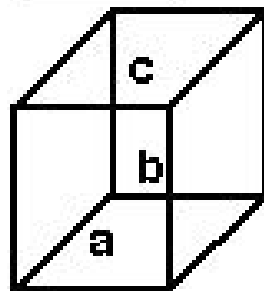
Tetragonal

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



Orthorhombic

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



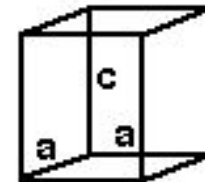
Rhombohedral

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



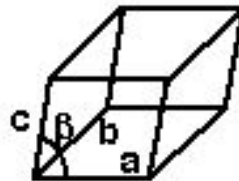
Hexagonal

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



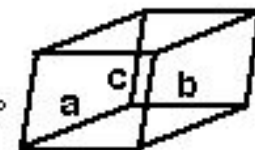
Monoclinic

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

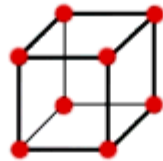


Triclinic

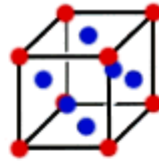
$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



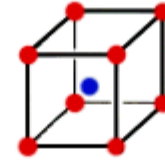
Fourteen Bravais Lattices



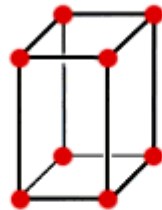
Simple cubic



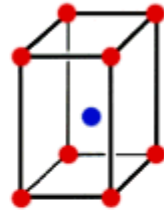
Face-centered cubic



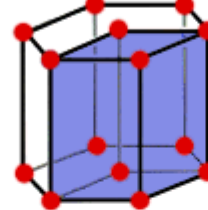
Body-centered cubic



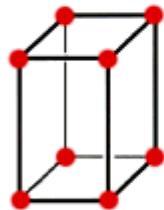
Simple tetragonal



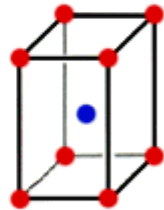
Body-centered tetragonal



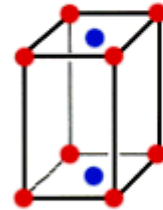
Hexagonal



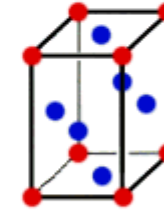
Simple orthorhombic



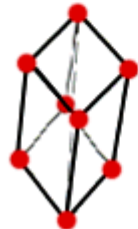
Body-centered orthorhombic



Base-centered orthorhombic



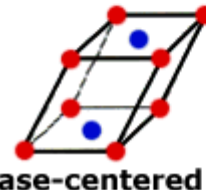
Face-centered orthorhombic



Rhombohedral



Simple monoclinic



Base-centered monoclinic



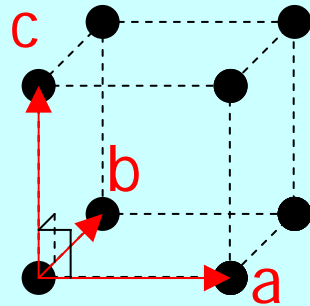
Triclinic

Simple Cubic (SC)

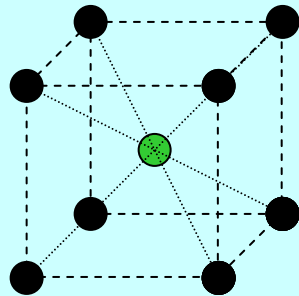
$$a = b = c$$

$$a \perp b \perp c$$

Conventional Cell = Primitive Cell

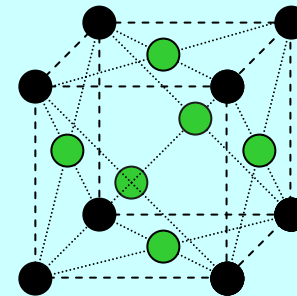


Add one atom at the center of the cube



Body-Centered Cubic (BCC)

Add one atom at the center of each face



Face-Centered Cubic (FCC)

Conventional Unit Cell \neq Primitive Cell

Primitive Cell

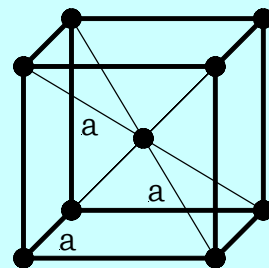
A *primitive cell* of the lattice = volume of space translated through all the vectors in a lattice that just fills all of space without overlapping or leaving voids.

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.

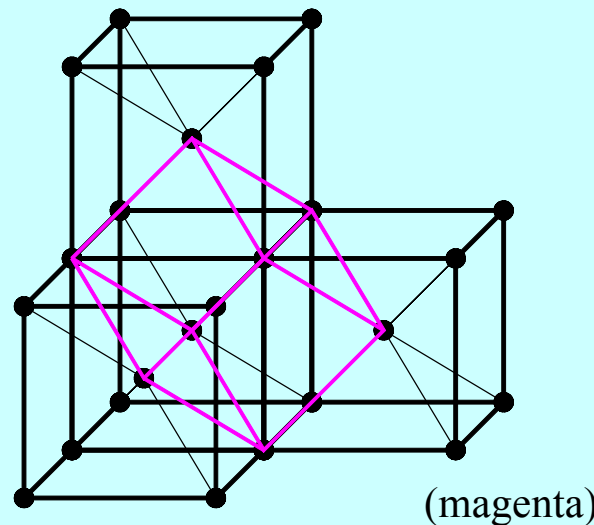
There is not one unique shape of a primitive cell, many possible shapes.

The primitive cell for the simple cubic lattice is equal to the simple cubic unit cell (they are identical).



Body-Centered
Cubic (I)

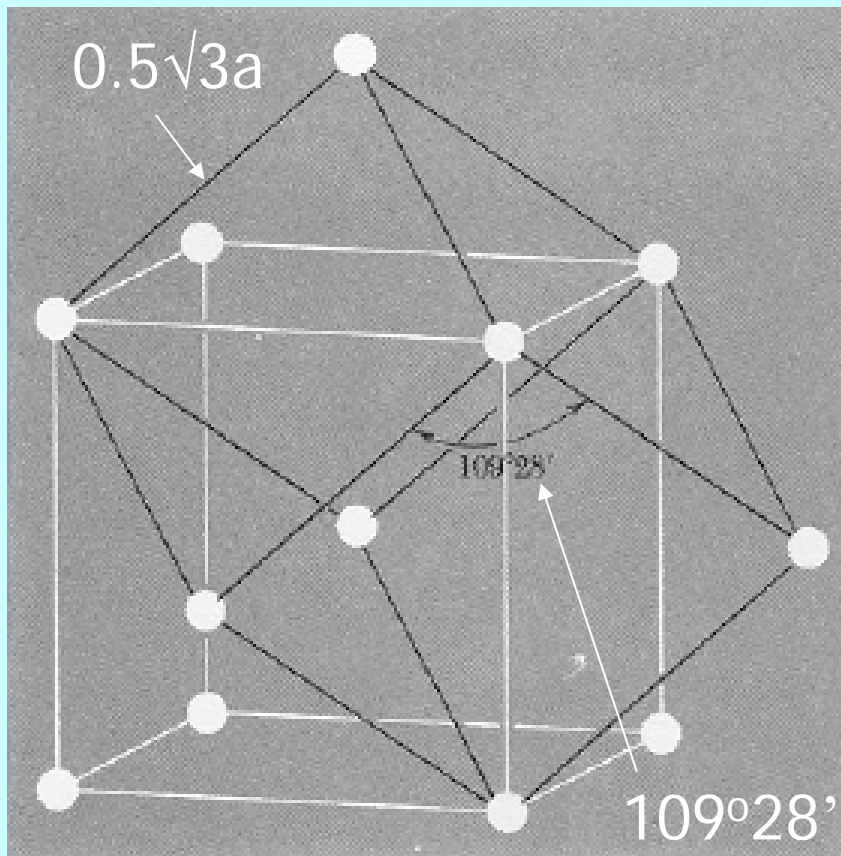
Unit Cell



Primitive Cell

Primitive Cell of BCC

- Rhombohedron primitive cell

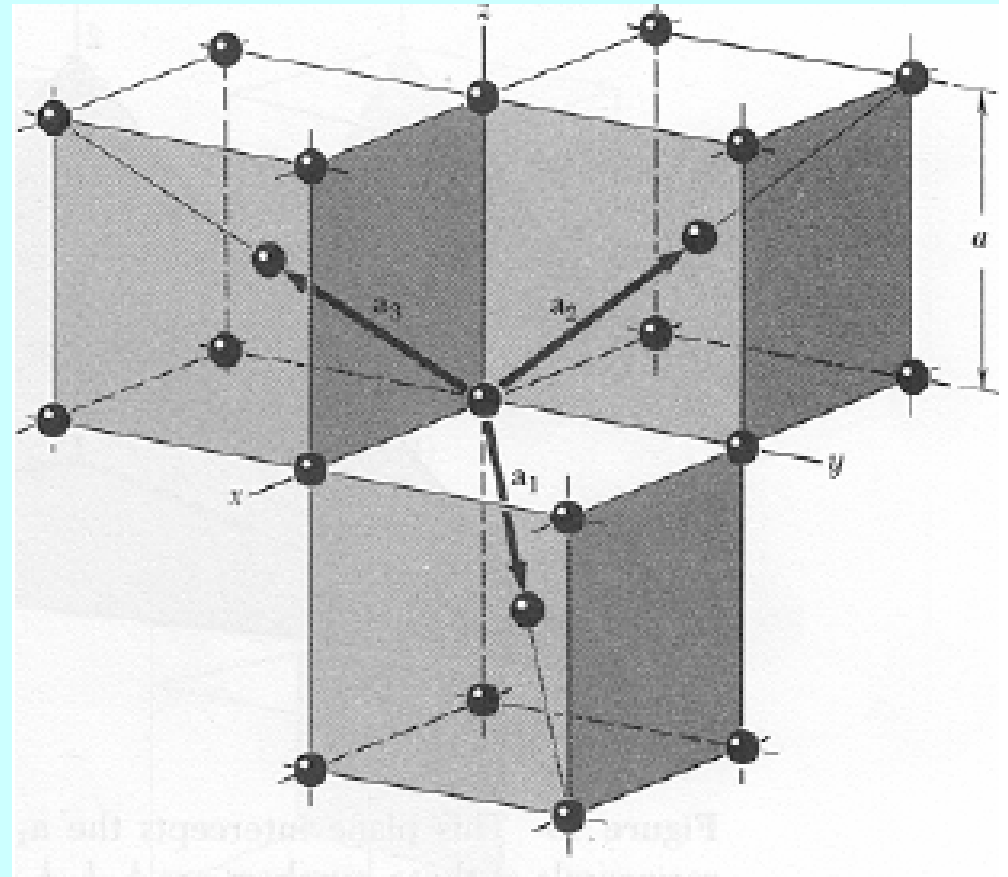
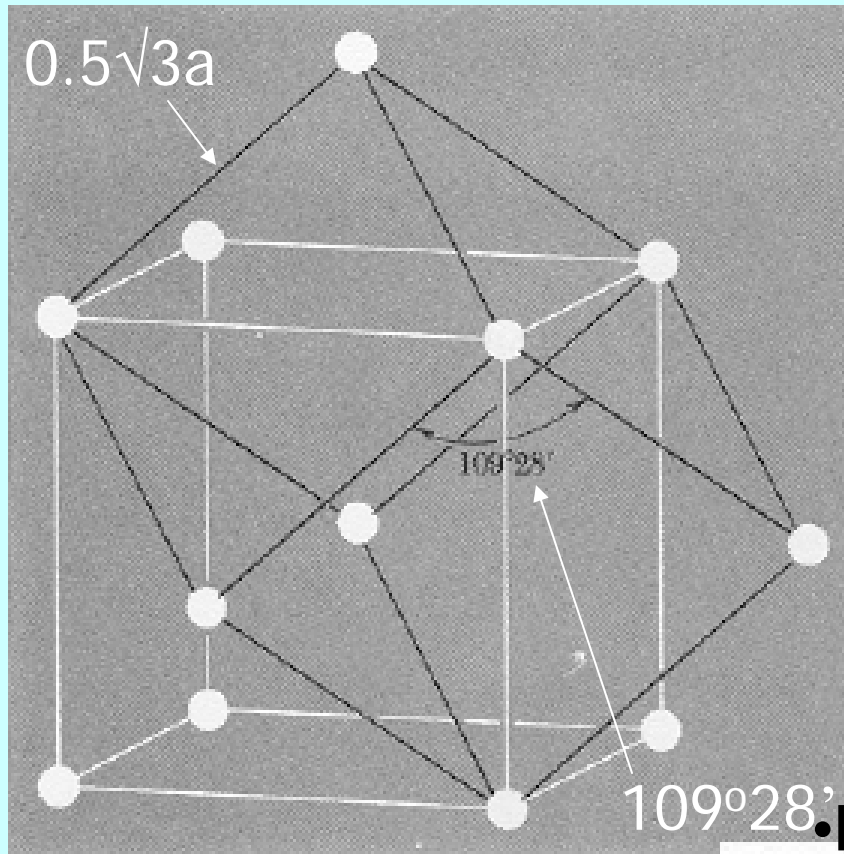


The primitive cell is smaller or equal in size to the unit cell.

The unit cells possesses the highest symmetry present in the lattice (for example Cubic).

Primitive Cell of BCC

- Rhombohedron primitive cell

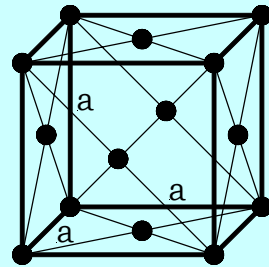


- Primitive Translation Vectors:

$$a_1 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z}) ; \quad a_2 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) ;$$

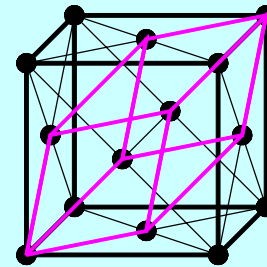
$$a_3 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) .$$

Nonprimitive Unit Cell vs. Primitive Cell

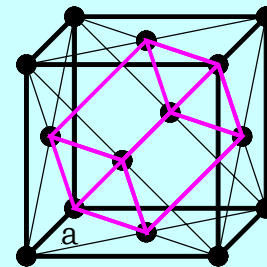


Face-Centered
Cubic (F)

Unit Cell



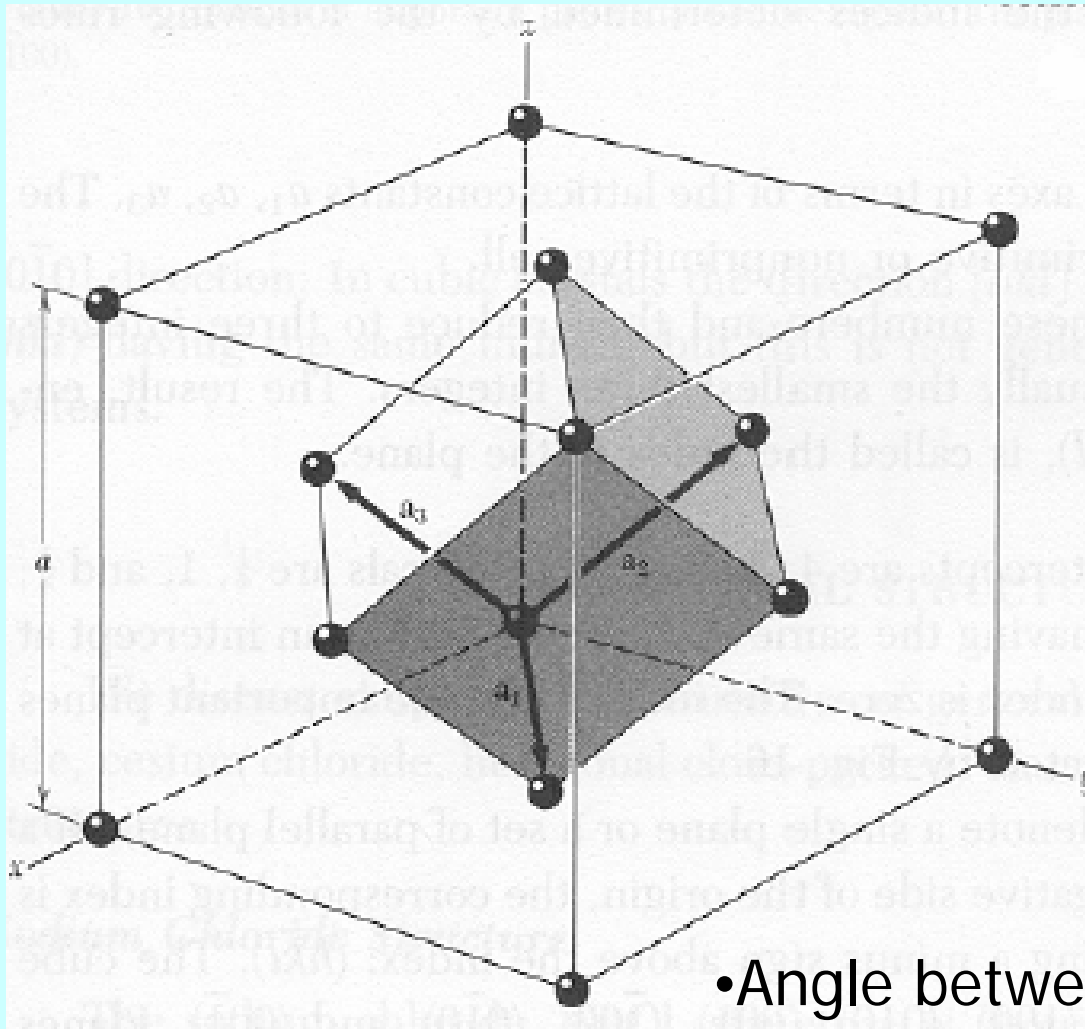
Primitive Cell



Rotated 90°

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

Primitive Cell of FCC

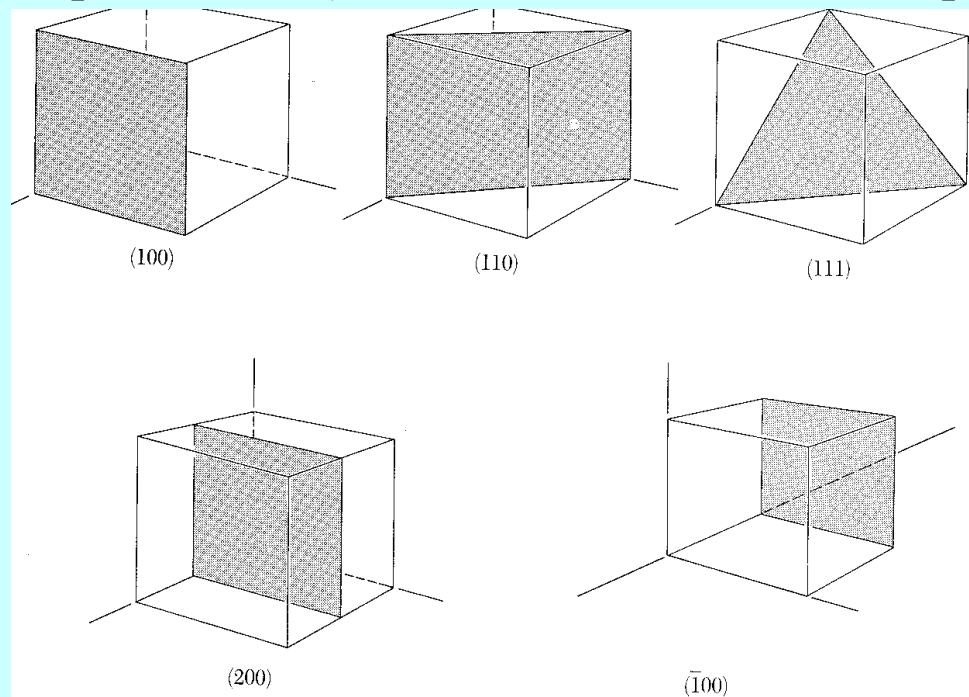


•Angle between a_1, a_2, a_3 : 60°

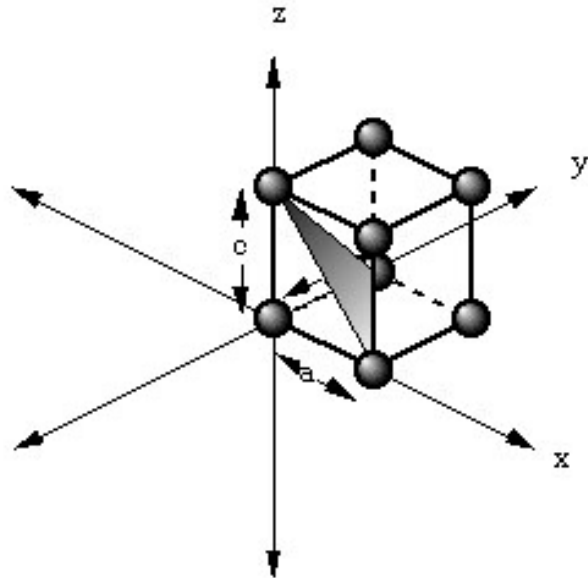
$$a_1 = \frac{1}{2}a(\hat{x} + \hat{y}) ; \quad a_2 = \frac{1}{2}a(\hat{y} + \hat{z}) ; \quad a_3 = \frac{1}{2}a(\hat{z} + \hat{x}) .$$

Index System for Crystal Planes (Miller Indices)

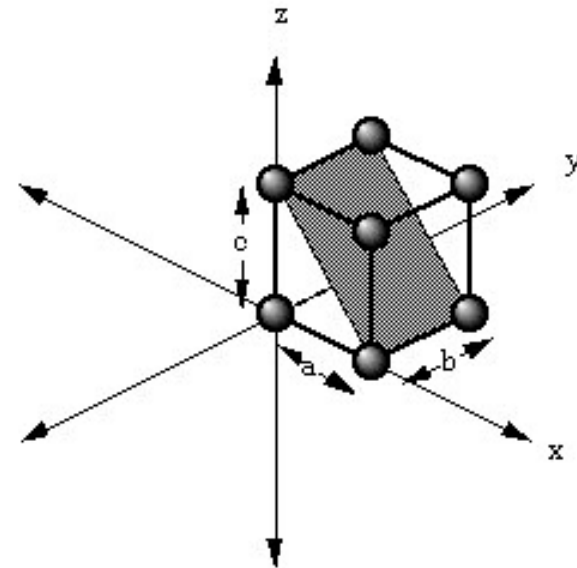
- 1) Find the intercepts on the axes in terms of the lattice constants a , b , c . The axes may be those of a primitive or nonprimitive unit cell.
- 2) Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result enclosed in parenthesis (hkl), is called the index of the plane.



Miller Indices

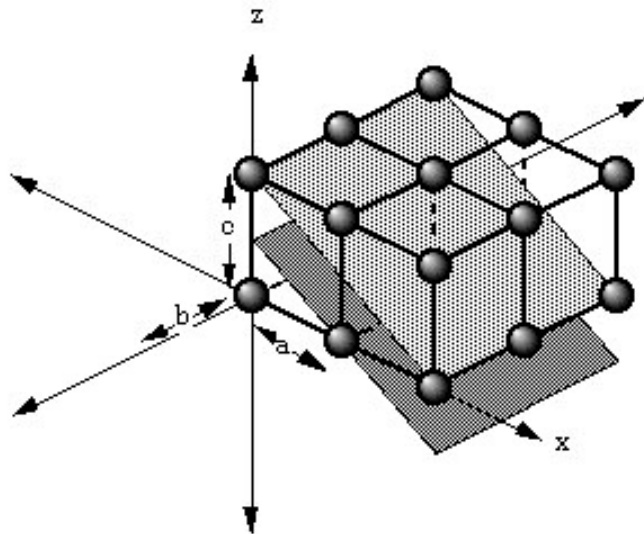


	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1
Miller indice	(111)		

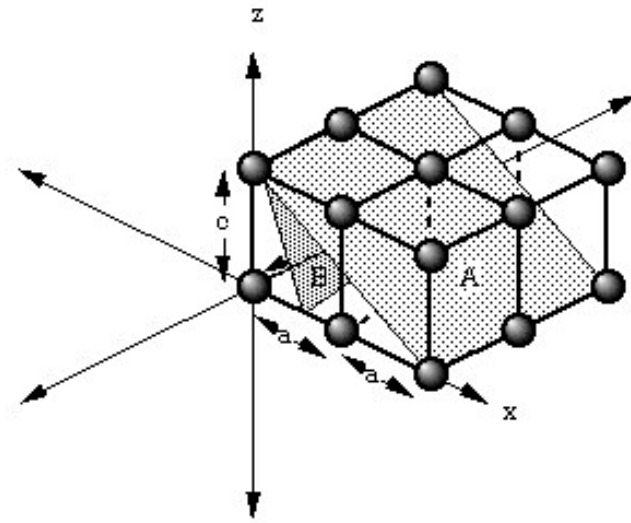


	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		

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)		

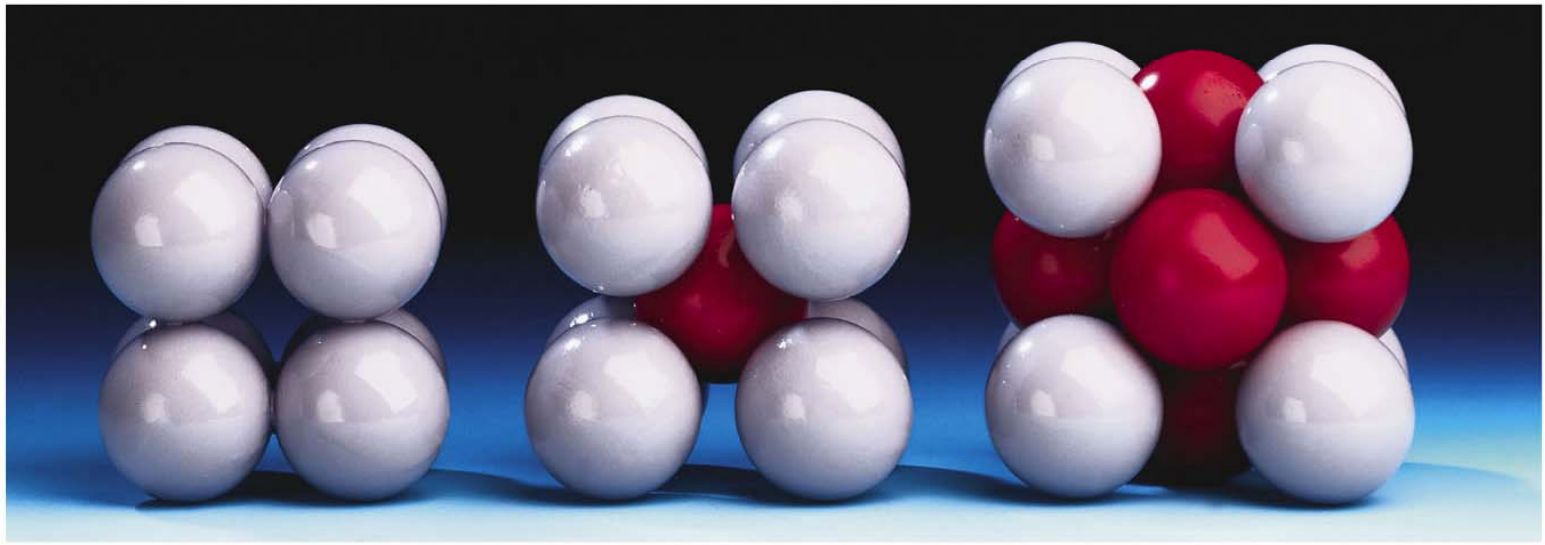
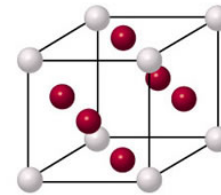
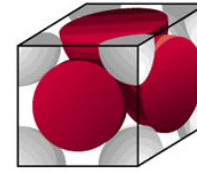
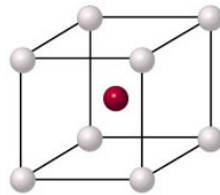
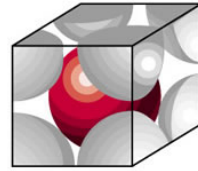
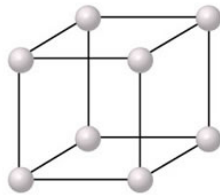
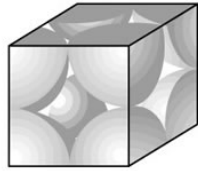


	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	∞	$\frac{1}{2}$	$\frac{1}{2}$	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	(102)			(201)		

Crystals and Crystal Bonding

- metallic (Cu, Fe, Au, Ba, alloys)
metallic bonding
- ionic (NaCl, CsCl, CaF₂, ...)
Ionic bonds, cations and anions, electrostatic interactions
- covalent (diamond, graphite, SiO₂, AlN,...)
atoms, covalent bonding
- molecular (Ar, C₆₀, HF, H₂O, organics, proteins)
molecules, van der Waals and hydrogen bonding

Three Cubic Cells



SC or Primitive (P)

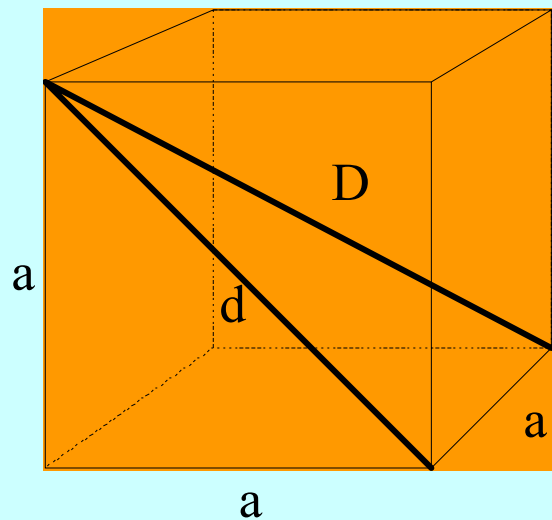
BCC (I)

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

Cube



a = edge

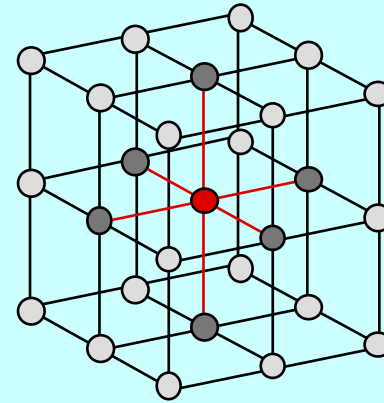
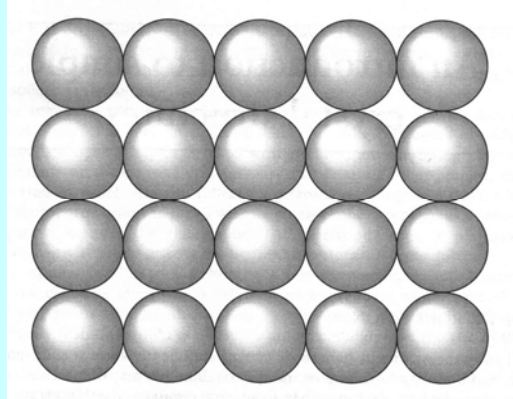
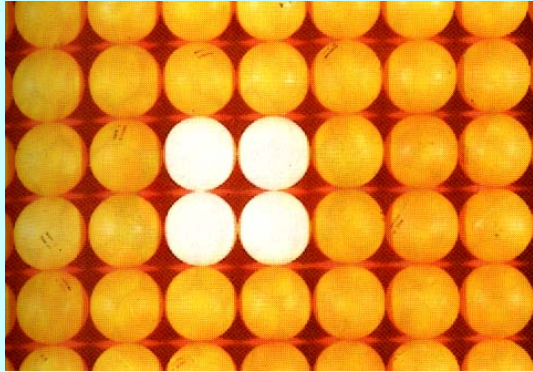
d = face diagonal
($d^2 = a^2 + a^2 = 2a^2$)

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

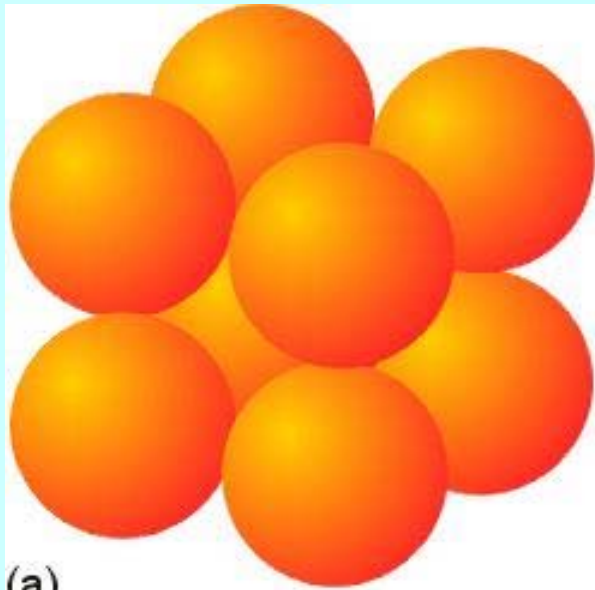
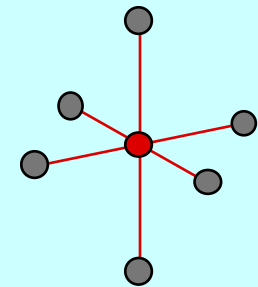
$$d = \sqrt{2} \cdot a$$

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

SC = Polonium

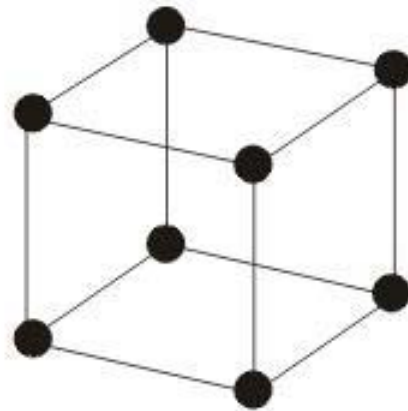


CN 6

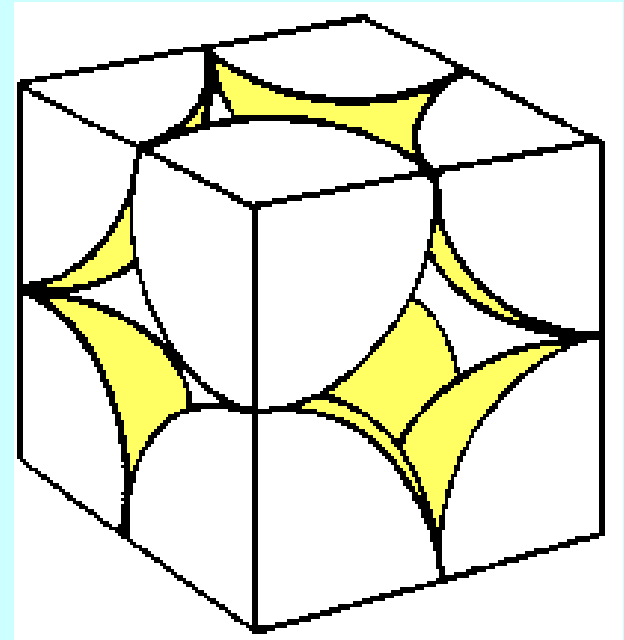


(a)

$Z = 1$

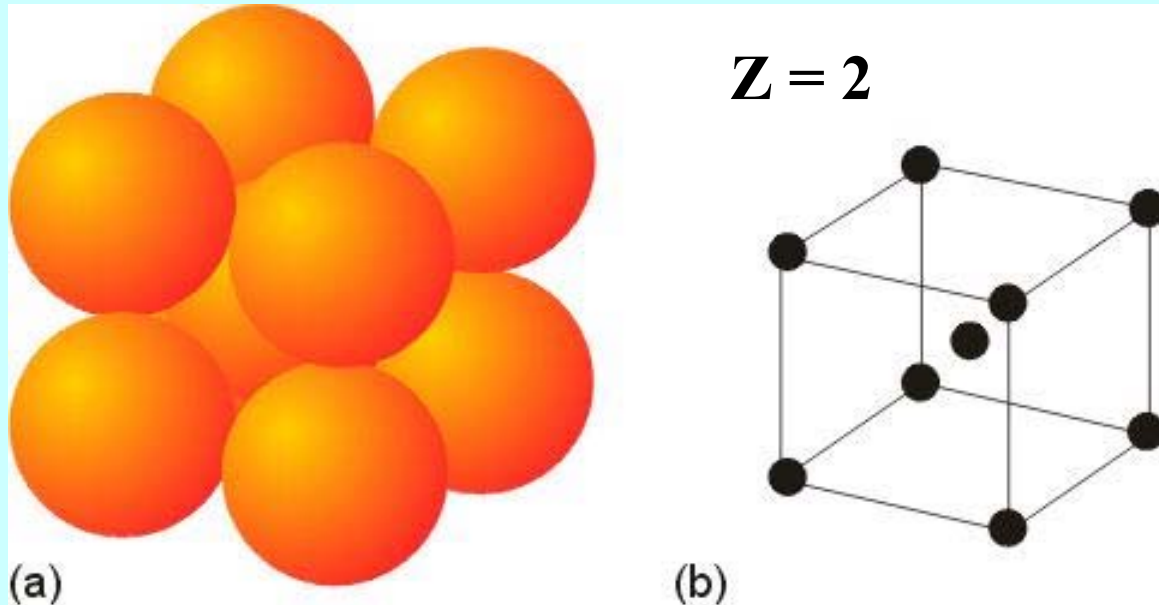


(b)



