Crystalline State

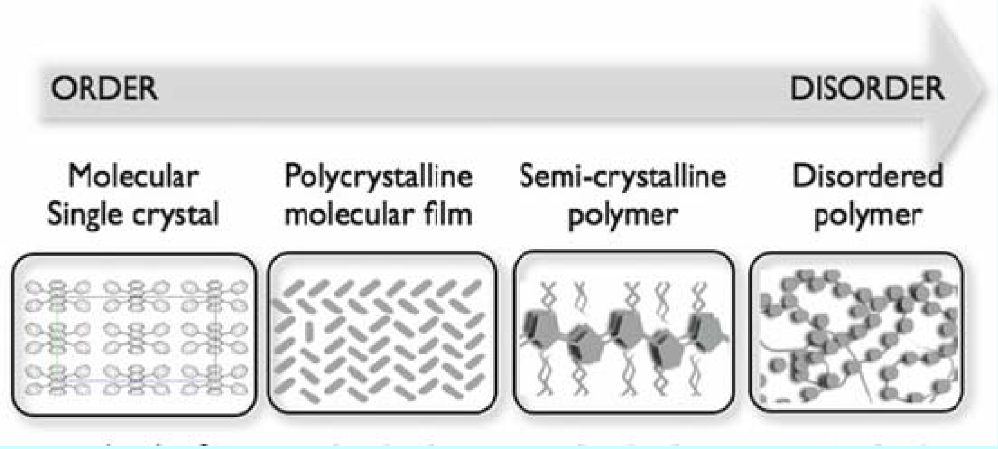
Basic Structural Chemistry

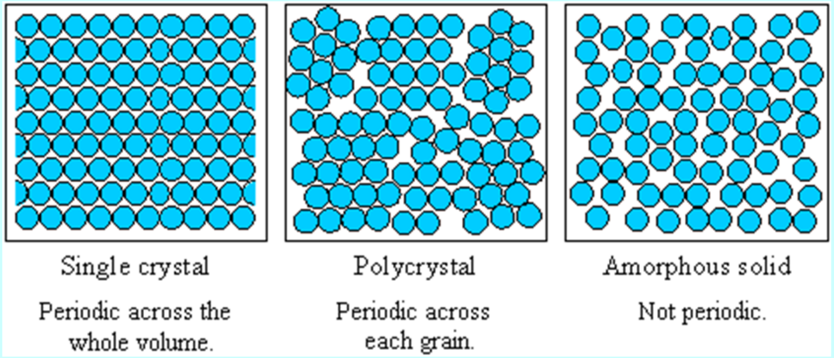
Structure Types

Lattice Energy

Pauling Rules

Degree of Crystallinity





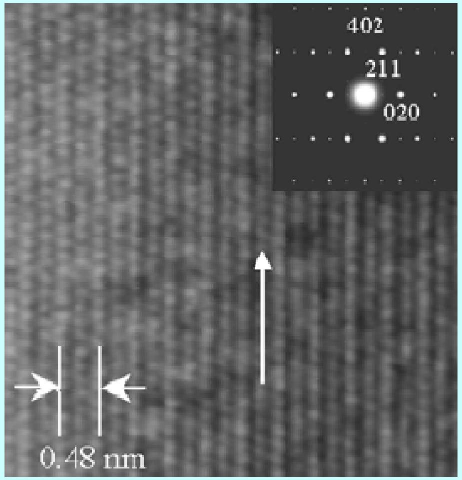
Crystalline – 3D long range order
- **Single-crystalline**
- **Polycrystalline - many crystallites of different sizes and orientations (random, oriented)**

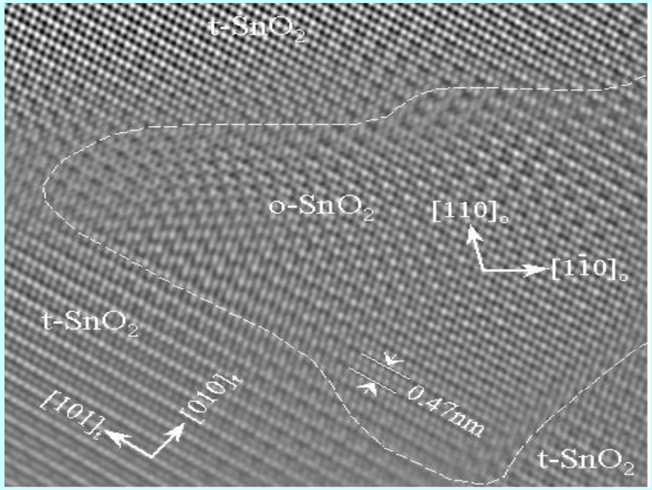
Paracrystalline - short and medium range order,
lacking long range order

Amorphous – no order, random

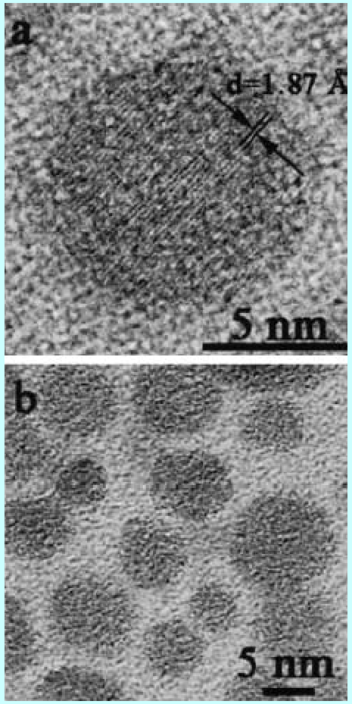
Degree of Crystallinity

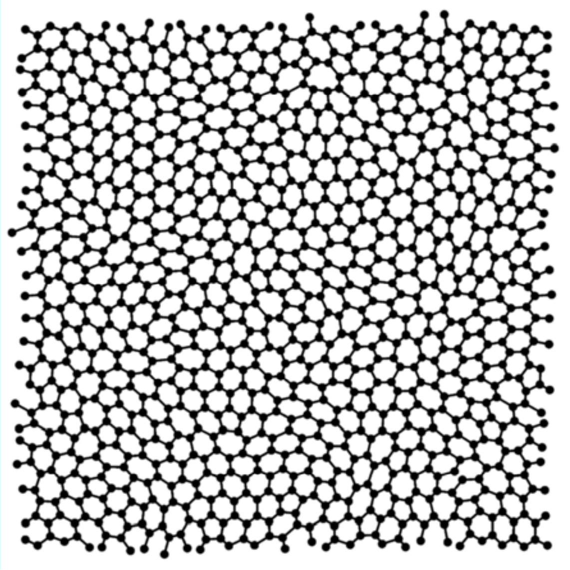
- Single Crystalline
- Polycrystalline
- Semicrystalline
- Amorphous





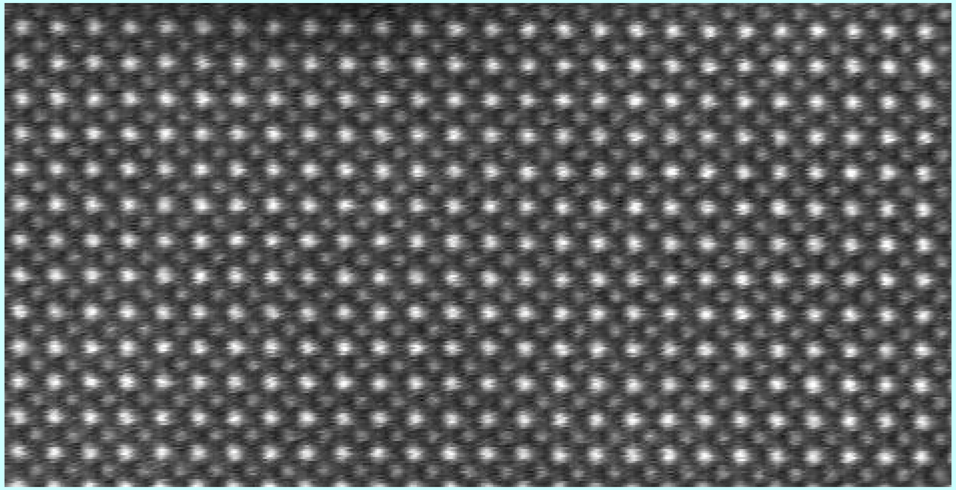
Grain boundaries



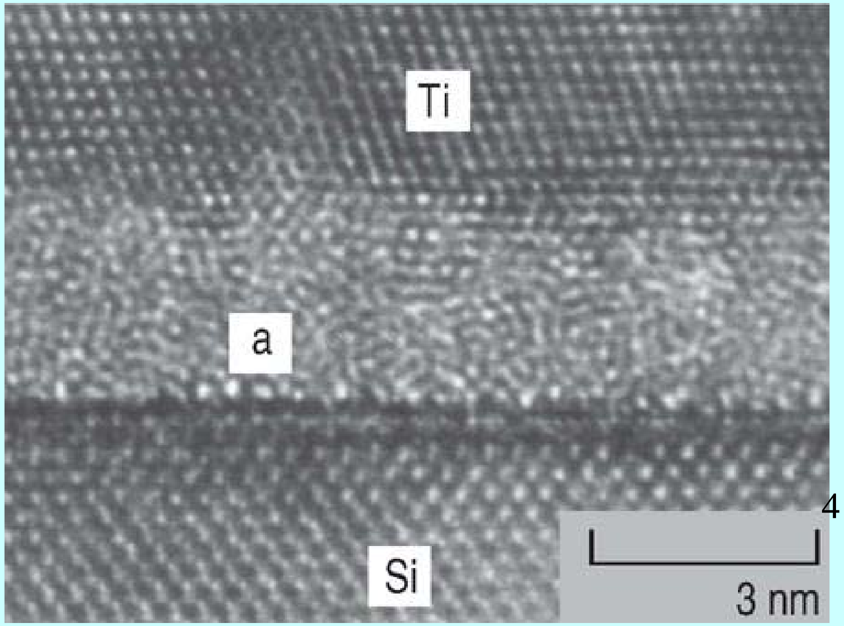


Degree of Crystallinity

A crystalline solid: HRTEM image of strontium titanate. Brighter atoms are Sr and darker are Ti.

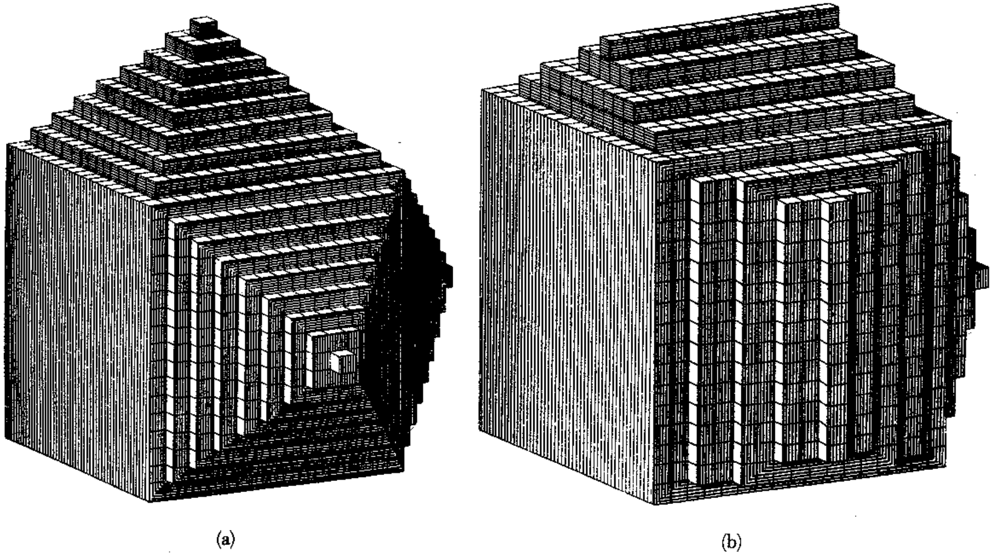


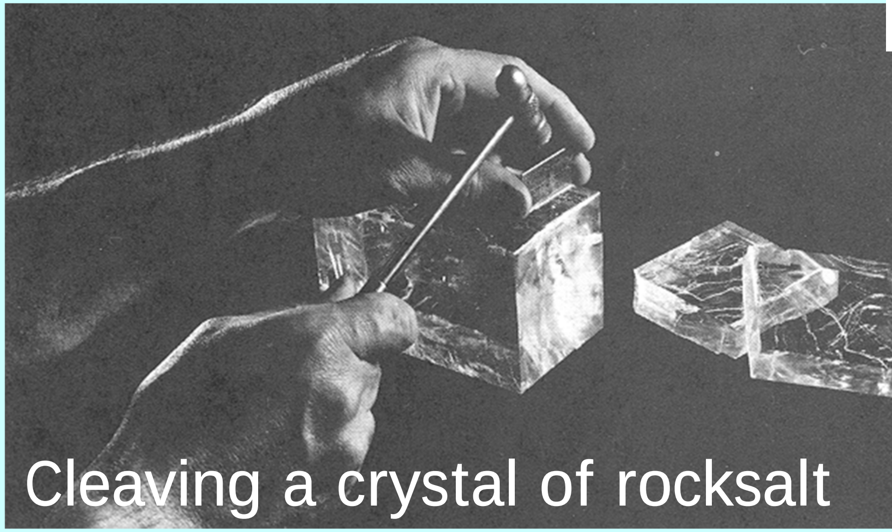
A TEM image of amorphous interlayer at the Ti/(001)Si interface in an as-deposited sample.