Space filling 52%

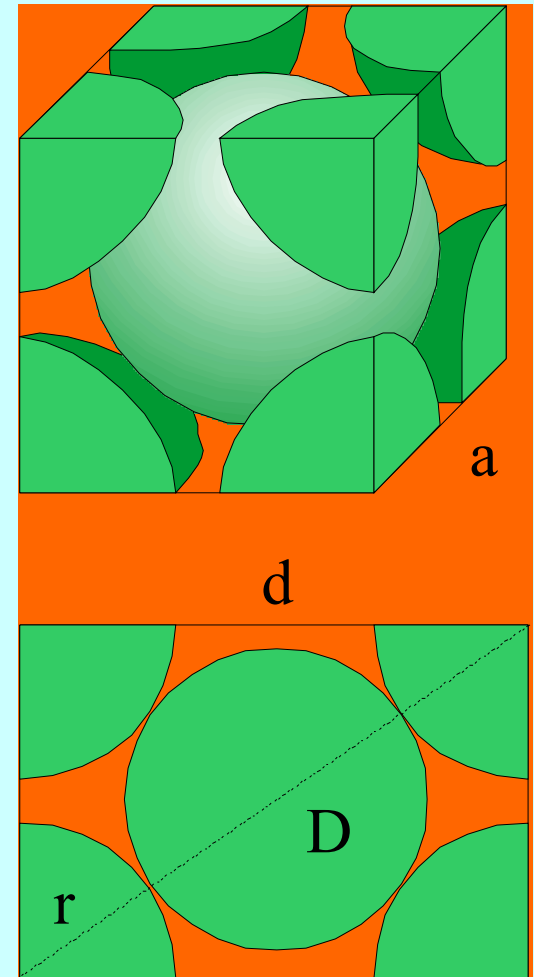
BCC = W, Tungsten



Space filling 68%

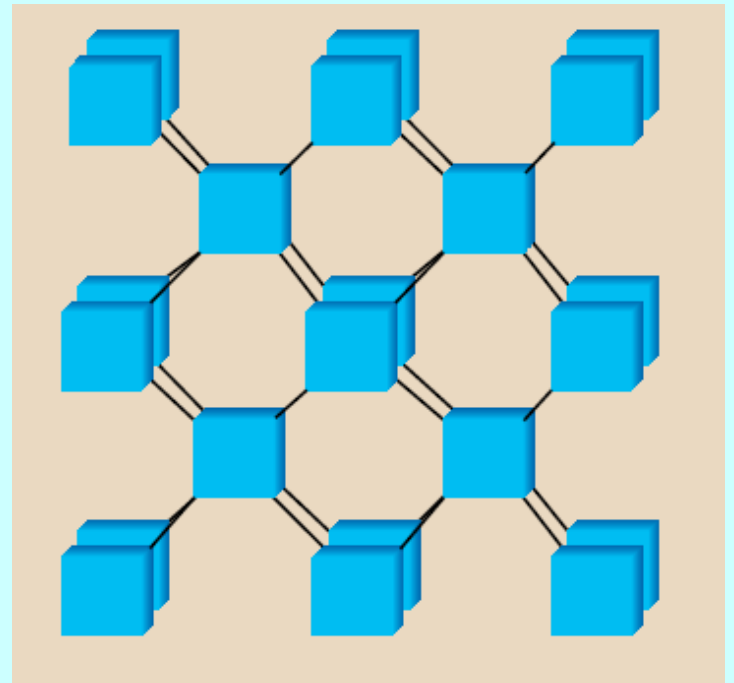
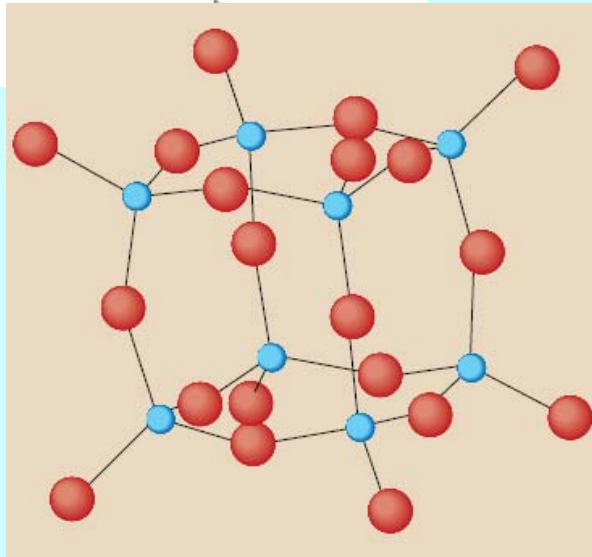
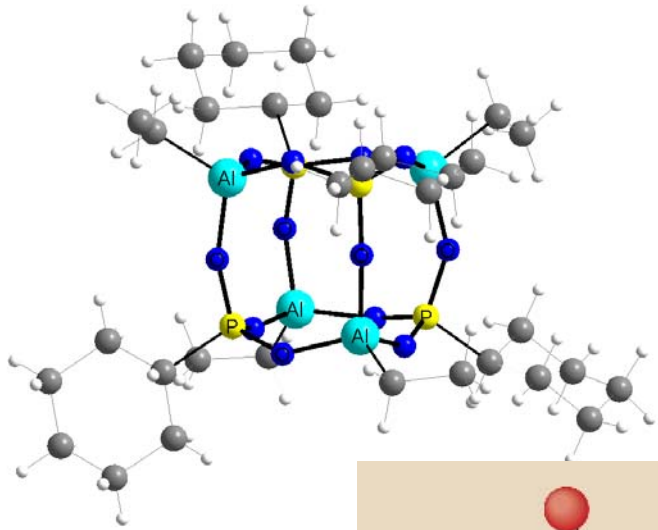
CN 8

Fe, Cr, V, Li-Cs, Ba

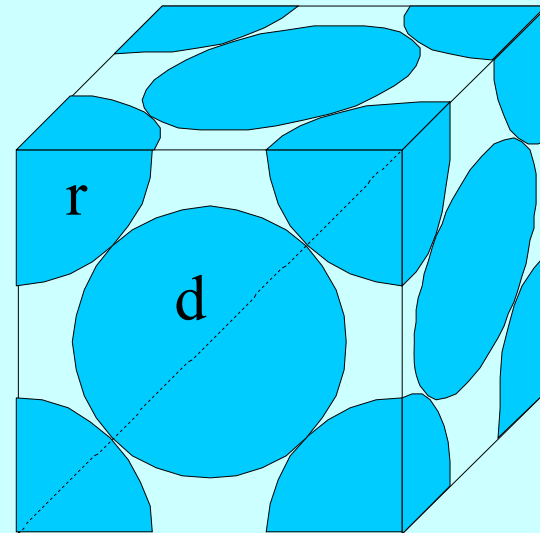
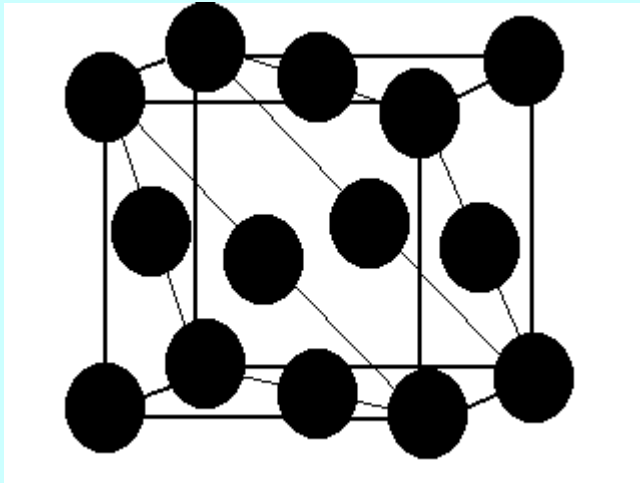




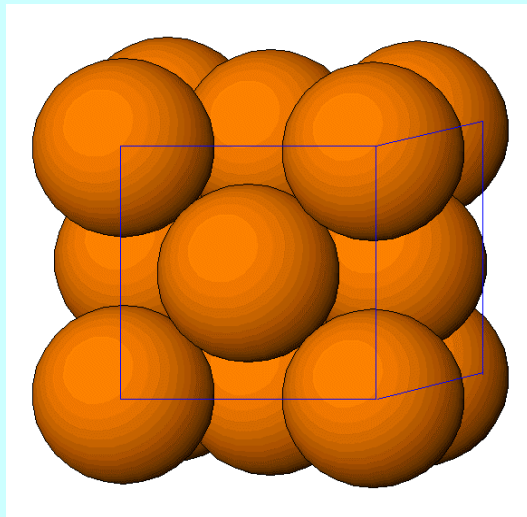
BCC



FCC = Copper, Cu = CCP



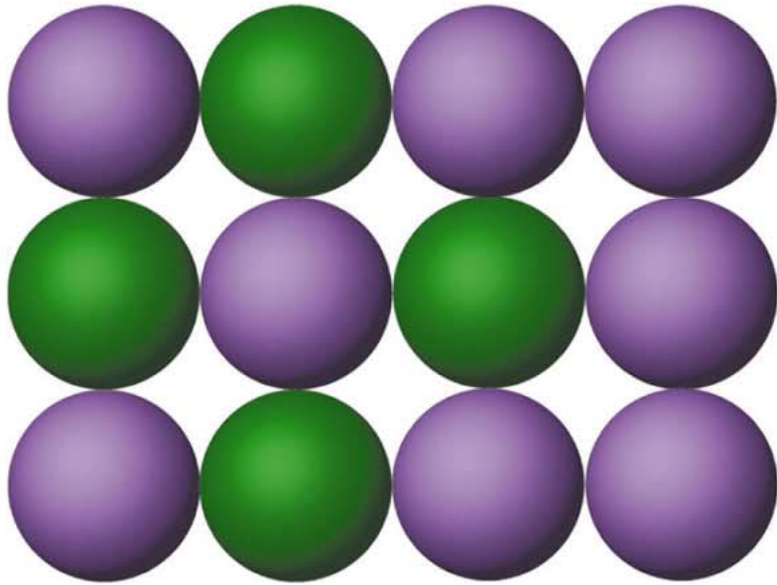
$$Z = 4$$



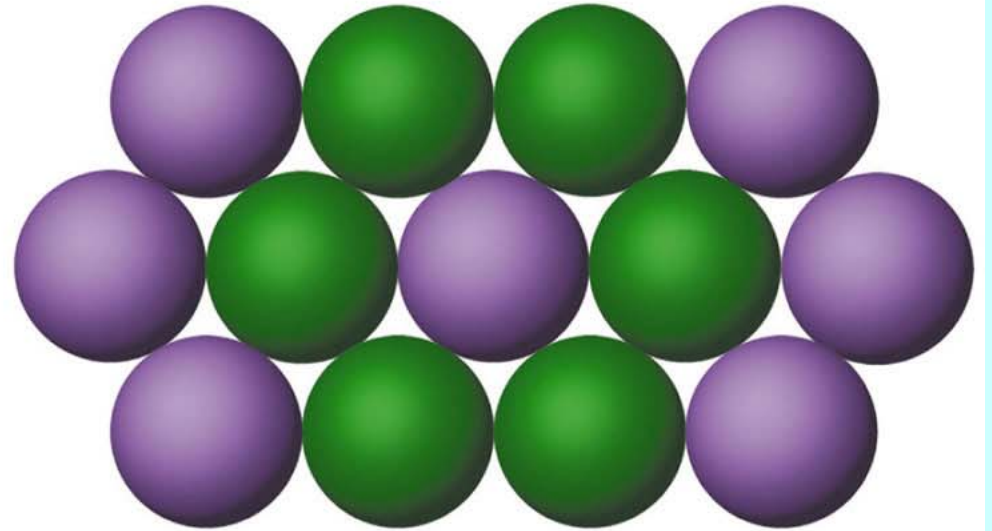
Space filling 74%

CN 12

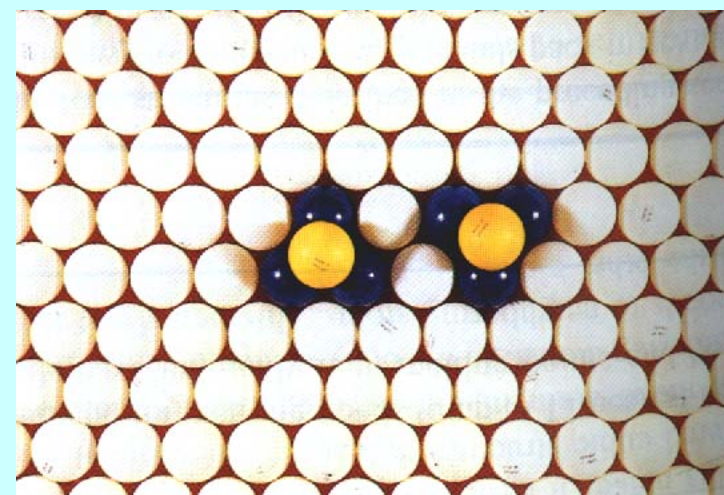
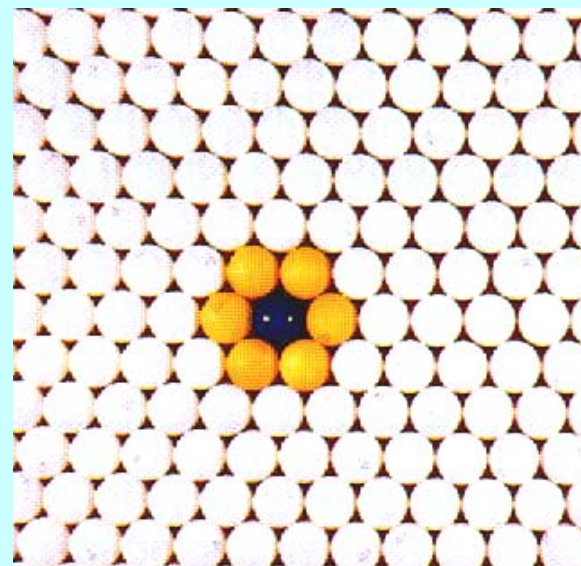
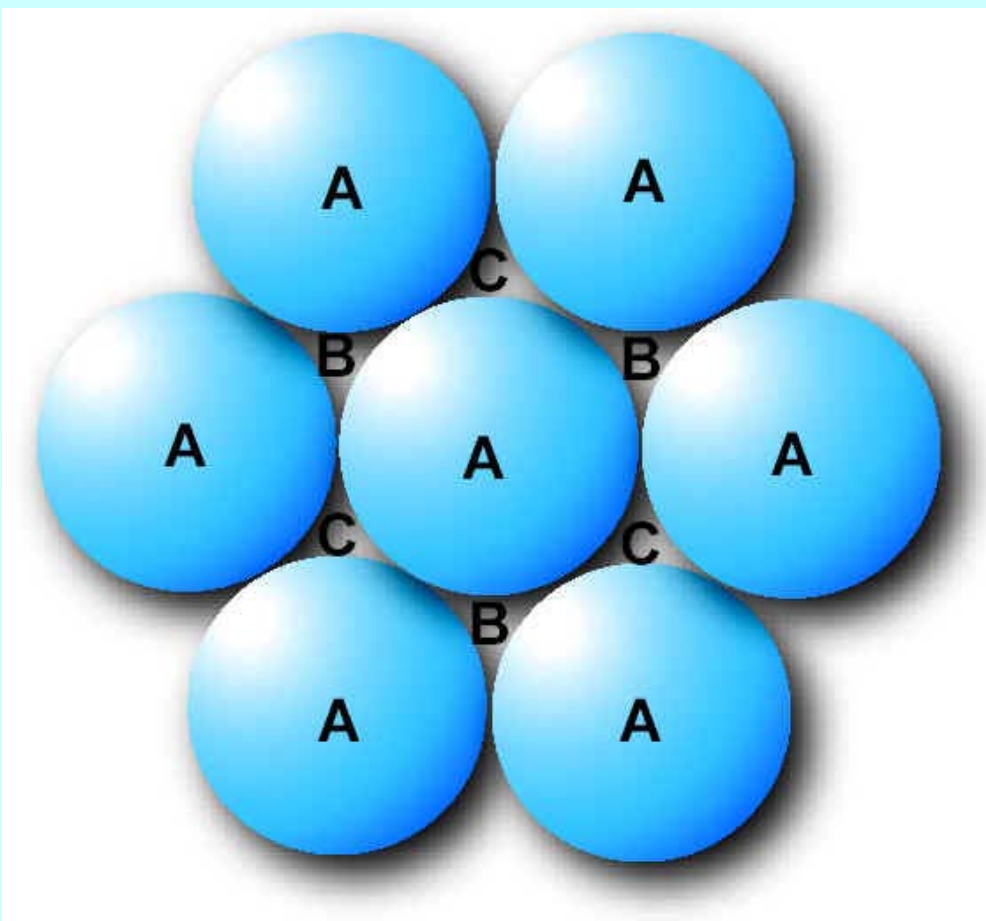
Close Packing in Plane 2D



(a) An "open" packing

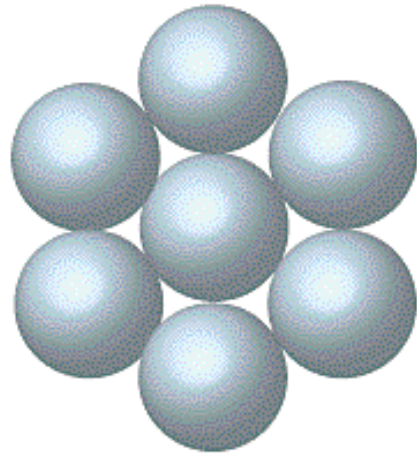


(b) Close packing

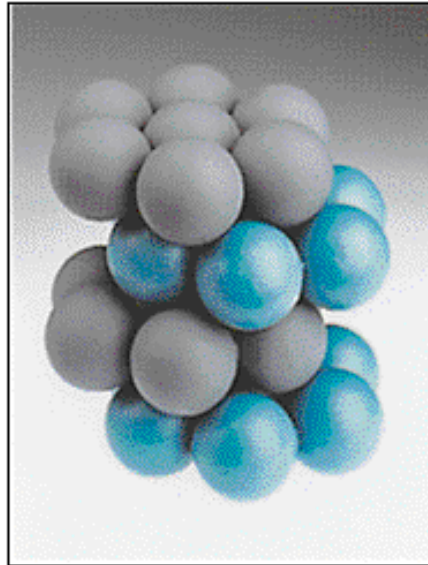


B and C holes cannot be occupied at the same time

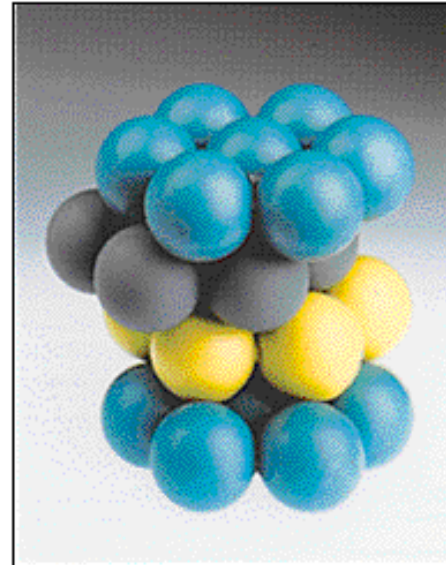
Close Packing in Space 3D



Close-packed layer of spheres



(b)



(c)

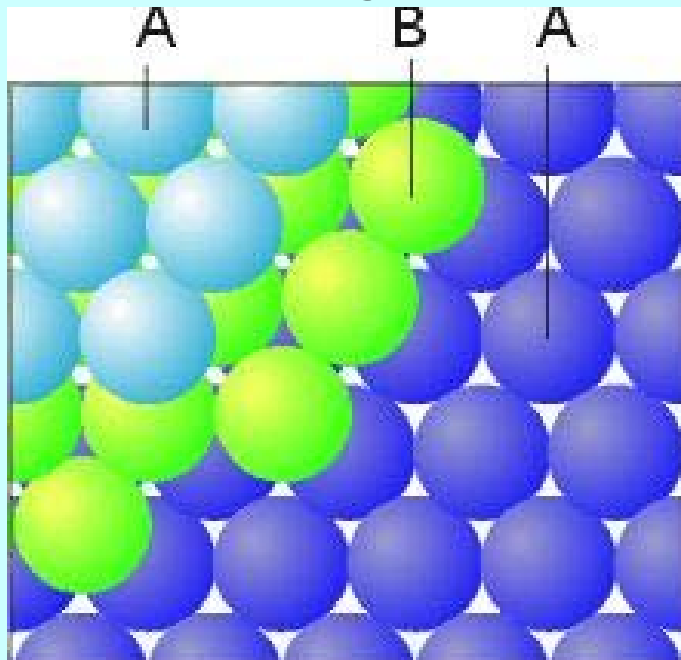


(a)

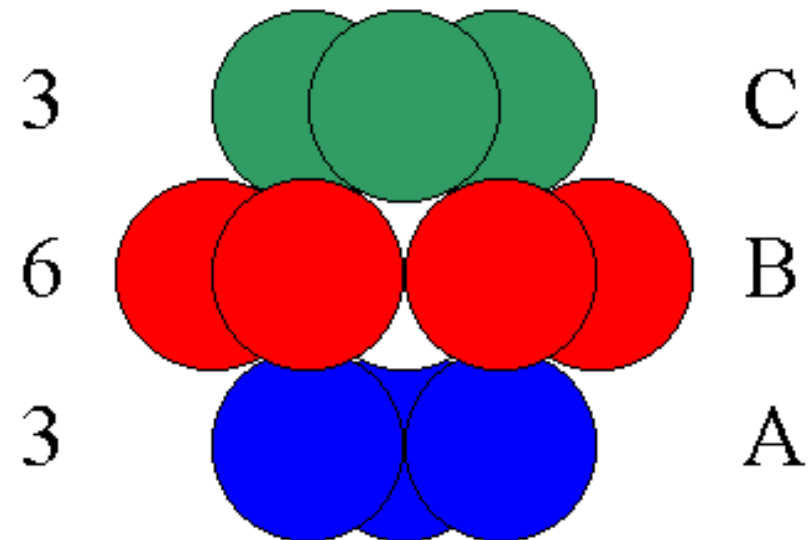
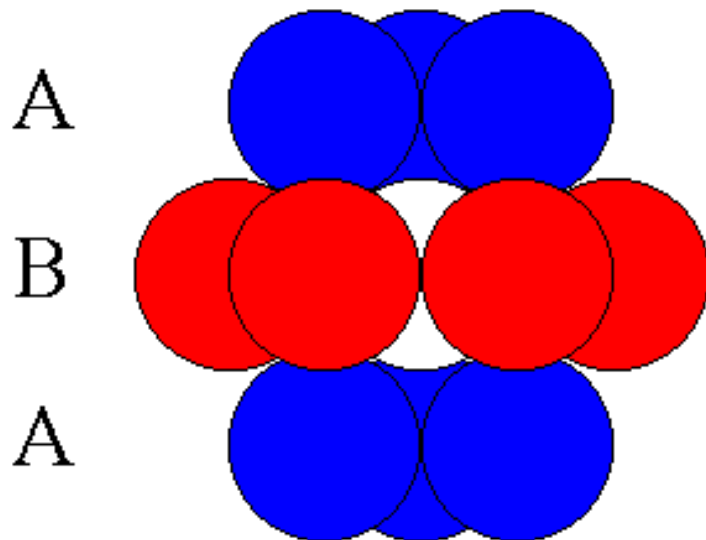
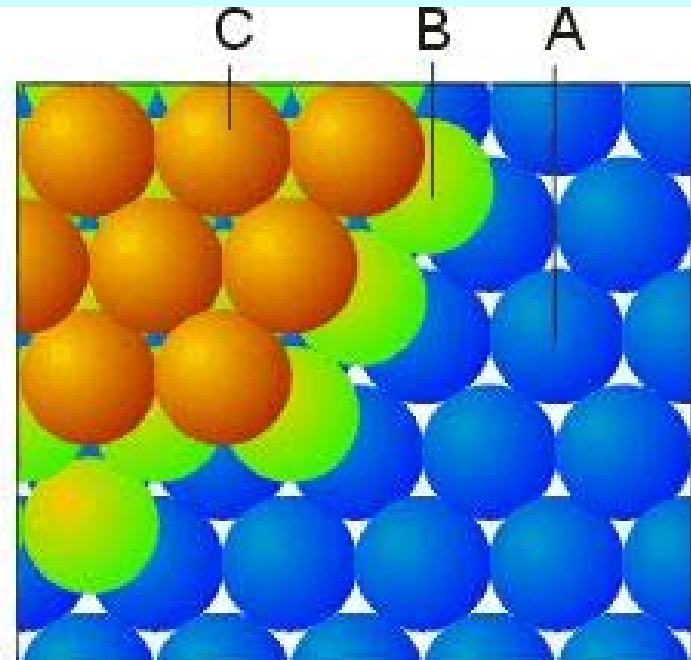
Hexagonal
HCP

Cubic
CCP

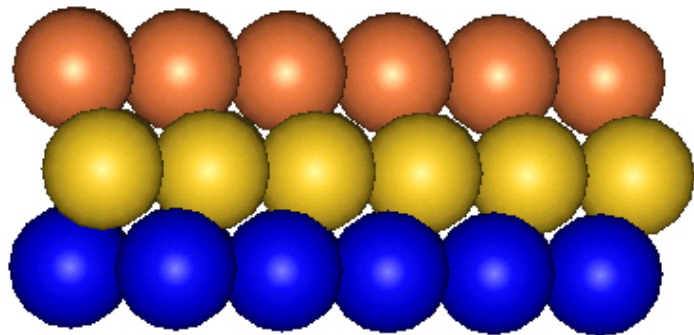
hexagonal



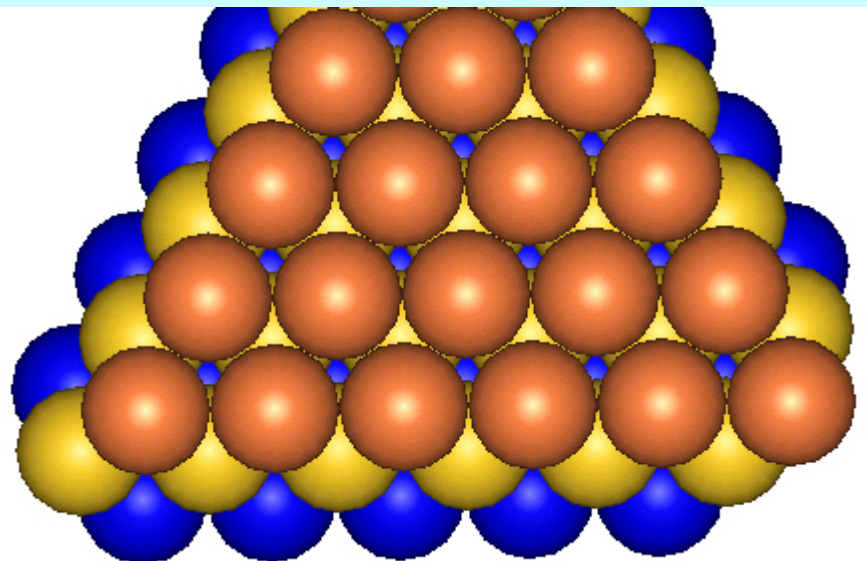
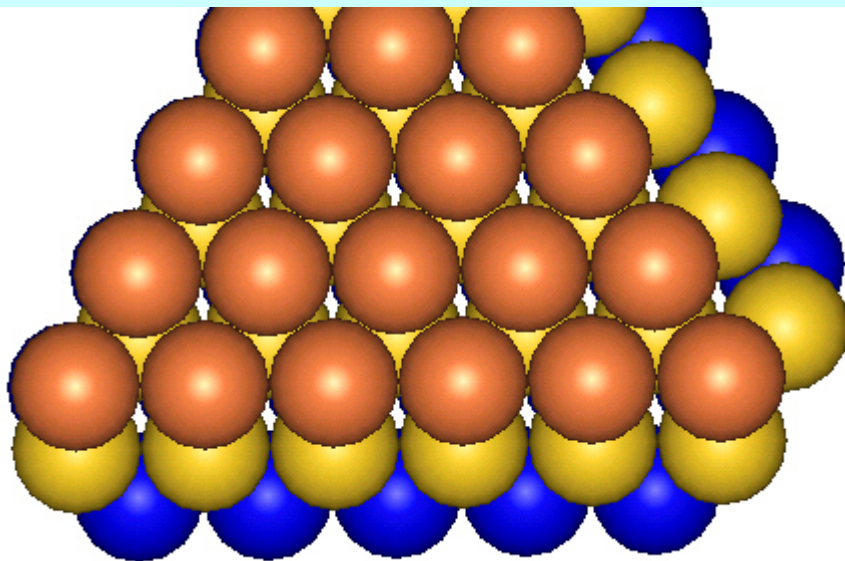
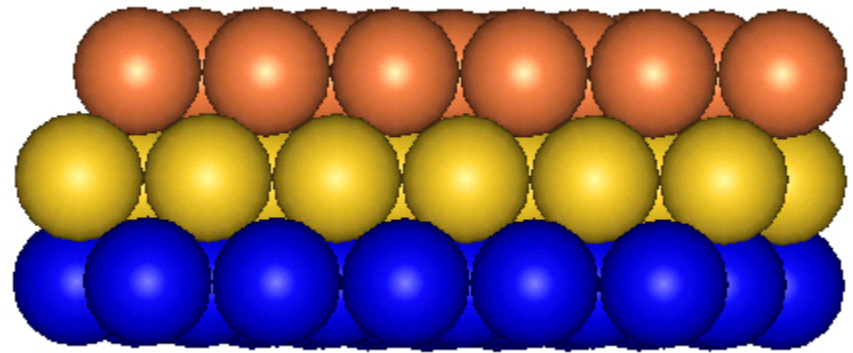
cubic

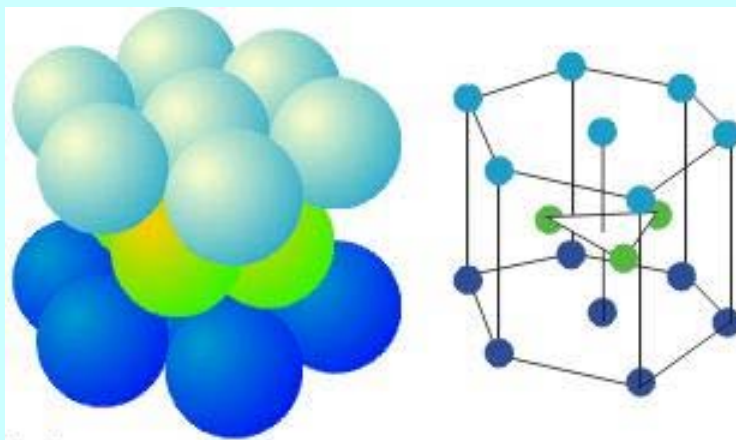


hexagonal

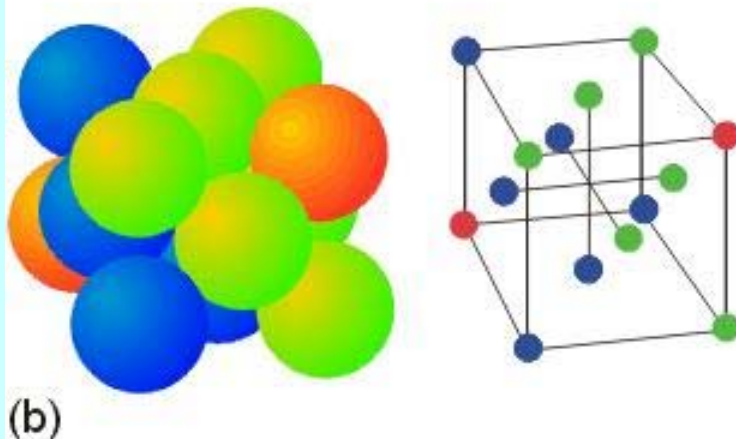


cubic



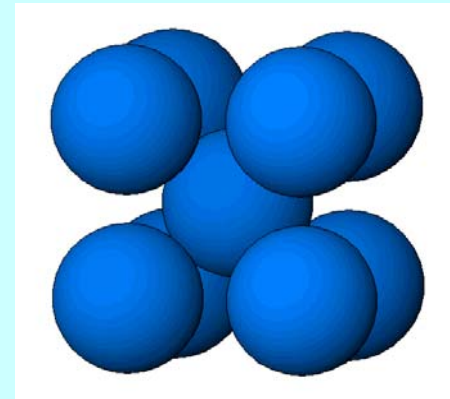


(a)

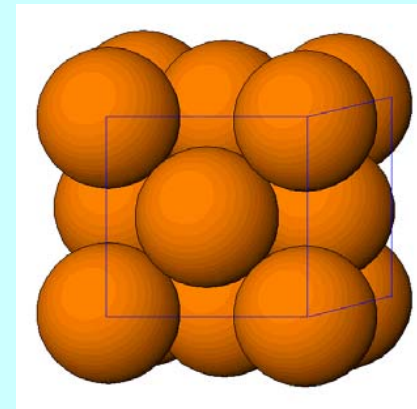


(b)

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



hexagonal

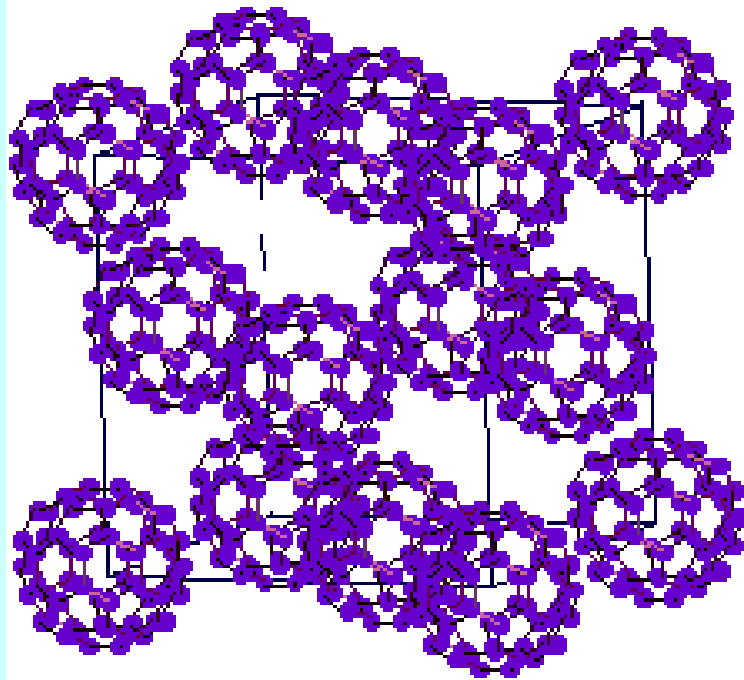


cubic

**Cu, Ca, Sr, Ag, Au, Ni, Rh, solid
Ne-Xe, F₂, C₆₀, opal (300 nm)**

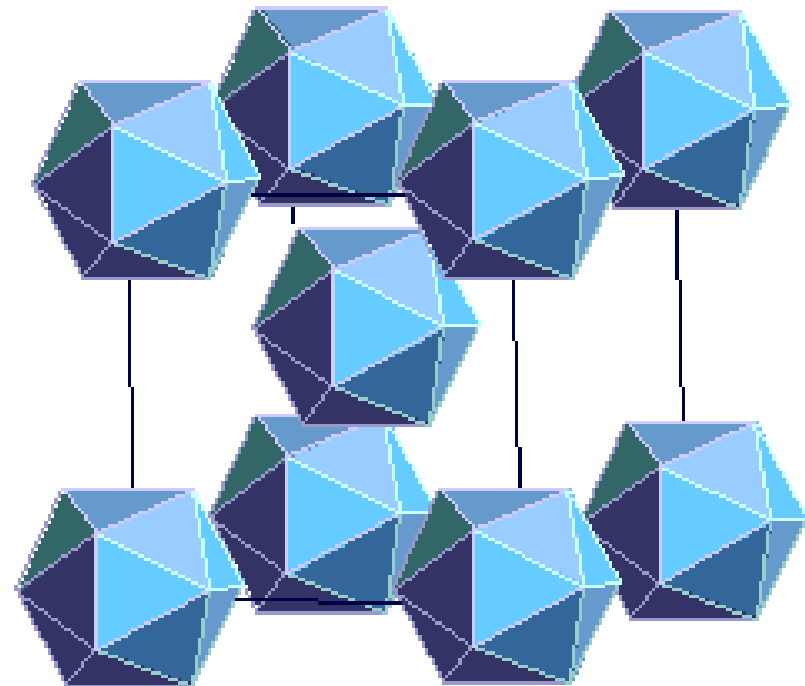
Structures with Larger Motifs

BUCKMINSTERFULLERENE

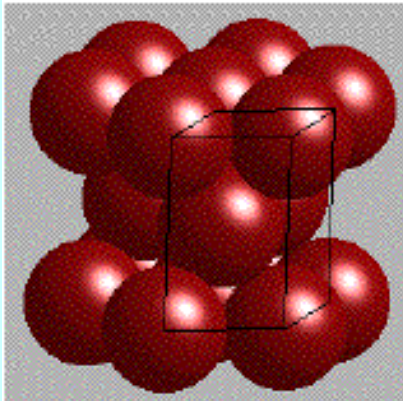


FCC

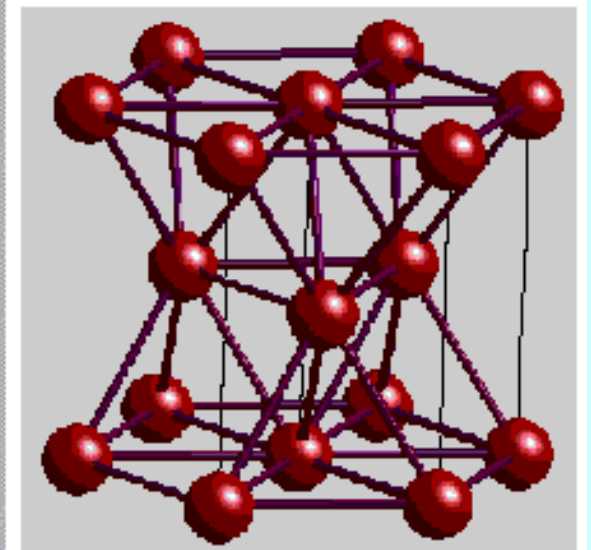
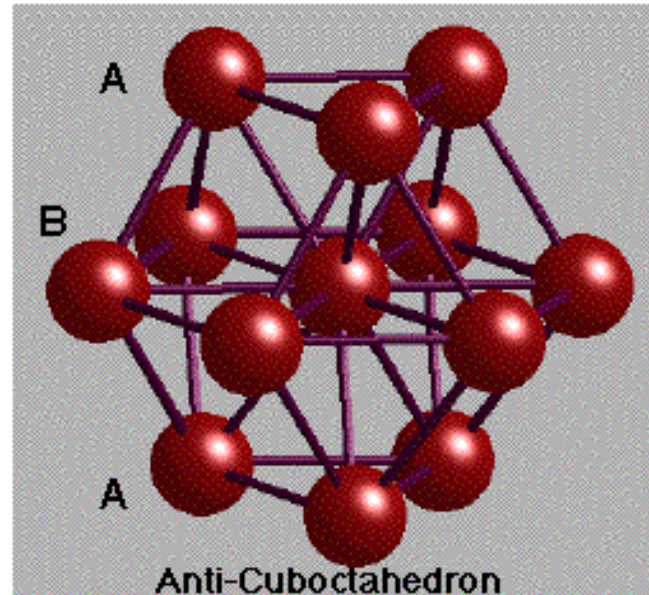
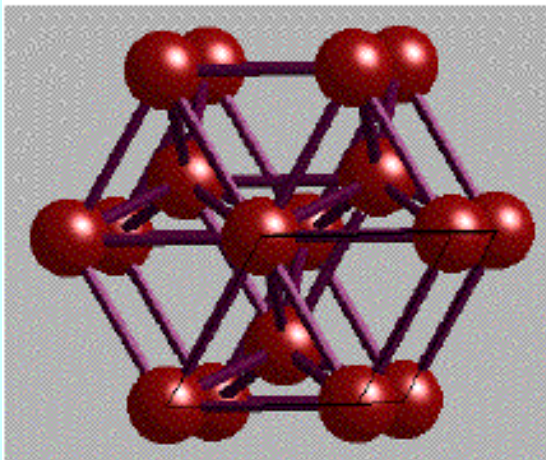
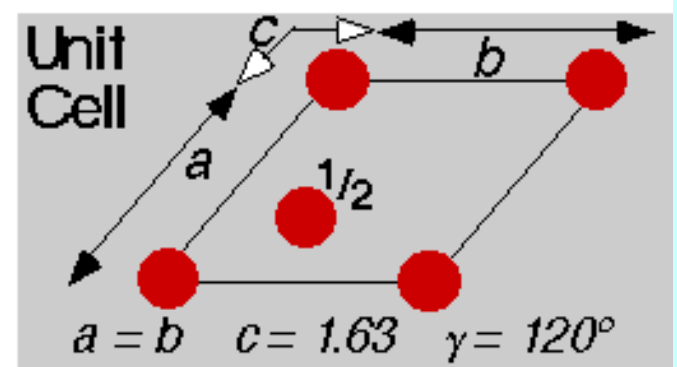
FOOT & MOUTH VIRUS