Crystal Structure

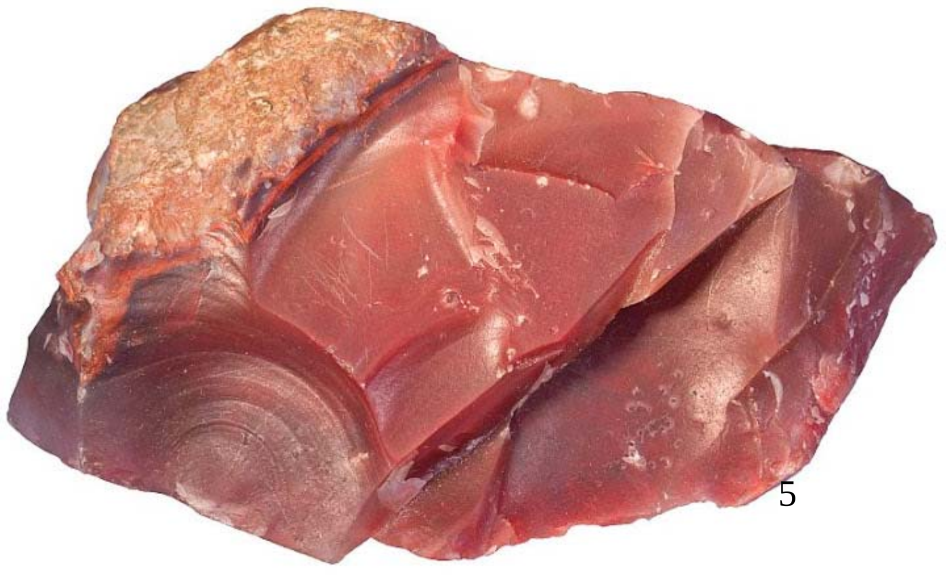
The building blocks of these two are identical, but different crystal faces are developed



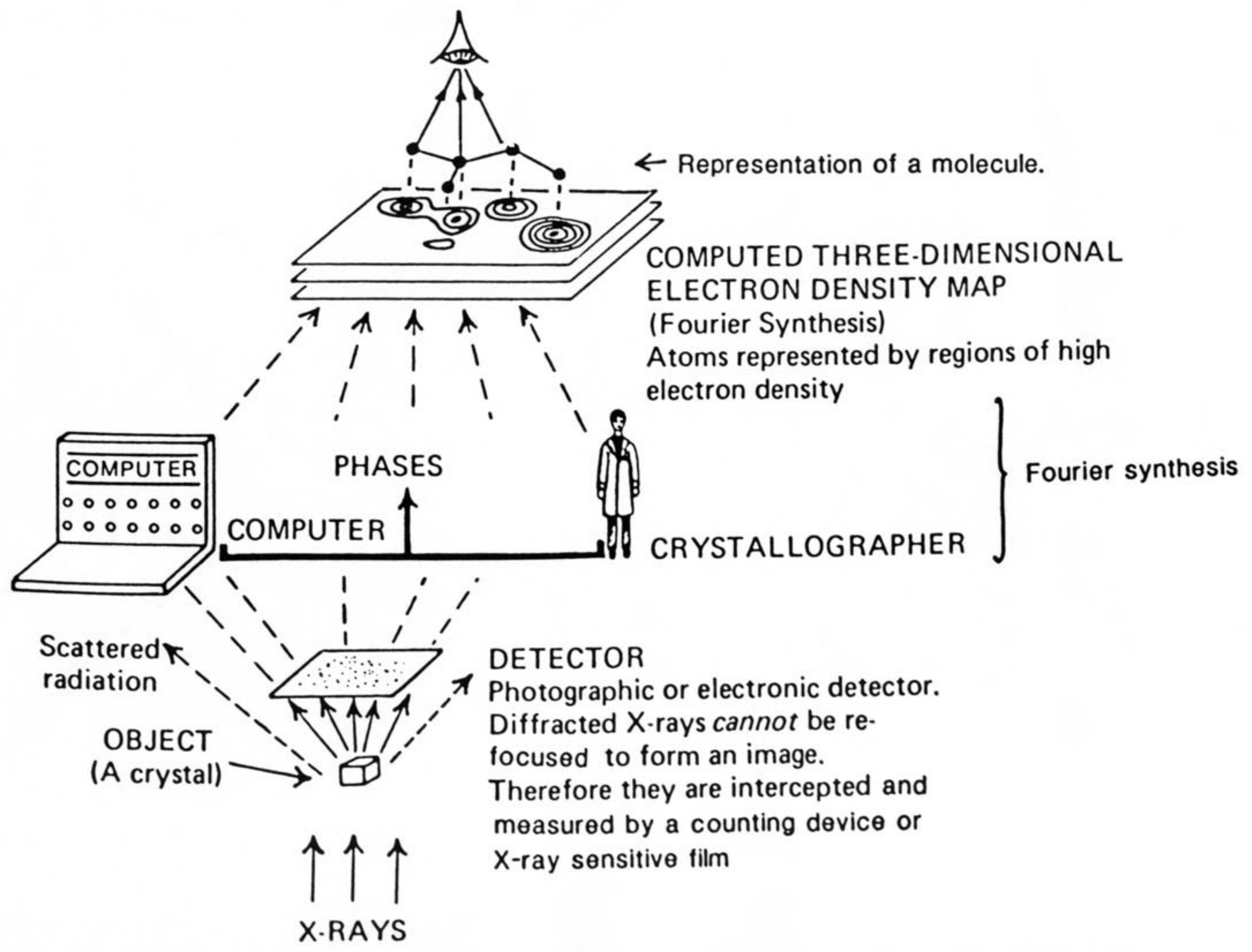


Cleaving a crystal of rocksalt

Conchoidal fracture in chalcedony



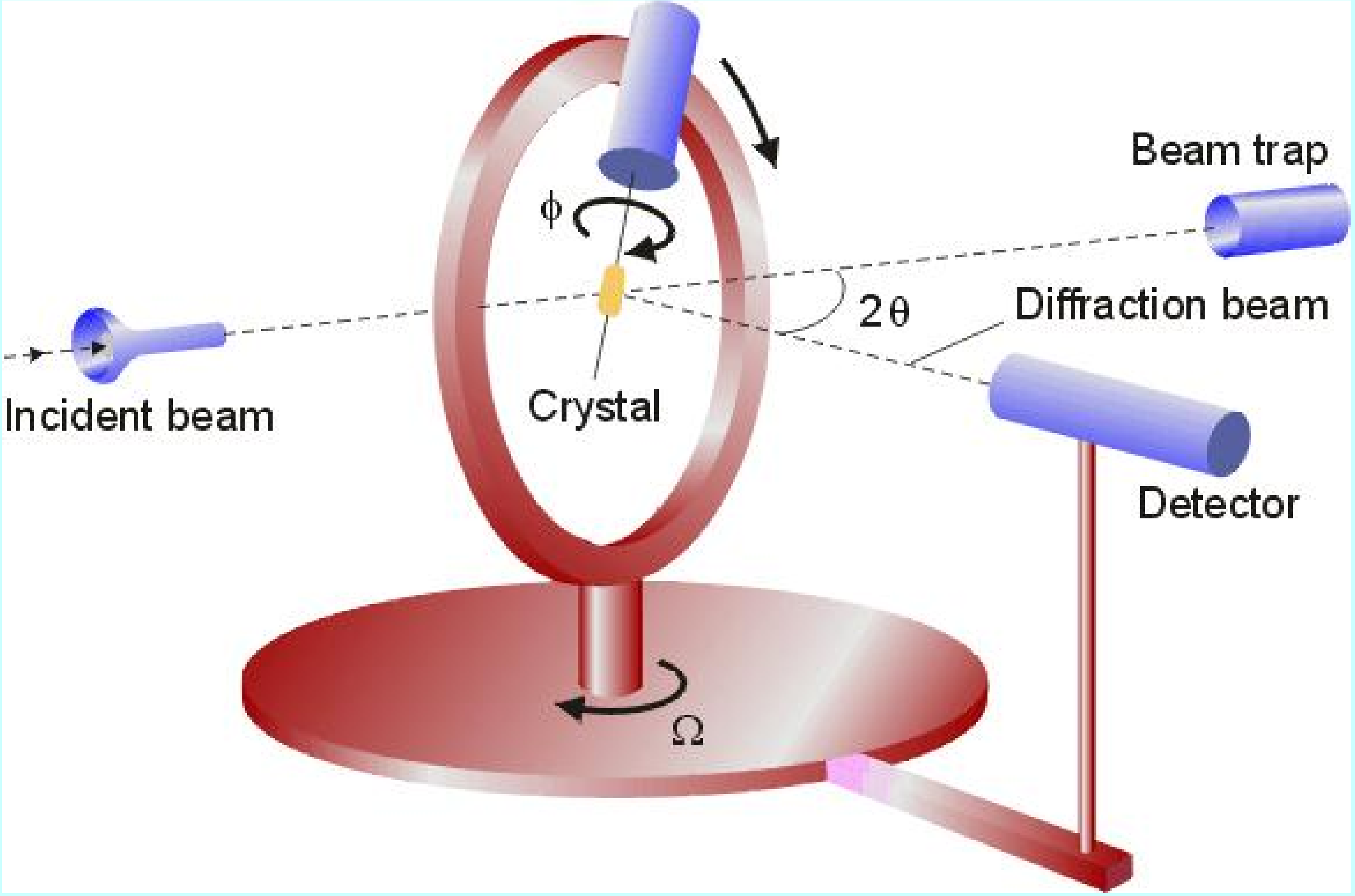
X-ray structure analysis with single crystals



Atoms represented by regions of high electron density

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

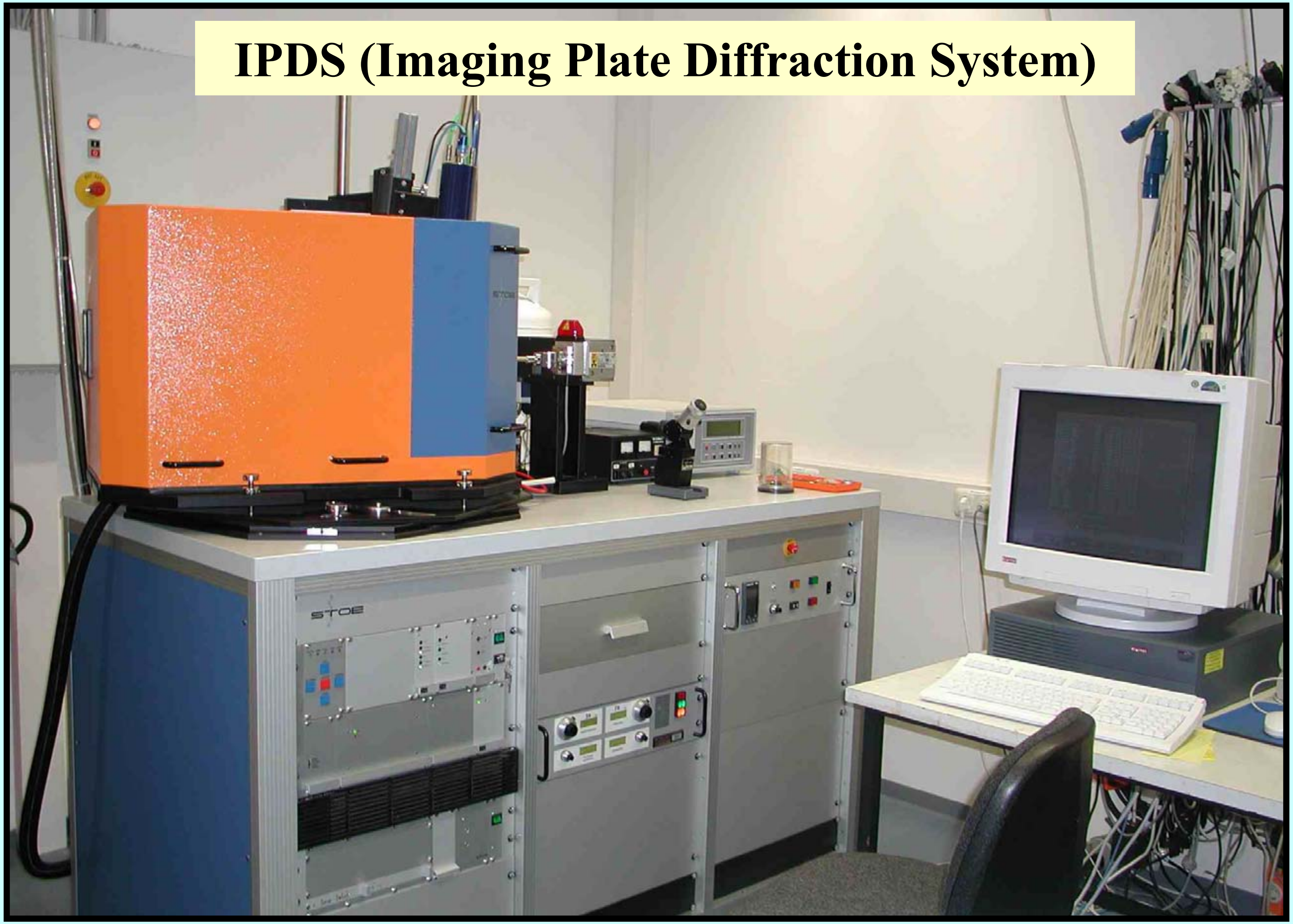
Single crystal X-ray diffraction structure analysis



a four circle X-ray diffractometer

CAD4 (Kappa Axis Diffractometer)

IPDS (Imaging Plate Diffraction System)



Crystals

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

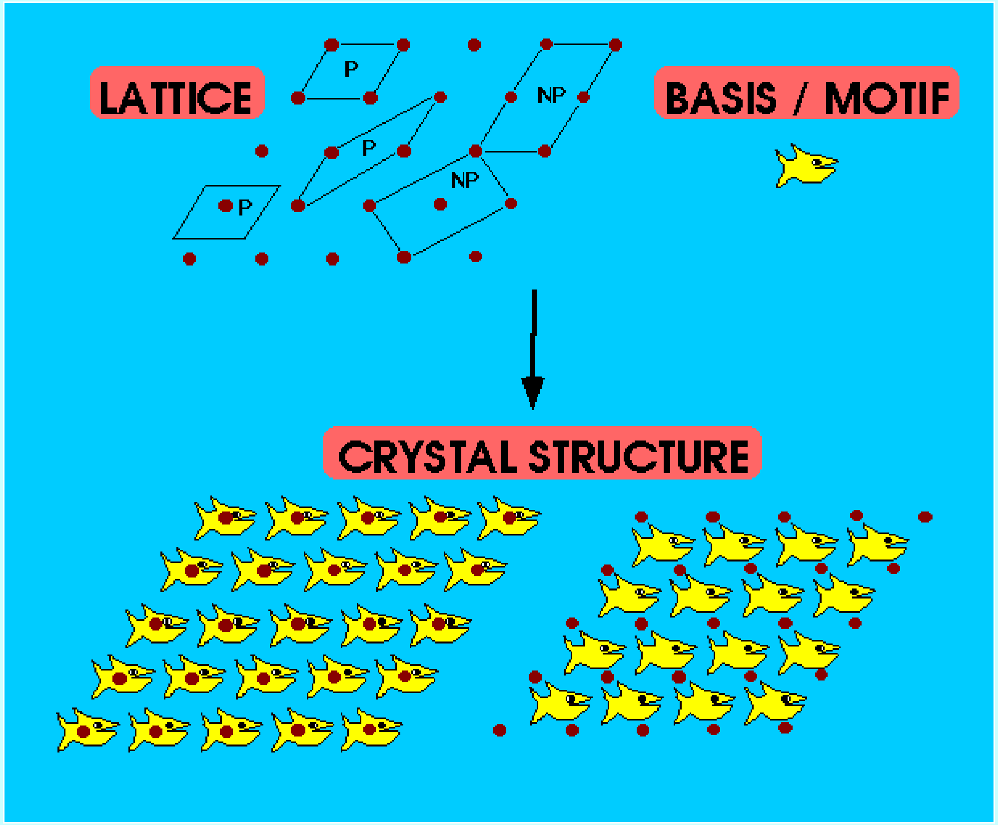
$$\overline{T} = n_1\overline{a} + n_2\overline{b} + n_3\overline{c}$$