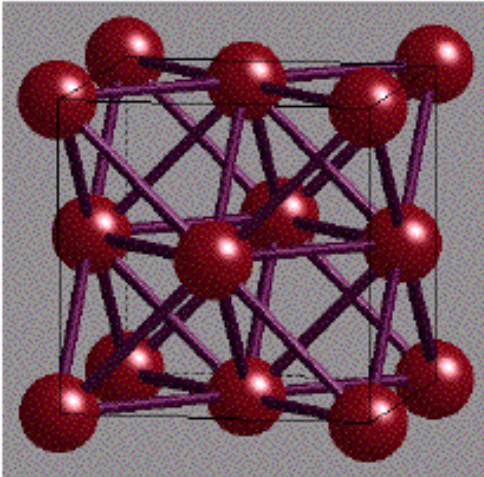
BCC



HEXAGONAL CLOSE-PACKING



CUBIC CLOSE-PACKING

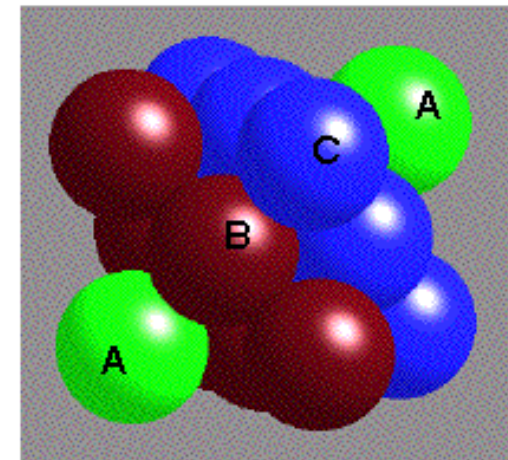
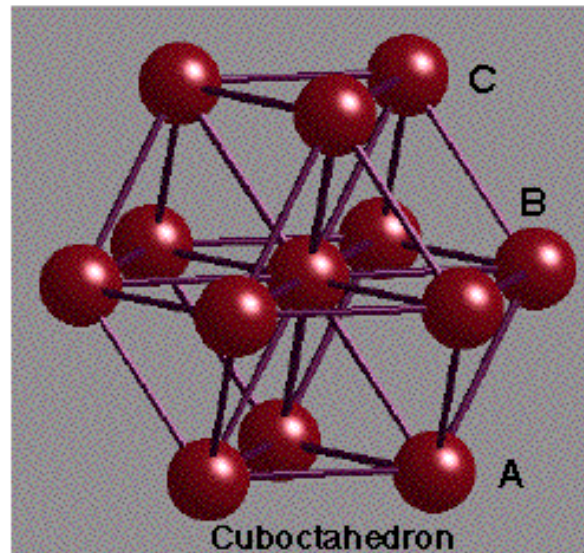
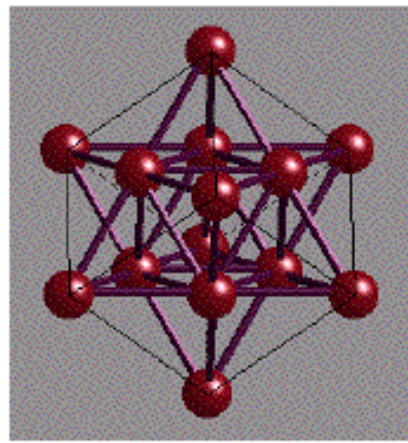
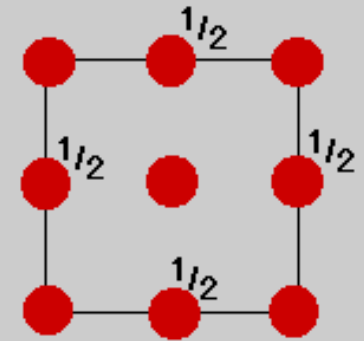


Face-Centred Cubic
(FCC) Unit Cell

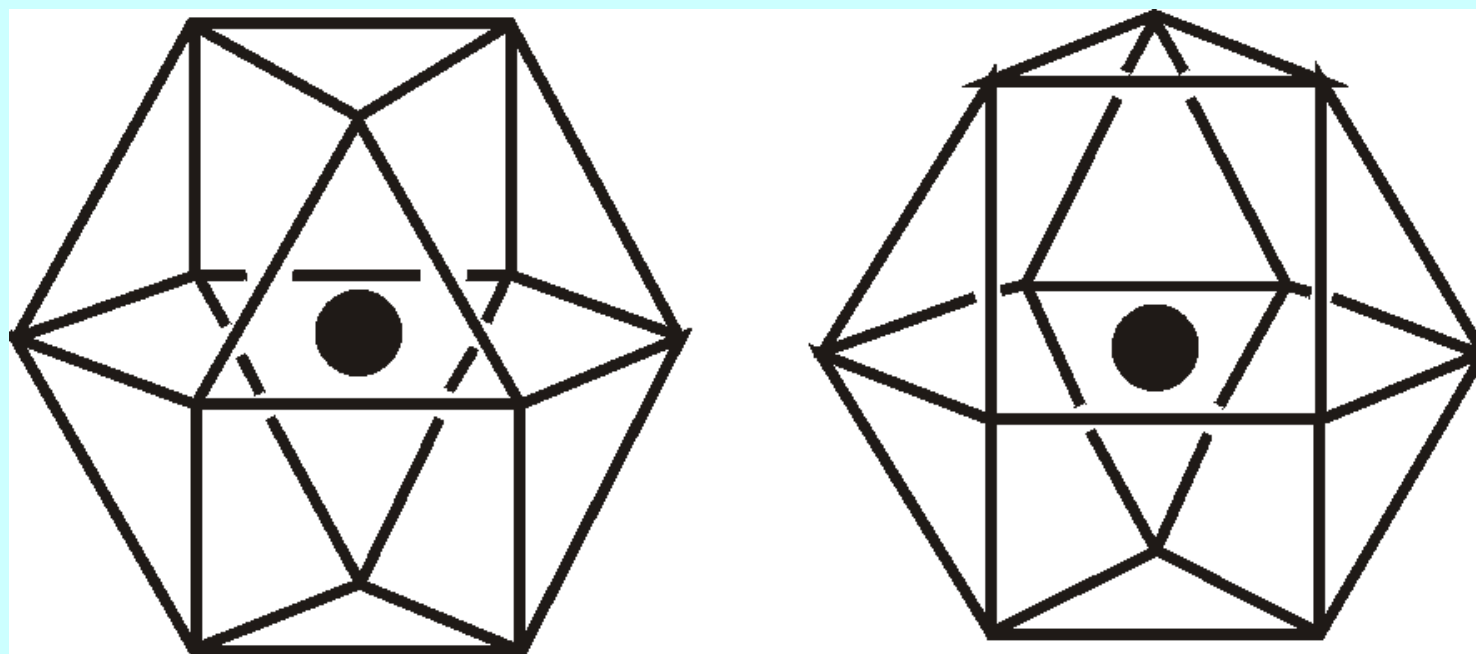
Unit
Cell

$$a = b = c$$

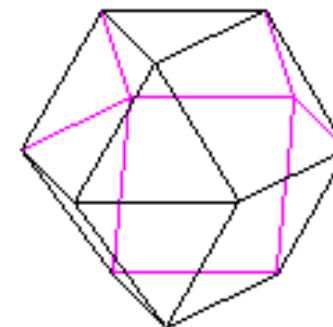
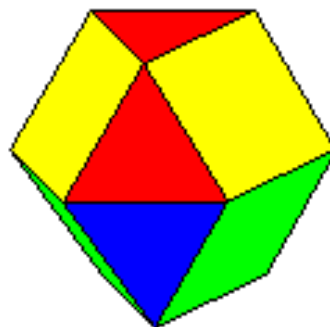
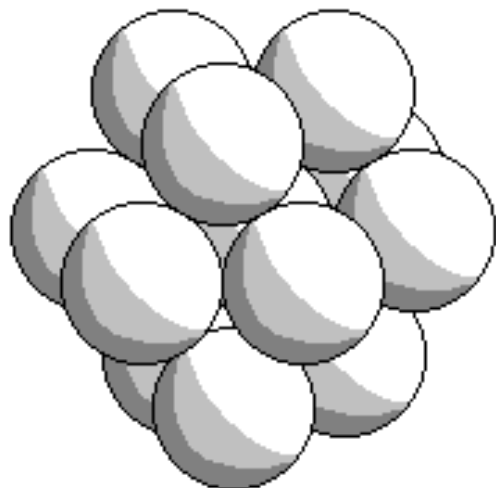
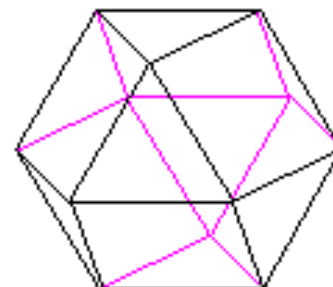
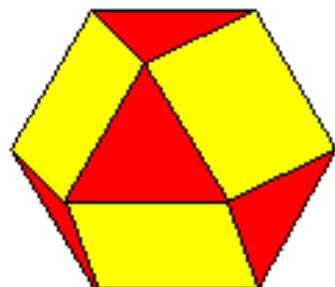
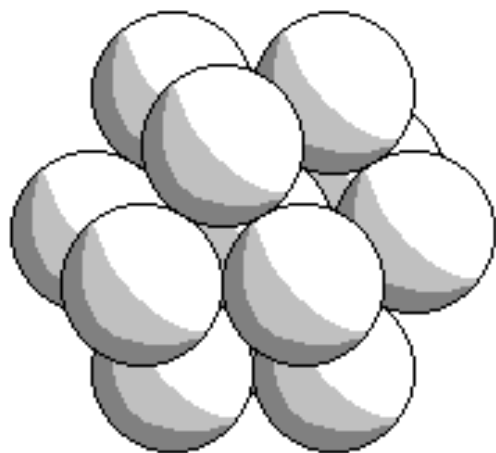
$$\alpha = \beta = \gamma = 90^\circ$$



Coordination Polyhedrons



Coordination Polyhedrons

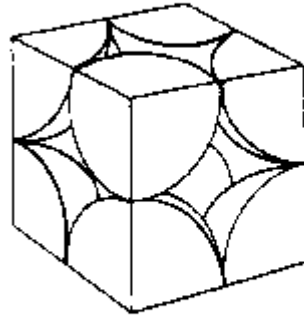


Space Filling

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
-----------------	--------------------	---------------------

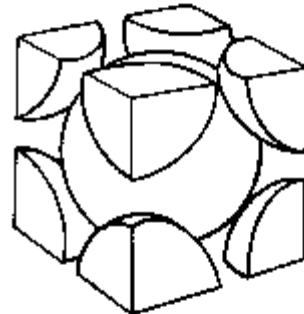
Simple cubic (sc)



52%

6

Body-centered cubic (bcc)



68%

8

Hexagonal close-packed (hcp)

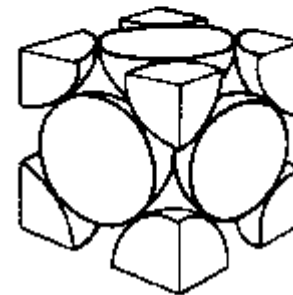
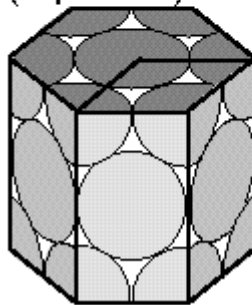
74%

12

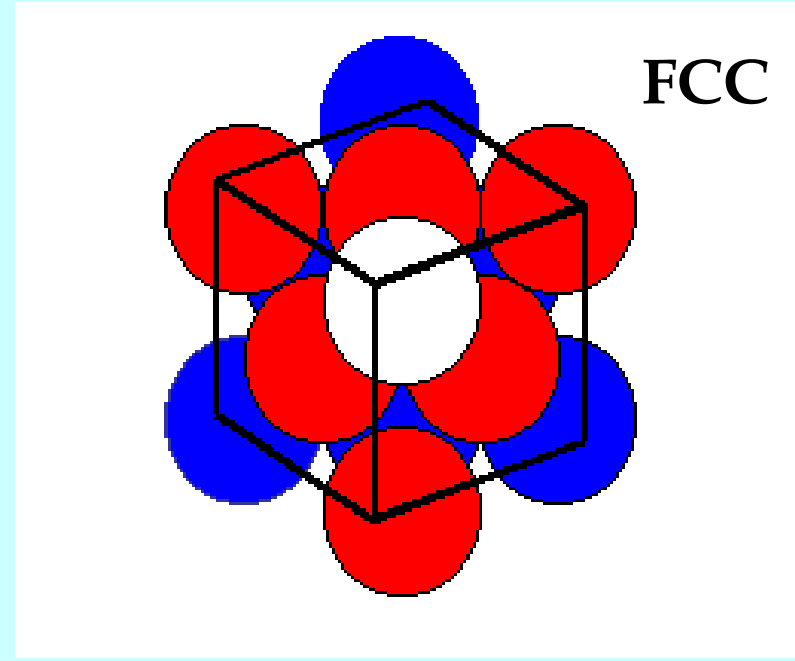
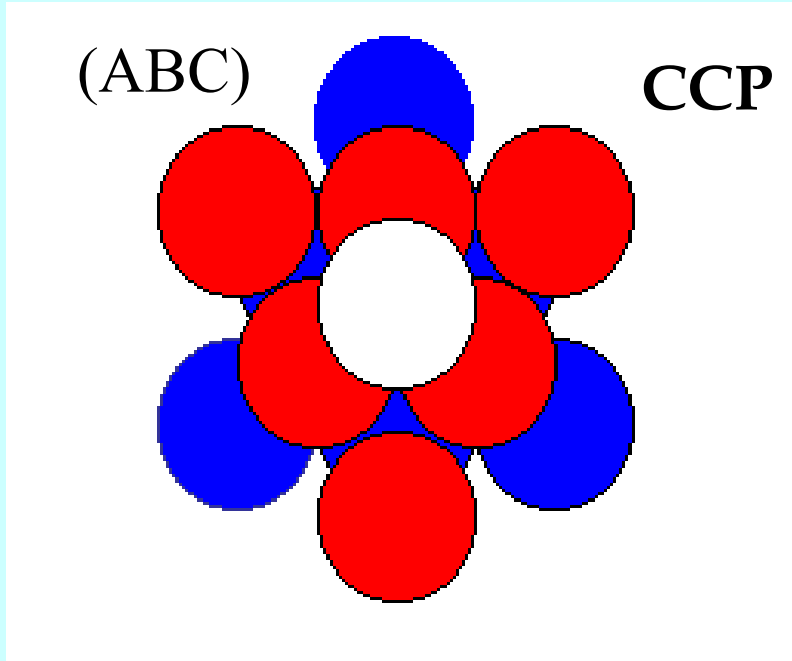
Cubic close-packed (ccp or fcc)

74%

12

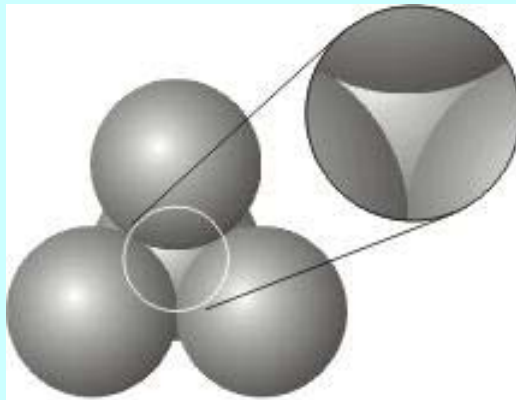


CCP = FCC

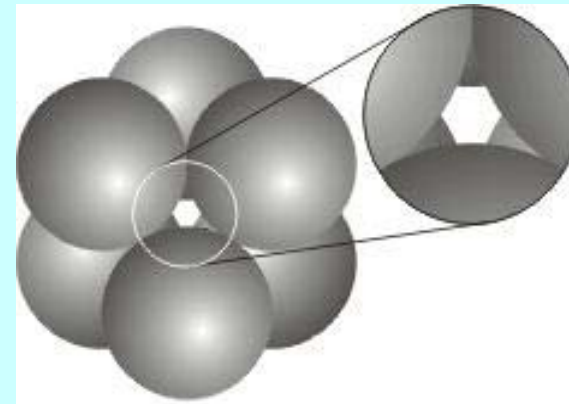


Close packed layers of CCP are oriented perpendicularly to the body diagonal of the cubic cell of FCC

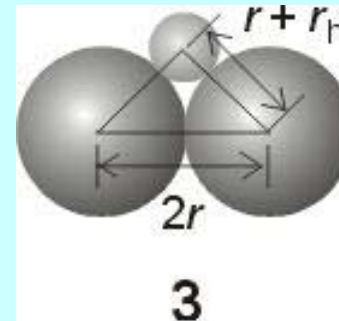
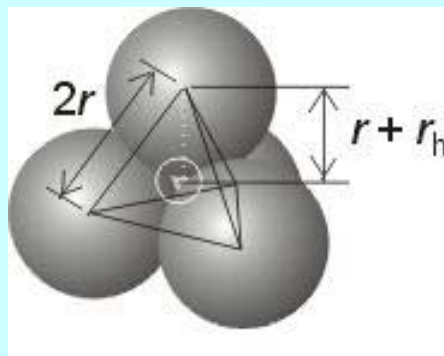
Two Types of Voids (Holes)



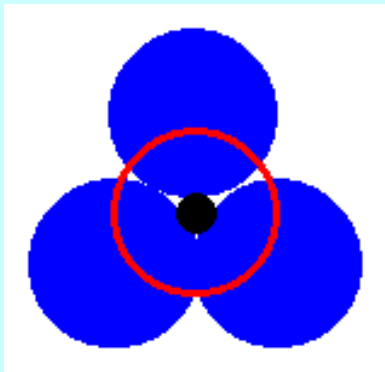
5 Tetrahedral hole



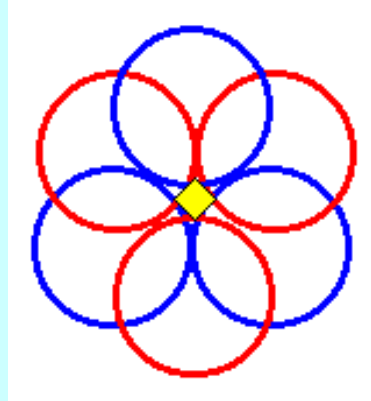
2 Octahedral hole



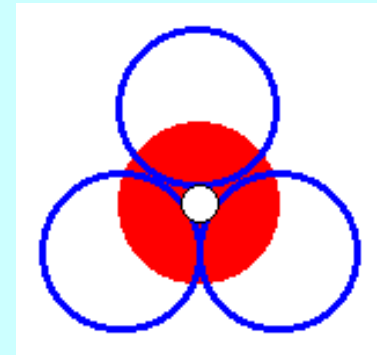
3



Tetrahedral Holes T+



Octahedral Holes

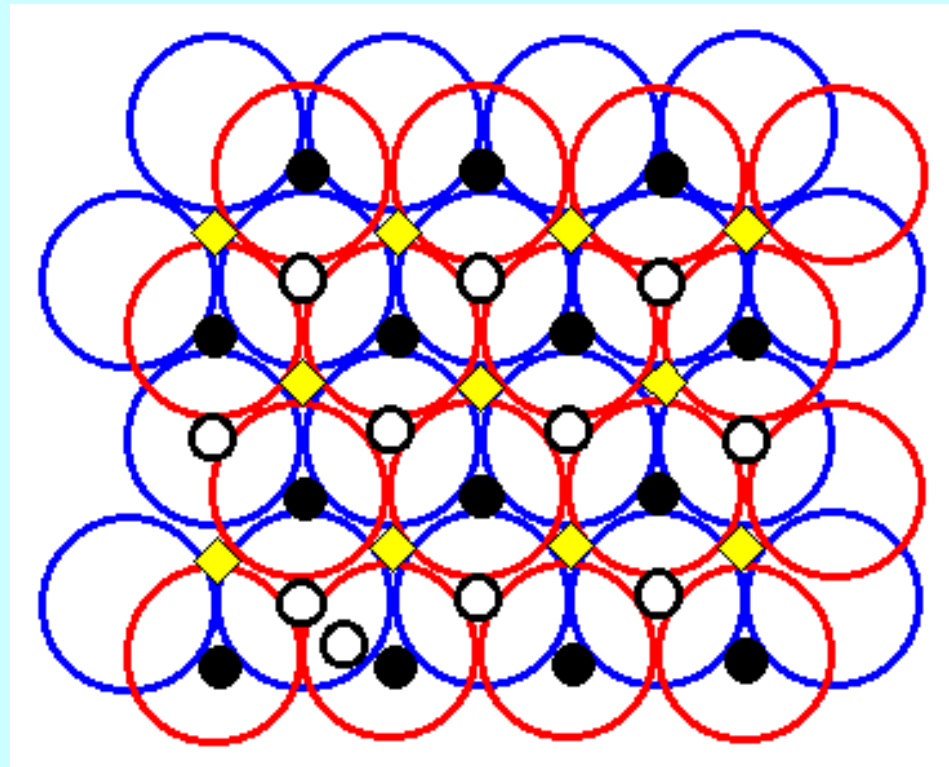


Tetrahedral Holes T-

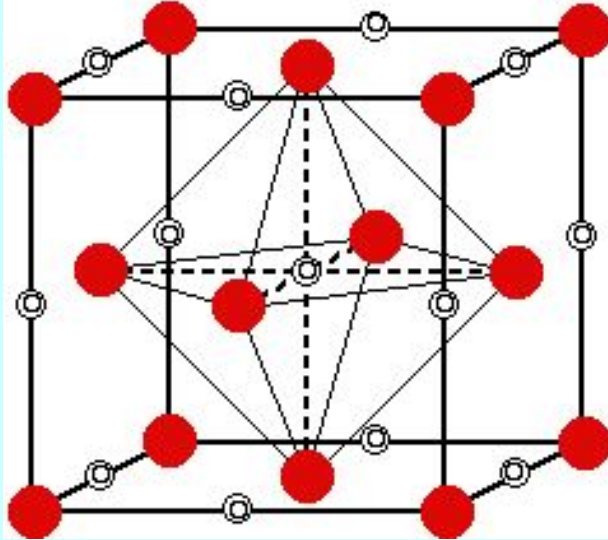
N cp atoms in lattice cell

N Octahedral Holes

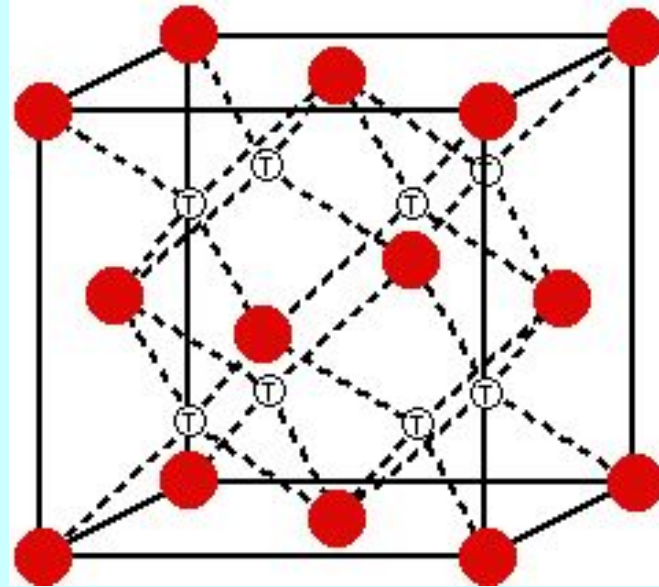
$2N$ Tetrahedral Holes



Two Types of Voids (Holes)

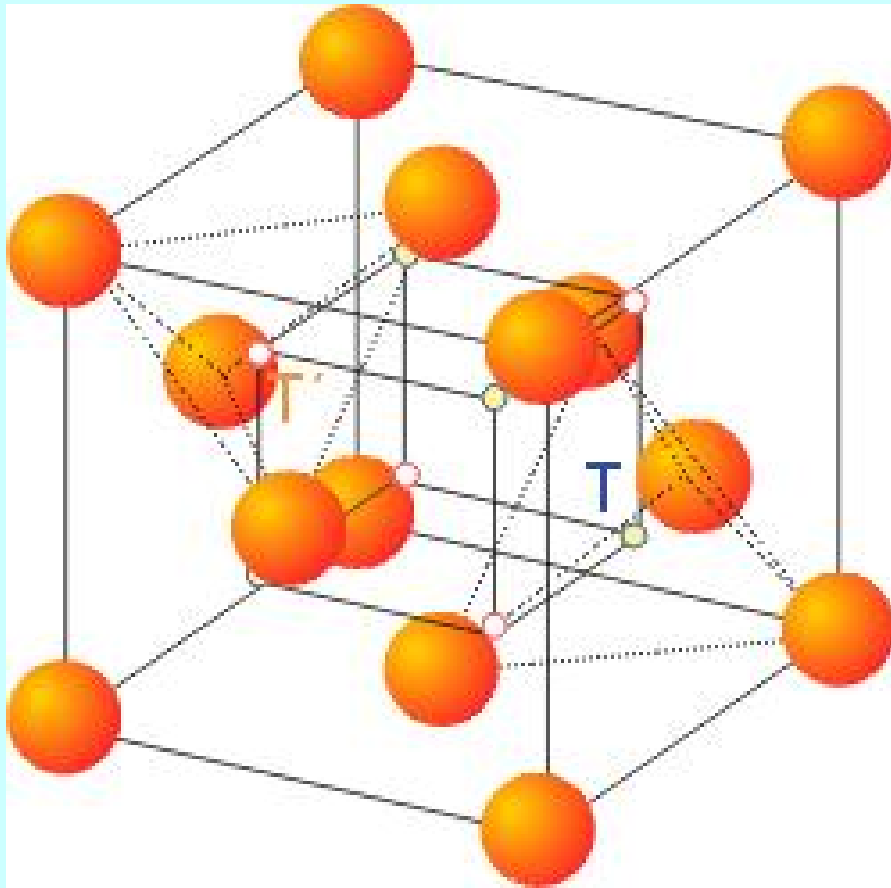


Octahedral Holes



Tetrahedral Holes

Tetrahedral Holes ($2N$)



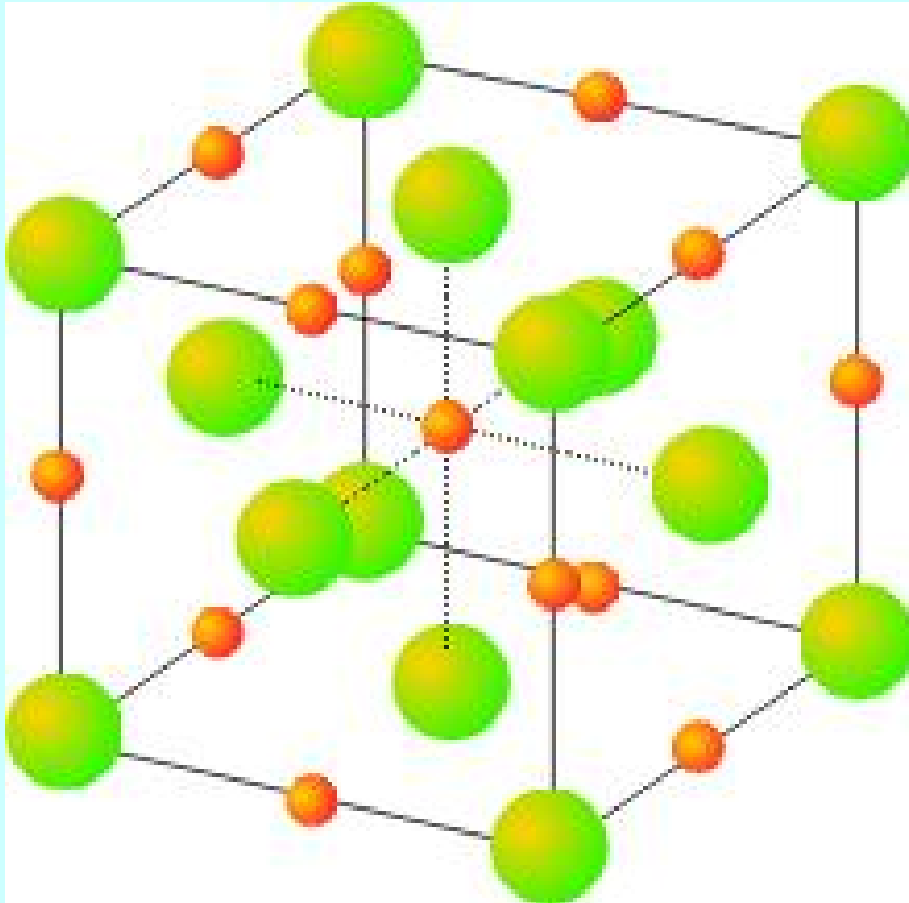
$$Z = \underline{4}$$

number of atoms in the
cell (N)

$$N = \underline{8}$$

number of tetrahedral
holes ($2N$)

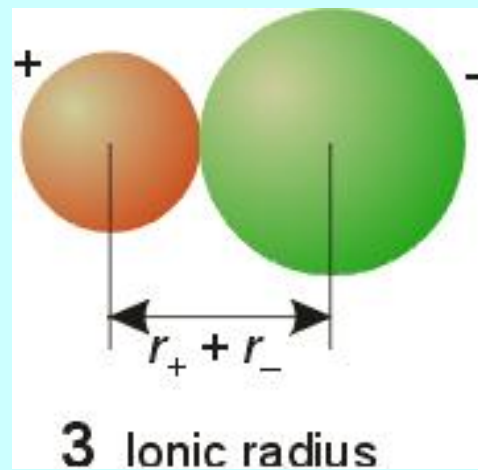
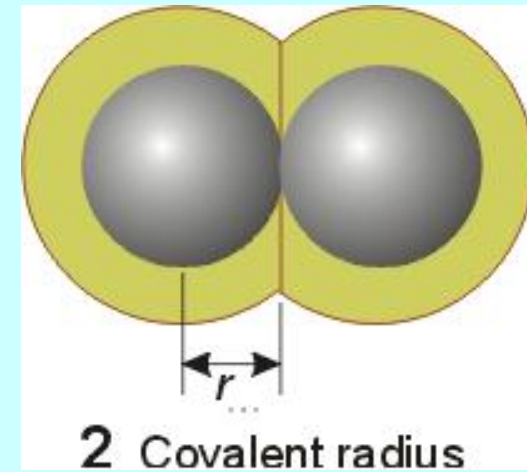
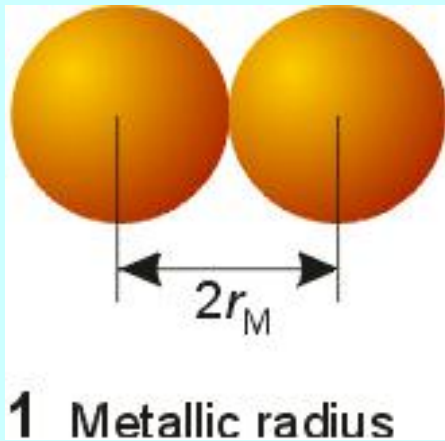
Octahedral Holes (N)



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

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

Different Types of Radii

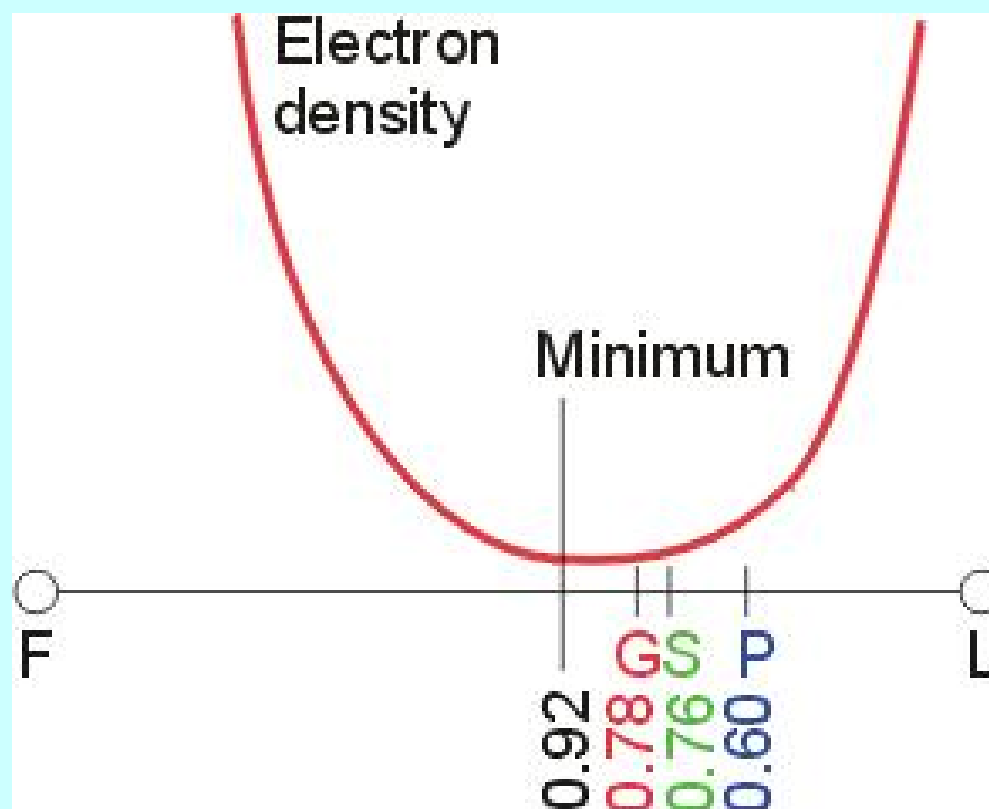


Variation of the electron density along the Li – F axis in LiF

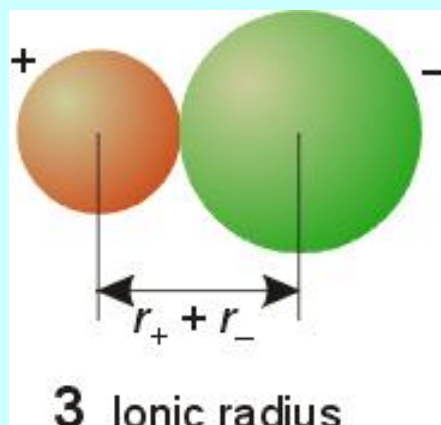
P – Pauling radius

G – Goldschmidt radius

S – Shannon radius.



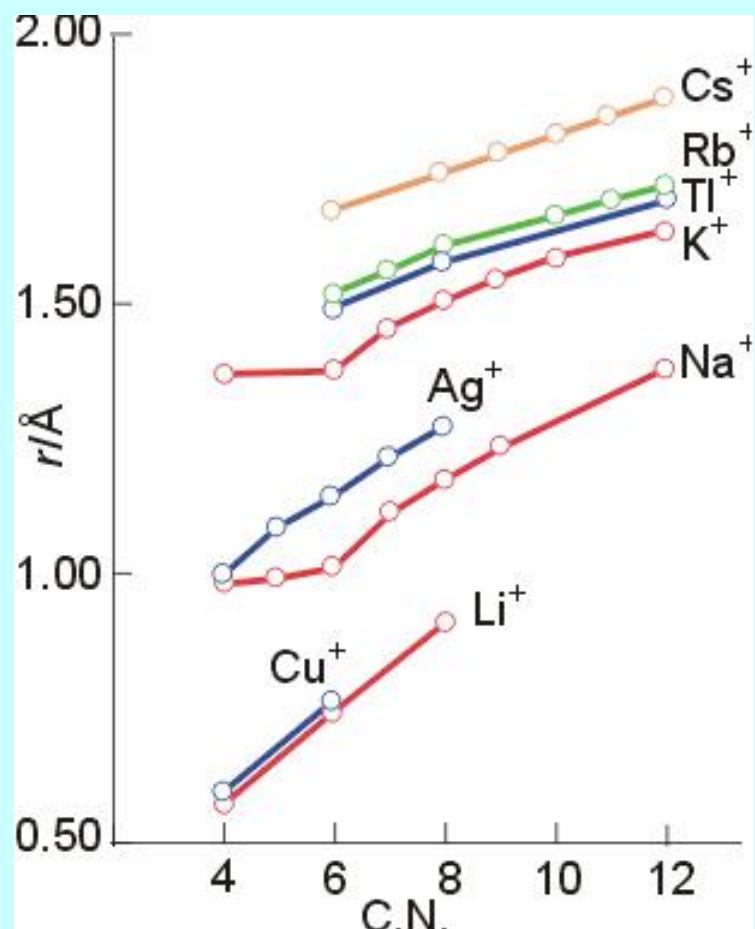
Variation of ionic radii with coordination number



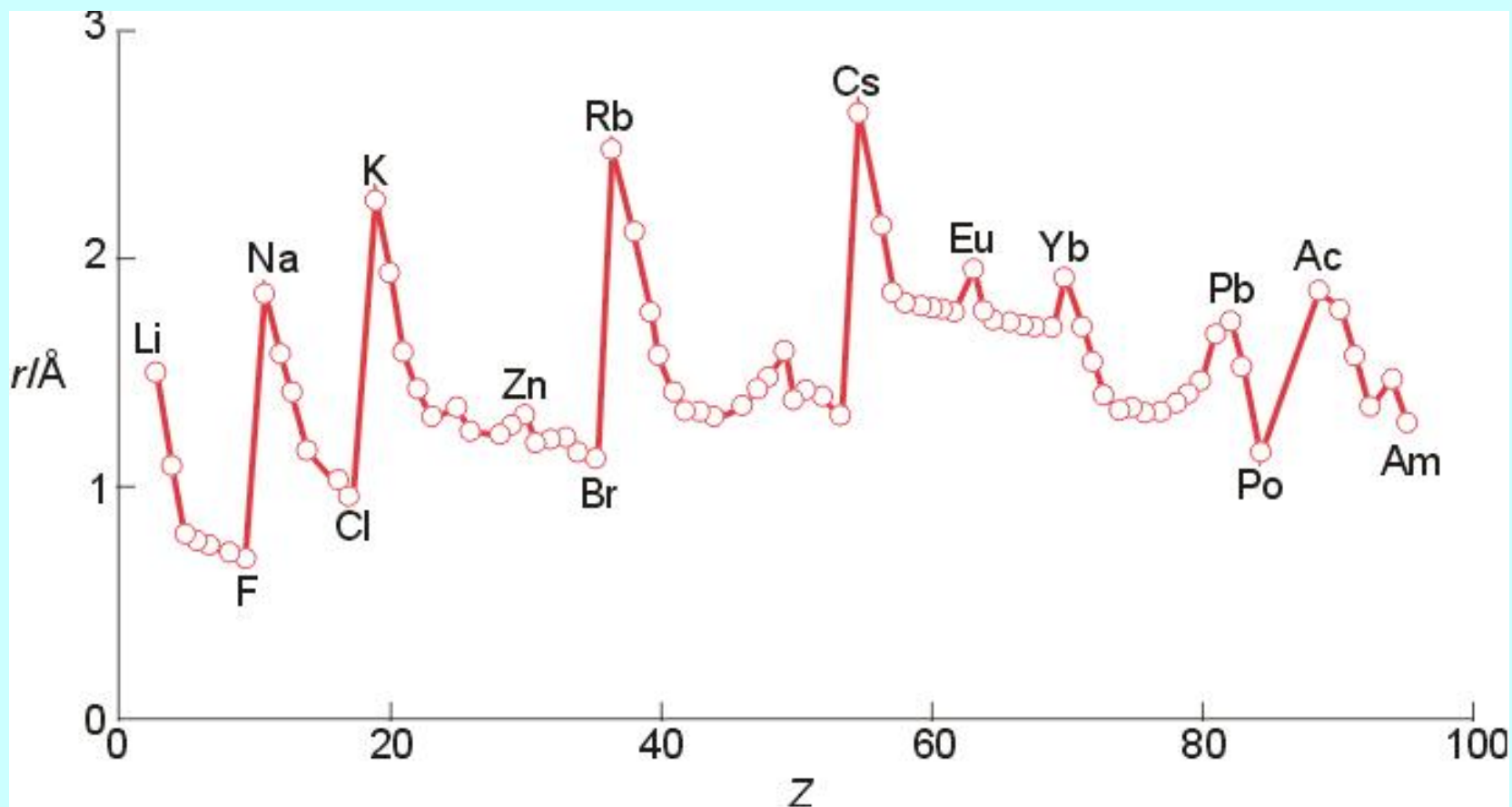
The radius of one ion was fixed to a reasonable value

($r(\text{O}^{2-}) = 140 \text{ pm}$) (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

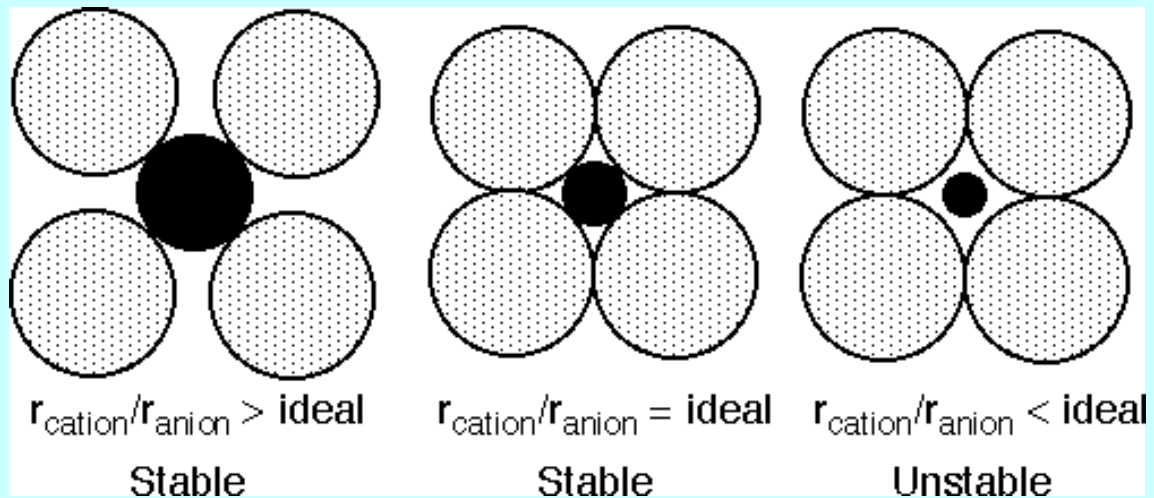
**3. Ionic radii increase with increasing coordination number
the higher the CN the bigger the ion**

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

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

**6. Frequently used for rationalization of structures:
„radius ratio“ $r(\text{cation})/r(\text{anion}) (< 1)$**

Cation/anion Radius Ratio

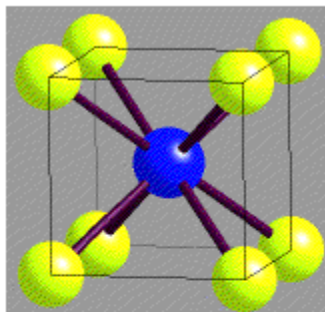


CN	r/R
12 – hcp/ccp	1.00 (substitution)
8 – cubic	0.732 – 1.00
6 – octahedral	0.414 – 0.732
4 – tetrahedral	0.225 – 0.414

optimal radius
ratio for
given CN
ions are in touch

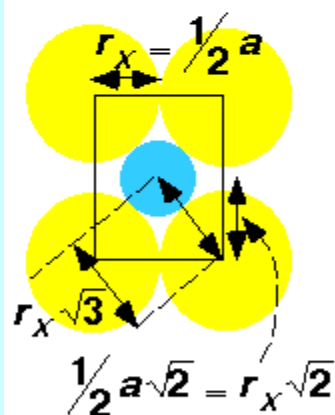
Limiting Radius Ratios

CsCl 8:8



unit cell

cell side a

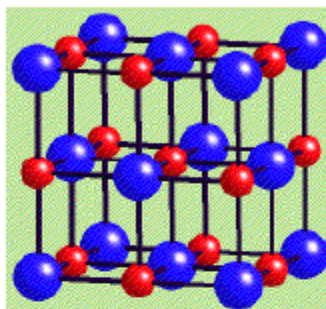


$$r_M + r_X = r_X \sqrt{3}$$

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

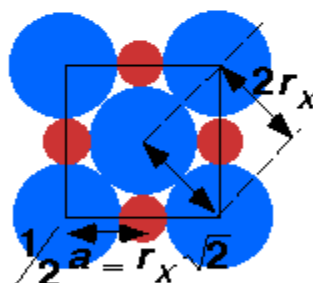
$$= 0.732$$

NaCl 6:6



unit cell

face diagonal $a\sqrt{2}$

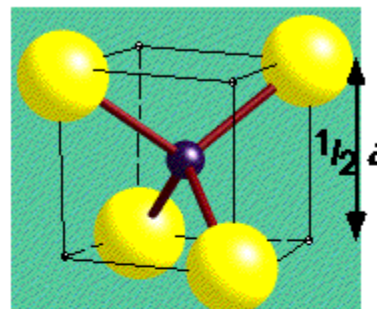


$$r_M + r_X = r_X \sqrt{2}$$

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

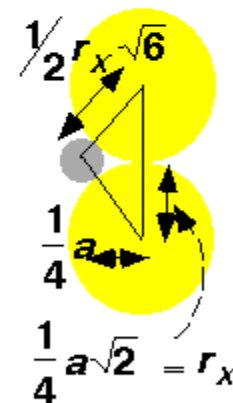
$$= 0.414$$

ZnS 4:4



1/8th unit cell

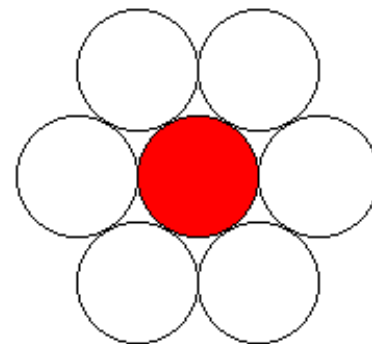
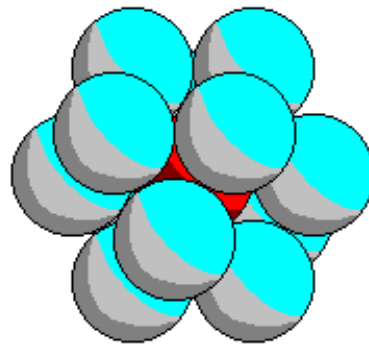
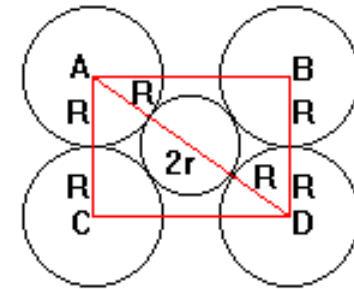
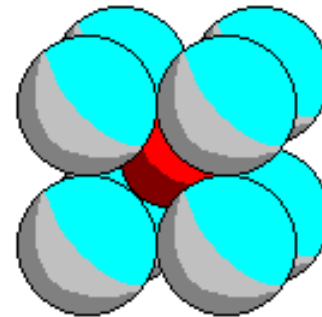
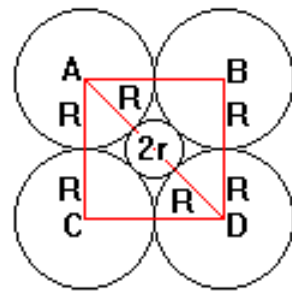
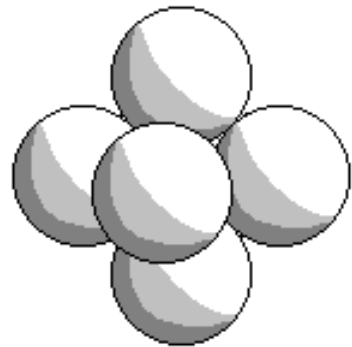
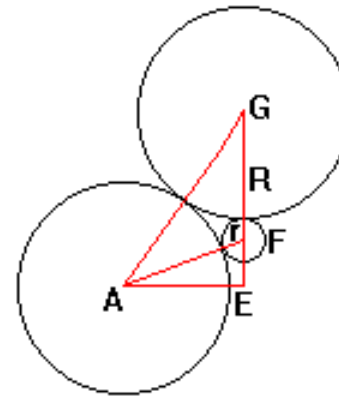
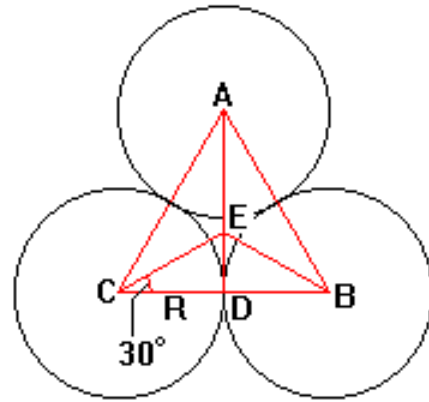
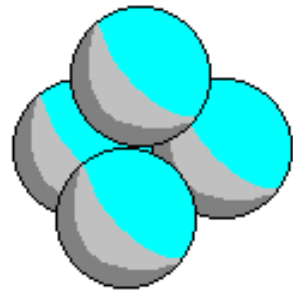
body diagonal $a\sqrt{3}$



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

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

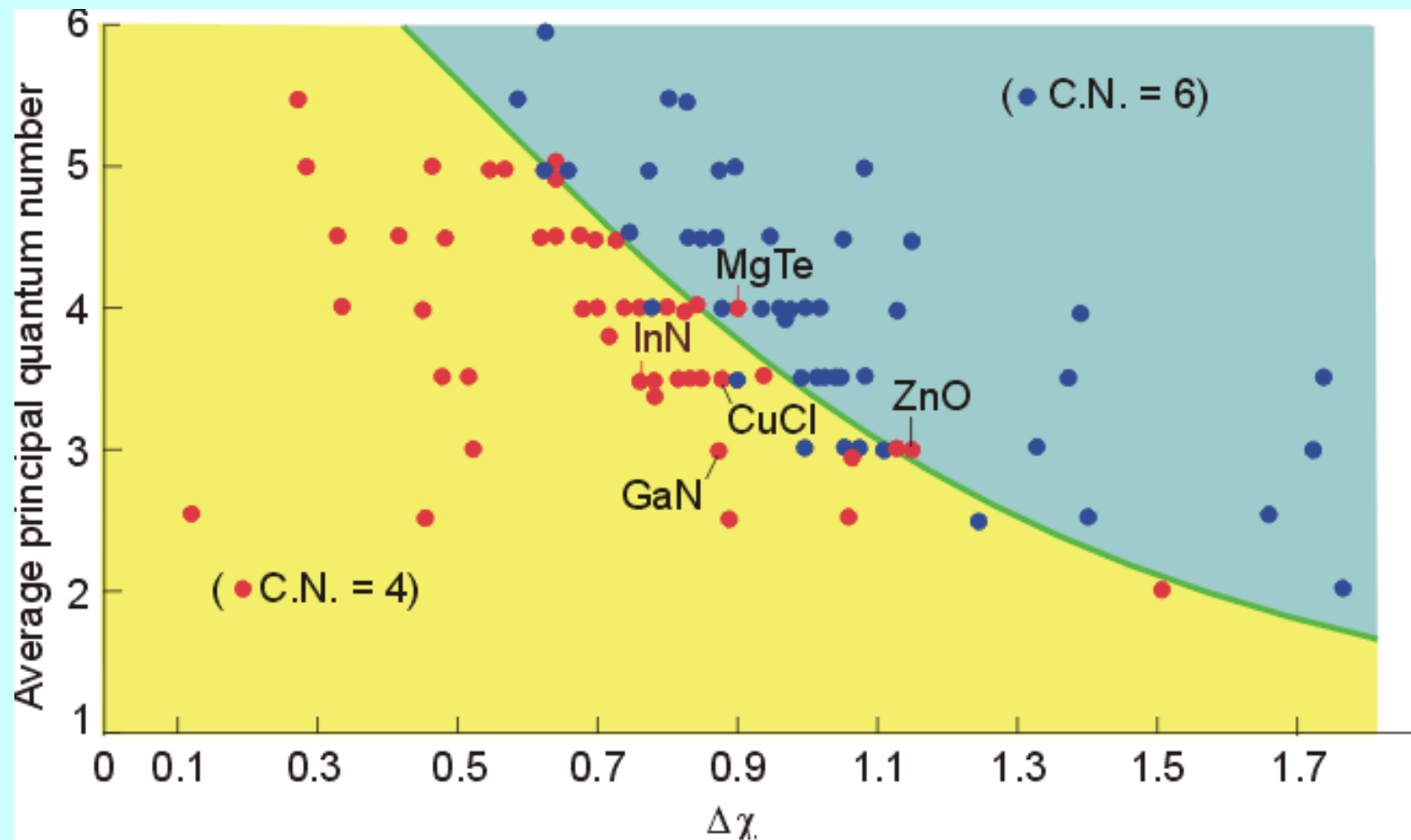
$$= 0.225$$



Structure Map

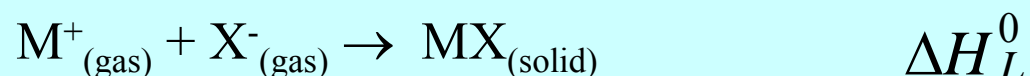
Dependence of the structure type (coordination number) on the electronegativity difference and the average principal quantum number (size and polarizability)

AB compounds



Lattice Enthalpy

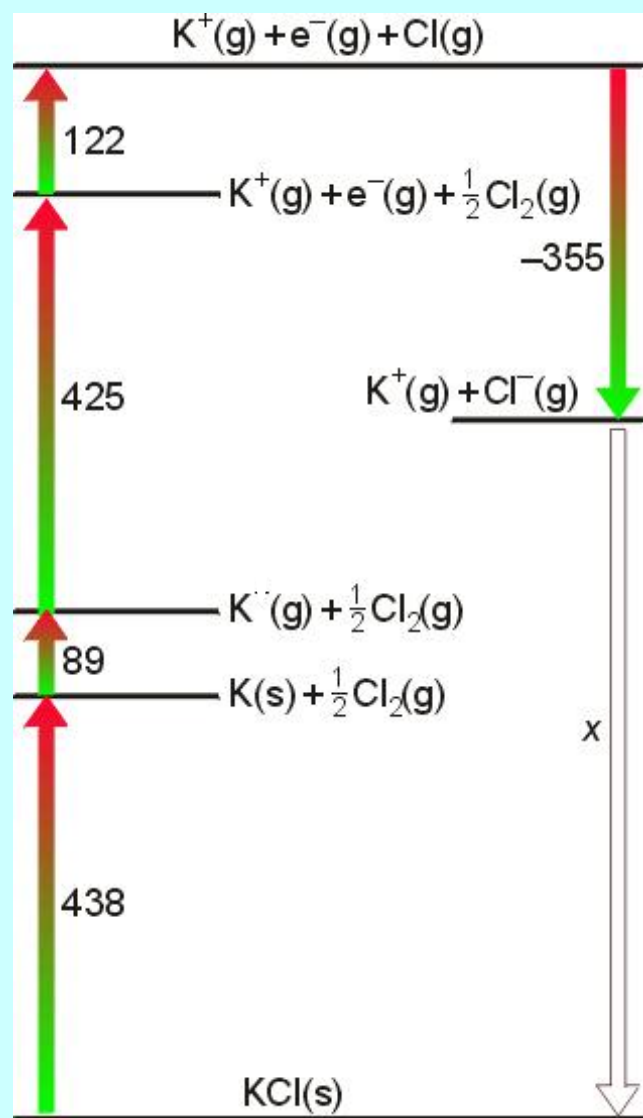
The lattice enthalpy change ΔH_L^0 is the standard molar enthalpy change for the following process:



Because the formation of a solid from a „gas of ions“ is always exothermic lattice enthalpies (defined in this way) are usually negative.

If entropy considerations are neglected the most stable crystal structure of a given compound is the one with the highest lattice enthalpy.

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



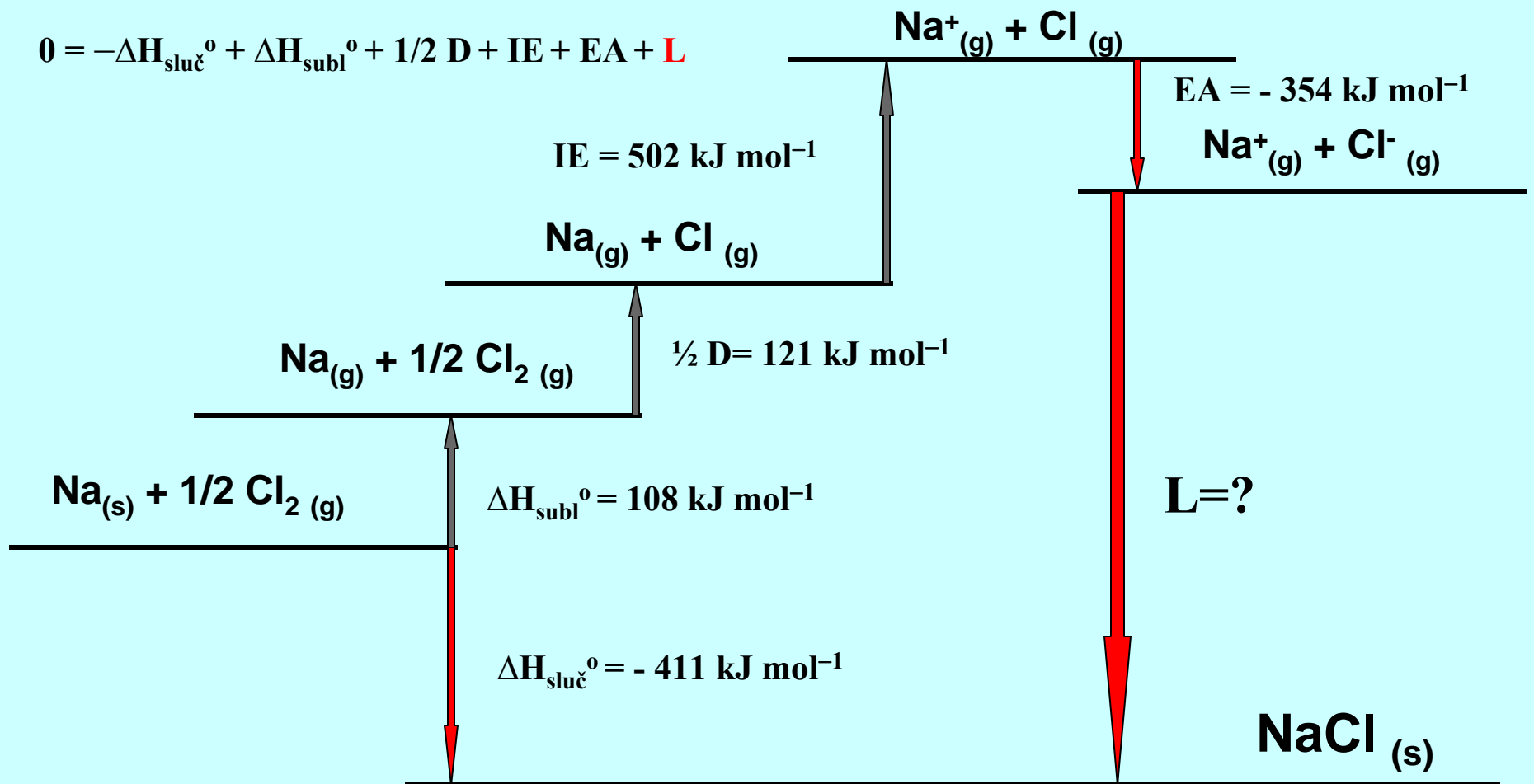
A Born-Haber cycle for KCl

(all enthalpies: kJ mol⁻¹ for normal conditions → standard enthalpies)

standard enthalpies of

- formation: 438
- sublimation: +89 (K)
- ionization: + 425 (K)
- atomization: +244 (Cl₂)
- electron affinity: -355 (Cl)
- lattice enthalpy: x

Born-Haber cycle

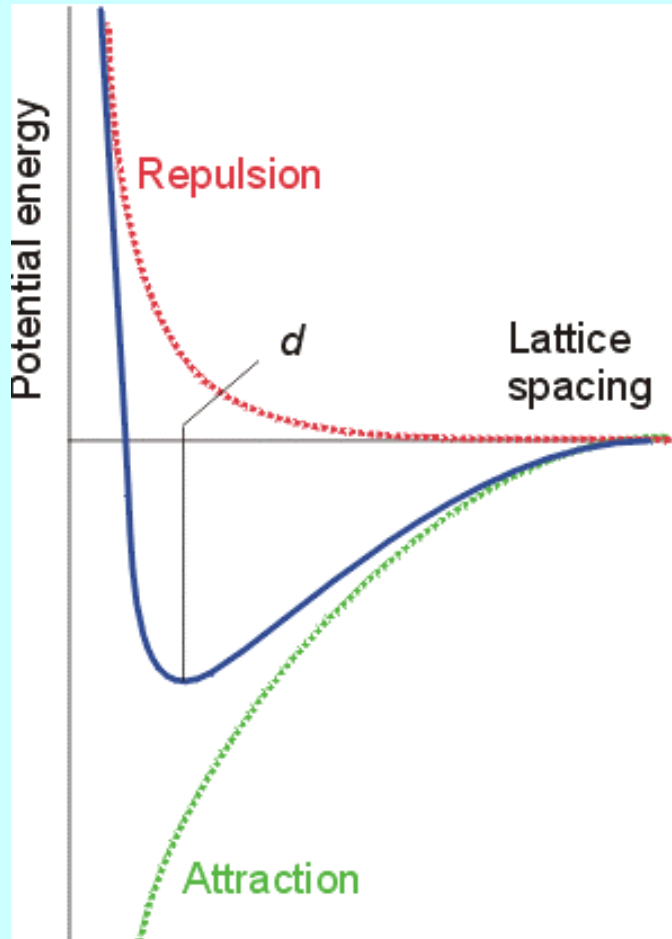


$$0 = 411 + 108 + 121 + 502 + (-354) + \mathbf{L}$$

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

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

Lattice Enthalpy



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

One ion pair

$$E_{\text{coul}} = (1/4\pi\epsilon_0) z_A z_B / d$$

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

n = Born exponent
(experimental measurement of compressibility)

Lattice Enthalpy

1 mol of ions

$$E_{\text{coul}} = N_A (e^2 / 4 \pi \epsilon_0) (z_A z_B / d) A$$

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

$$L = N_A A \frac{z_A z_B e^2}{4 \pi \epsilon_0 d} + N_A \frac{B}{d^n}$$

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

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

Calculation of lattice enthalpies

Coulombic contributions to lattice enthalpies

$$V_{AB} = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_{AB}} N$$

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

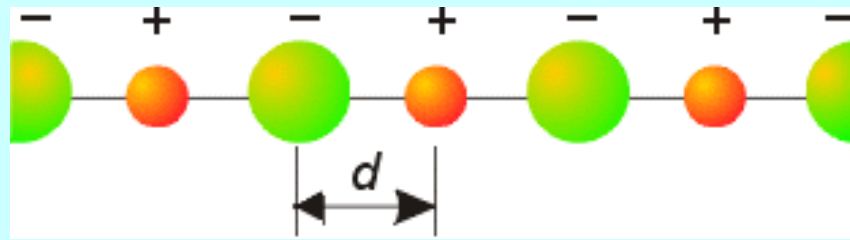
e: elementary charge

ϵ_0 : dielectric constant (vacuum permittivity)

r_{AB} : shortest distance between cation and anion

Madelung Constant

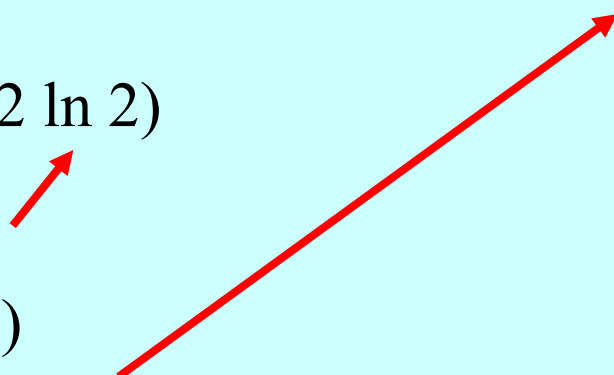
Count all interactions in the crystal lattice



$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + \dots]$$

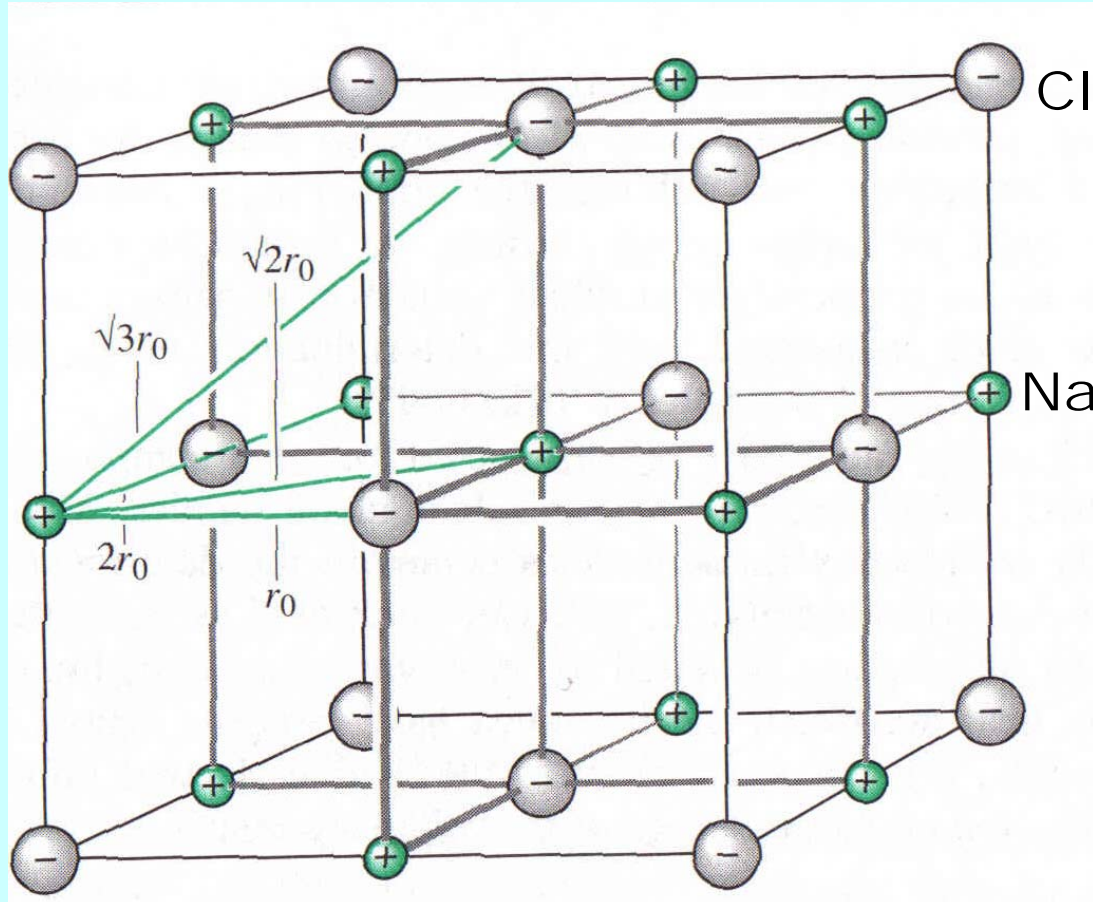
$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * (2 \ln 2)$$

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



Two red arrows originate from the text. One arrow points from the phrase 'sum of convergent series' to the term '(2 ln 2)' in the second equation. The other arrow points from the same phrase to the entire second equation.

Calculation of the Madelung constant



3D ionic solids:
Coulomb attraction and
repulsion

Madelung constants:

CsCl: 1.763

NaCl: 1.748

ZnS: 1.641 (wurtzite)

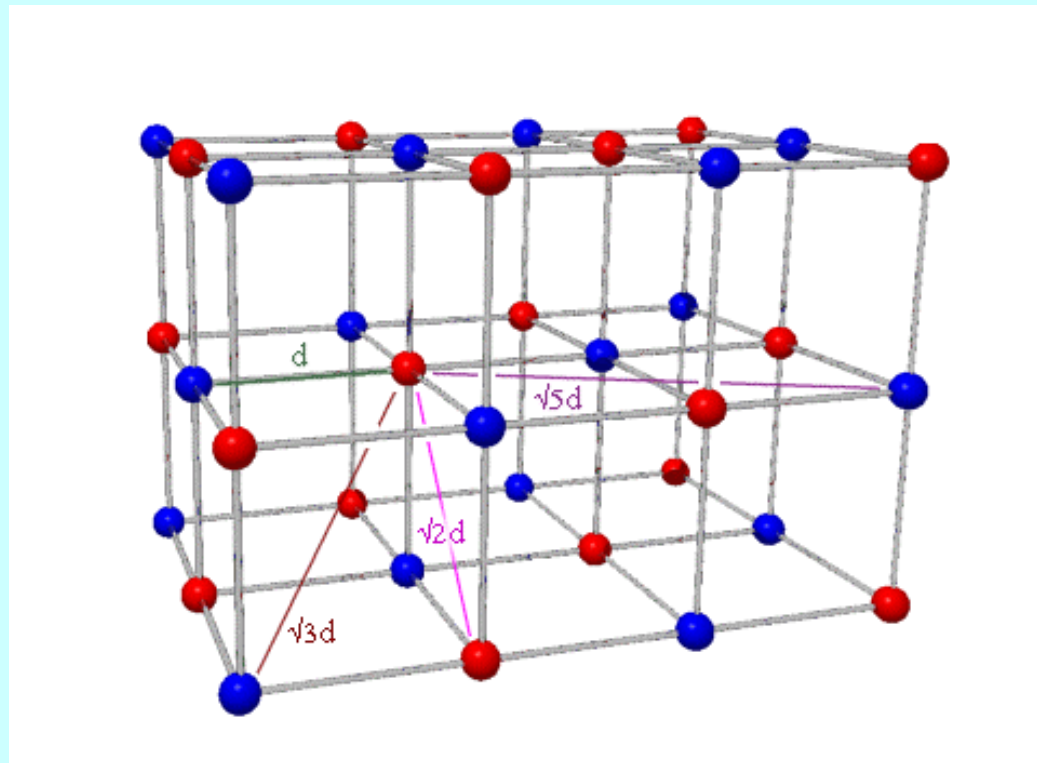
ZnS: 1.638 (sphalerite)

ion pair: 1.0000 (!)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \dots = 1.748\dots \text{ (NaCl)}$$

(infinite summation)

Madelung constant for NaCl



$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) \dots]$$

convergent series

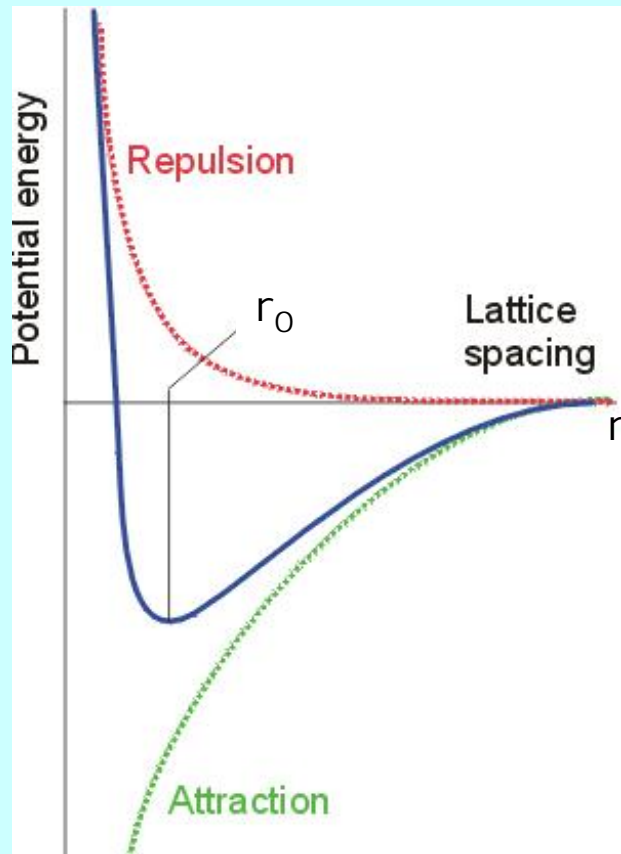
$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * A$$

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:

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

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

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

(set first derivative of the sum to zero)

$$\Delta H_L^0 = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_0} N \left(1 - \frac{1}{n}\right)$$

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

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

Most important advantage of the Kapustinski equation

- it is possible to apply the equation for lattice calculations of crystals with polyatomic ions (e.g. KNO_3 , $(\text{NH}_4)_2\text{SO}_4$...).
- a set of „thermochemical radii“ was derived for further calculations of lattice enthalpies

Table 1.13 Thermochemical radii of polyatomic ions*

<i>Ion</i>	<i>pm</i>	<i>Ion</i>	<i>pm</i>	<i>Ion</i>	<i>pm</i>
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

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 d} \left(1 + \frac{1}{n} \right)$$

Born – Mayer

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 d} \left(1 - \frac{d^*}{d} \right)$$

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

$$d^* = 0.345 \text{ \AA}$$

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	<i>M</i>	CN	stoichm	<i>M / v</i>
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 ₂ O ₃	4.172	(6,4)	A ₂ B ₃	0.834

$v =$ the number of ions in one formula unit

Lattice Enthalpy of NaCl

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

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

Lattice Enthalpy consists of ionic and covalent contribution

Applications of lattice enthalpy calculations:

- thermal stabilities of ionic solids
- stabilities of oxidation states of cations
- Solubility of salts in water
- calculations of electron affinity data
- lattice enthalpies and stabilities of „non existent“ compounds

Pauling's Rules

Five principles which could be used to determine the structures of complex ionic/covalent crystals

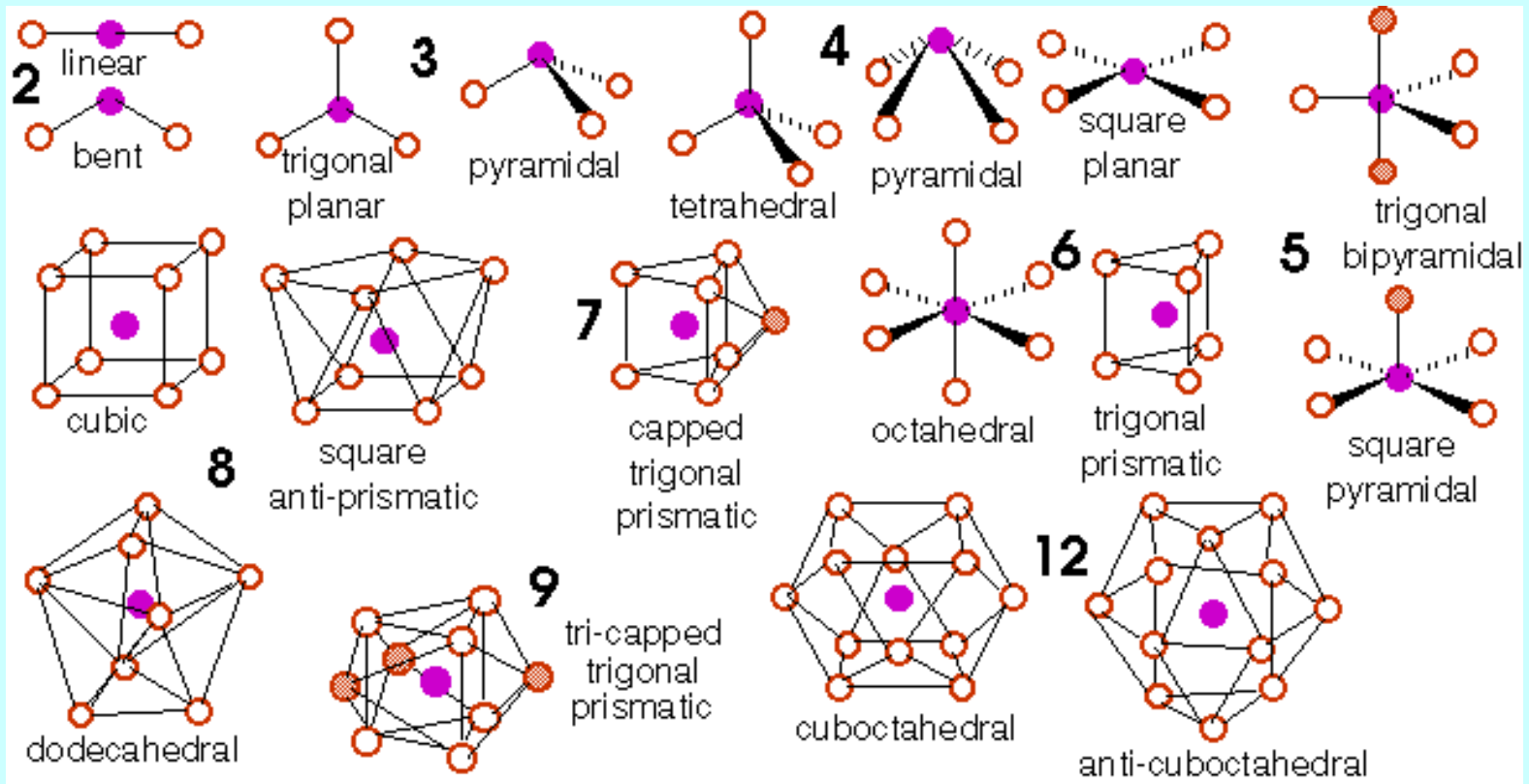
Pauling's Rule no. 1 Coordination Polyhedra

A coordinated polyhedron of anions is formed about each cation.