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

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

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

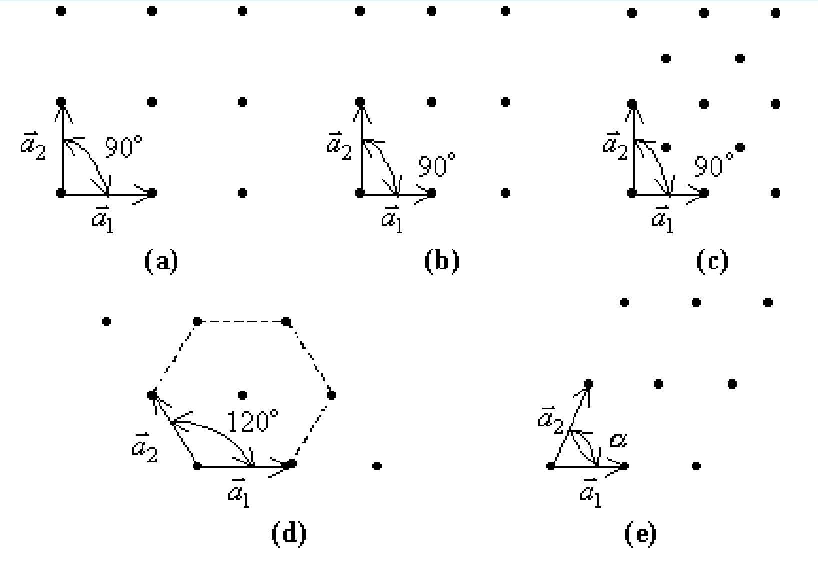
Planar Lattice 2D



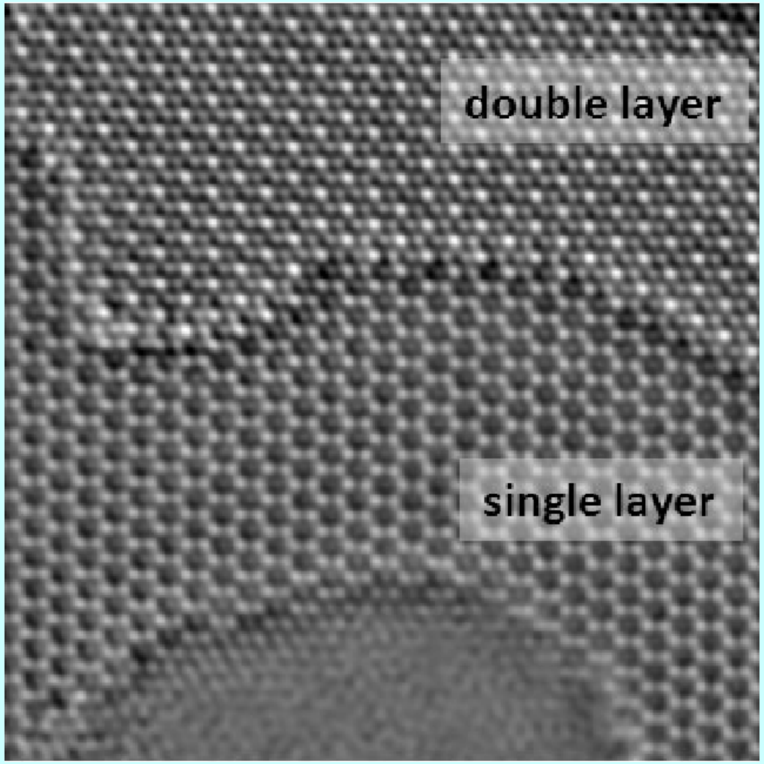
LATTICE
A lattice is the geometrical pattern formed by points representing the locations of these basis or motifs.

BASIS OR MOTIFS
Basis are the positions of the atoms inside the unit cell.

Five Planar Lattices

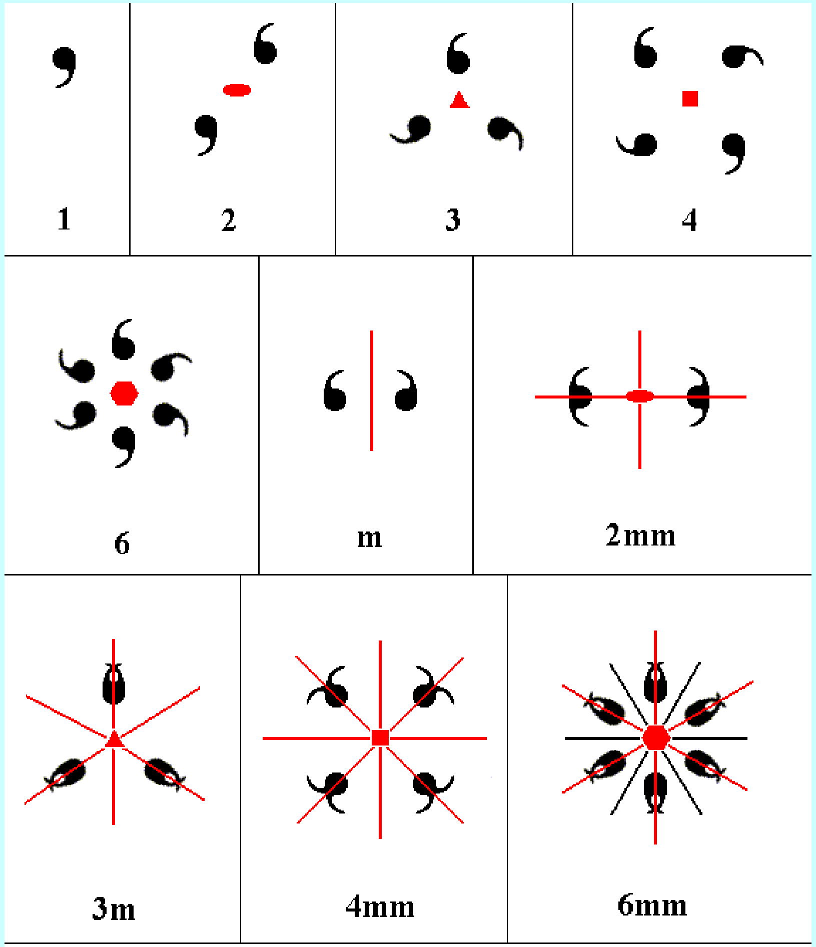


Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2$, $\alpha = 90°$
Rectangular	2	$a_1 \neq a_2$, $\alpha = 90°$
Hexagonal	1	$a_1 = a_2$, $\alpha = 120°$
Oblique	1	$a_1 \neq a_2$, $\alpha \neq 120°$, $\alpha \neq 90°$