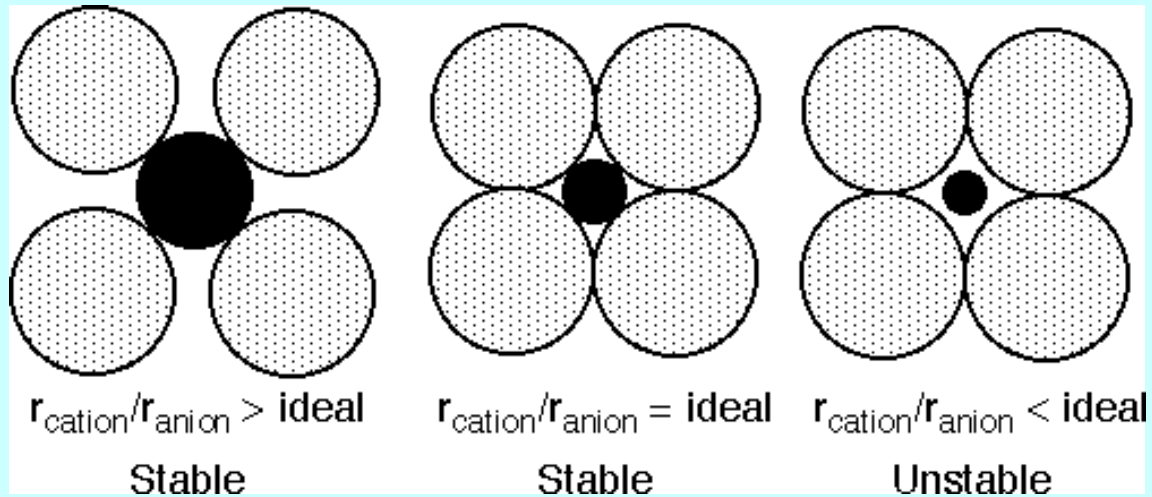
Cation-Anion distance is determined by sums of ionic radii.

Cation coordination environment is determined by radius ratio.

Coordination Polyhedra



Cation/Anion Radius Ratio



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

Ionic Radii

R.D. Shannon and C.T. Prewitt, Acta Cryst. B25, 925-945 (1969)

R.D. Shannon, Acta Cryst. A32, 751-767 (1976)

As the coordination number (CN) increases, the Ionic Radius increases

Sr²⁺

CN	Radius, Å
6	1.32
8	1.40
9	1.45
10	1.50
12	1.58

As the oxidation state increases, cations get smaller
(6-fold coordination, in Å)

Mn ²⁺	0.810
Mn ³⁺	0.785
Mn ⁴⁺	0.670

Ti ²⁺	1.000
Ti ³⁺	0.810
Ti ⁴⁺	0.745

Ionic Radii

The radius increases down a group in the periodic table.

The exception - 4d/5d series in the transition metals - the lanthanide contraction

(6-fold coordination, in Å)

Al³⁺ 0.675

Ga³⁺ 0.760

In³⁺ 0.940

Tl³⁺ 1.025

Ti⁴⁺ 0.745

Zr⁴⁺ 0.86

Hf⁴⁺ 0.85

Right to left across the periodic table the radius decreases

(6 coordinate radii, in Å)

La³⁺ 1.172

Nd³⁺ 1.123

Gd³⁺ 1.078

Lu³⁺ 1.001

Pauling's Rules

Pauling's Rule no. 2 Bond Strength

The bond valence sum of each ion equals its oxidation state.

The valence of an ion (V_i , equal to the oxidation state of the ion) is equal to a sum of the valences of its bonds (s_{ij}).

In a stable ionic structure the charge on an ion is balanced by the sum of electrostatic bond strengths (s_{ij}) to the ions in its coordination polyhedron.

TiO₂ (Rutile) Ti - oxidation state of +4, coordinated to 6 oxygens.

$$V_{\text{Ti}} = 4 = 6 (s_{ij}) \quad s_{ij} = 2/3$$

The bond valence of oxygen, coordinated by 3 Ti atoms

$$V_{\text{O}} = 3 (s_{ij}) = 3 (-2/3) = -2$$

Each bond has a valence of s_{ij} with respect to the cation and $-s_{ij}$ with respect to the anion.

Bond Strength

Correlation of the valence of a bond s_{ij} with the bond distance d_{ij} .

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

$b = 0.37$, R_{ij} is determined empirically from structures where bond distances and ideal valences are accurately known.

Tables of R_{ij} values for given bonding pairs (i.e. Nb-O, Cr-N, Mg-F, etc.) have been calculated, just as tables of ionic radii are available.

Use of the bond valence concept

A) To check experimentally determined structures for correctness, or bonding instabilities

B) To predict new structures

C) To locate light atoms such as hydrogen or Li ion, which are hard to find experimentally

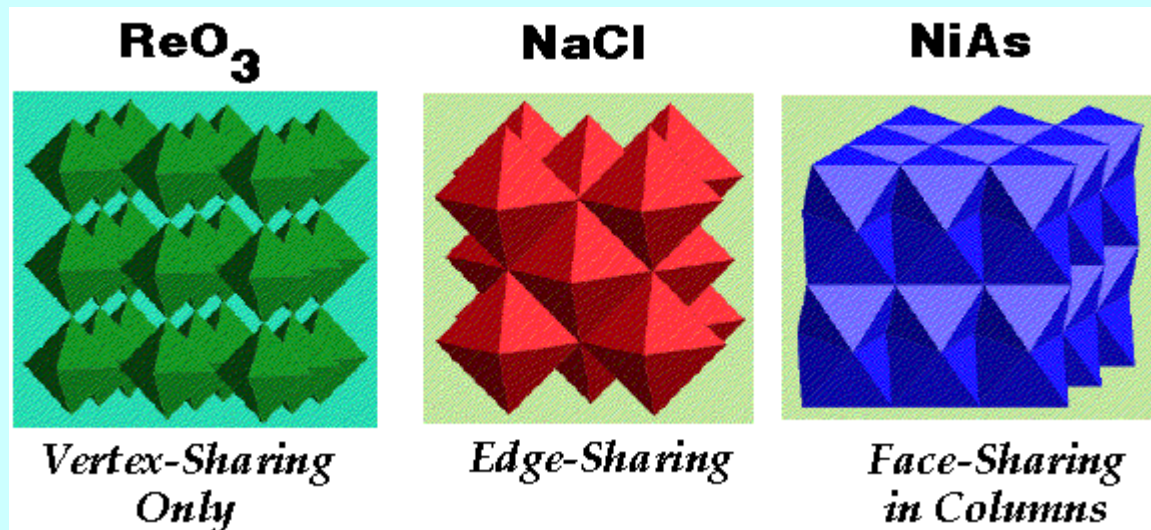
D) To determine ordering of ions which are hard to differentiate experimentally, such as Al^{3+} and Si^{4+} , or O^{2-} and F^-

Pauling's Rules

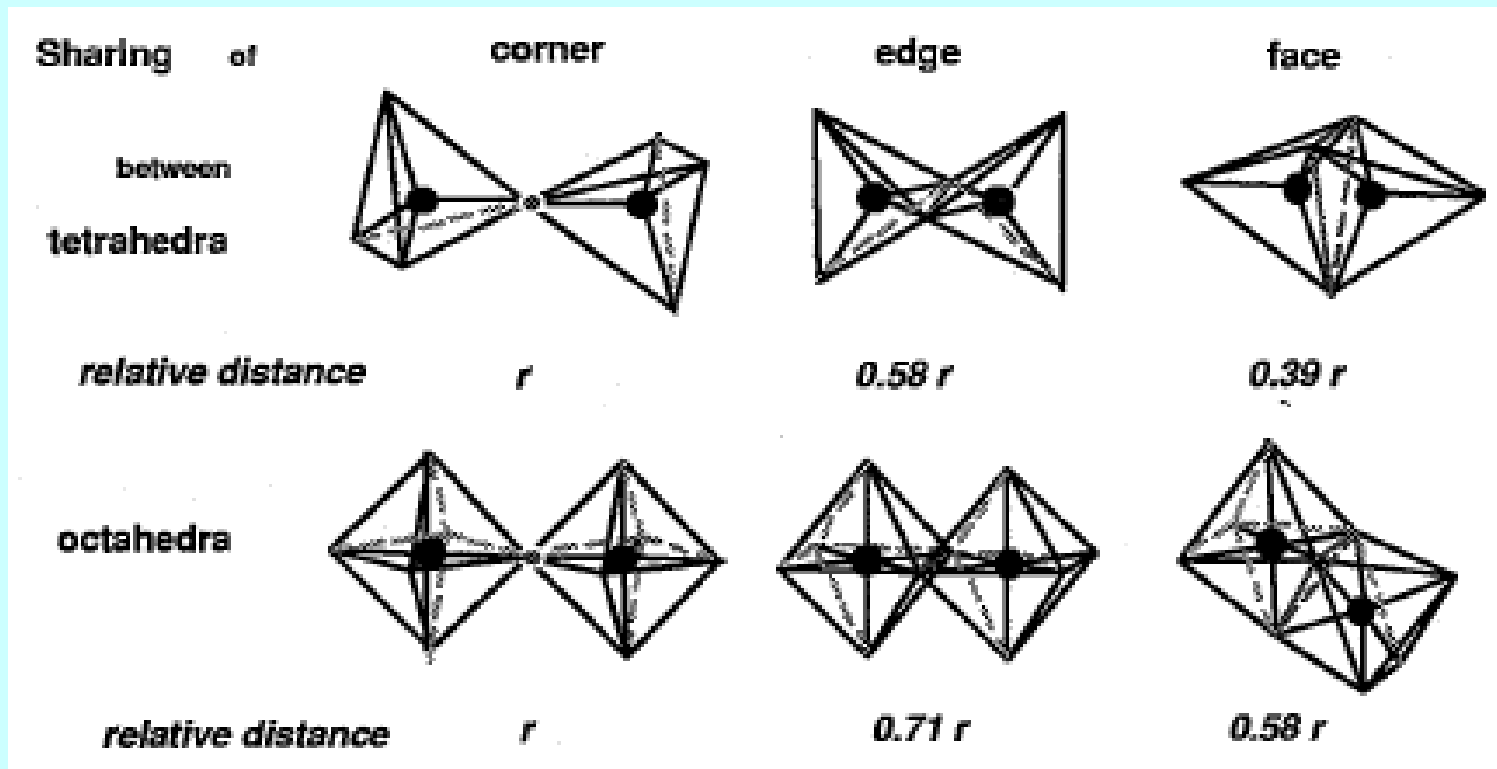
Pauling's Rule no. 3 Polyhedral Linking

The presence of shared edges, and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small coordination number.

Avoid shared polyhedral edges and/or faces.



Polyhedral Linking



The Coulombic interactions - maximize the cation-anion interactions (attractive), and minimize the anion-anion and cation-cation interactions (repulsive).

The cation-anion interactions are maximized by increasing the coordination number and decreasing the cation-anion distance. If ions too close - electron-electron repulsions.

The cation-cation distances as a function of the cation-anion distance (M-X)

Polyhedron/Sharing	Corner	Edge	Face
2 Tetrahedra	2 M-X	1.16 MX	0.67 MX
2 Octahedra	2 M-X	1.41 MX	1.16 MX

The cation-cation distance decreases, (the Coulomb repulsion increases) as the

- degree of sharing increases (corner < edge < face)
- CN decreases (cubic < octahedral < tetrahedral)
- cation oxidation state increases (this leads to a stronger Coulomb repulsion)

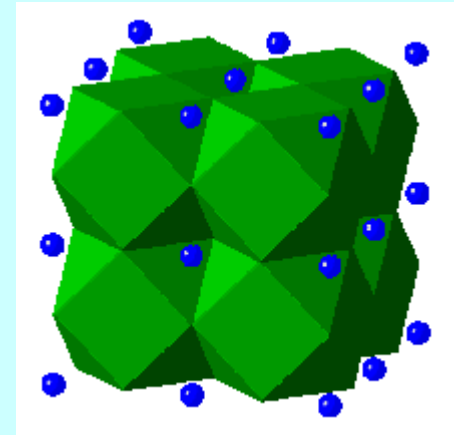
Pauling's Rules

Pauling's Rule no. 4 Cation Evasion

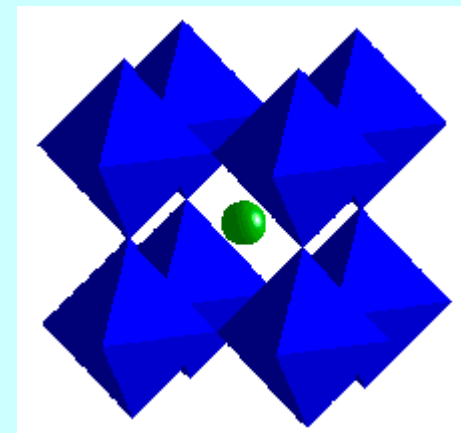
In a crystal containing different cations those with large valence and small coord. number tend not to share anions.

Perovskite, CaTiO_3

Ca^{II} 12-coordinate CaO_{12} cuboctahedra share **FACES**



Ti^{IV} 6-coordinate TiO_6 octahedra share only **VERTICES**



Pauling's Rules

Pauling's Rule no. 5 Environmental Homogeneity the rule of parsimony

The number of chemically different coordination environments for a given ion tends to be small.

Once the optimal chemical environment for an ion is found, if possible all ions of that type should have the same environment.

Characteristic Structures of Solids = Structure Types

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

Fluorite CaF₂ BaCl₂, K₂O, PbO₂ ...

Lithium bismutide Li₃Bi

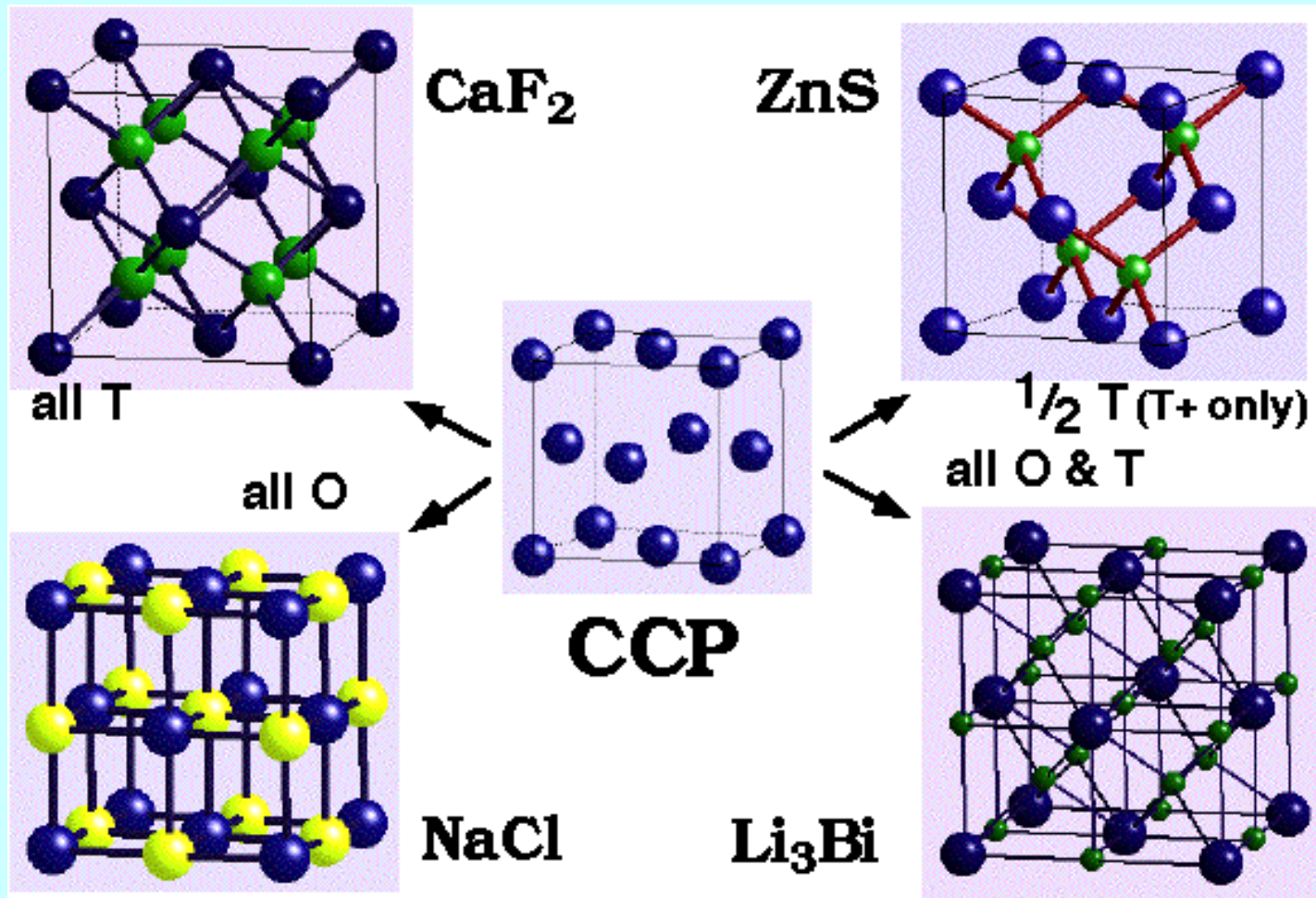
Sphalerite (zinc blende) ZnS CuCl, HgS, GaAs ...

Nickel arsenide NiAs FeS, PtSn, CoS ...

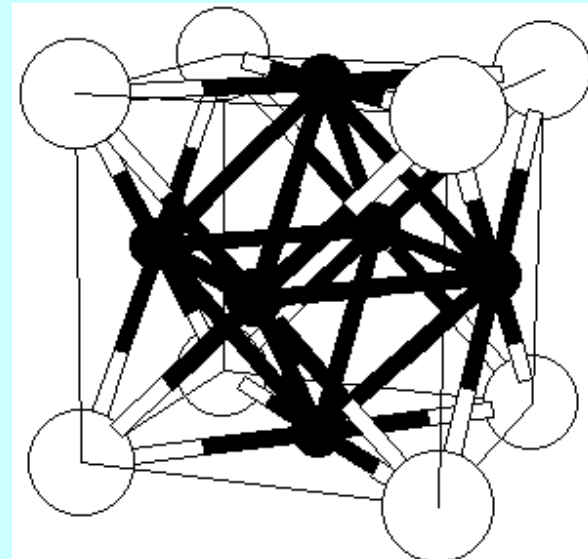
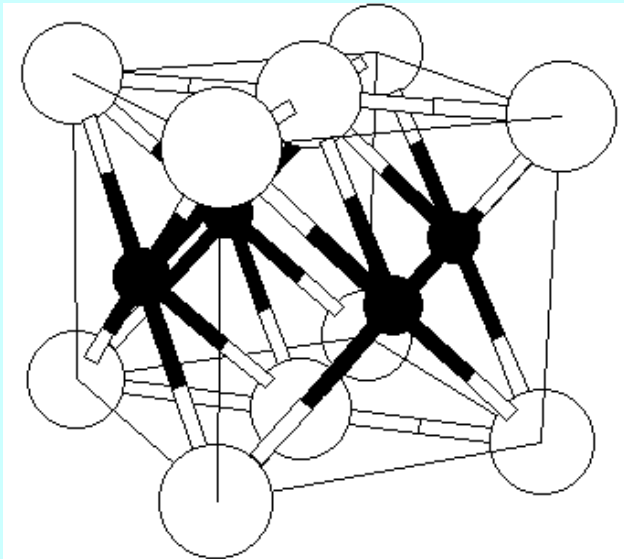
Wurtzite ZnS ZnO, MnS, SiC

Rhenium diboride ReB₂

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

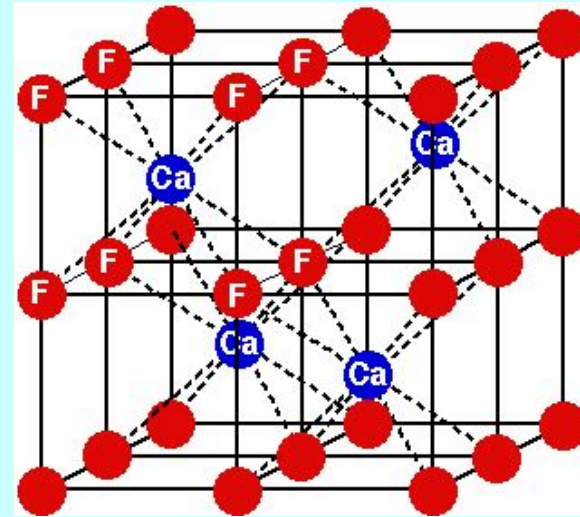
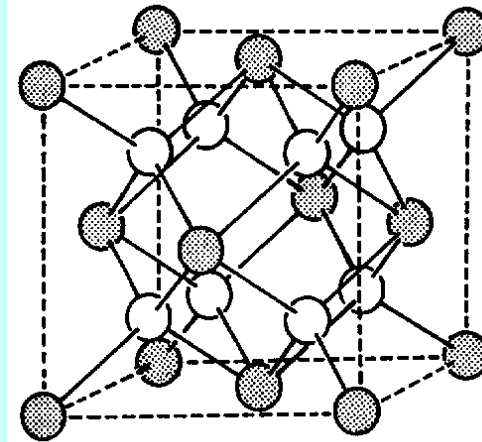
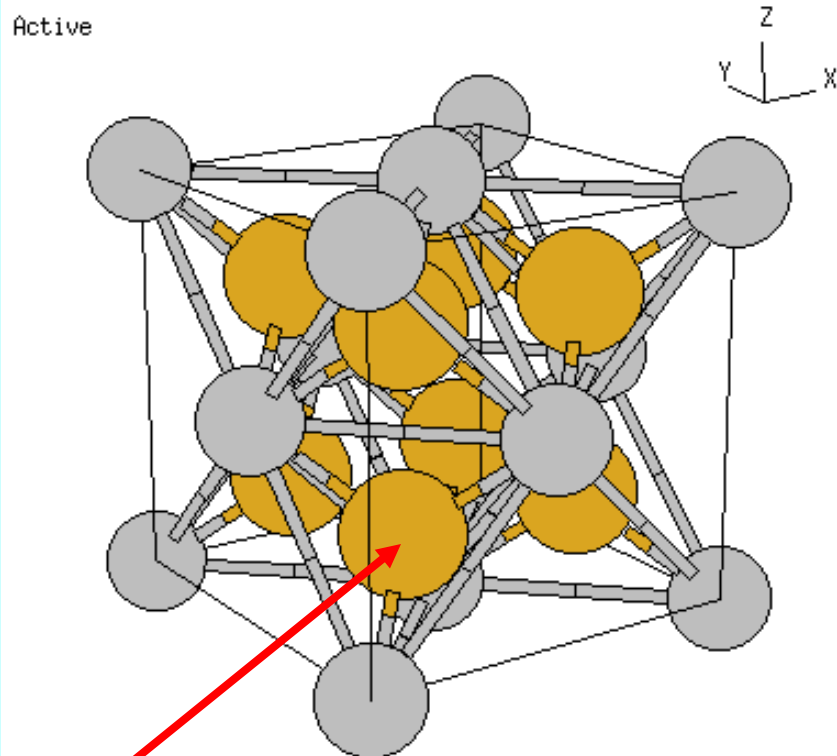
<u>o/t</u>	fcc(ccp)	hcp
all <u>o</u> ct.	NaCl	NiAs
all <u>t</u> etr.	CaF ₂	ReB ₂
<u>o/t</u> (all)	Li ₃ Bi	(Na ₃ As) (!) problem
½ <u>t</u>	sphalerite (ZnS)	wurtzite (ZnS)
½ <u>o</u>	CdCl ₂	CdI ₂

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).

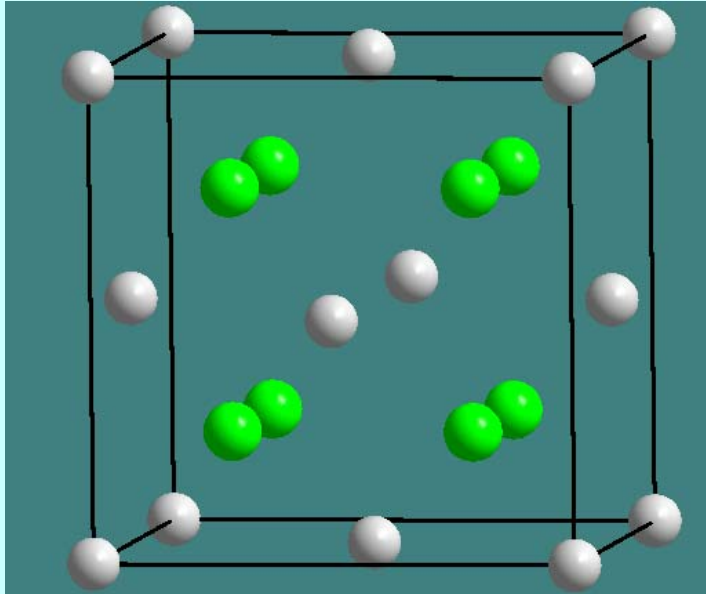
Fluorite (CaF_2 , antiferroite Li_2O)



F / Li

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

Fluorite structures (CaF_2 , antifluorite Li_2O)



Oxides: Na_2O , K_2O , UO_2 ,
 ZrO_2 , ThO_2

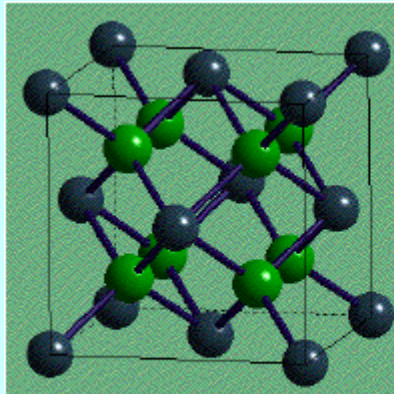
**alkali metal sulfides,
selenides and tellurides**

$\text{K}_2[\text{PtCl}_6]$, $(\text{NH}_4)_2[\text{PtCl}_6]$,
 $\text{Cs}_2[\text{SiF}_6]$,
 $[\text{Fe}(\text{NH}_3)_6][\text{TaF}_6]_2$.

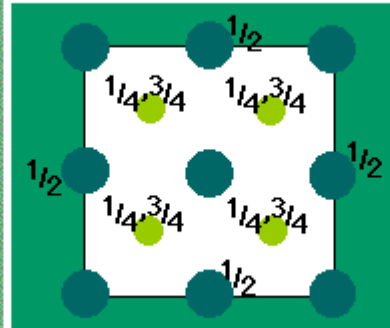
CaF_2 , SrF_2 , SrCl_2 , BaF_2 , BaCl_2 , CdF_2 , HgF_2 , EuF_2 , $\beta\text{-PbF}_2$, PbO_2

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

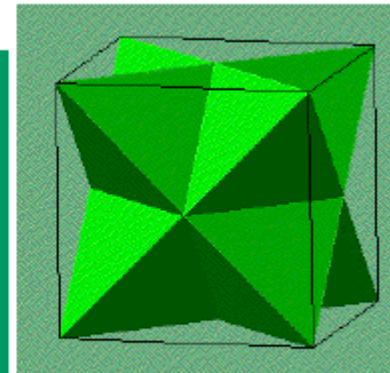
Fluorite structures (CaF_2 , antifluorite Li_2O)



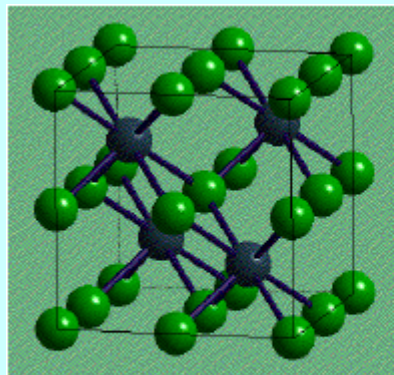
Fluorite A-cell



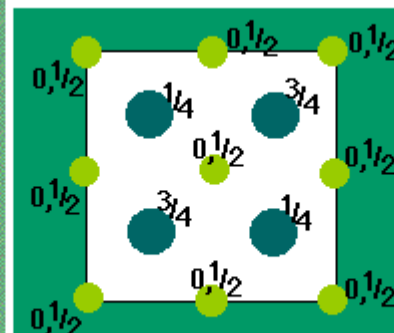
Plan view



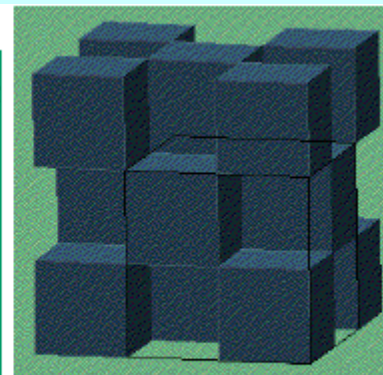
FCa_4 Tetrahedra



Fluorite B-cell

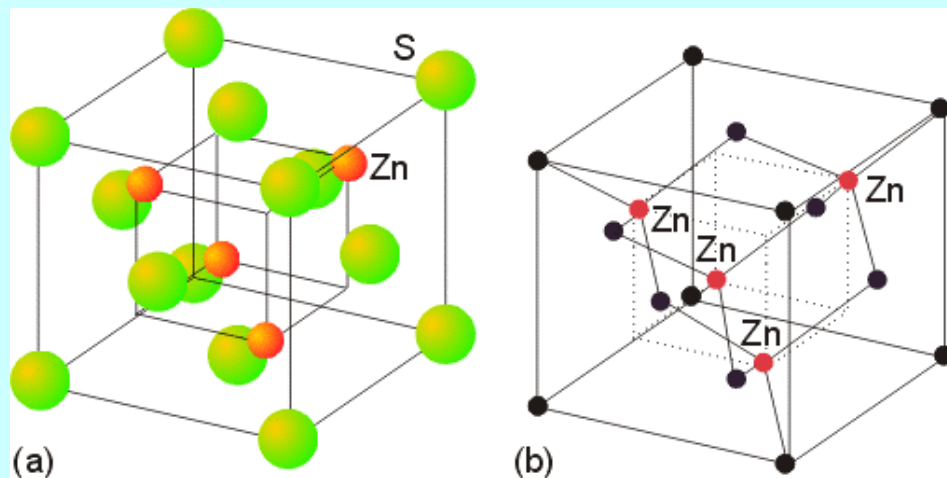
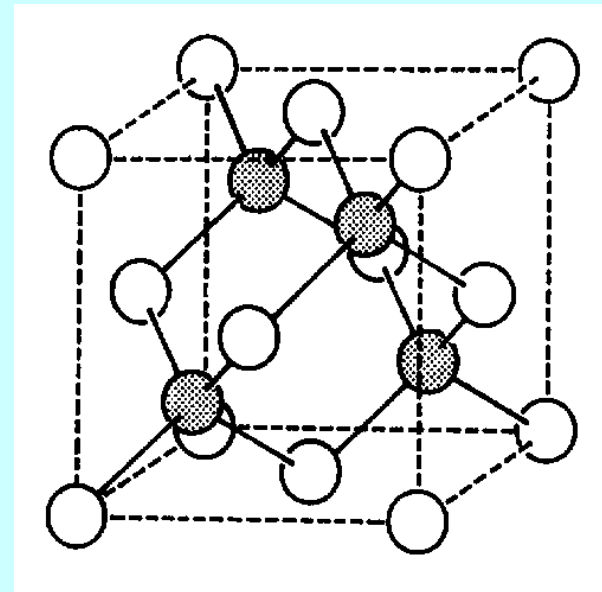
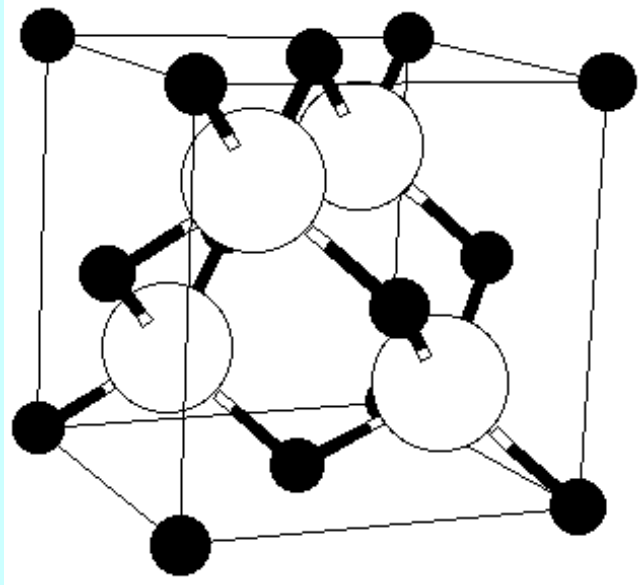


Plan view



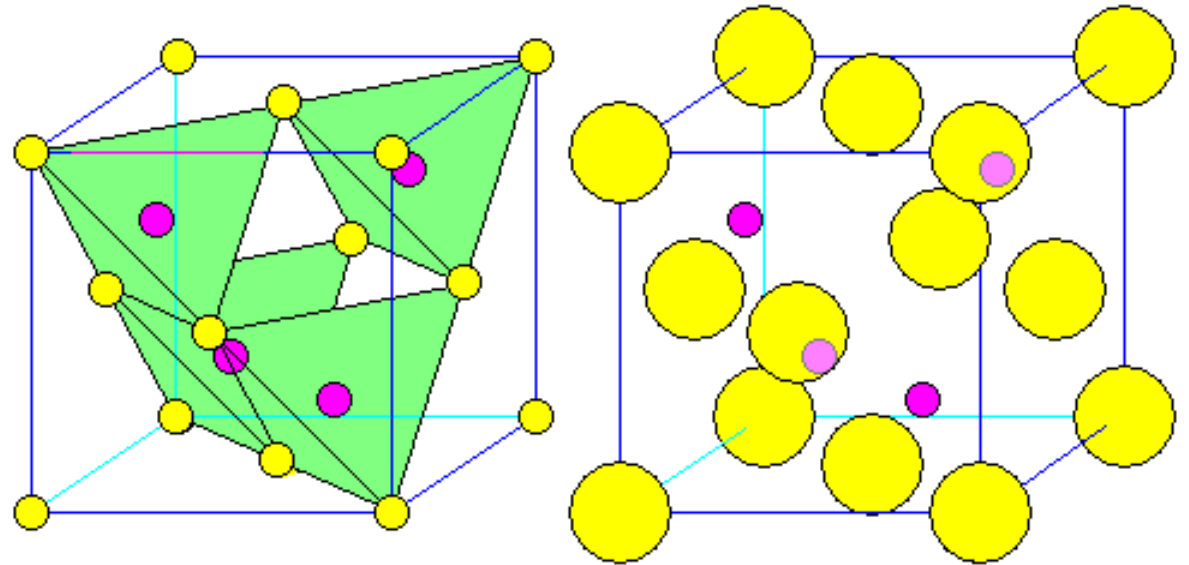
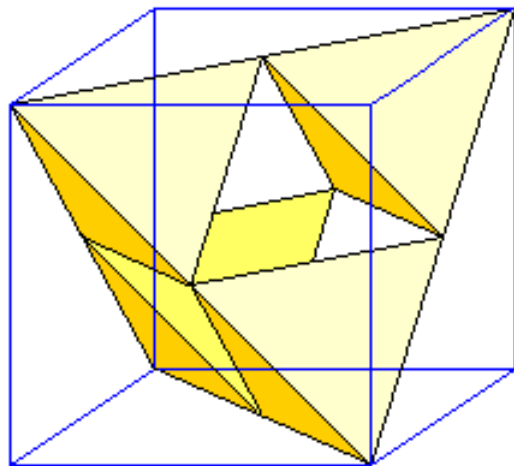
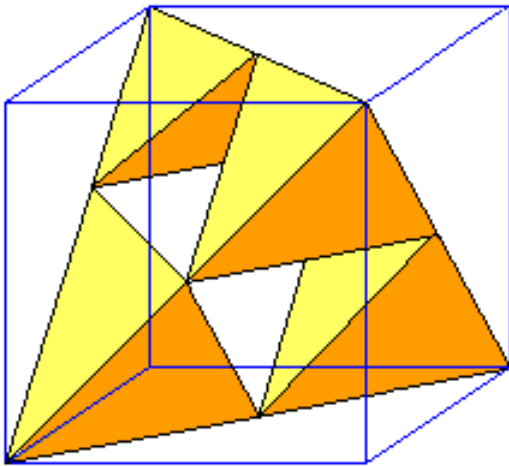
CaF_8 Cubes

Sphalerite (zincblende, ZnS)



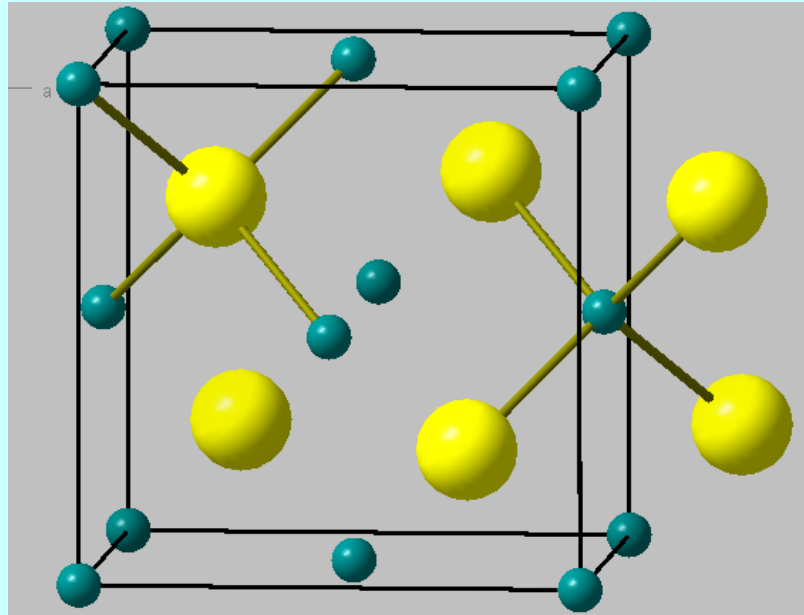
**Cubic close packing of anions
with 1/2 tetrahedral holes
filled by cations**