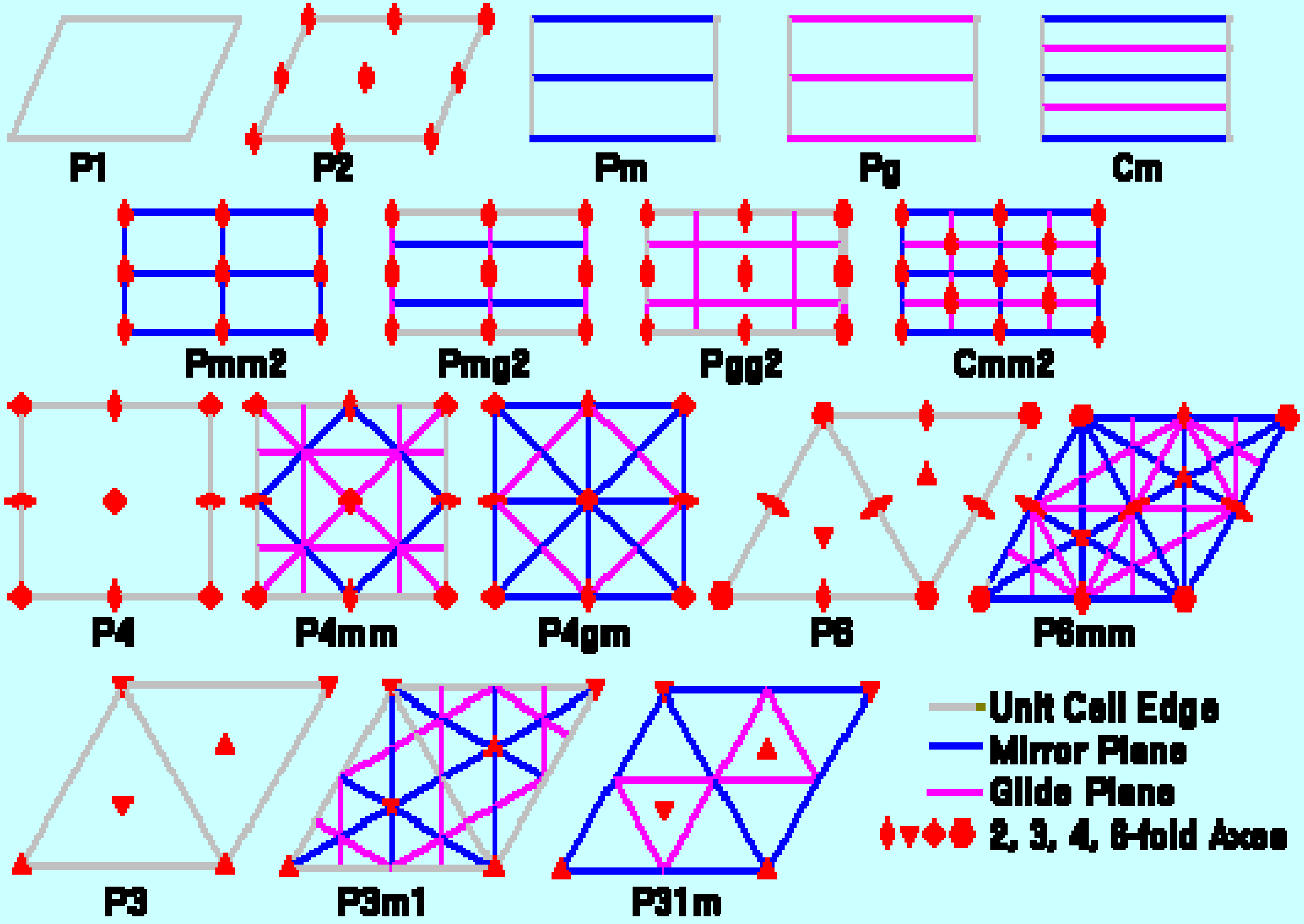
graphene

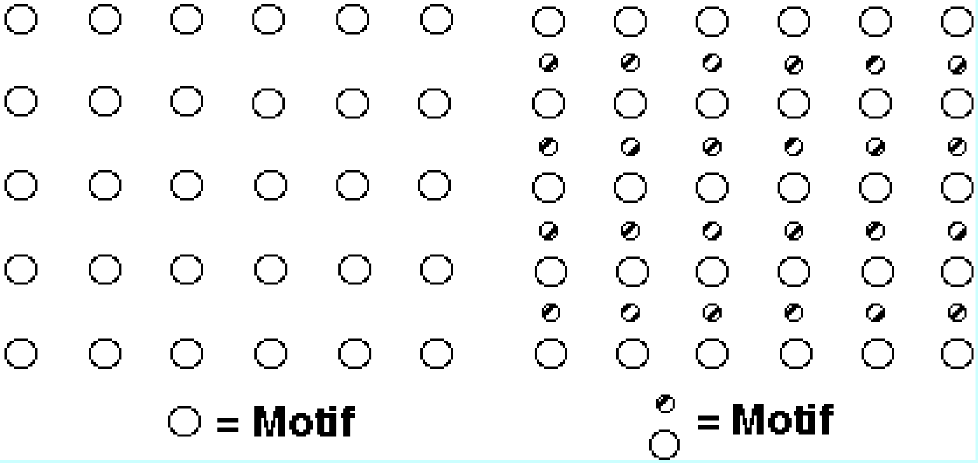
Ten Planar Point Groups

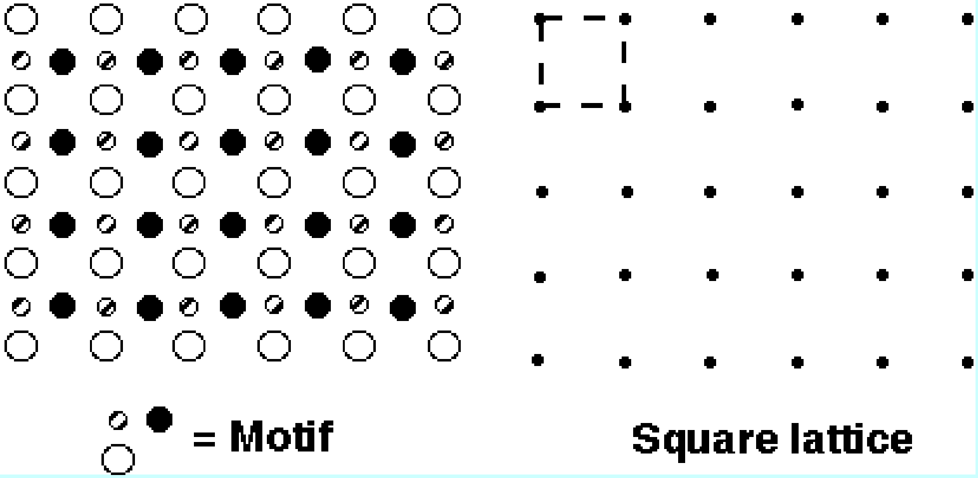


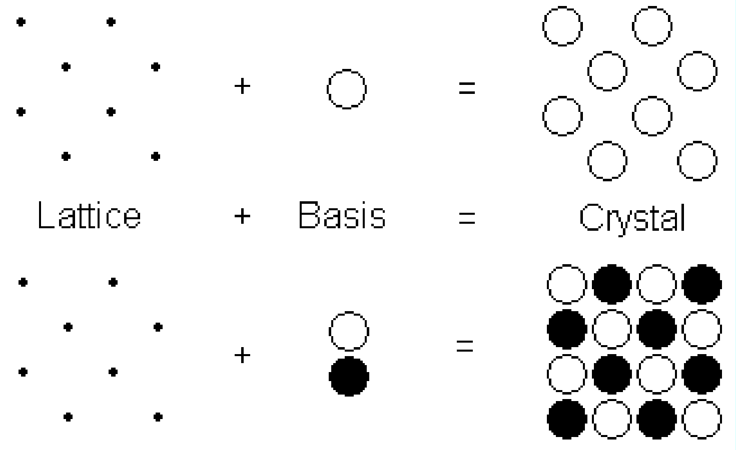
The Ten Planar Point Groups

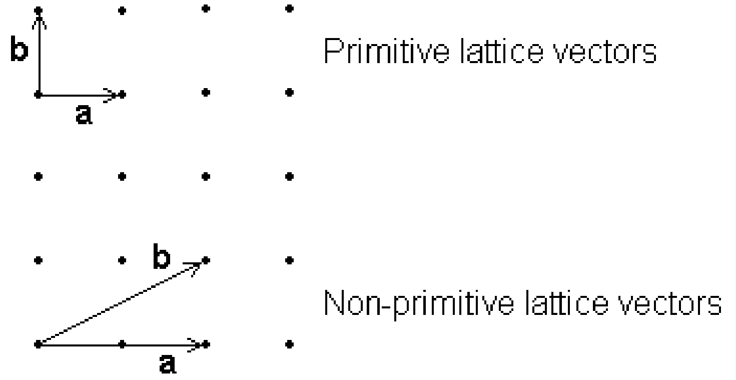
17 Plane Space Groups

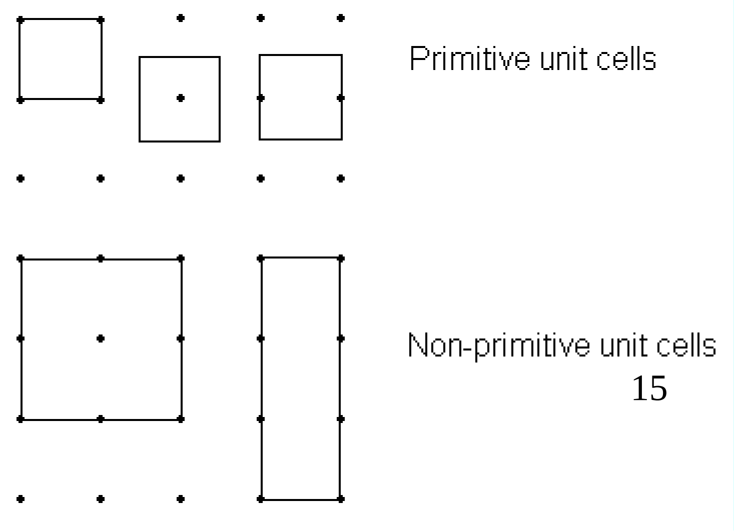


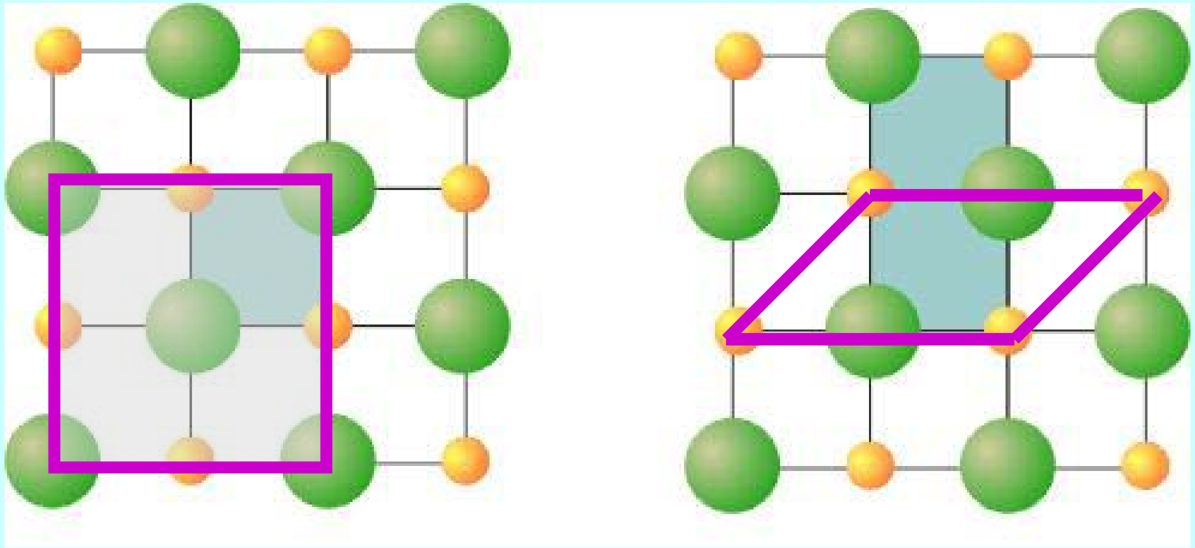

= Motif
= Motif


= Motif
Square lattice


+
=
Lattice
+
Basis
=
Crystal
+
=


b
a
Primitive lattice vectors
b
a
Non-primitive lattice vectors


Primitive unit cells
Non-primitive unit cells

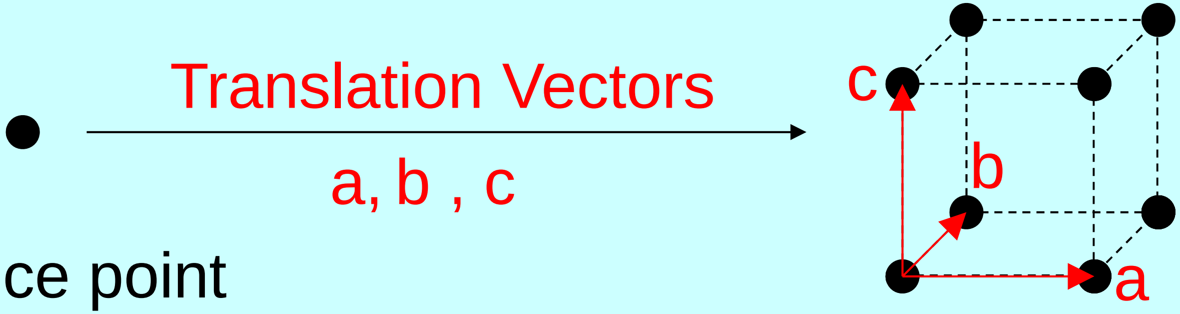


Unit Cell: An „imaginary“ parallel sided region of a structure from which the entire crystal can be constructed by purely translational displacements. It contains one unit of the translationally repeating pattern. Content of a unit cell represents its chemical composition. The unit cells that are commonly formed by joining neighbouring lattice points by straight lines, are called primitive unit cells.

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

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

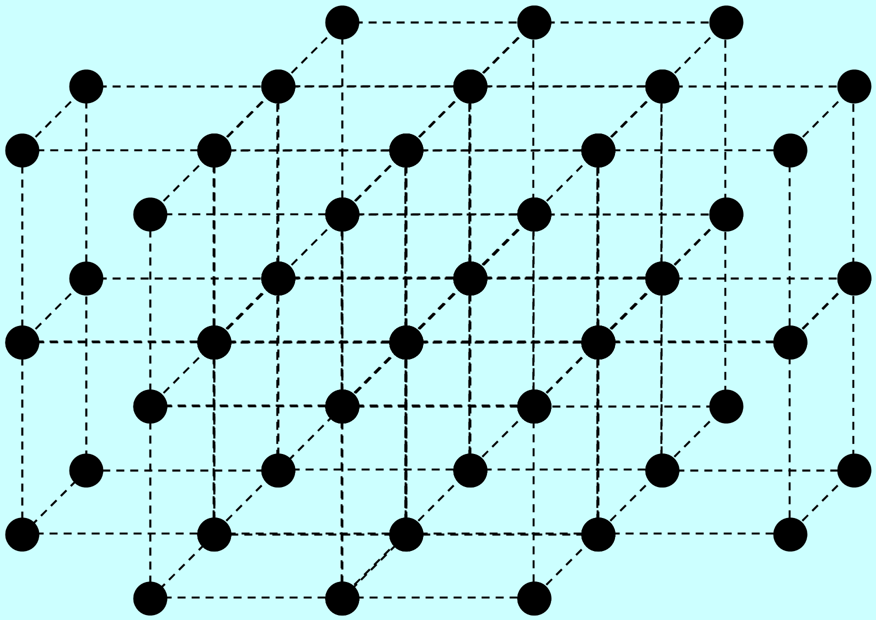
Crystal = Periodic Arrays of Atoms



Translation Vectors

a, b , c

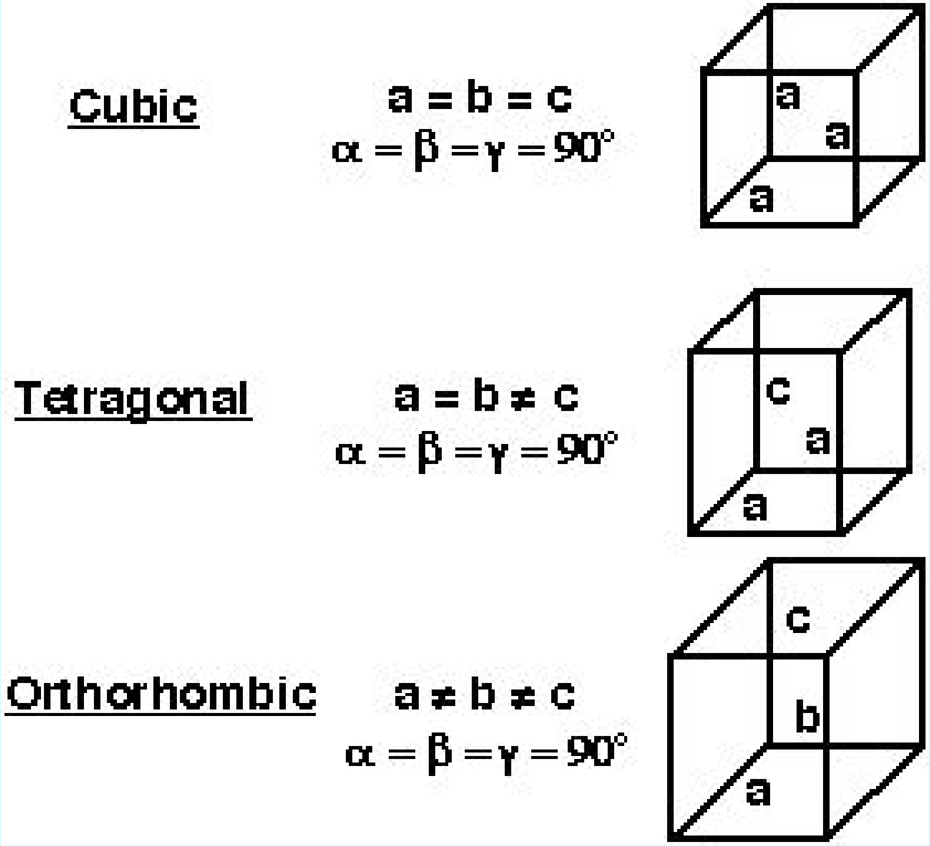
Lattice point
(Atom, molecule, group of molecules,…)



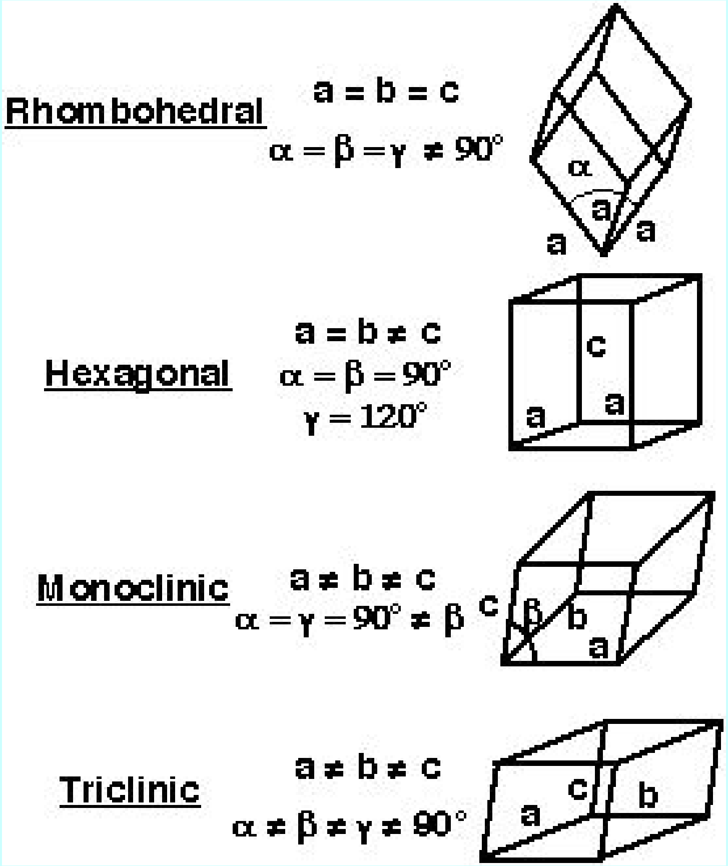
Primitive Cell:

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

Seven Crystal Systems



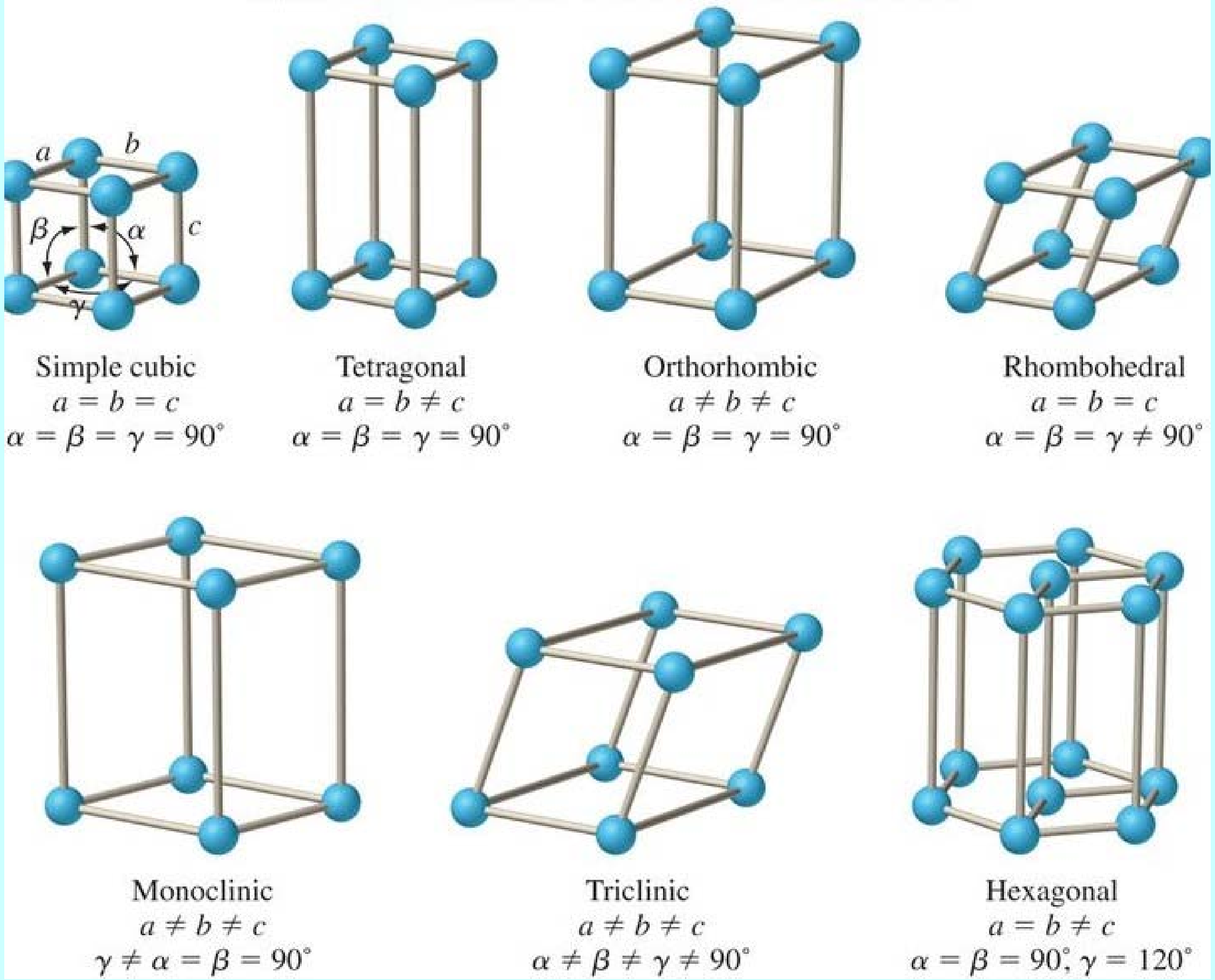
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90°$
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$



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

All angles 90°

Seven Crystal Systems



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

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

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

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

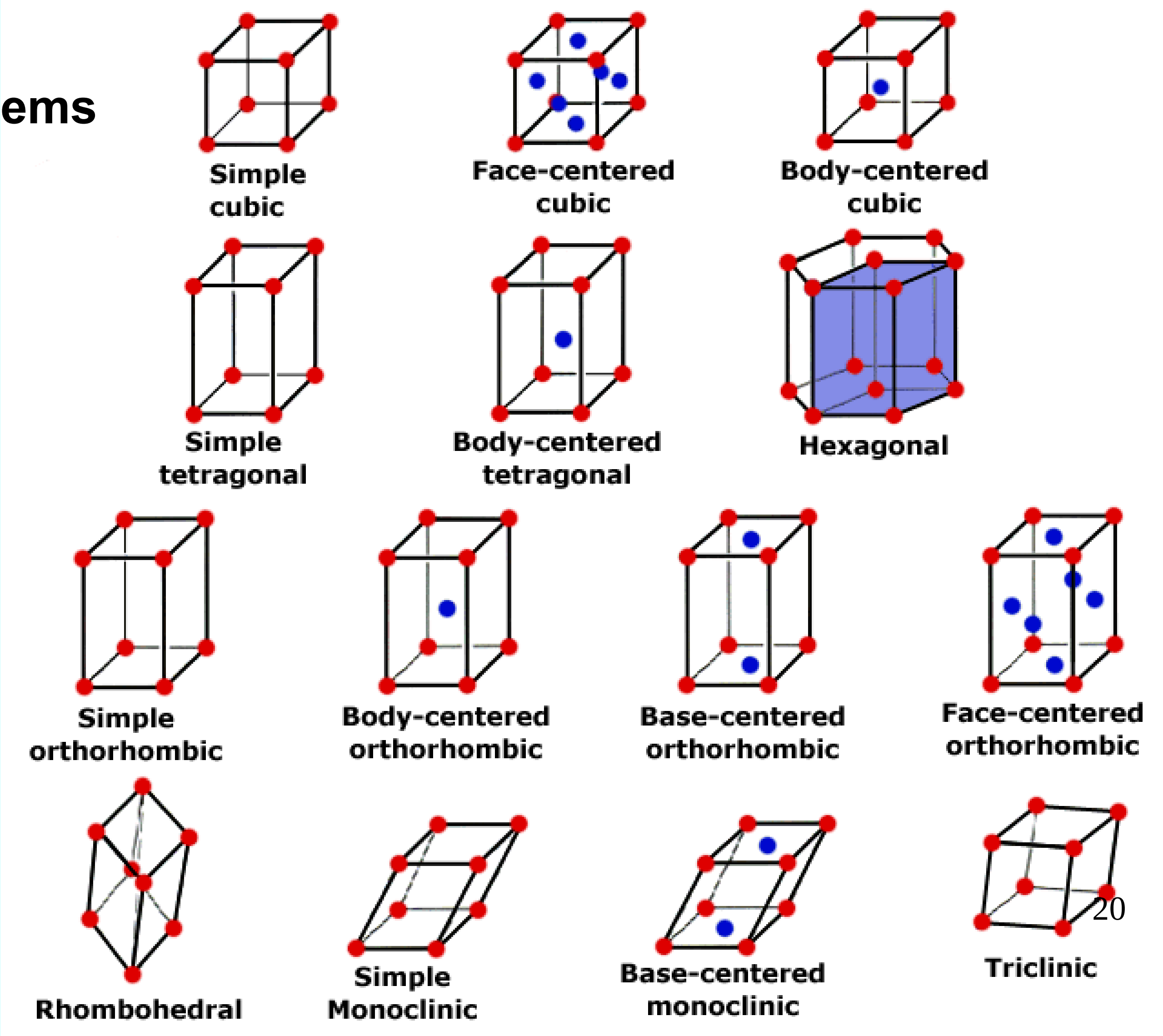
Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90^\circ$

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

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

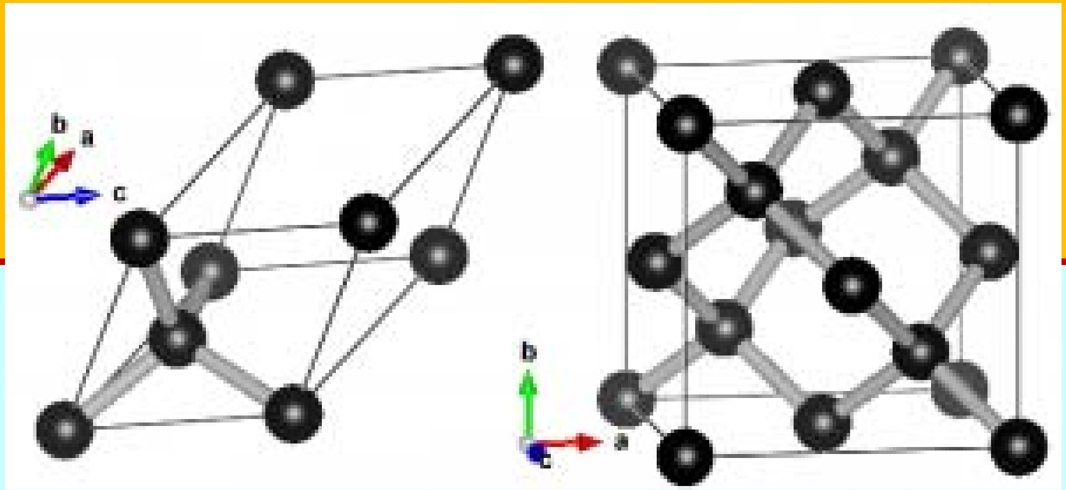
Fourteen Bravais Lattices

Seven Crystal Systems
+ Centering



3D Lattices and Space Groups

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

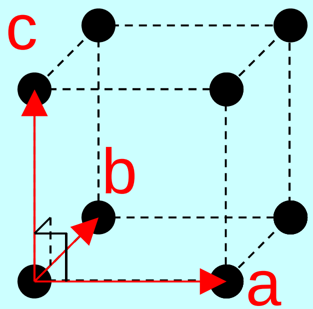


Simple Cubic (SC)

Conventional Cell = Primitive Cell

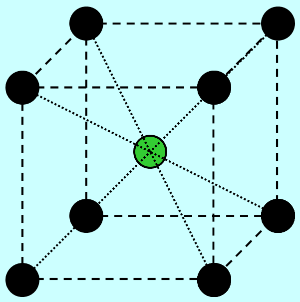
a = b = c

a ⊥ b ⊥ c

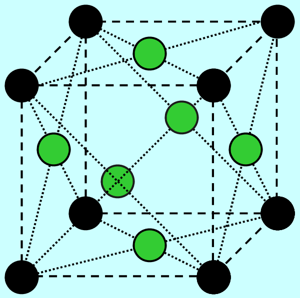


Add one atom at the center of the cube

Add one atom at the center of each face



Body-Centered Cubic (BCC)



Face-Centered Cubic (FCC)

Conventional Unit Cell ≠ Primitive Cell

Primitive Cell

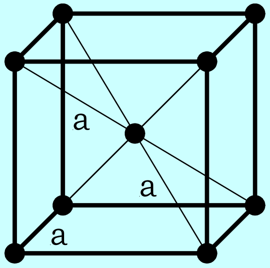
A ***primitive cell*** of the lattice = volume of space translated through all the vectors in a lattice that just fills all of space without overlapping or leaving voids.

A primitive cell contains just **one** Bravais **lattice point**.

The primitive cell is the smallest cell that can be translated throughout space to completely recreate the entire lattice.

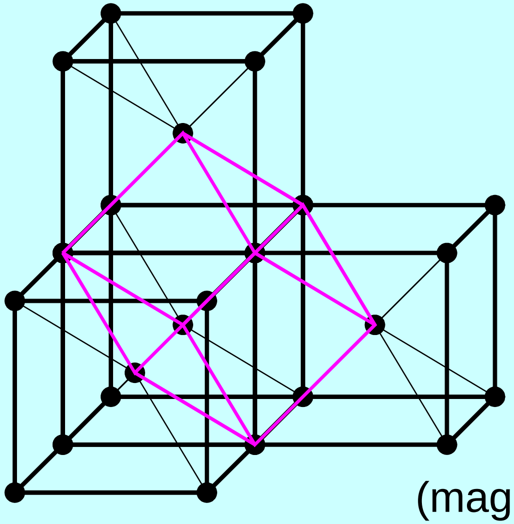
There is not one unique shape of a primitive cell, many possible shapes.

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



Body-Centered
Cubic (I)

Unit Cell



(magenta)

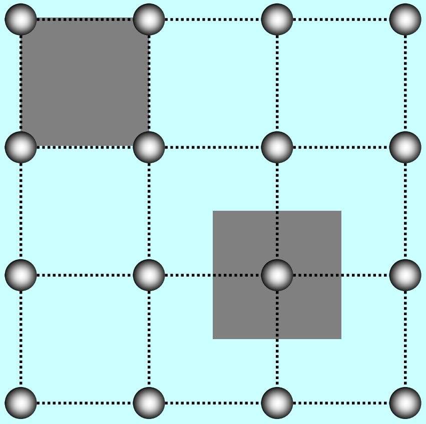
Primitive Cell

Primitive Cell

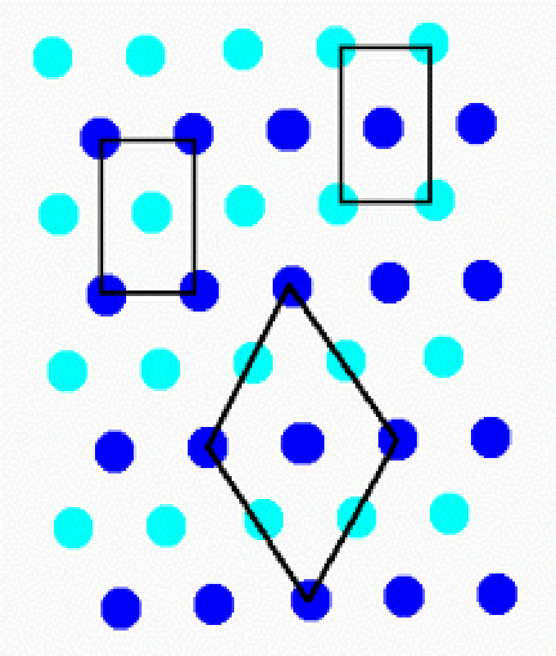
A ***primitive cell*** of the lattice may be constructed in 2 ways:

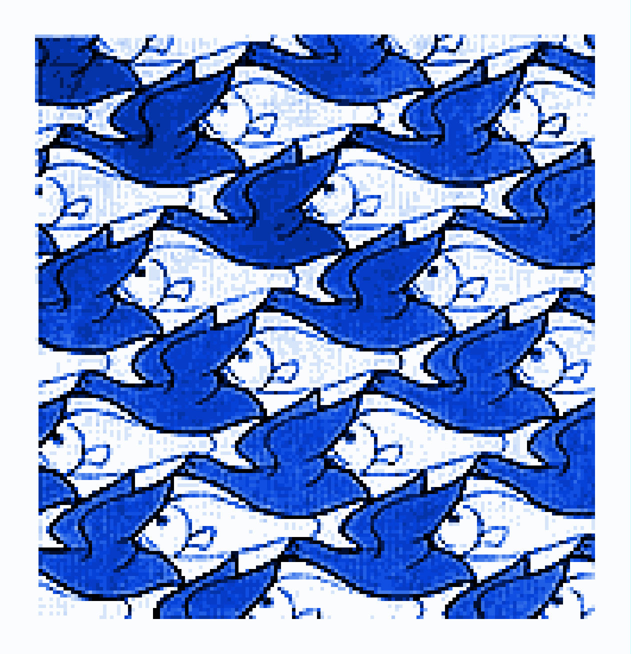
- The primitive cell may have the lattice point confined at its CENTER = the WIGNER-SEITZ cell

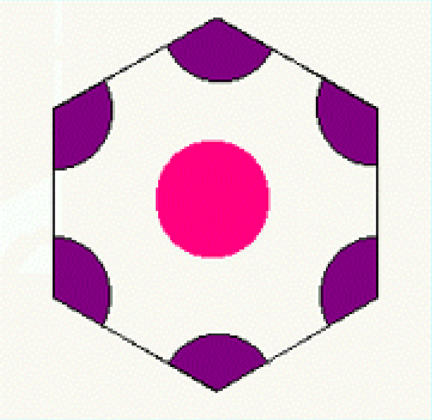
- The primitive cell may be formed by constructing lines BETWEEN lattice points, the lattice points lie at the VERTICES of the cell



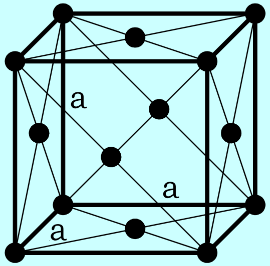
Primitive Cell





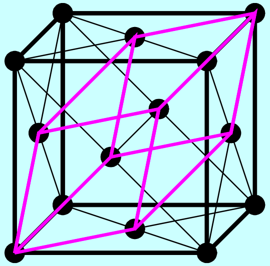


Nonprimitive Unit Cell vs. Primitive Cell

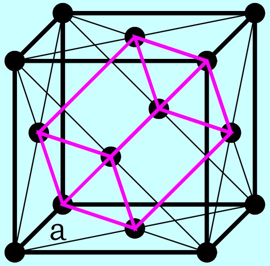


Face-Centered
Cubic (F)

Unit Cell



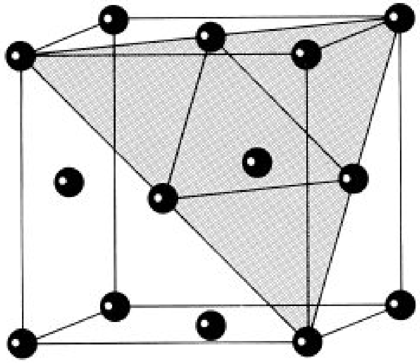
Primitive Cell



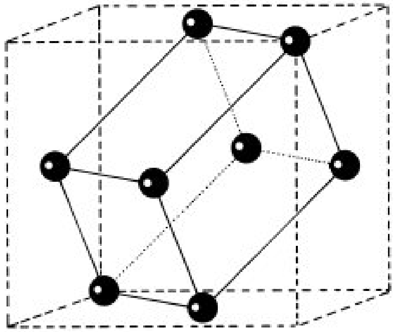
Rotated 90º

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

Nonprimitive Unit Cell vs. Primitive Cell



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

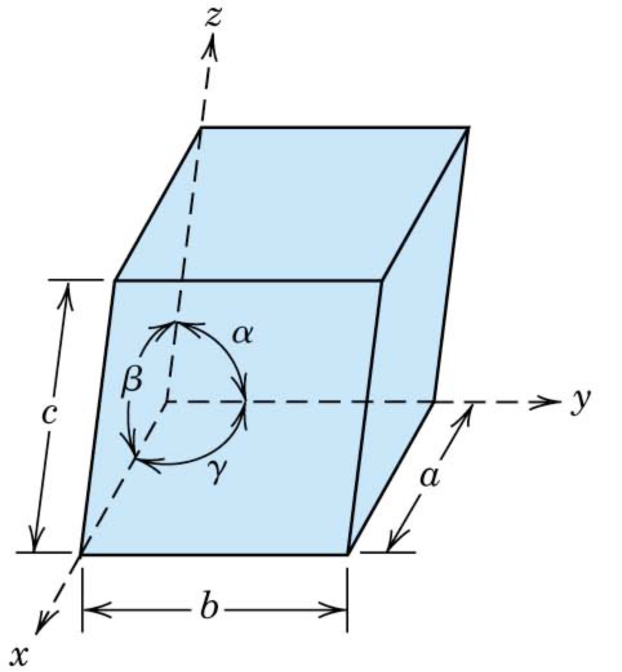


(*b*) Primitive rhombohedral unit cell

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

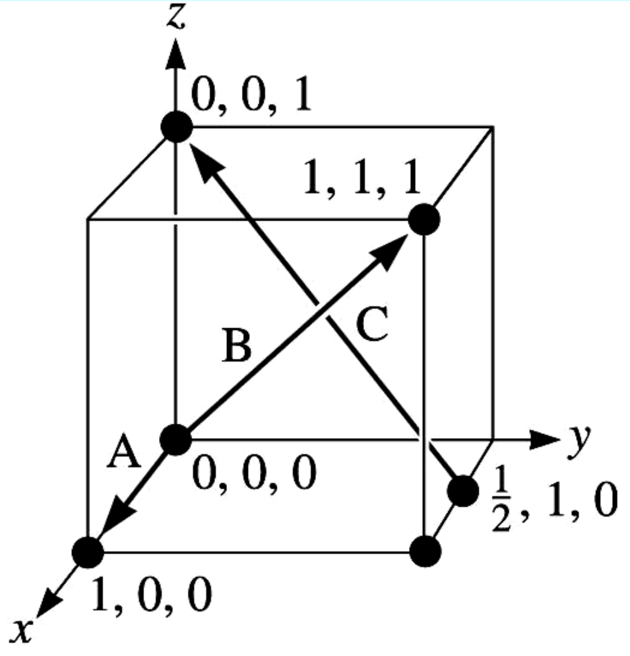
Index System for Points

1) **Coordinates within a unit cell**
2) **Express the coordinates u v w as fractions of unit cell vectors (lattice parameters) a, b, and c**
3) **Entire lattice can be referenced by one unit cell**



Central point coordinates?