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

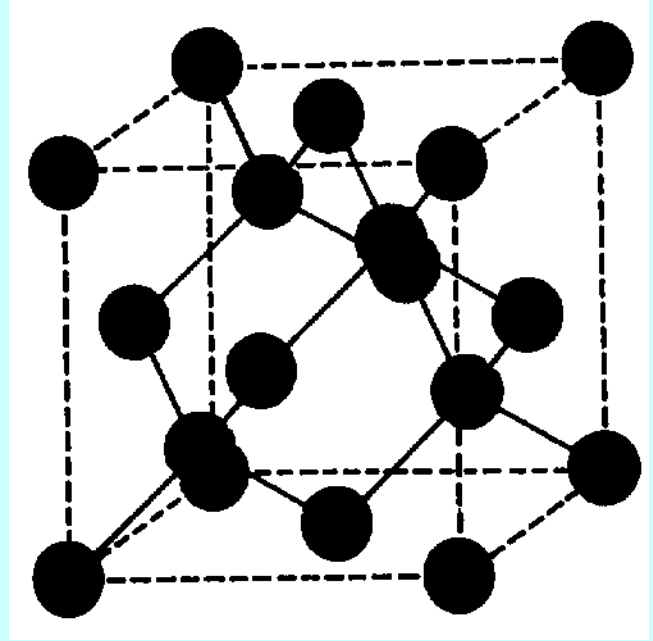
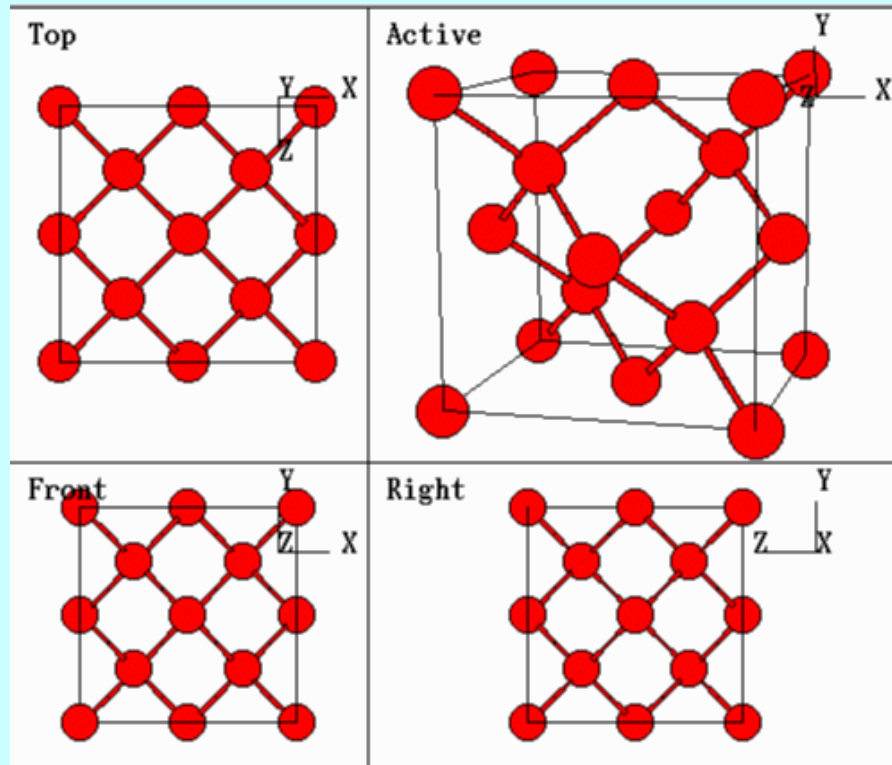
Halogenides: AgI, CuF, CuCl, CuBr, CuI, NH₄F

Borides: PB, AsB

Carbides: β -SiC

Nitrides: BN

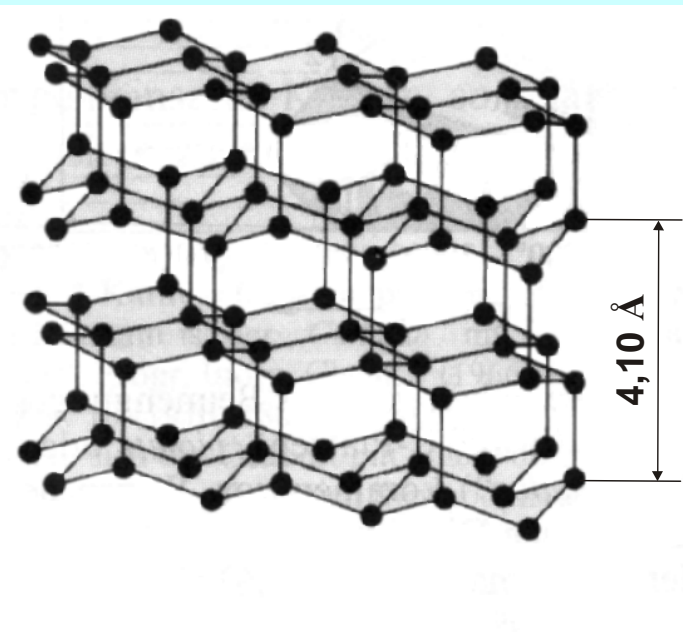
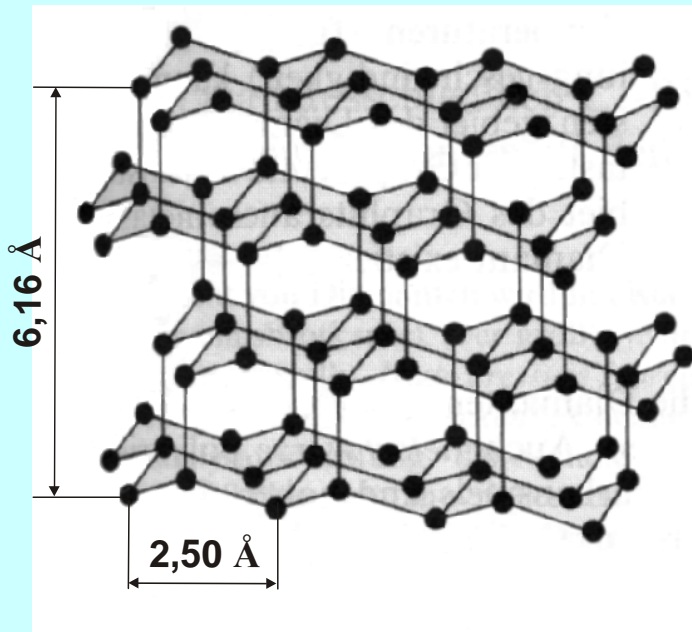
Diamond



Diamond

cubic

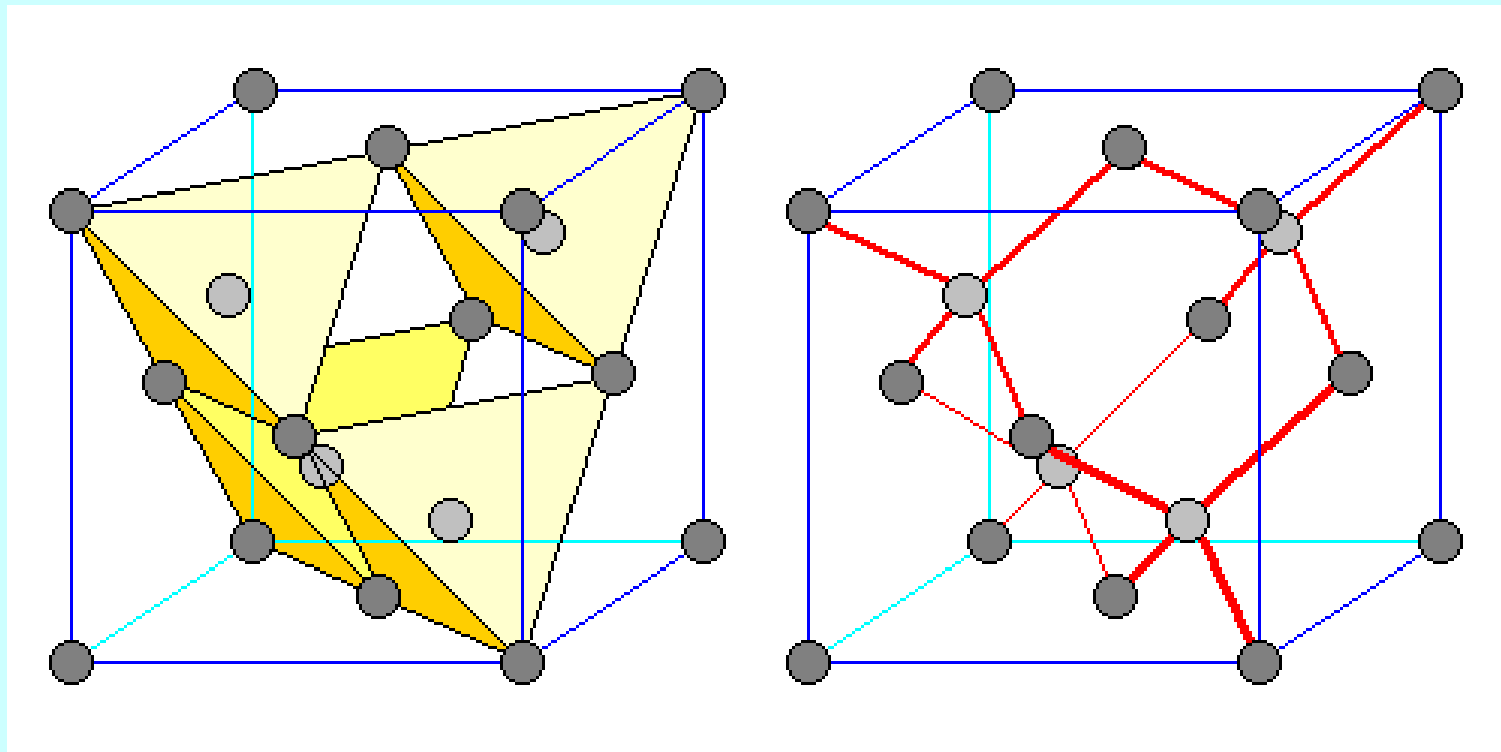
hexagonal



SiO₂ cristobalite

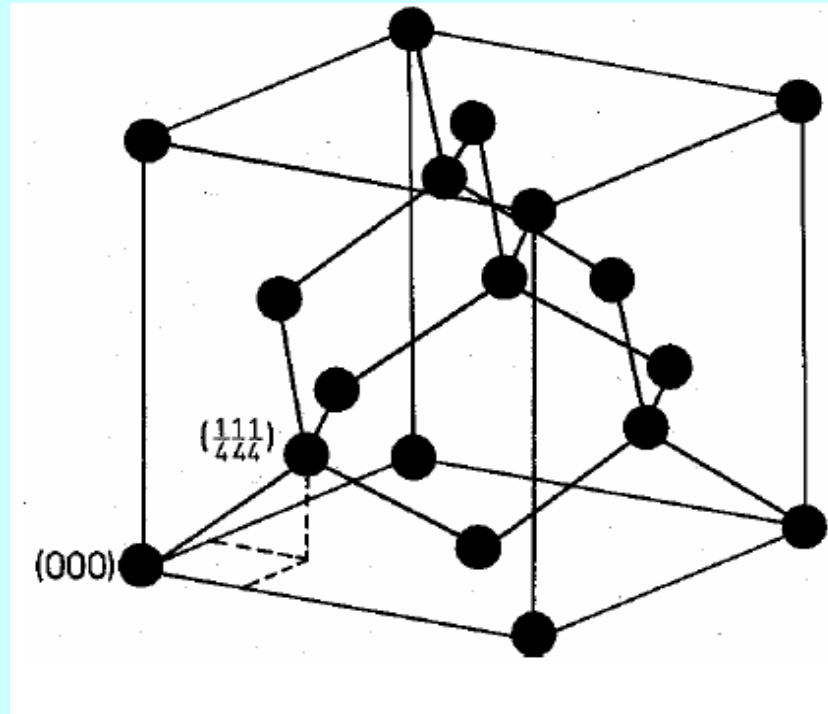
SiO₂ tridymite
ice

Cubic Diamond



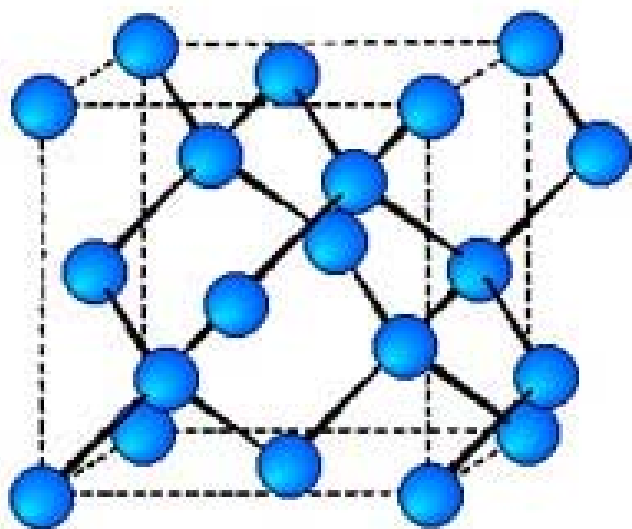
Diamond Structure

C, Si, Ge, α -Sn



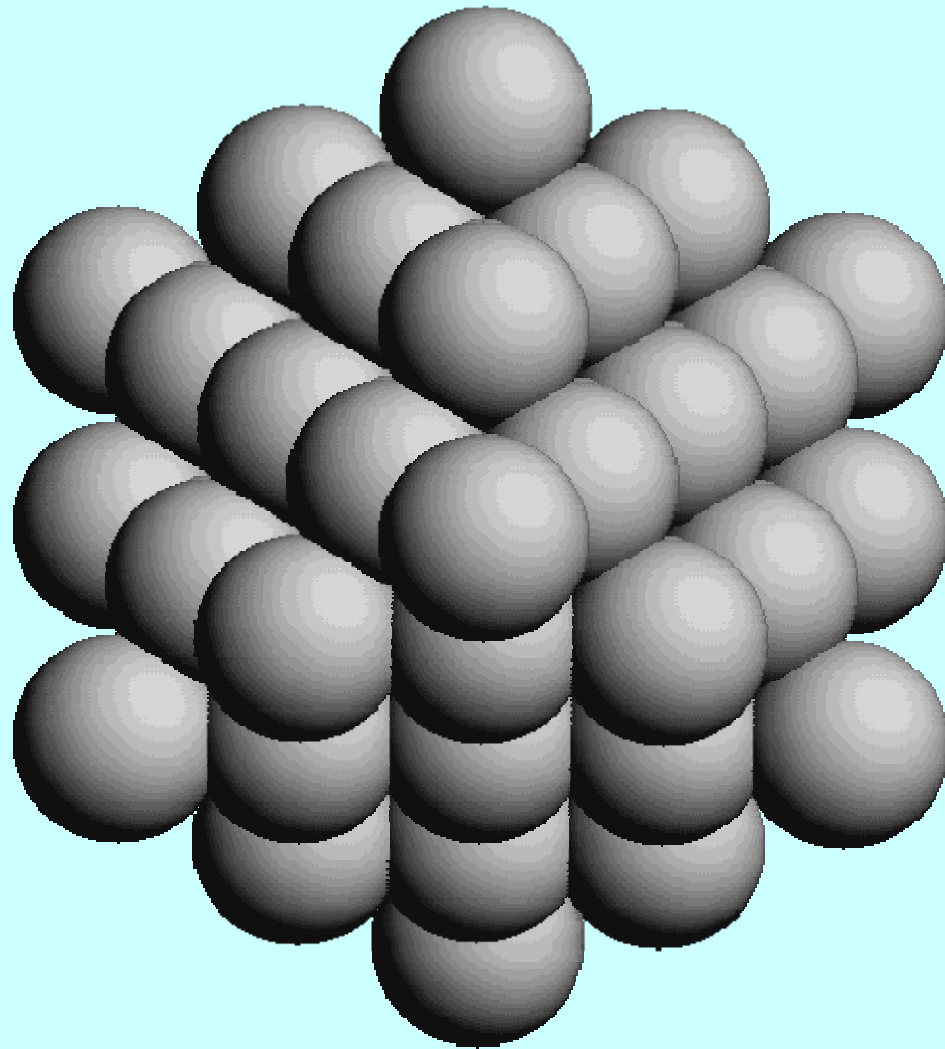
- Add 4 atoms to a FCC
- Tetrahedral bond arrangement
- Each atom has 4 nearest neighbors and 12 next nearest neighbors

Elements of the 14th Group

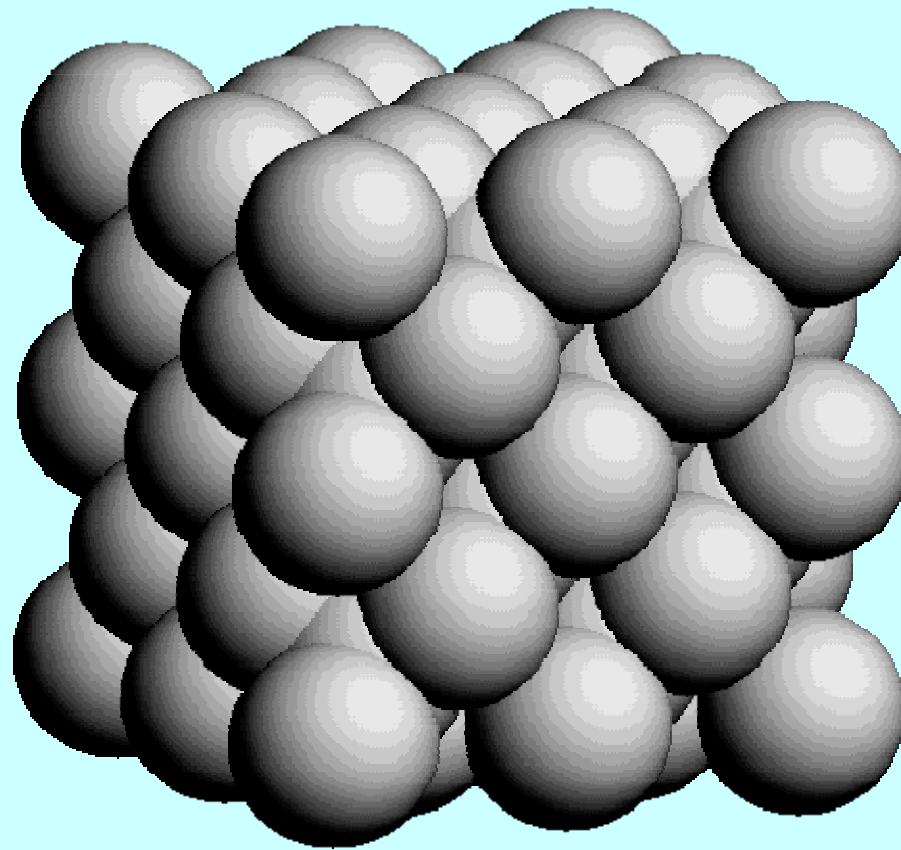


	a (Å)	d (g.cm ⁻³)
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
α -Sn	6.489	7.285

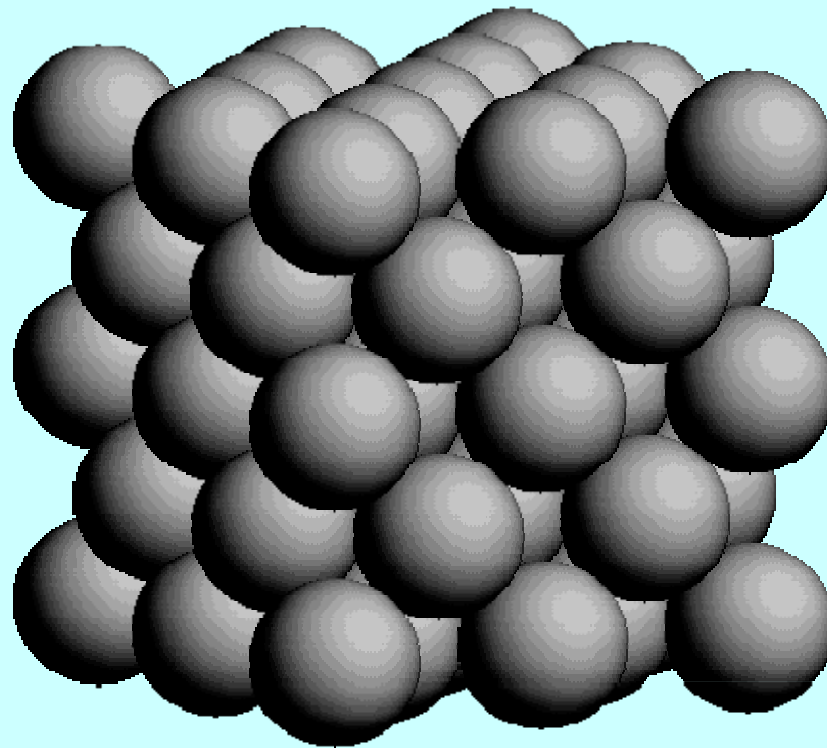
Diamond Lattice (111) Hard Sphere Model



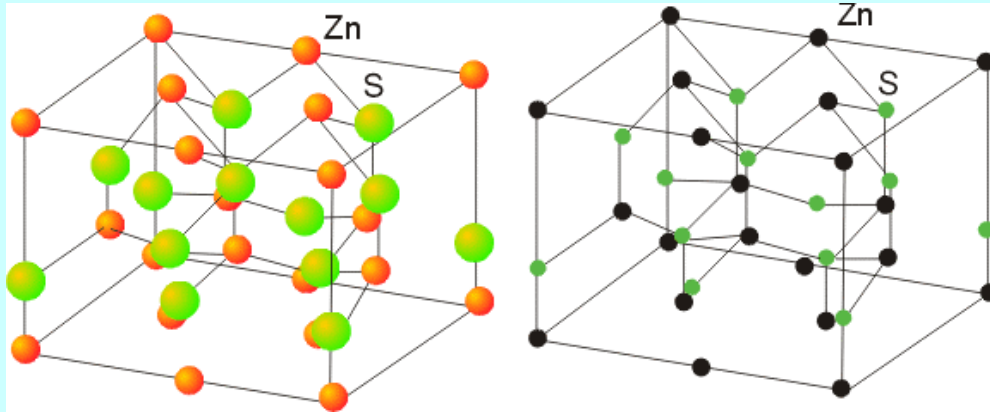
Diamond Lattice (111) Hard Sphere Model



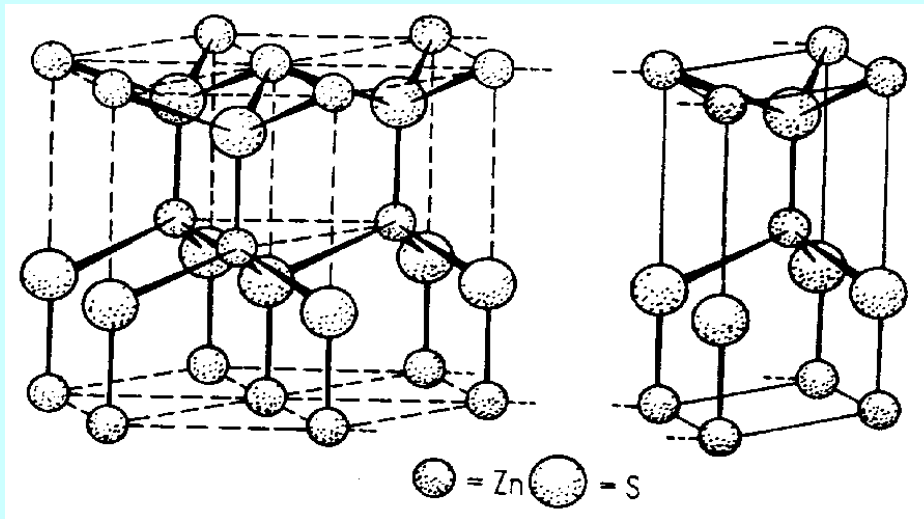
Face Centered Cubic Lattice (111) Hard Sphere Model



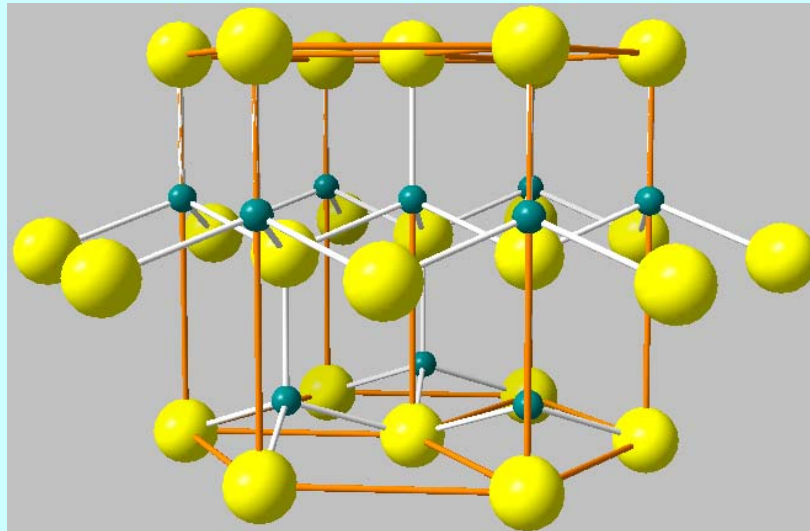
Wurzite, ZnS



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



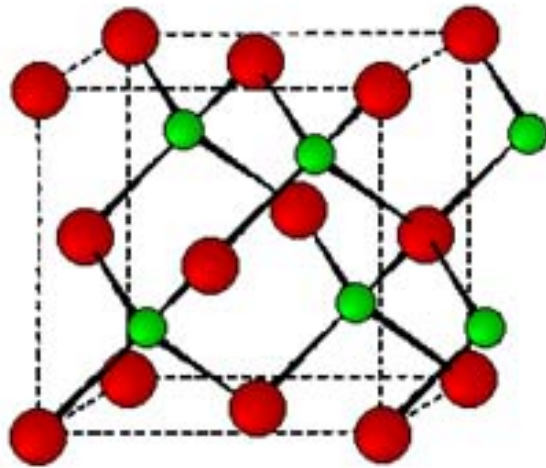
Wurzite, ZnS



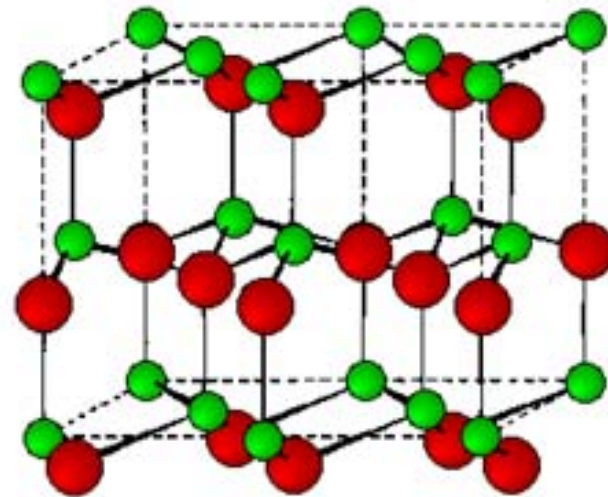
ZnO, ZnS, ZnSe, ZnTe, BeO, CdS, CdSe, MnS, AgI, AlN

Semiconductors of 13-15 and 12-16 type

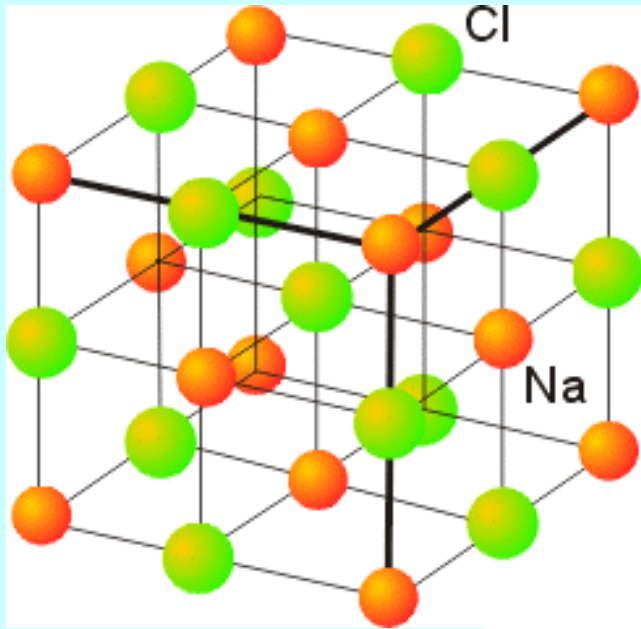
Structure of III-V and II-VI
Compound Semiconductors



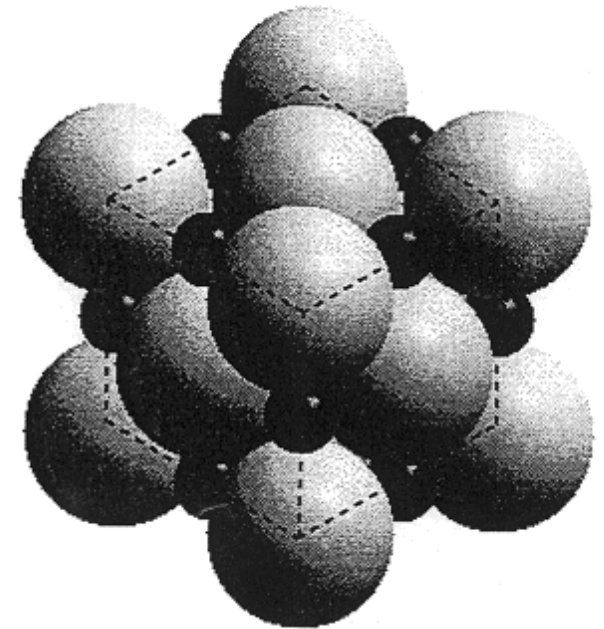
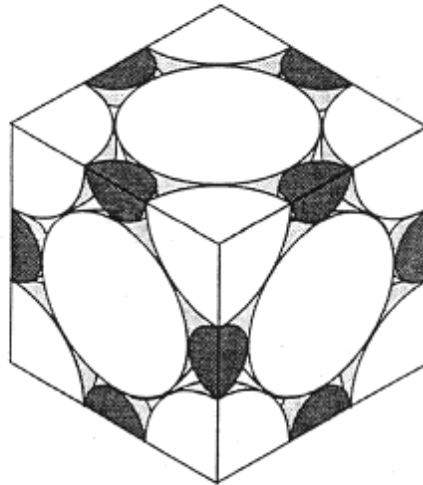
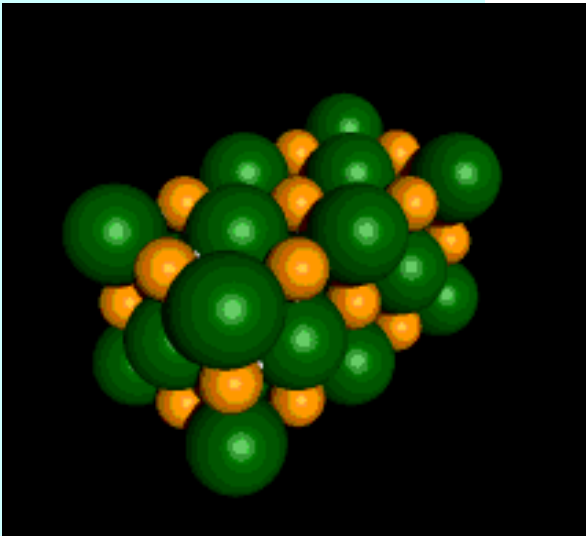
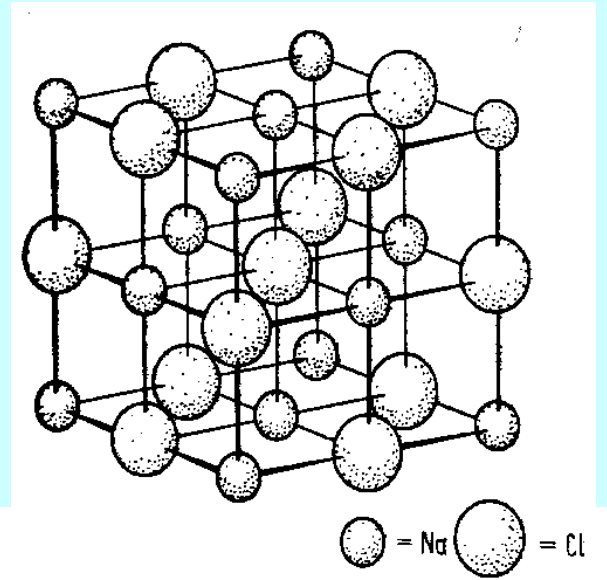
Zinc blende



Wurtzite

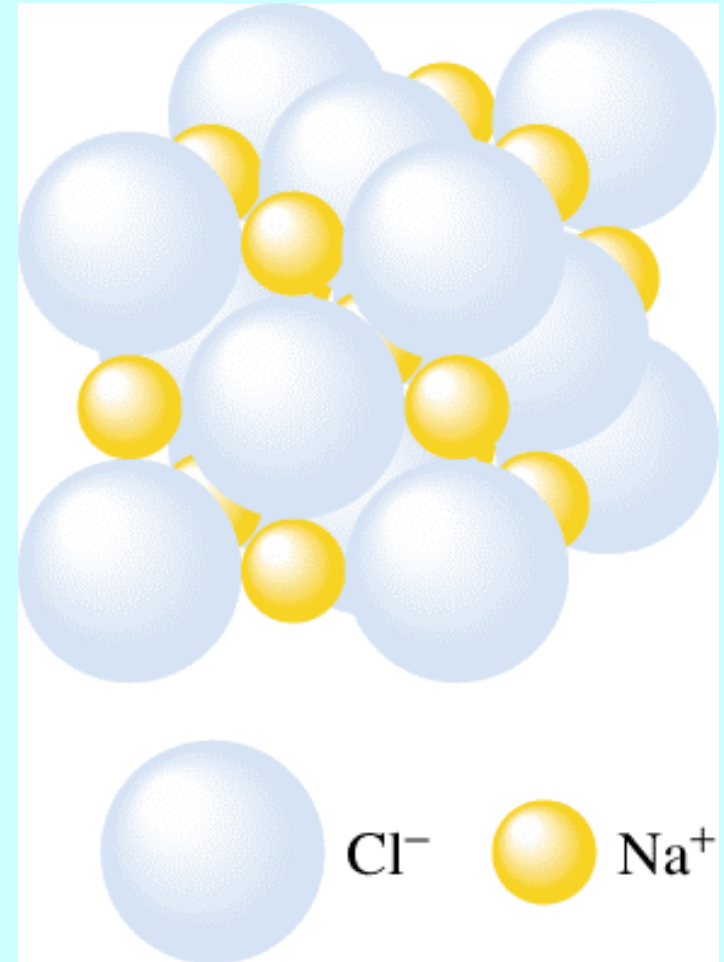
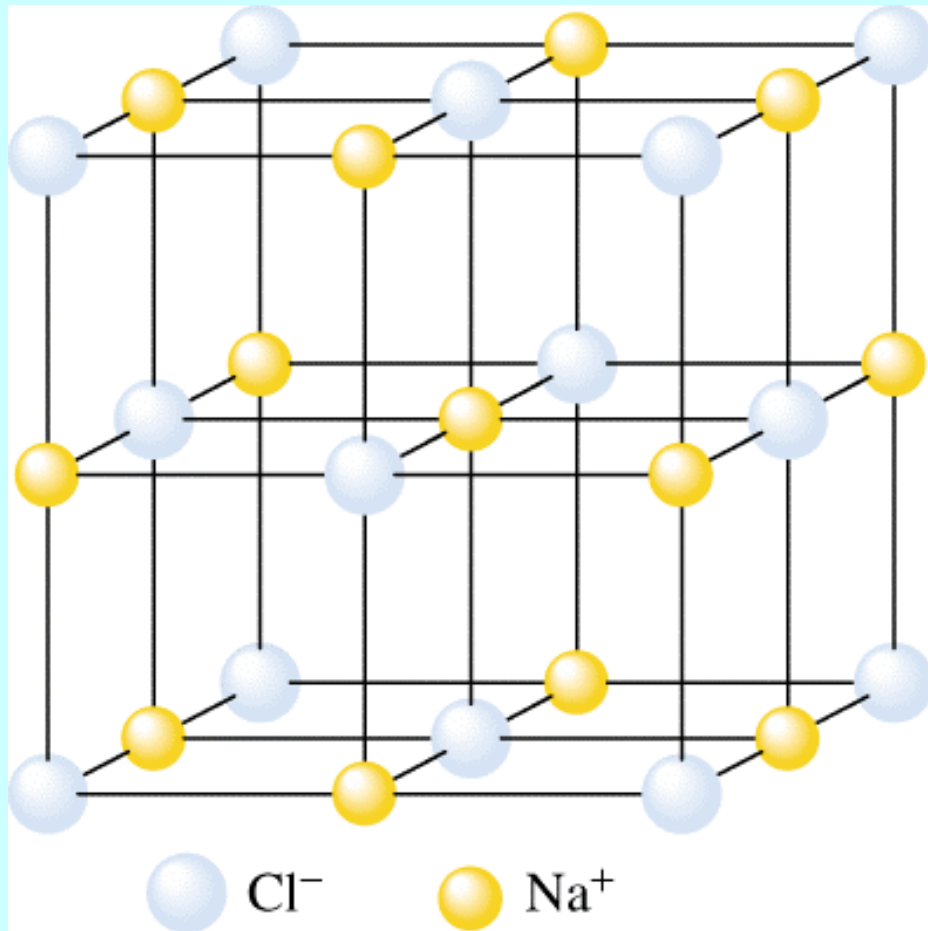