Index System for Directions (Miller Indices)



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

u1 v1 w1 and u2 v2 w2

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

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

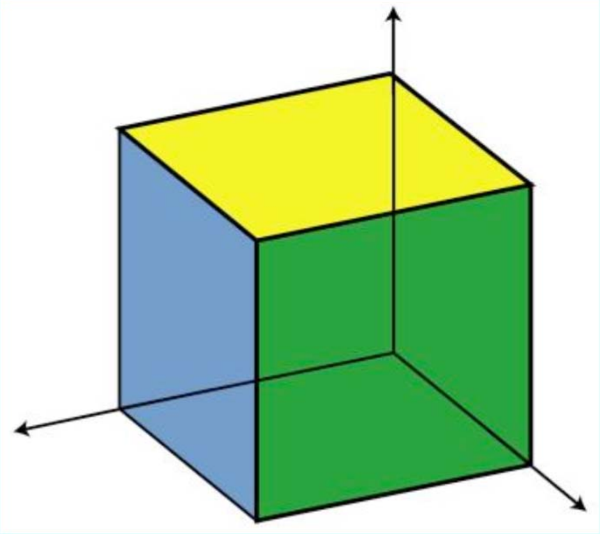
3) Clear fractions from the differences to give indices in lowest integer values.

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

5) Negative = a bar over the integer.

A = [100]
B = [111]
C = [1¯2¯2]

Index System for Directions
(Miller Indices)



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

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

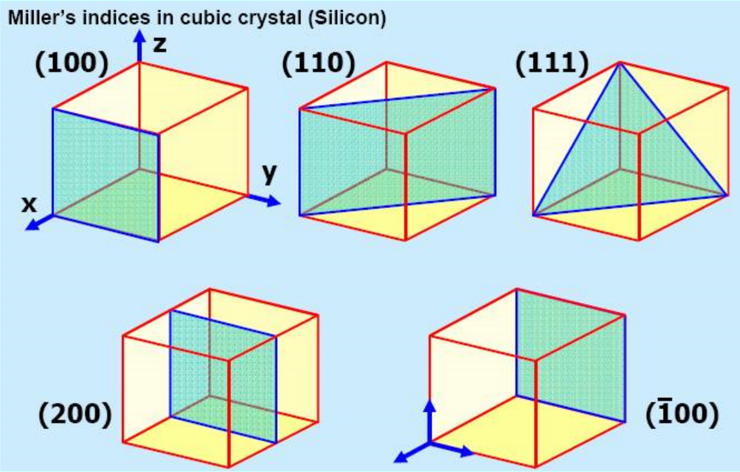
[1 0 0], [1¯ 0 0], [0 1 0], [0 1¯ 0], [0 0 1], [0 0 1¯]

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

Angled brackets denote a family of crystallographic directions.

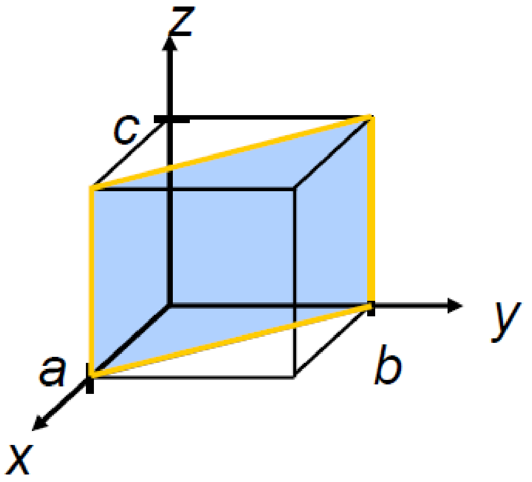
Index System for Crystal Planes (Miller Indices)

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

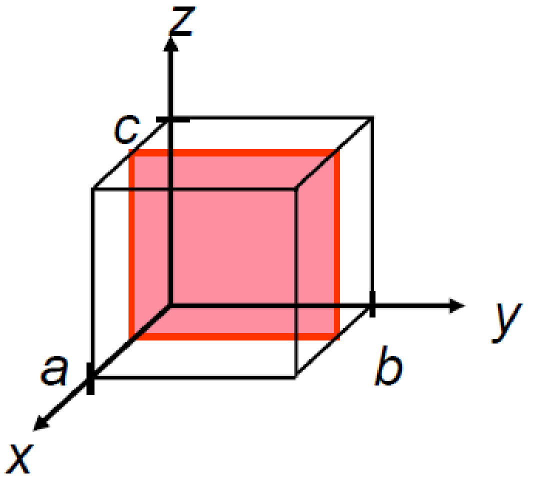


Index System for Crystal Planes (Miller Indices)

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



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

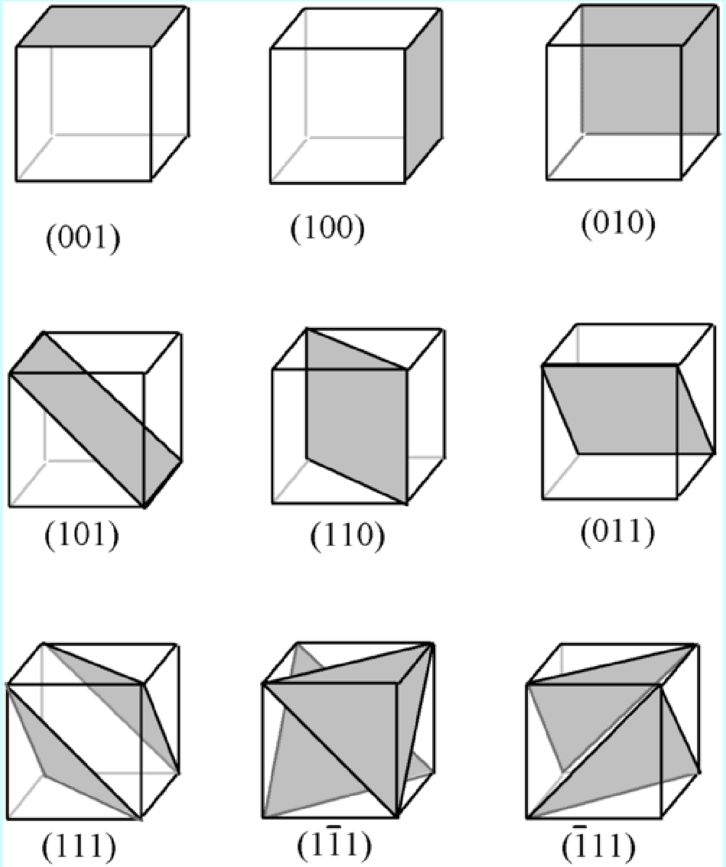


Index System for Crystal Planes
(Miller Indices)

Cubic system - planes having the same indices regardless of order or sign are equivalent

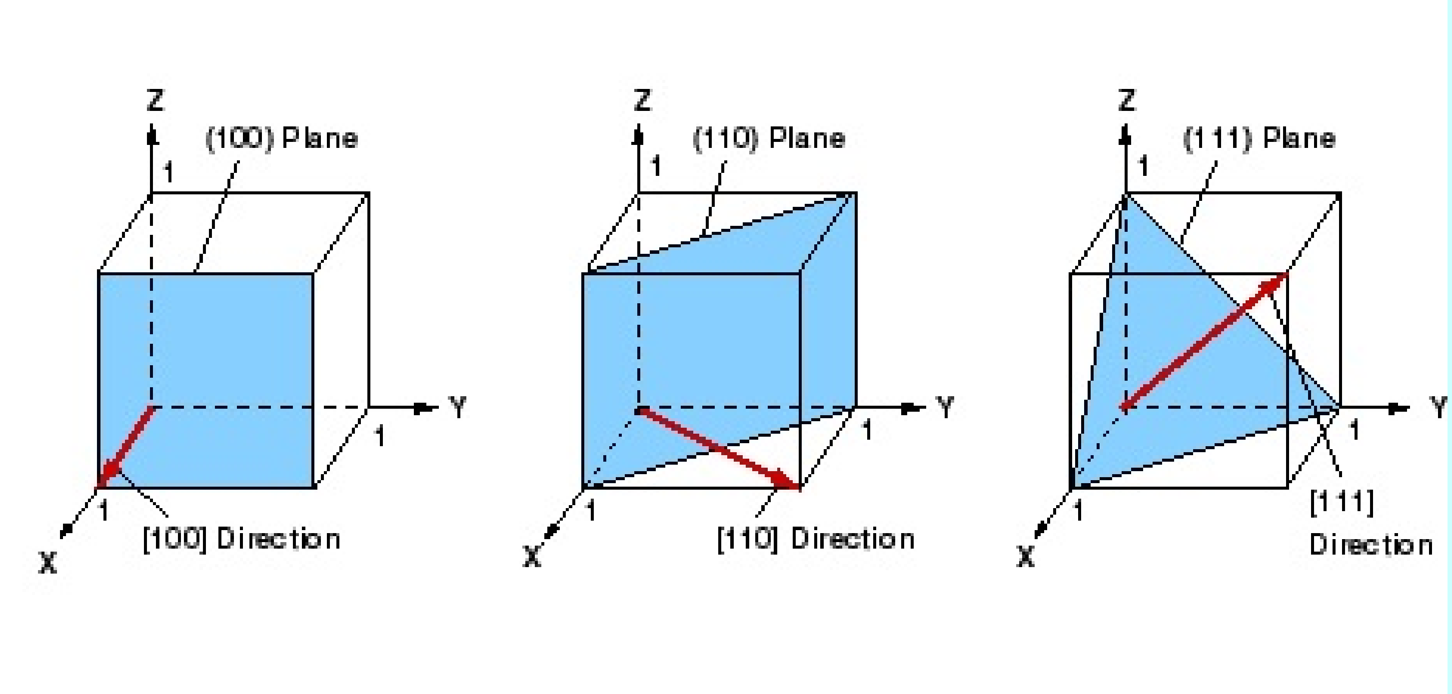
(111), (11¯1), (111¯) ….
belong to {111} family

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

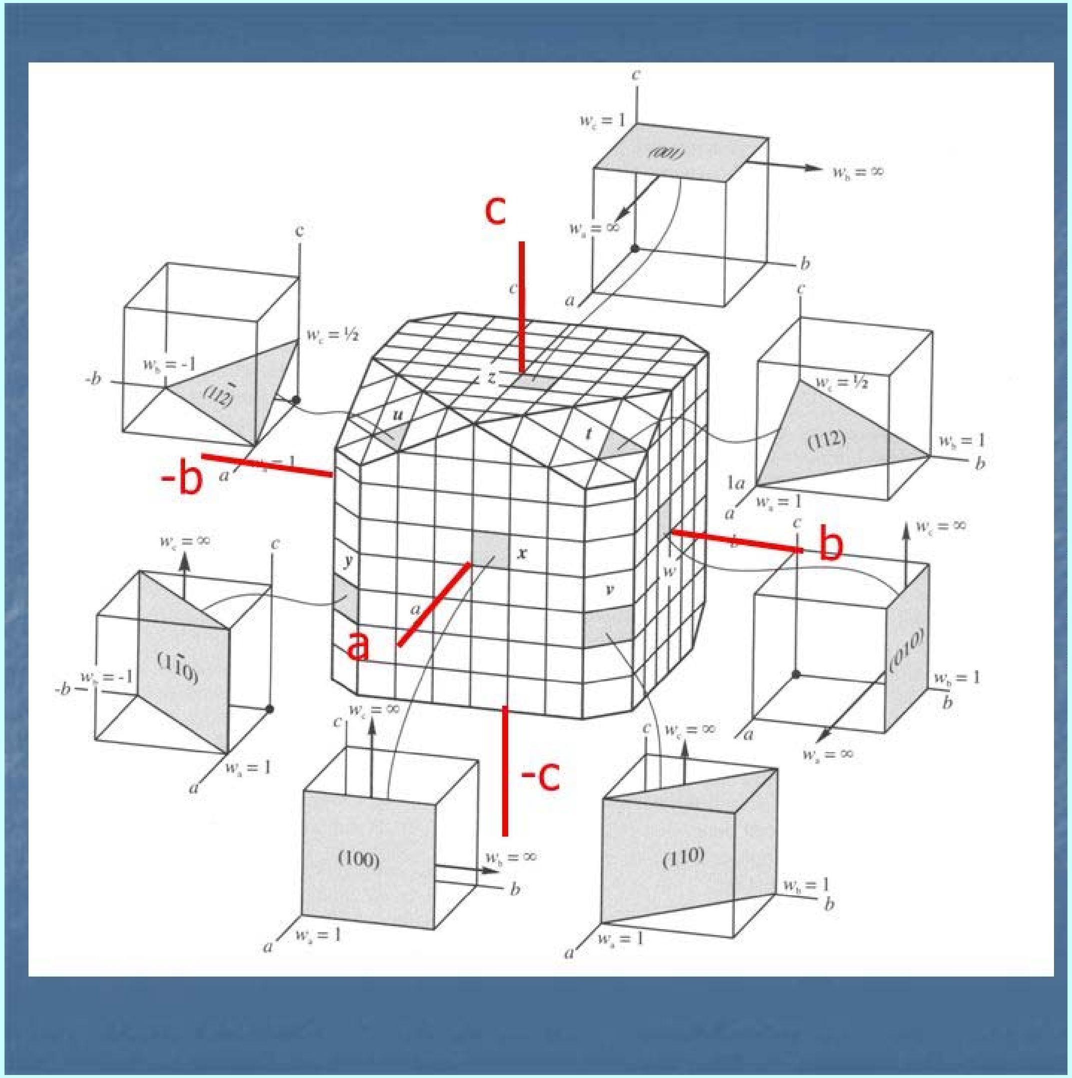


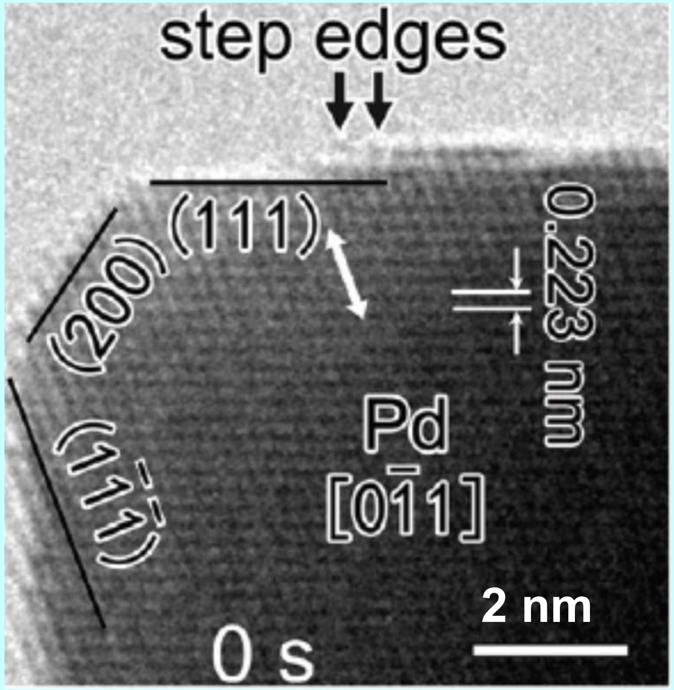
Index System for Crystal Planes
(Miller Indices)

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



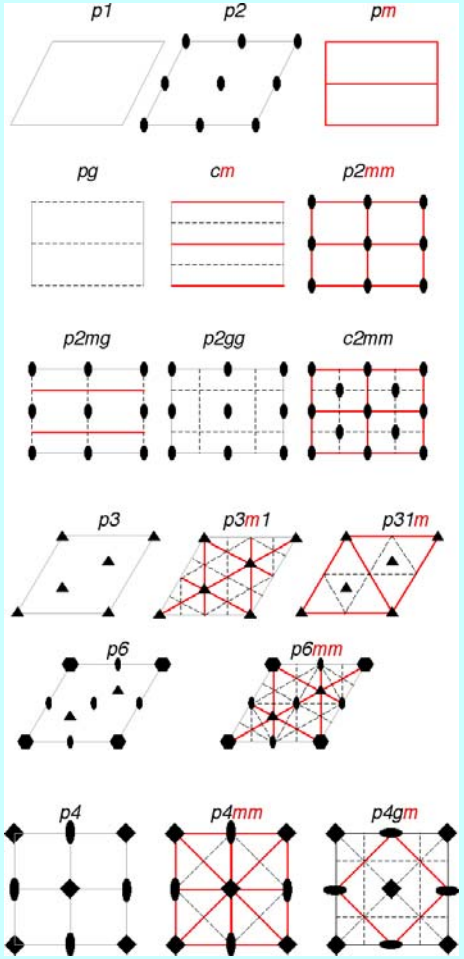
Index System for Crystal Planes (Miller Indices)





Quasiperiodic Crystals

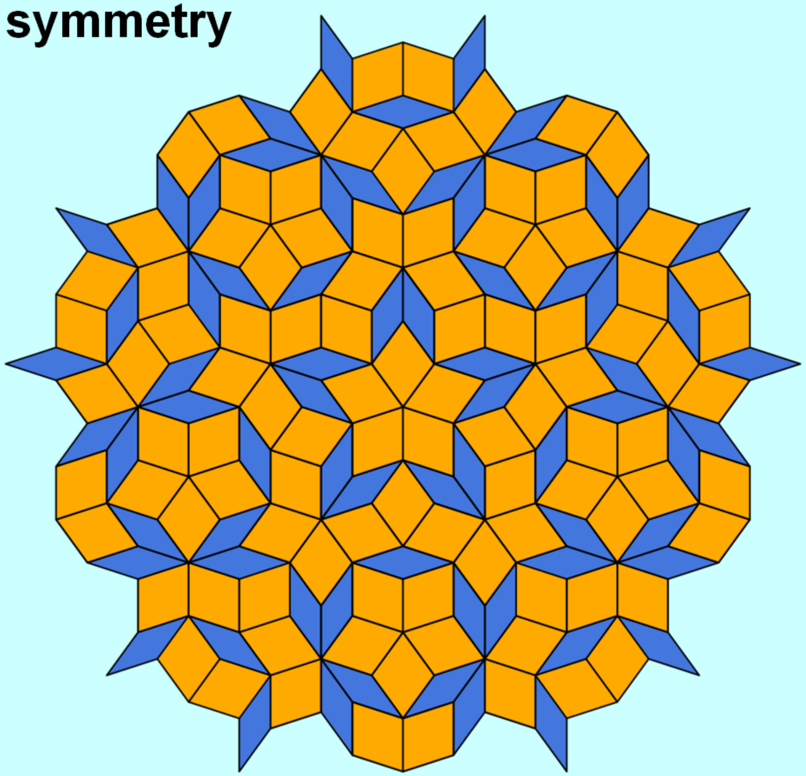
Quasiperiodic crystal = a structure that is ordered but not periodic continuously fills all available space, but it lacks translational symmetry



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

Five-fold symmetry

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

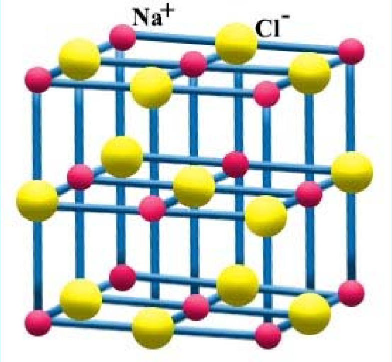


Crystals and Crystal Bonding

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

  metallic bonding, electron delocalization
- **ionic** (NaCl, CsCl, CaF_2, ...)

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

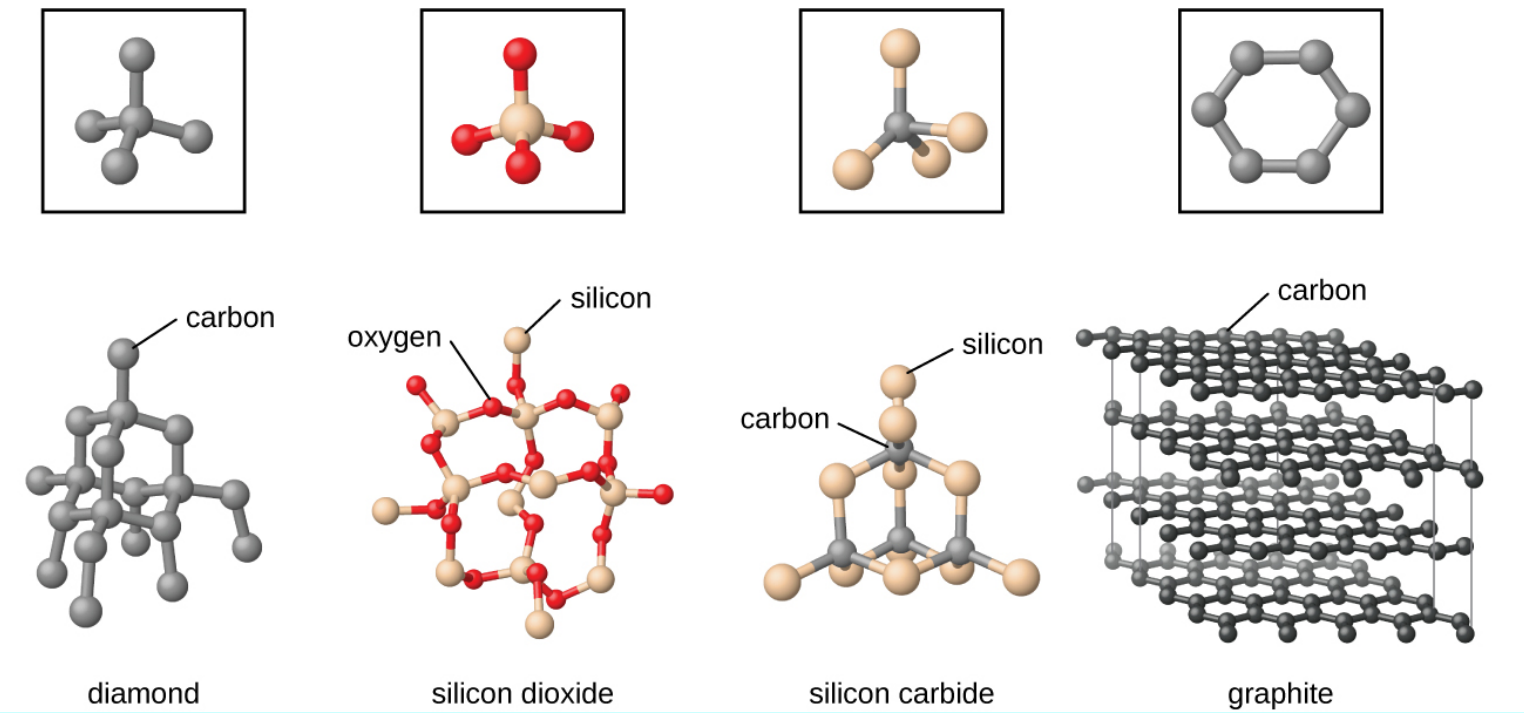


- **covalent network solid** (diamond, graphite, SiO_2, AlN,...)

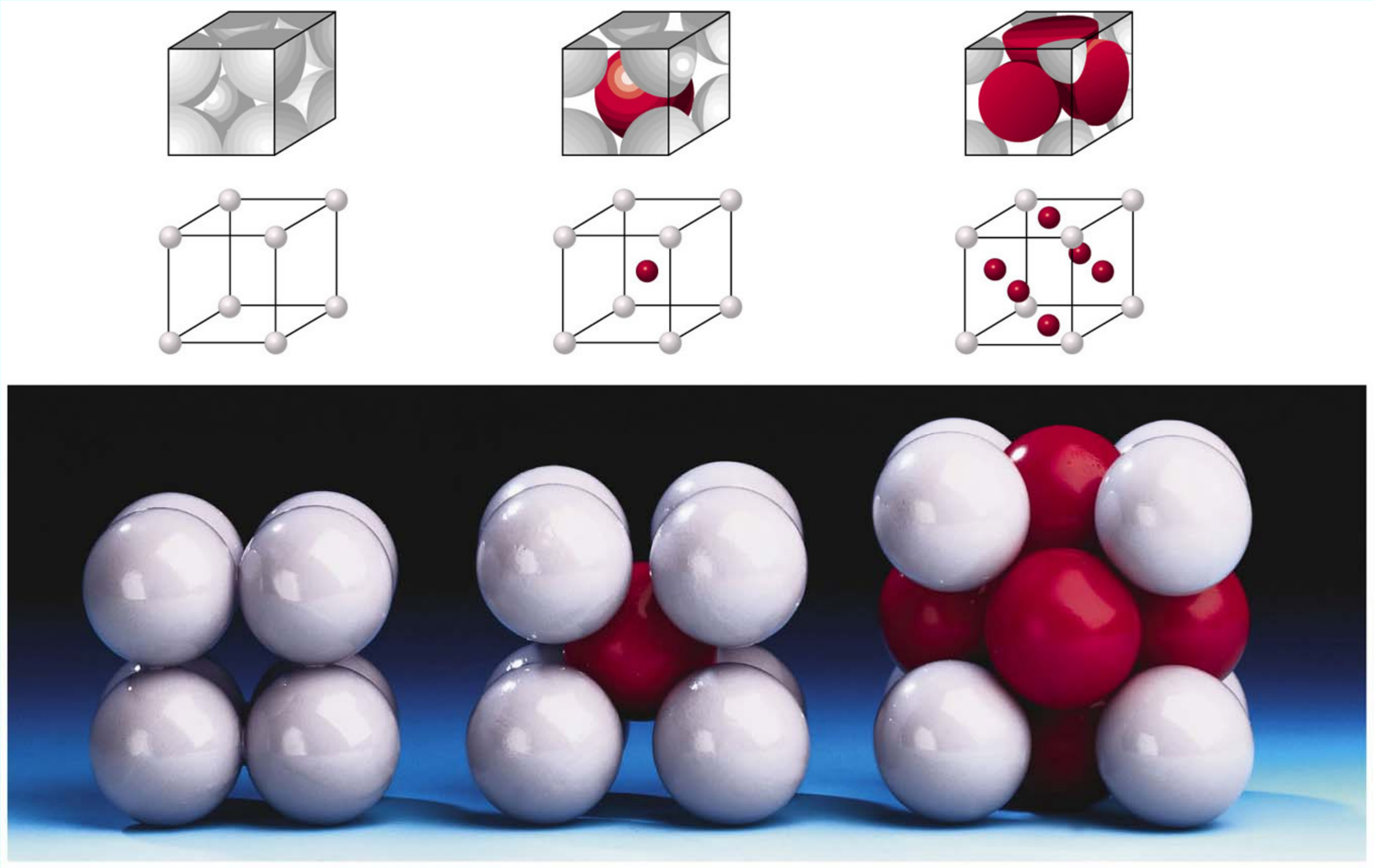
  atoms, covalent bonding, a chemical compound (or element) in which the atoms are bonded by covalent bonds in a continuous network extending throughout the material, there are no individual molecules, the entire crystal or amorphous solid may be considered a macromolecule
- **molecular** (Ar, C_{60}, HF, H_2O, organics, proteins)