Rock Salt, NaCl

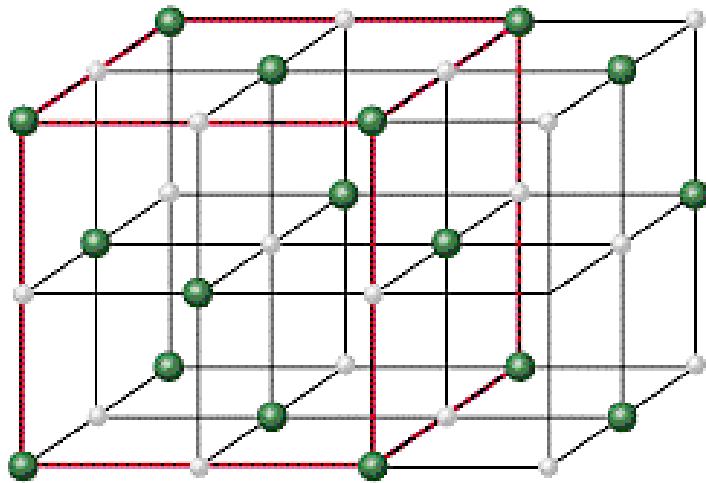


Cubic close packing of anions with all octahedral holes filled by cations

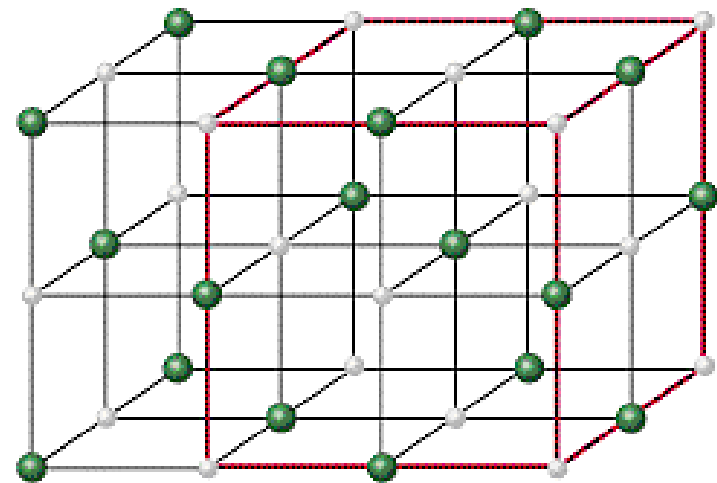
Rock Salt, NaCl



Rock Salt, NaCl



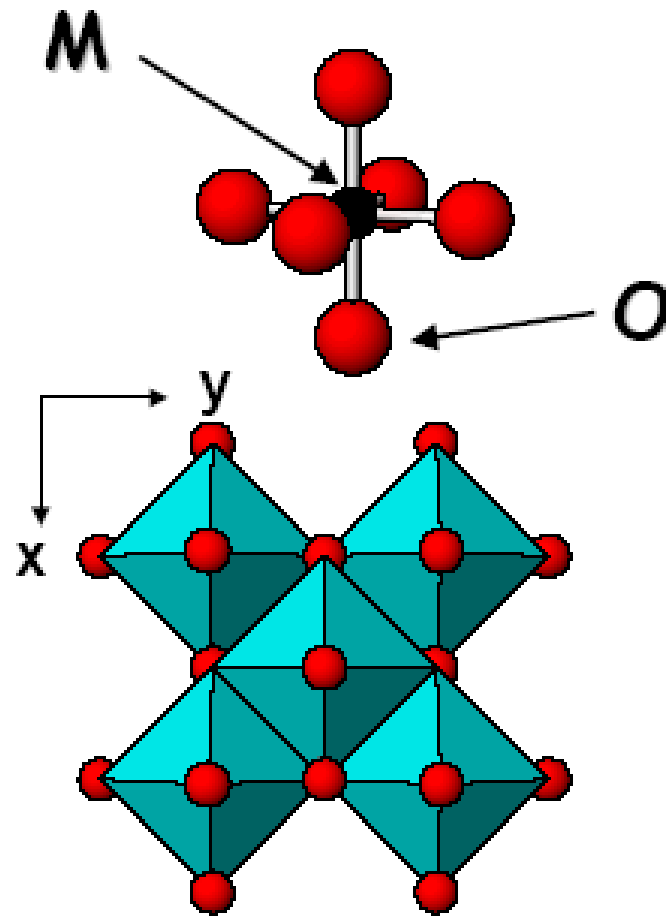
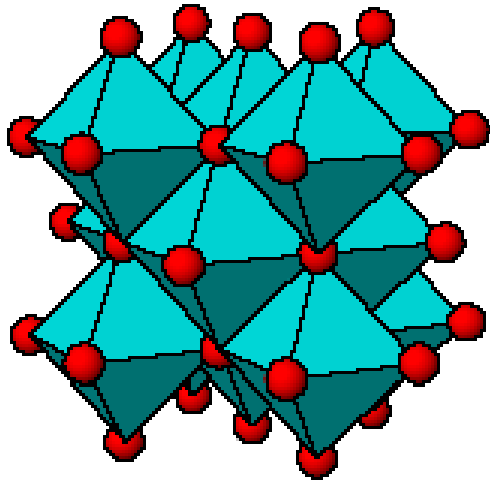
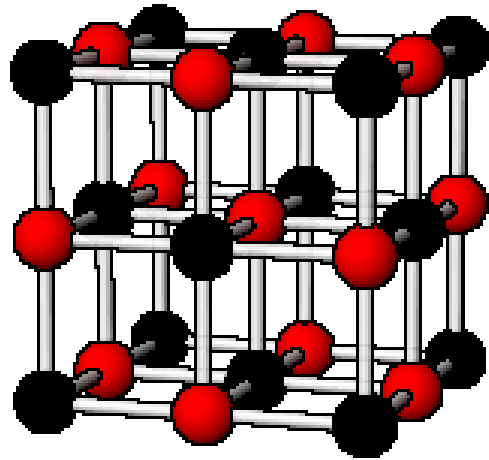
(a)



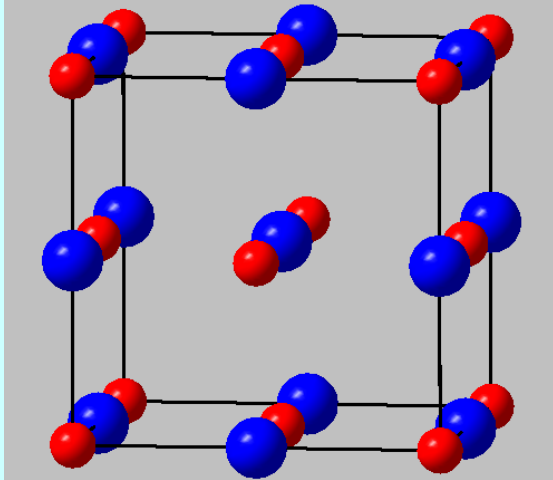
(b)

Anion and cation sublattices

Rock Salt Crystal Structure



Rock salt structures (NaCl)



Hydrides: LiH, NaH, KH,
 NH_4BH_4 – H_2 storage material

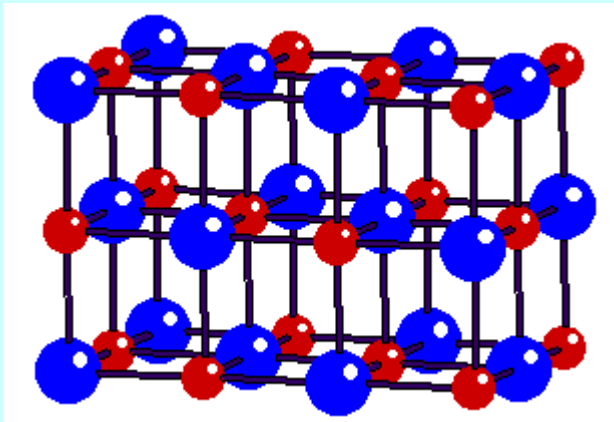
Borides: ZrB, HfB

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



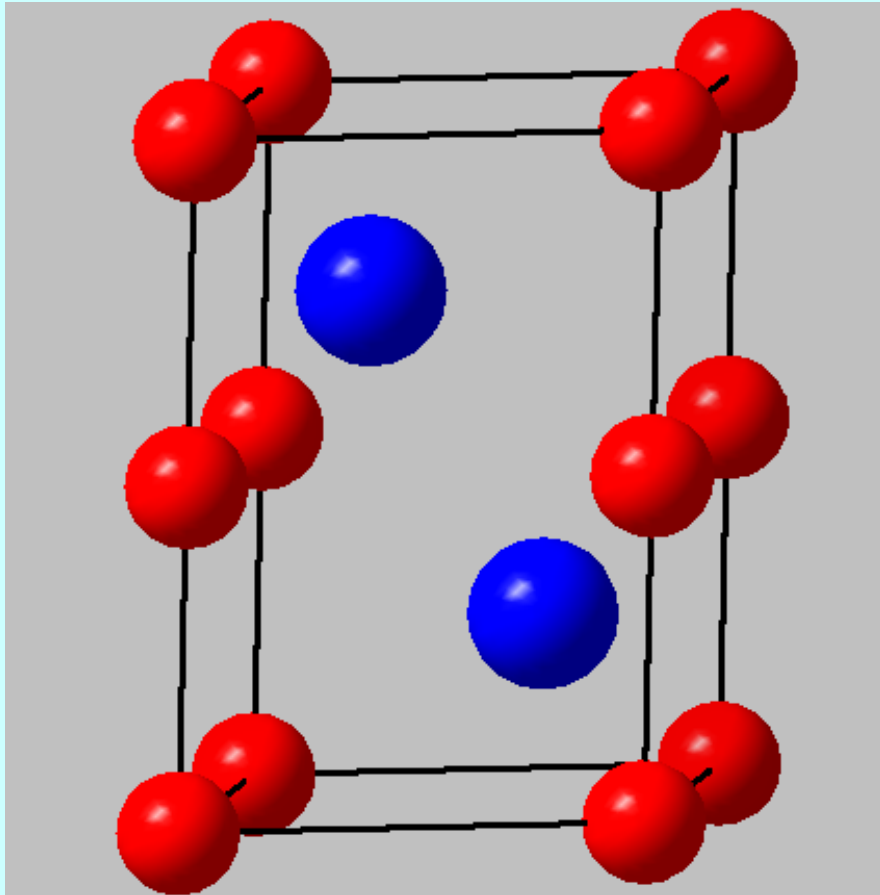
Halides: LiF, LiCl, LiBr, LiI, NaF, NaBr, NaI, KF,
KCl, KBr, KI, RbF, RbCl, RbBr, AgCl, AgF, AgBr

Intermetallics: SnAs

Other

FeS_2 (pyrite), CaC_2 , NaO_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,**

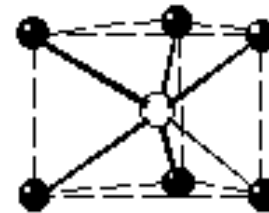
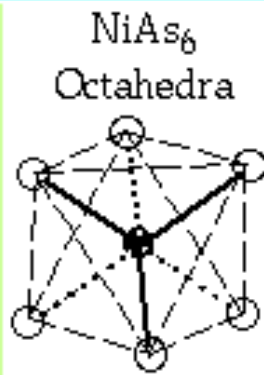
PtB (anti-NiAs structure)

NiAs - type

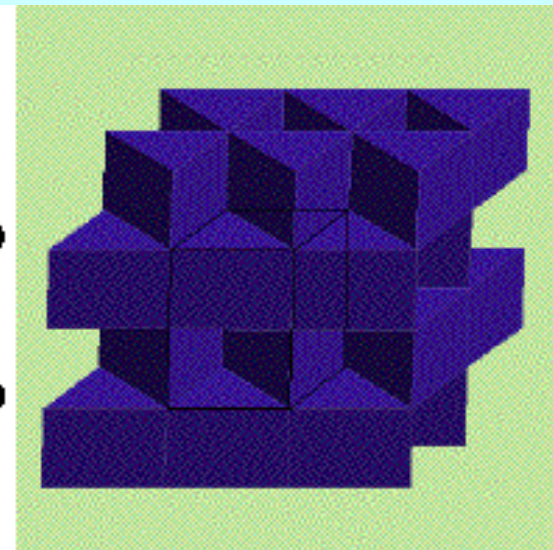
Hexagonal close packing of anions with all octahedral holes filled by cations



NiAs₆ Octahedra

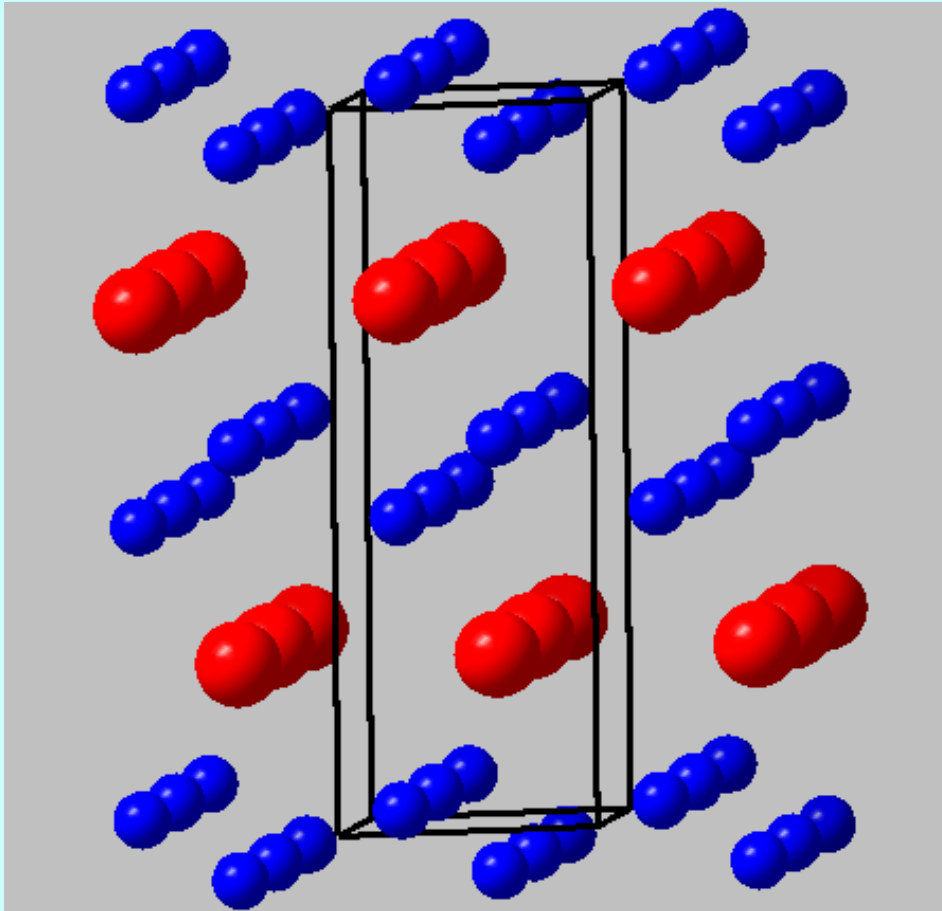


**AsNi₆
Trigonal
Prisms**



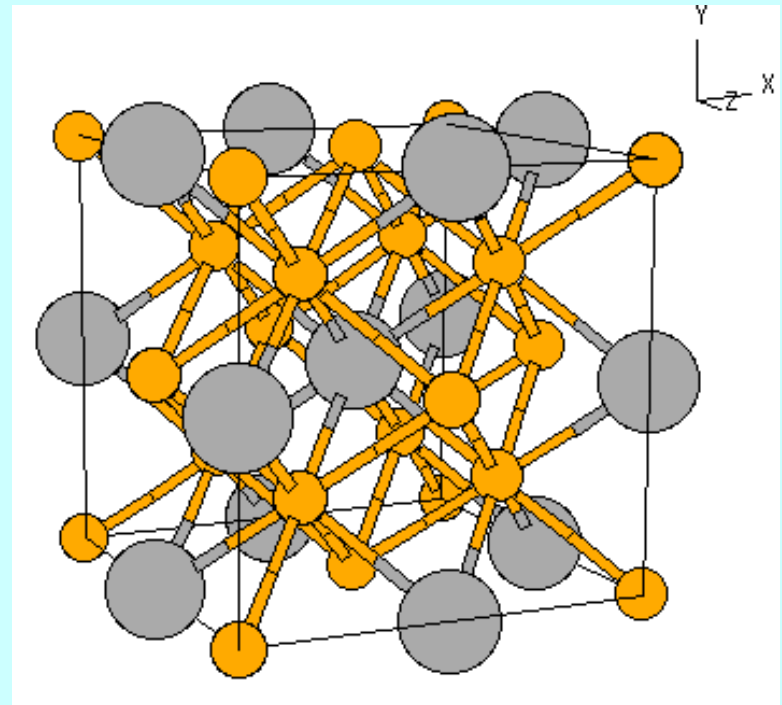
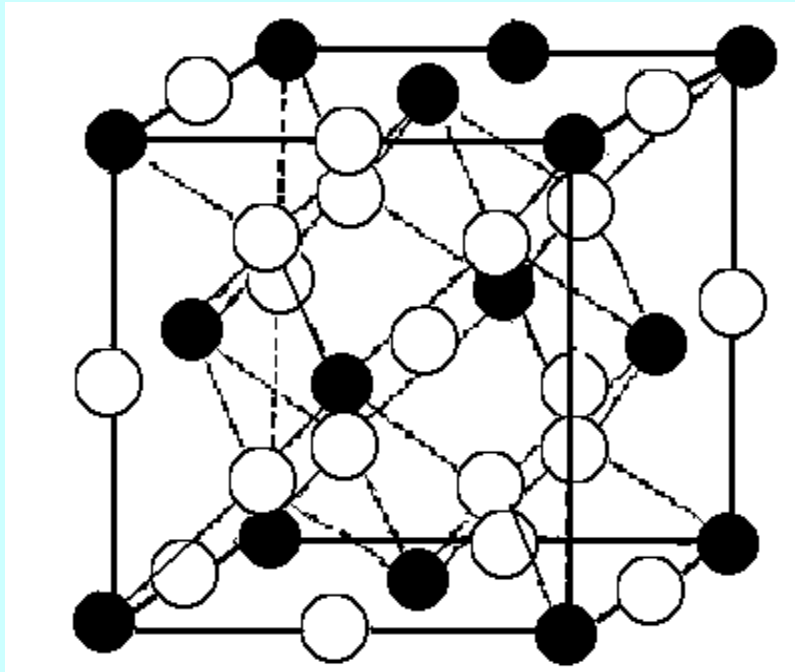
AsNi₆ Trigonal Prisms

ReB₂ - type



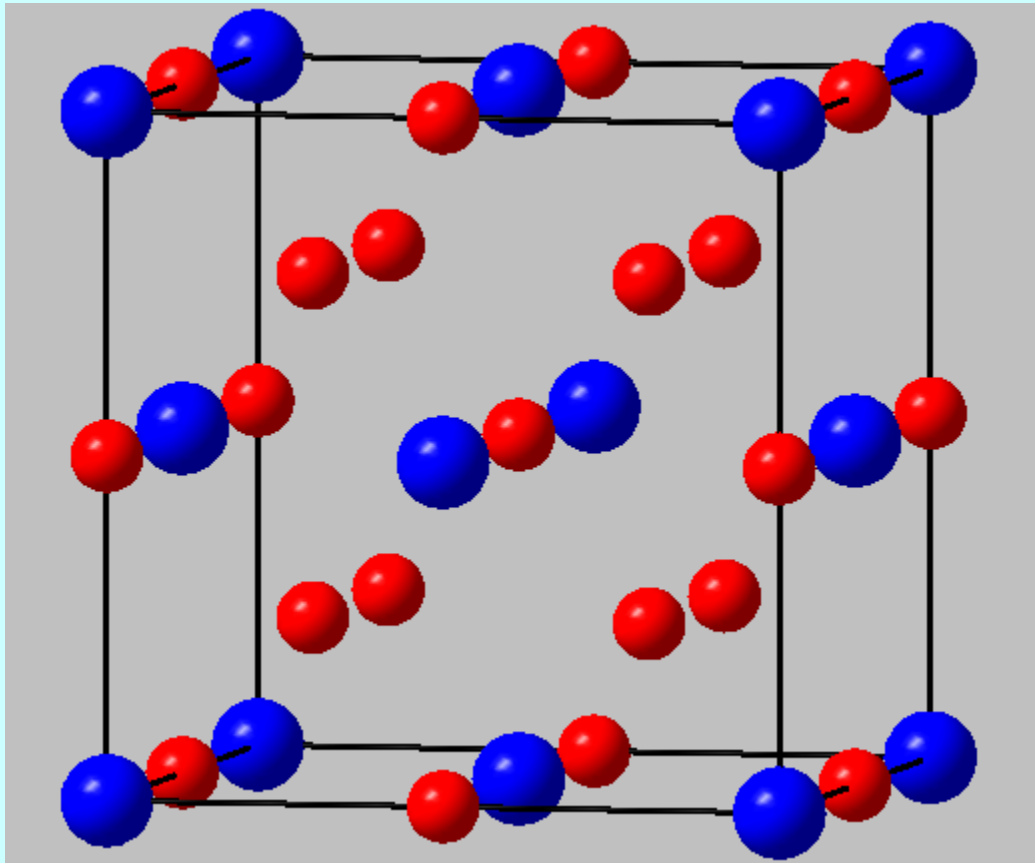
**Hexagonal close packing of
anions with all tetrahedral holes
filled by cations**

Li_3Bi - type (anti BiF_3)



$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_3[\text{Fe}(\text{CN})_6]$
bcc

Li_3Bi - type (anti BiF_3)

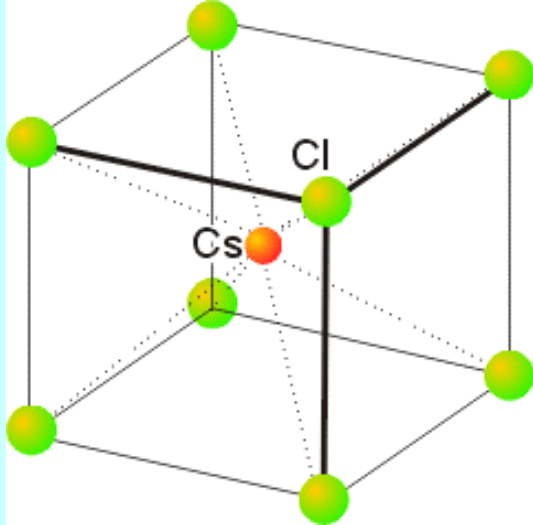


Fe_3Al

$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$

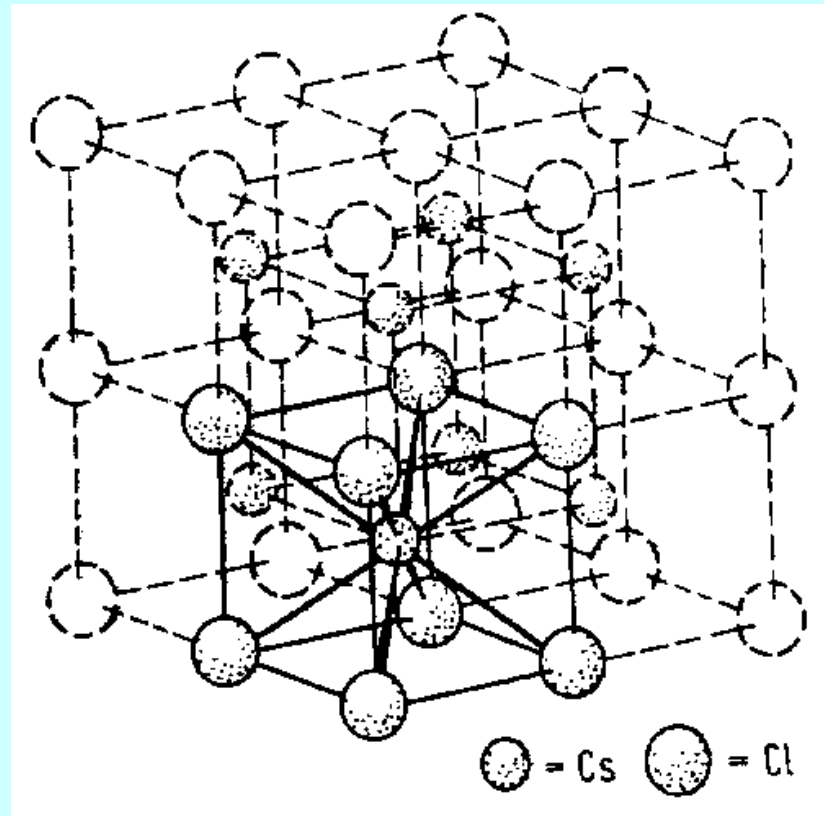
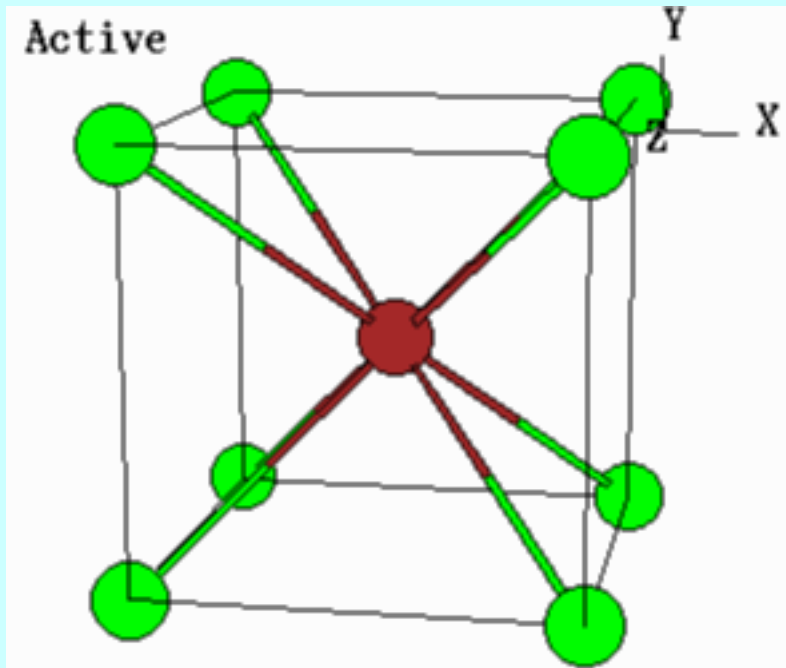
$\text{K}_3[\text{Fe}(\text{CN})_6]$

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



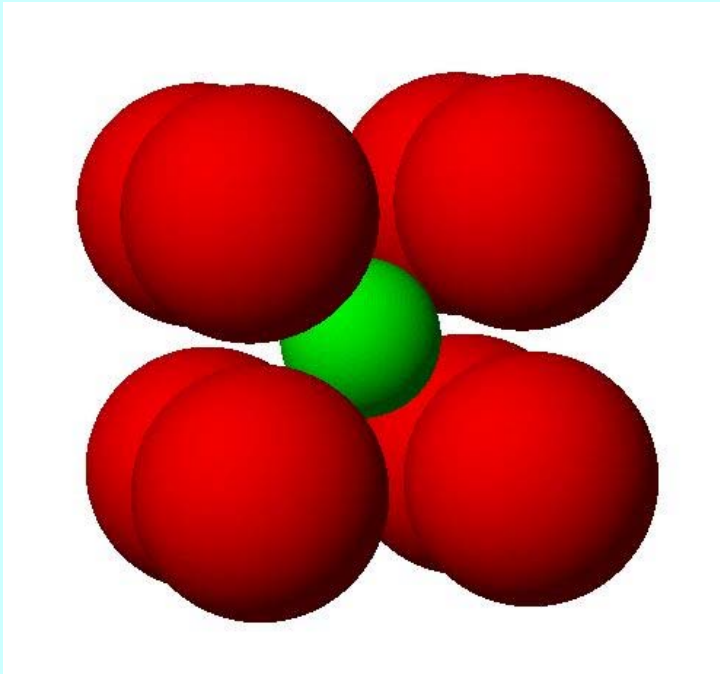
CsCl

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

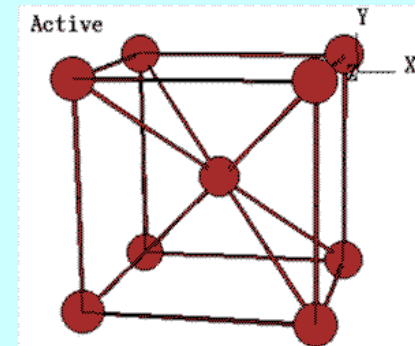
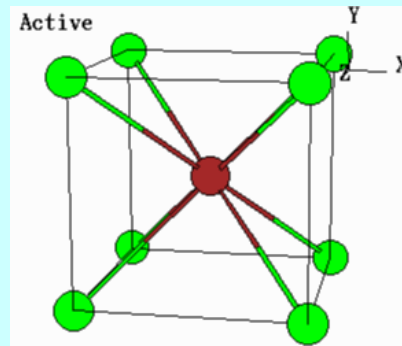


Primitive cubic packing of CsCl_8 cubes sharing all faces

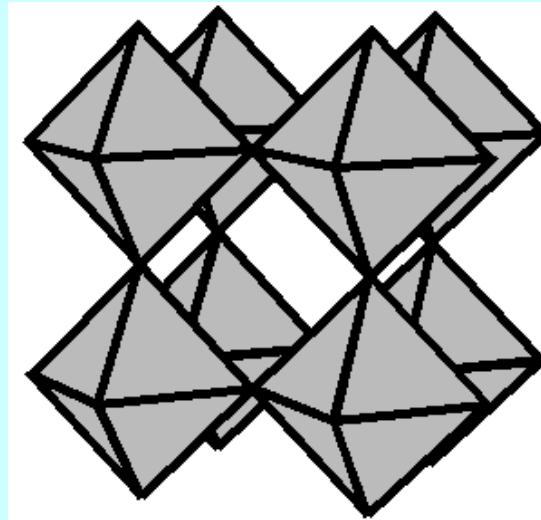
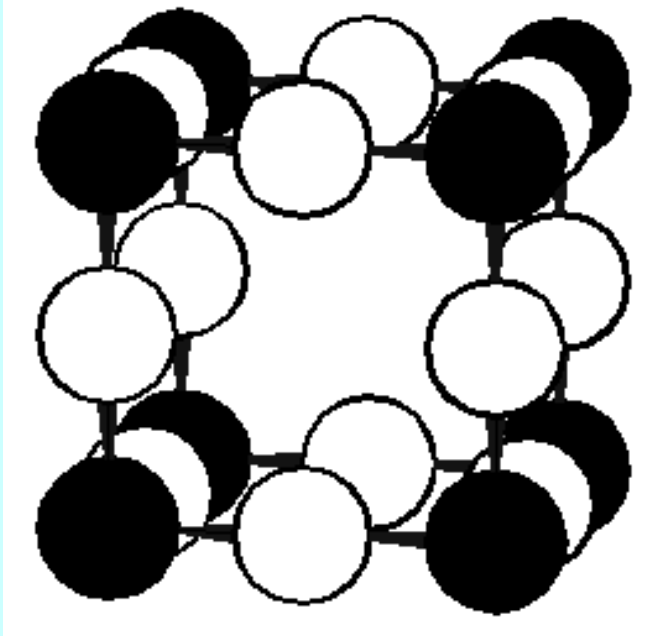
CsCl



CsCl is not BCC



CsBr, CsI, CsCN, NH₄Cl, NH₄Br, TlCl, TlBr, TlI, CuZn, CuPd, LiHg



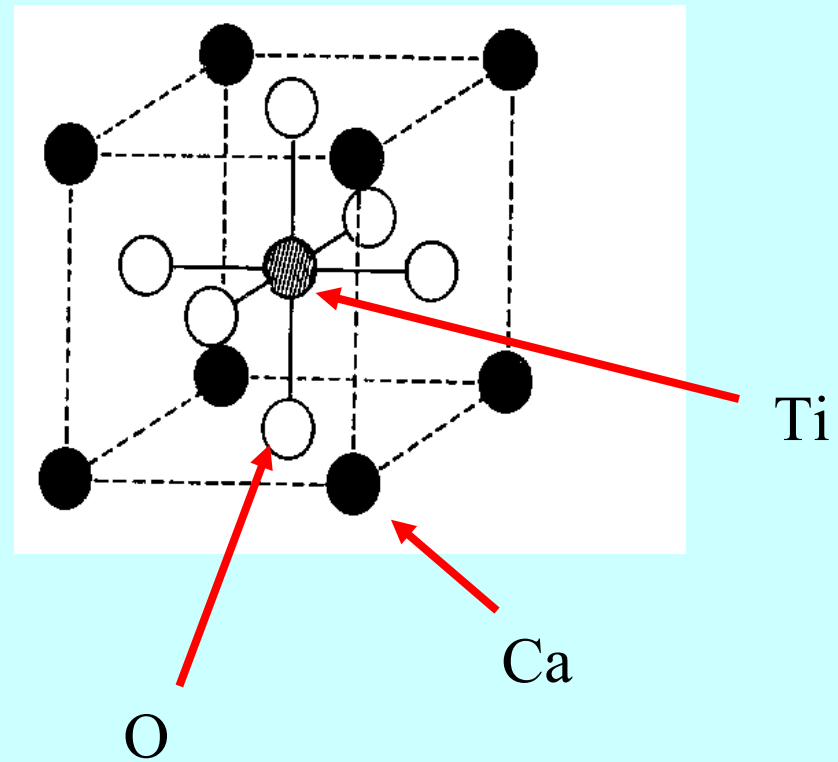
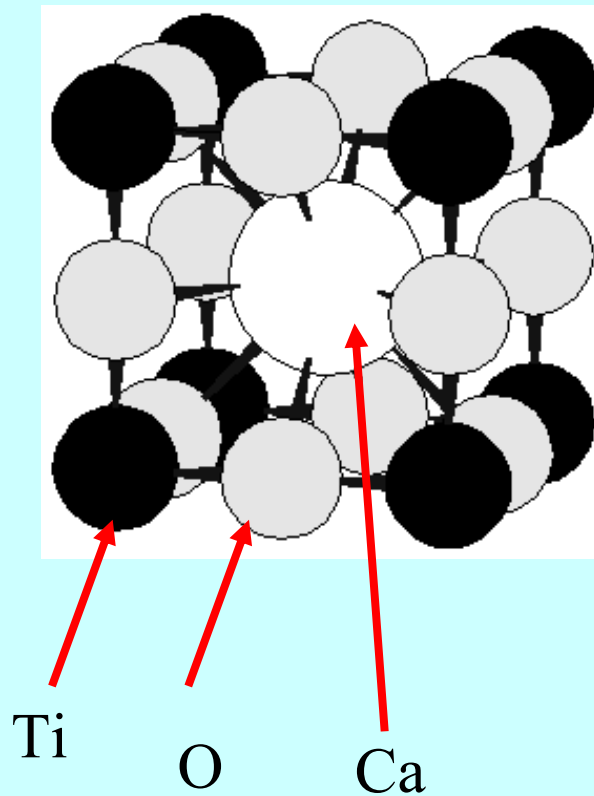
SC of ReO₆ octahedra

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



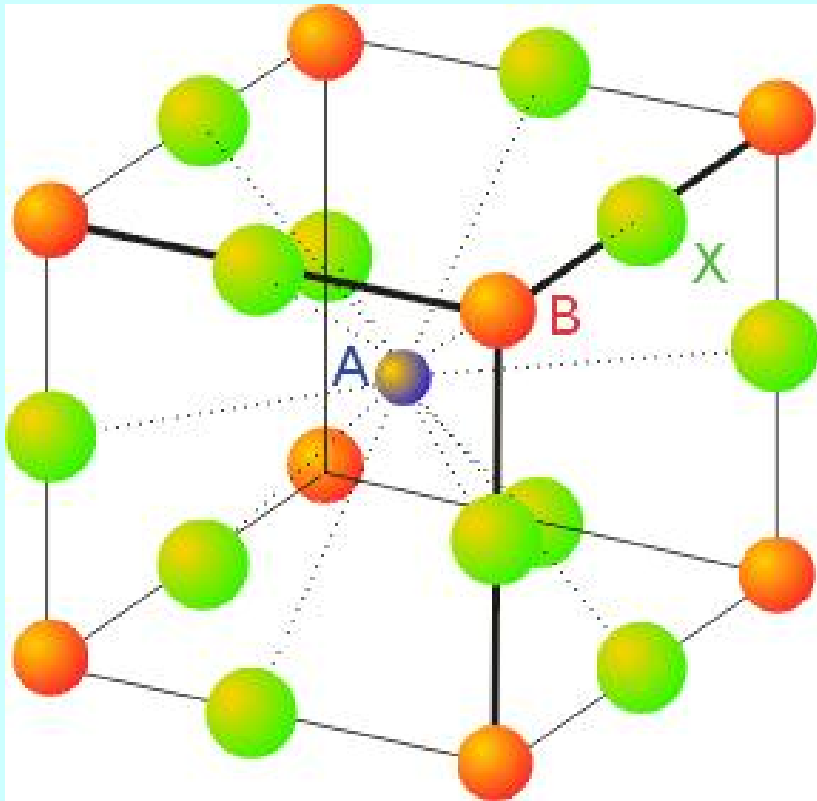
Perovskite, CaTiO_3

Two equivalent 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)

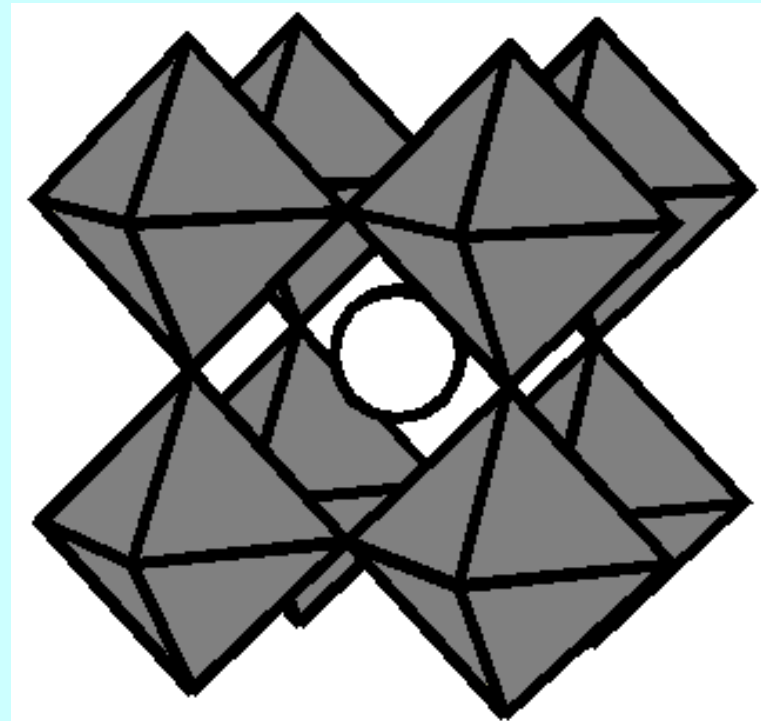
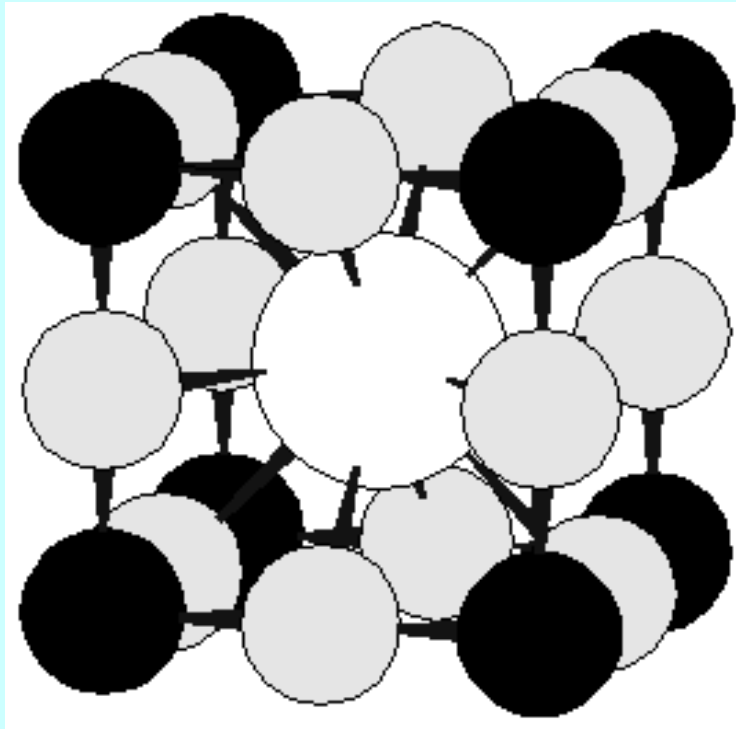
preferred structure of piezoelectric,
ferroelectric and superconducting
materials

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

Goldschmidt's tolerance factor

Perovskite, CaTiO_3

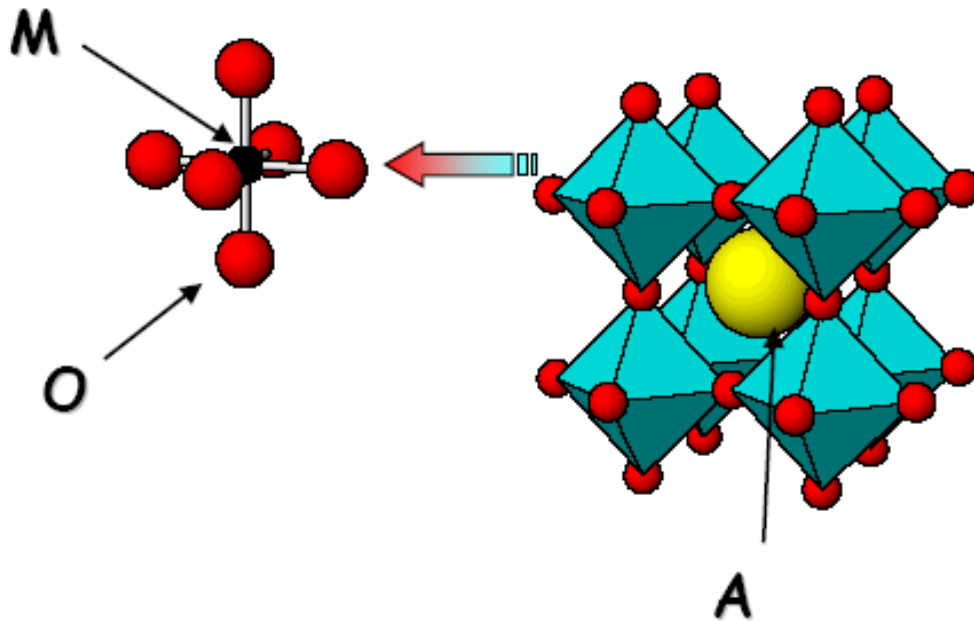
Cubic "close packing" of A and X with 1/4 octahedral holes filled by B cations



Similarity to CsCl

Perovskite, CaTiO_3

Perovskite Crystal Structure

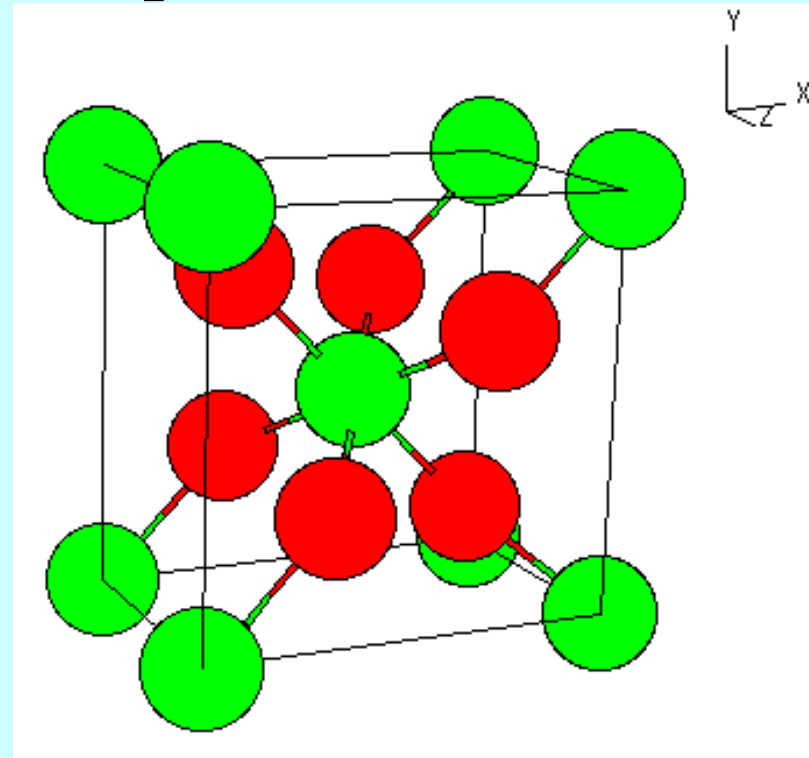
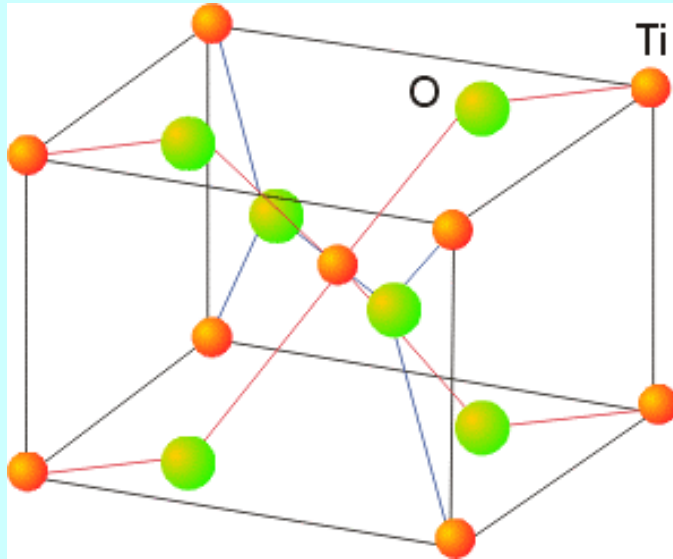


MgSiO_3 , CaSiO_3

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

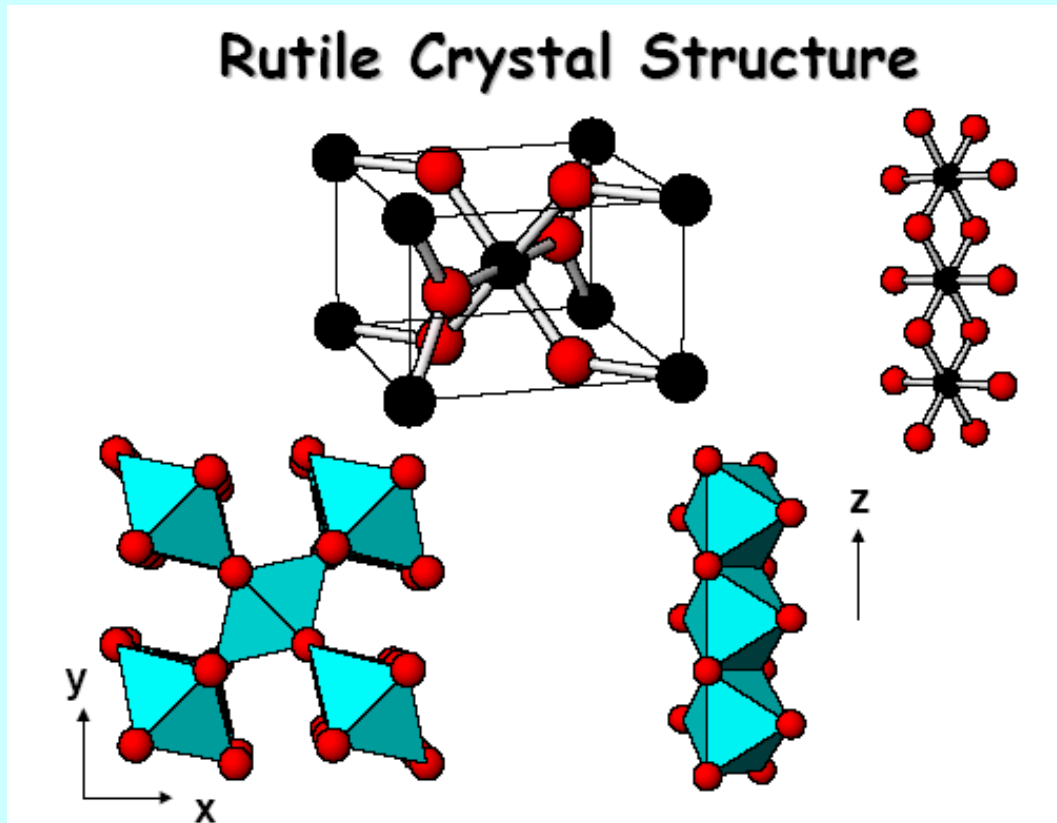


$$\text{CN}(A) / \text{CN}(B) = y / x$$

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

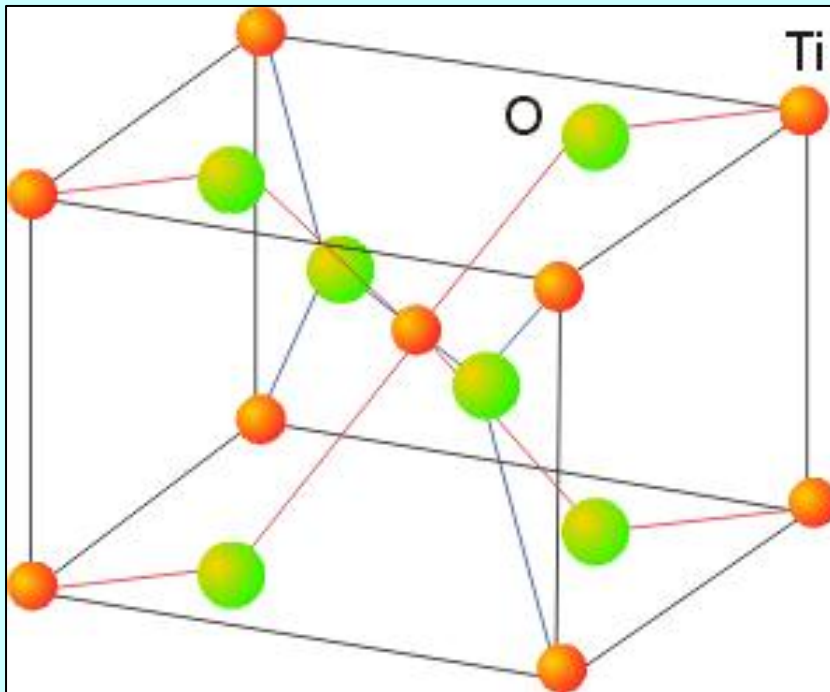
Rutile, TiO_2

Rutile Crystal Structure



GeO_2 , CrO_2 , IrO_2 , MoO_2 , NbO_2 , $\beta\text{-MnO}_2$, OsO_2 , VO_2
($>340\text{K}$), RuO_2 , CoF_2 , FeF_2 , MgF_2 , MnF_2

The rutile structure: TiO_2

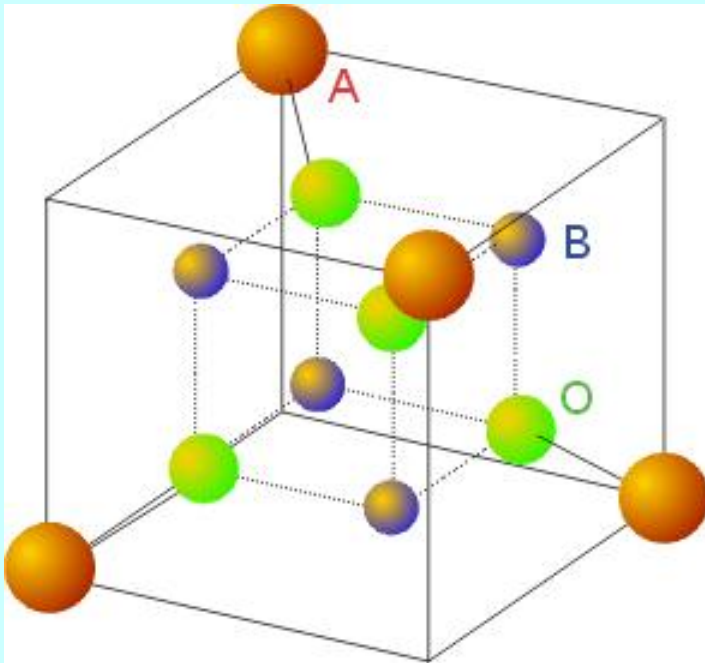


TiO_6 – octahedra

OTi_3 – trigonal planar

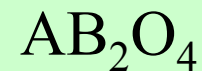
(alternative to CaF_2 for highly charged smaller cations)

The spinel structure: MgAl_2O_4

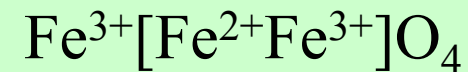
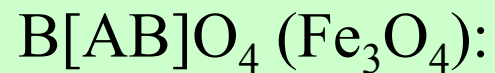


fcc array of O^{2-} ions, A^{2+} occupies $1/8$ of the tetrahedral and B^{3+} $1/2$ of the octahedral holes

→ normal spinel:



→ inverse spinel:



→ basis structure for several magnetic materials

Spinel

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

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

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

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

Garnets



Naturally occurring 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:

pyrospite 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	$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$
Almandine	$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
Spessartine	$\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$
Uvarovite	$\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$
Grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
Andradite	$\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$

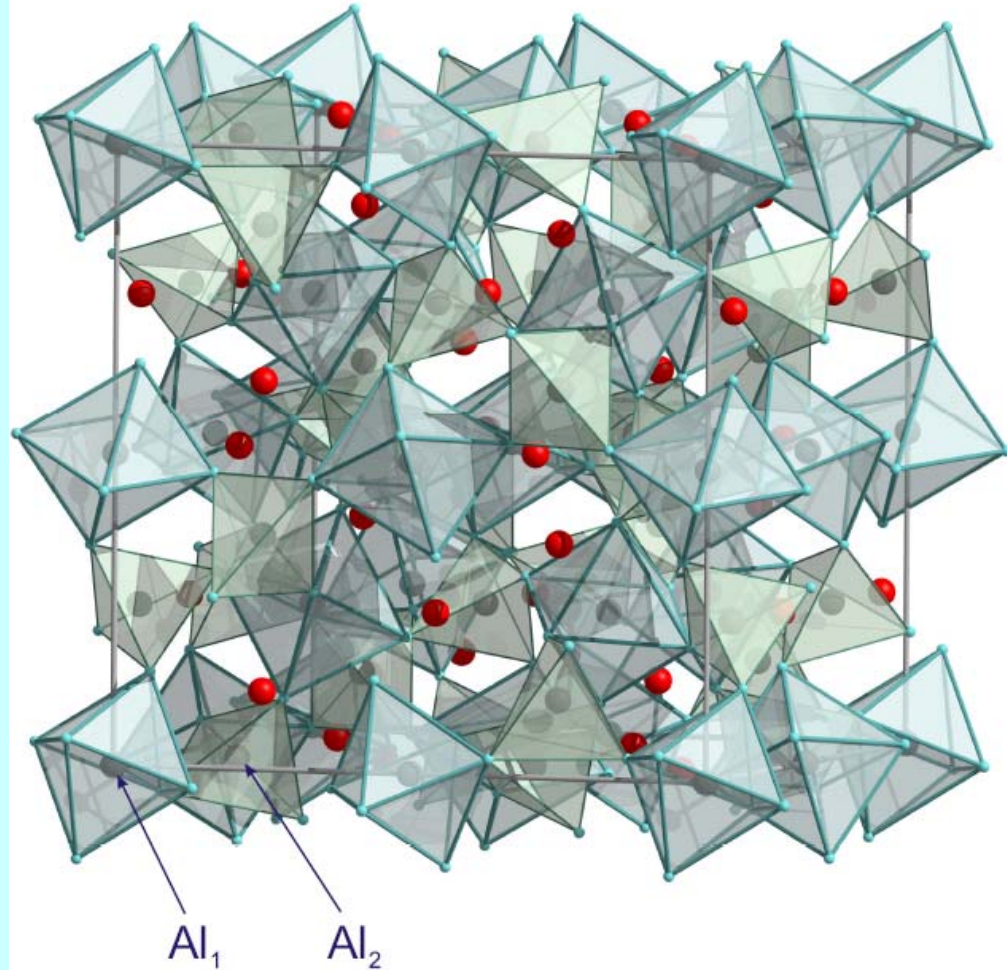
Garnets

Garnet $Y_3Al_5O_{12}$

Y_3 = red - dodecahedral
trivalent cations, large size

Al_5 = blue
2 octahedral
3 tetrahedral

O_{12}



Layered Structures

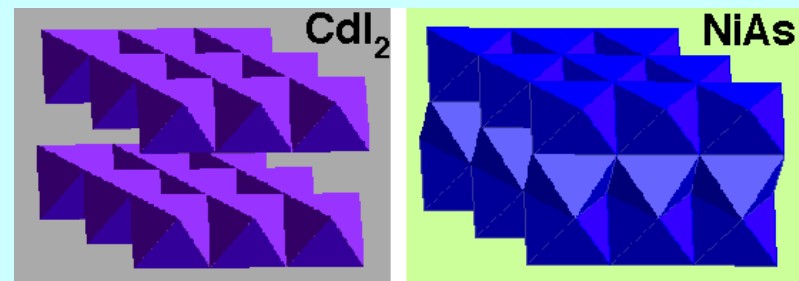
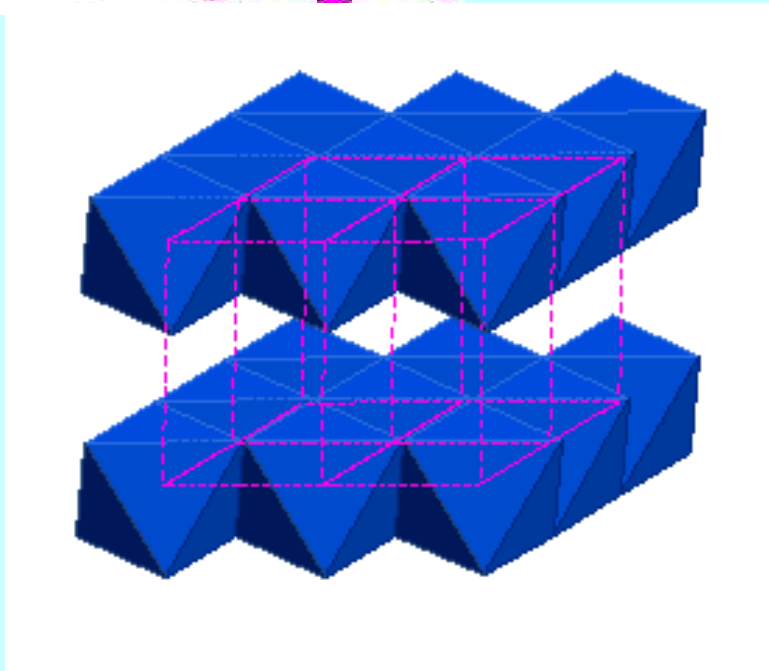
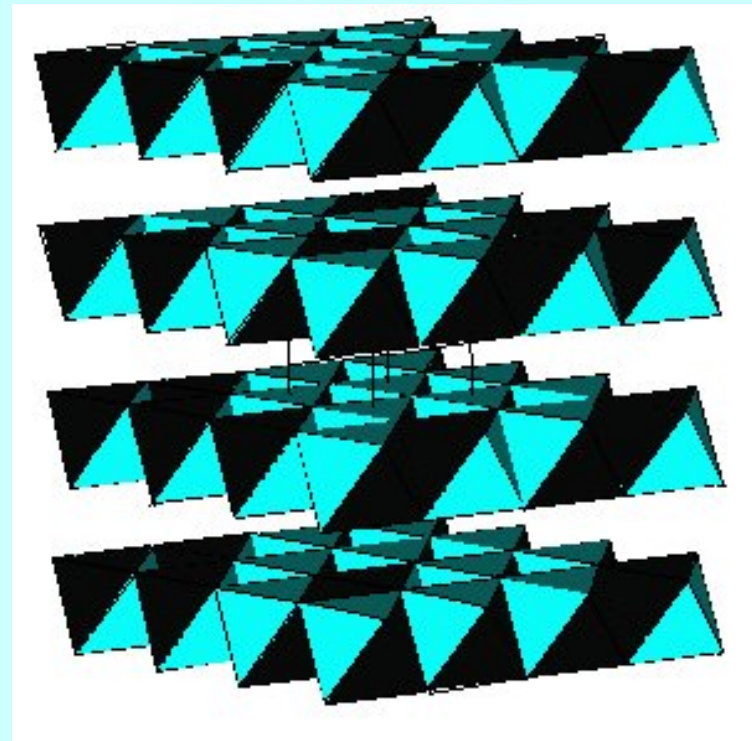
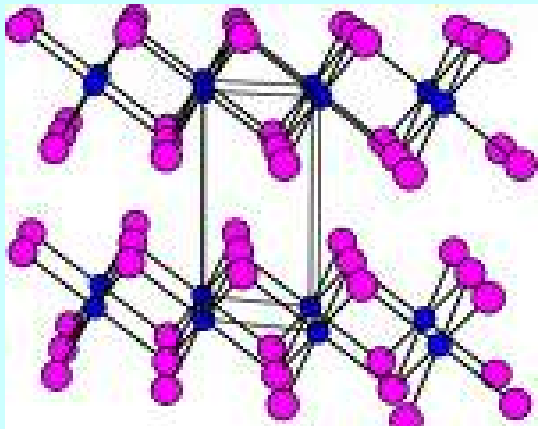
CdI₂ Hexagonal close packing of anions with 1/2 octahedral holes filled by cations

CoI₂, FeI₂, MgI₂, MnI₂, PbI₂, ThI₂, TiI₂, TmI₂, VI₂, YbI₂, ZnI₂, VBr₂, TiBr₂, MnBr₂, FeBr₂, CoBr₂, TiCl₂, TiS₂, TaS₂.

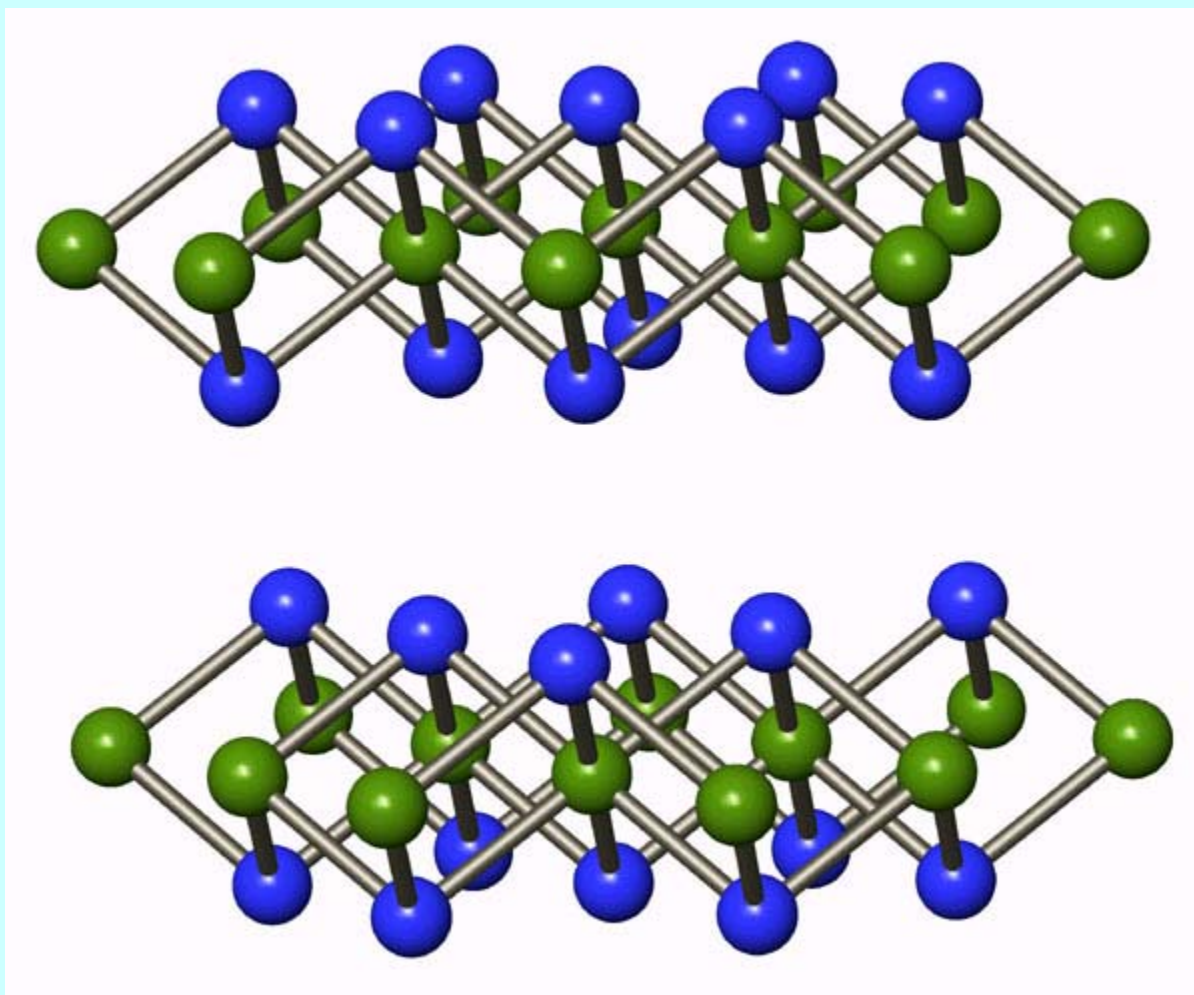
CdCl₂ Cubic close packing of anions with 1/2 octahedral holes filled by cations

CdCl₂, CdBr₂, CoCl₂, FeCl₂, MgCl₂, MnCl₂, NiCl₂, NiI₂, ZnBr₂, ZnI₂, Cs₂O* (anti-CdCl₂ structure)

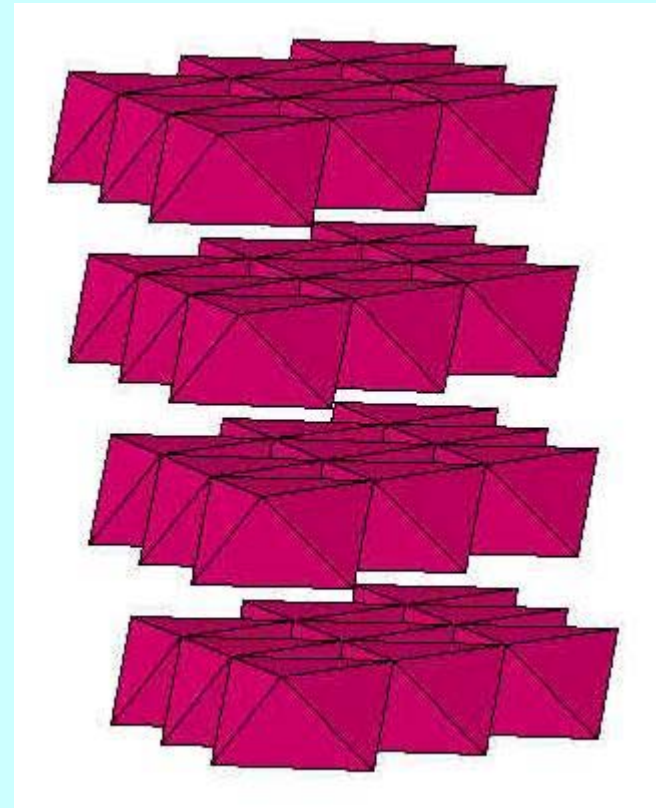
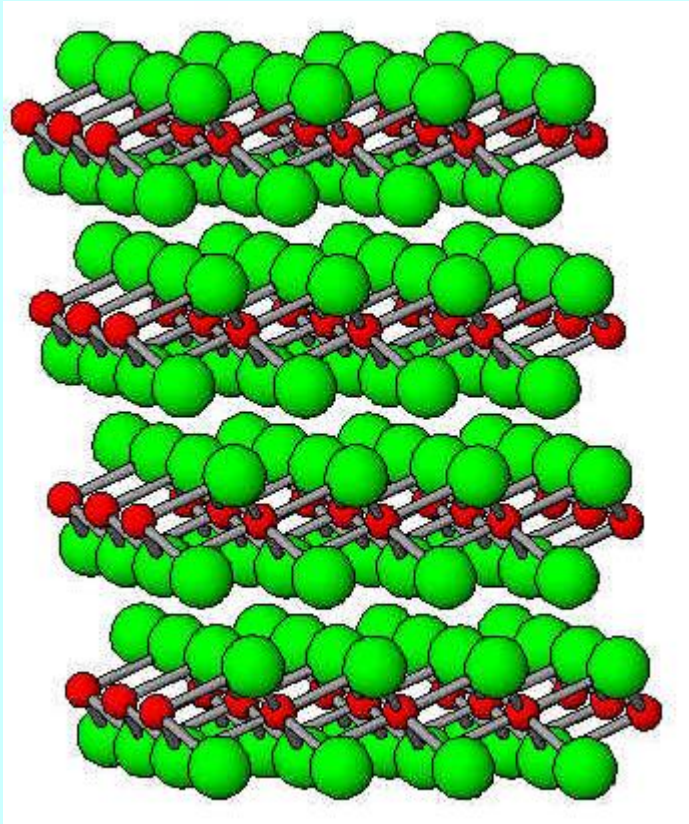
CdI_2 Hexagonal Close Packing



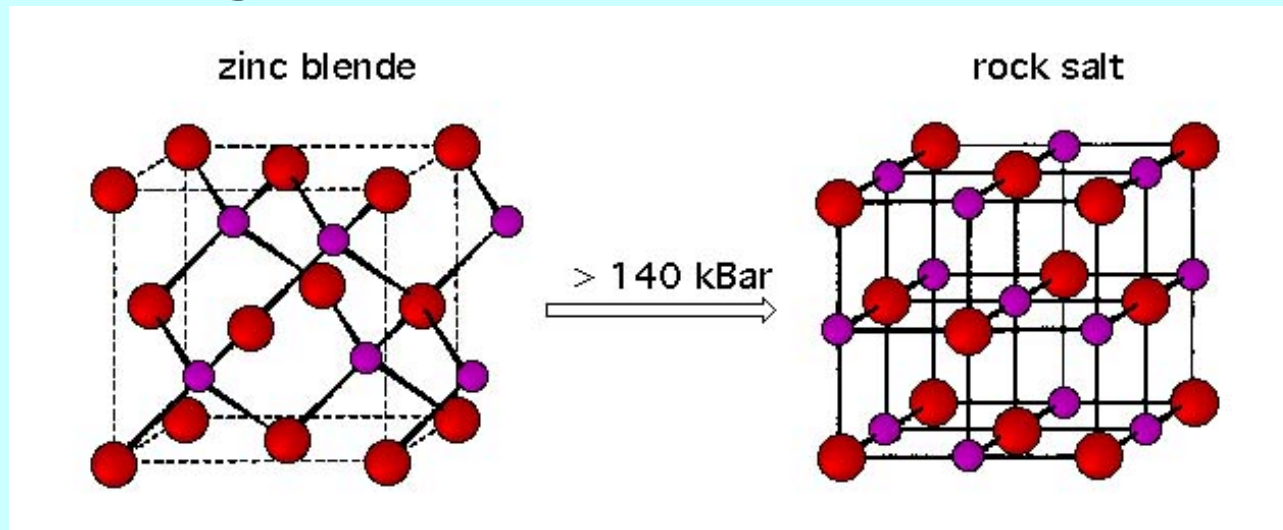
CdCl_2 Cubic Close Packing



CdCl_2 Cubic close packing



High Pressure Transformations

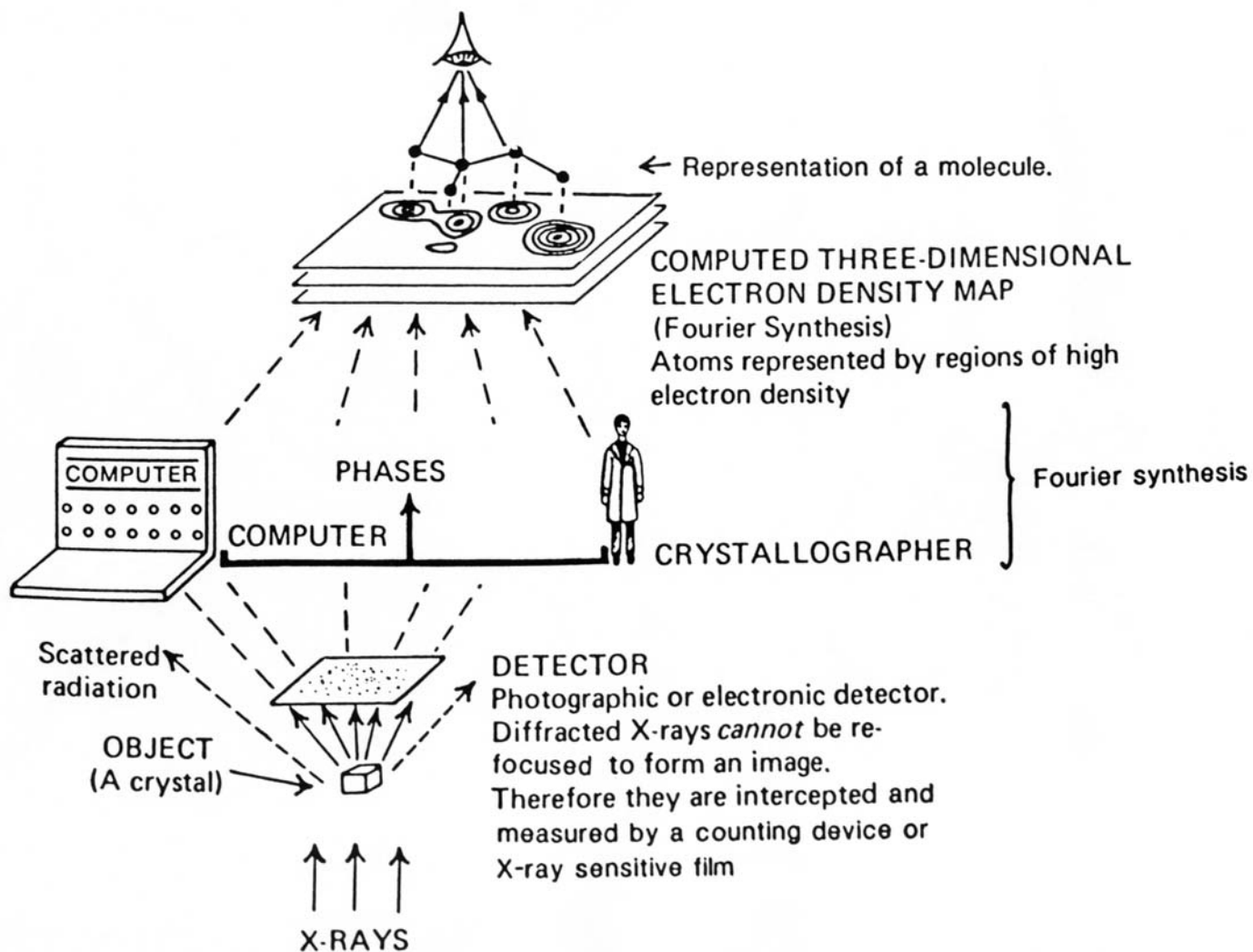


- high pressure phases
- higher density
- higher coordination number
- higher symmetry
- transition to from nonmetal to metal
- band mixing
- longer bonds

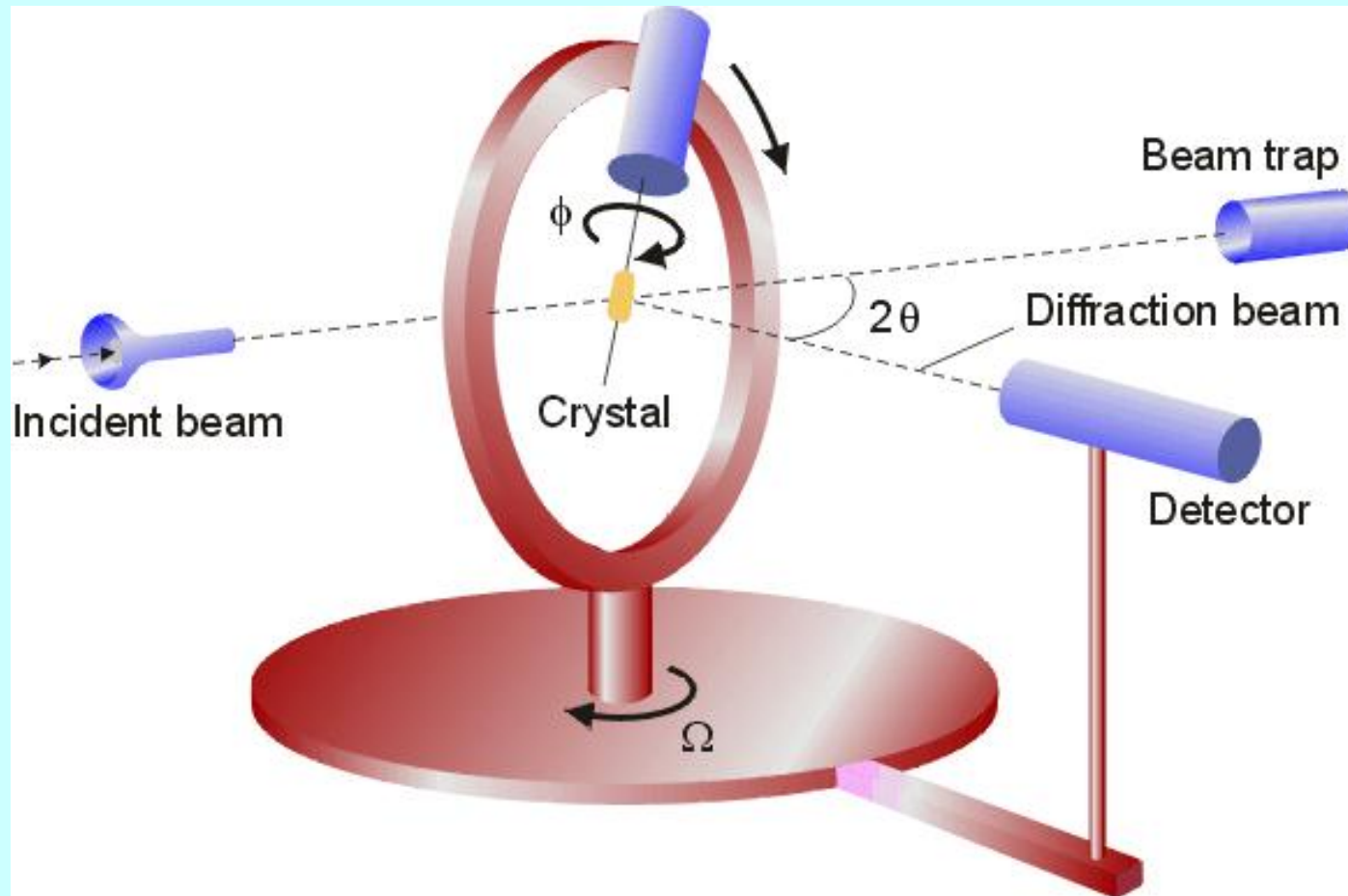
Pressure/Coordination Number Rule: increasing pressure – higher CN

Pressure/Distance Paradox: increasing pressure – longer bonds

X-ray structure analysis with single crystals



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



CAD4 (Kappa Axis Diffractometer)



IPDS (Imaging Plate Diffraction System)