  molecules, van der Waals and hydrogen bonding

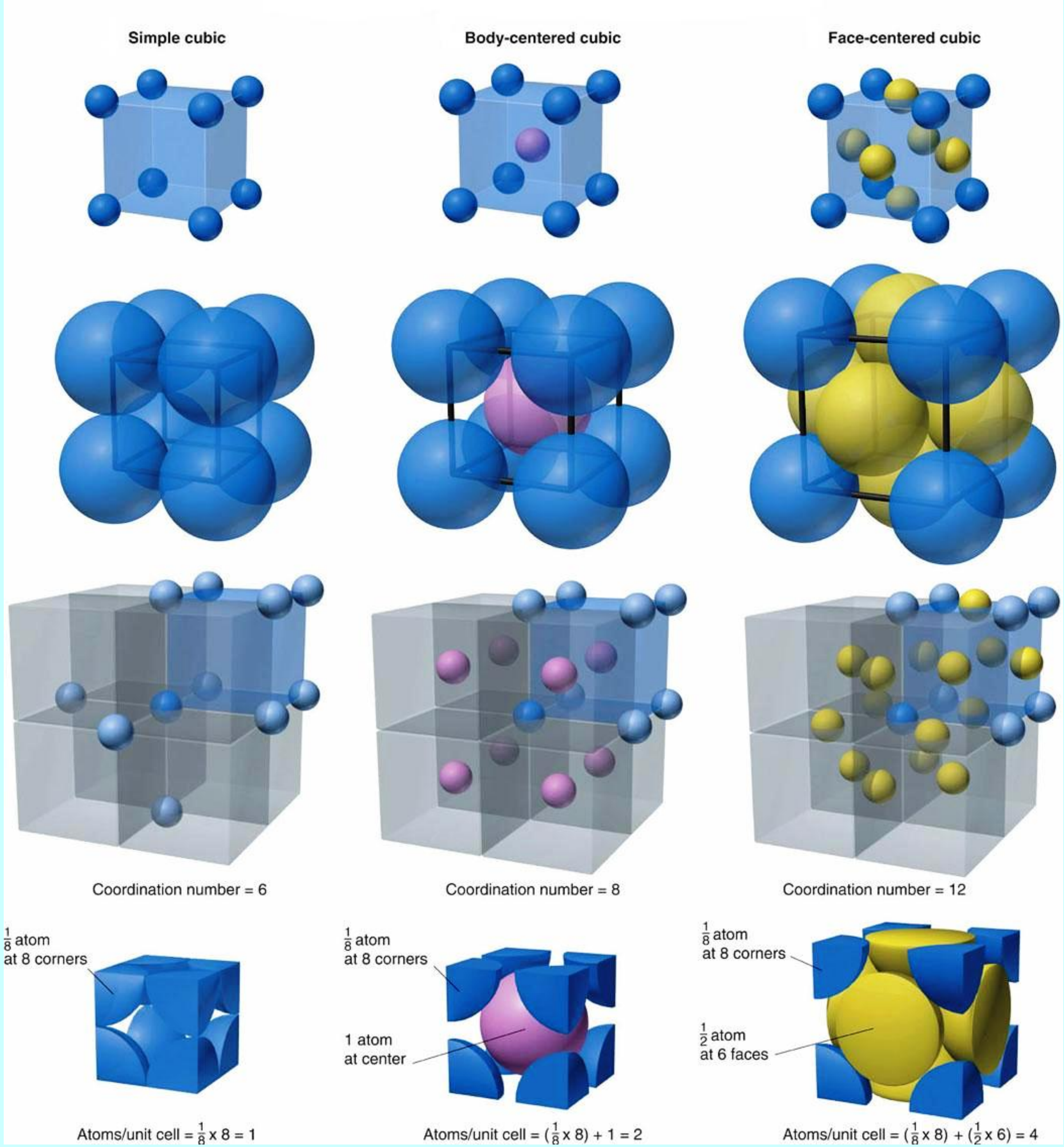
Covalent network solids



Three Cubic Cells



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


Simple cubic
Body-centered cubic
Face-centered cubic
Coordination number = 6
Coordination number = 8
Coordination number = 12
$\frac{1}{8}$ atom at 8 corners
Atoms/unit cell = $\frac{1}{8}$ x 8 = 1
$\frac{1}{8}$ atom at 8 corners
1 atom at center
Atoms/unit cell = ($\frac{1}{8}$ x 8) + 1 = 2
$\frac{1}{8}$ atom at 8 corners
$\frac{1}{2}$ atom at 6 faces
Atoms/unit cell = ($\frac{1}{8}$ x 8) + ($\frac{1}{2}$ x 6) = 4

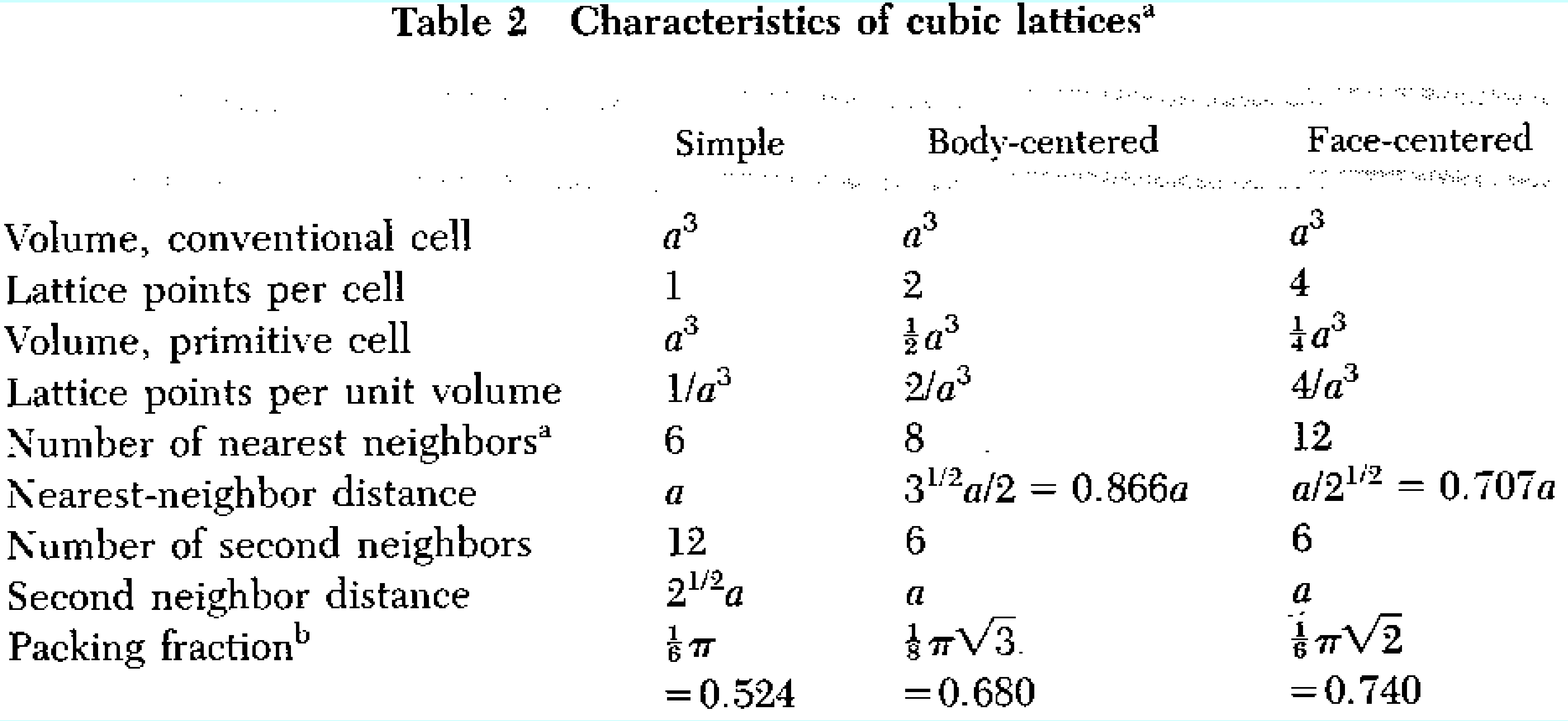
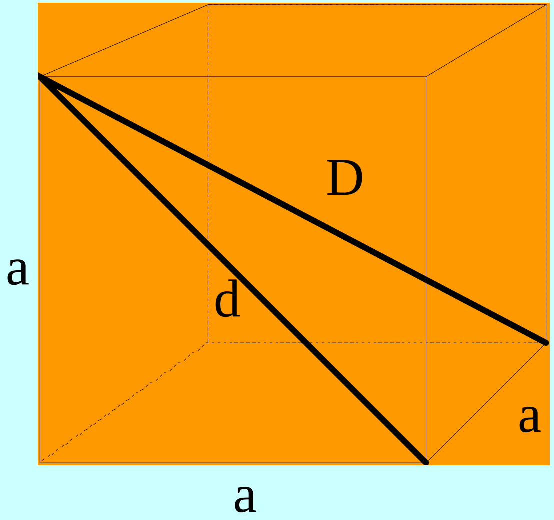


Table 2 Characteristics of cubic lattices[a]

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

Cube



a = edge

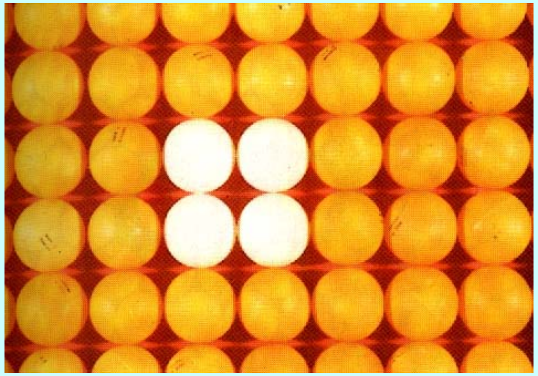
d = face diagonl
$(d^2 = a^2 + a^2 = 2a^2)$

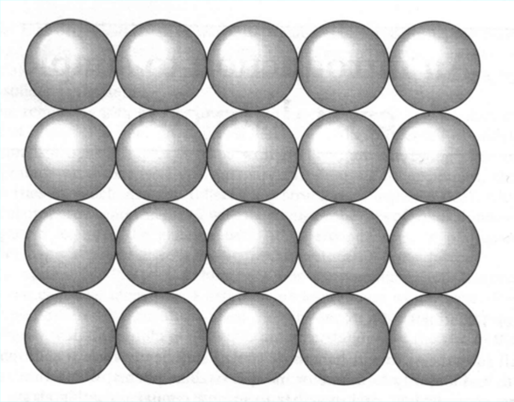
D = body diagonal
$(D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2)$

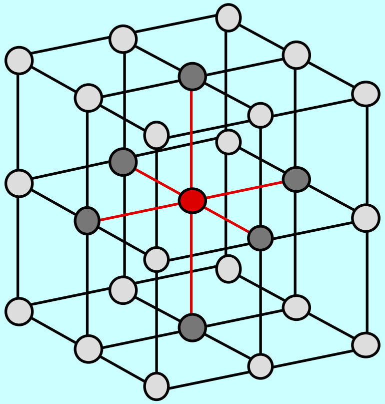
$$d = \sqrt{2} \cdot \mathrm{a}$$

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

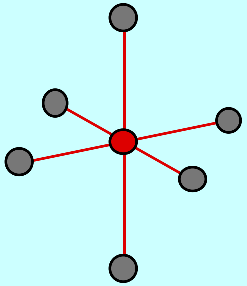
Simple Cubic SC = Polonium

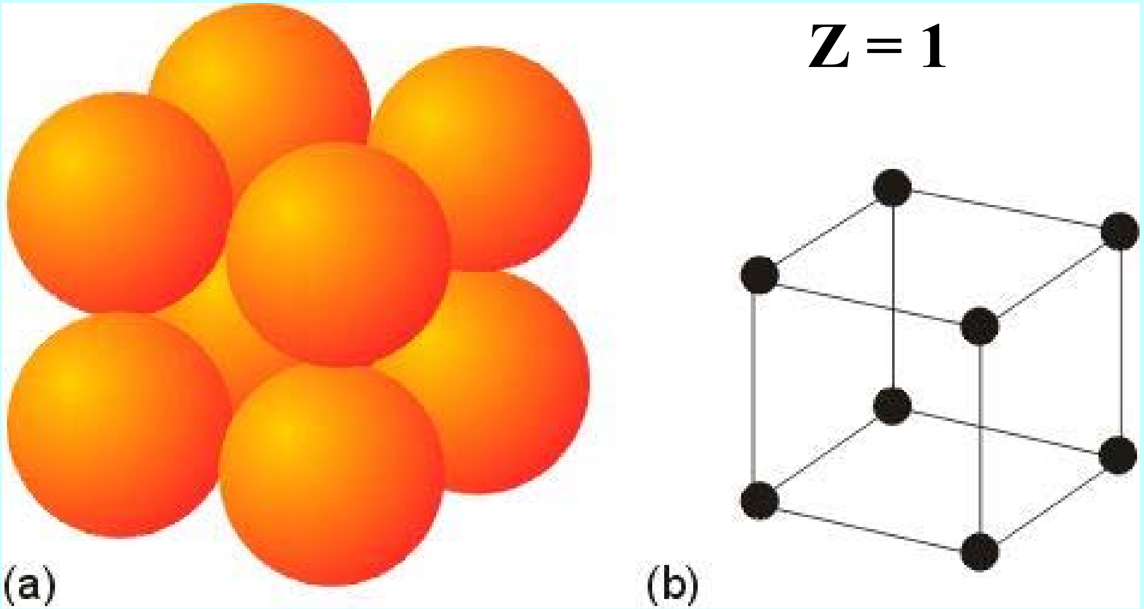




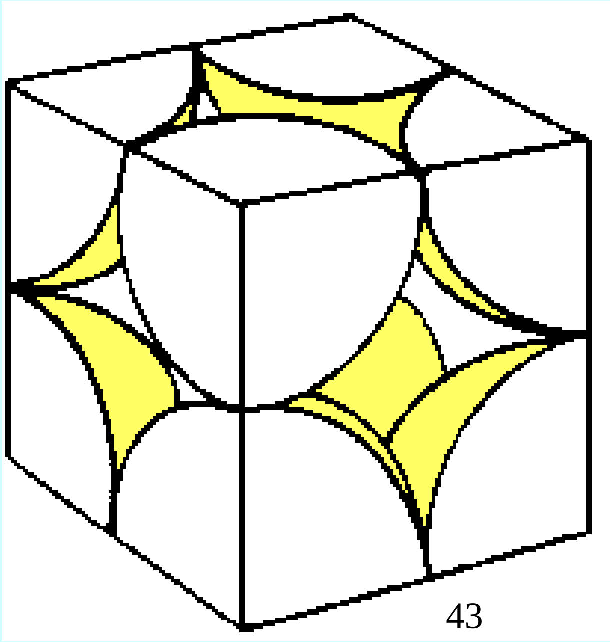


CN 6



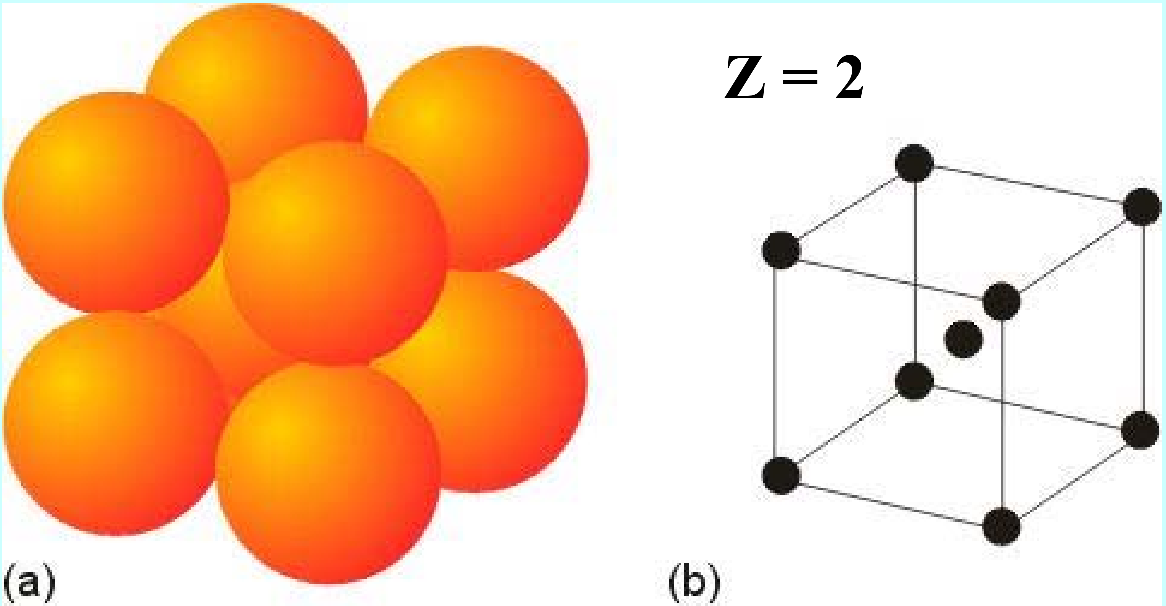


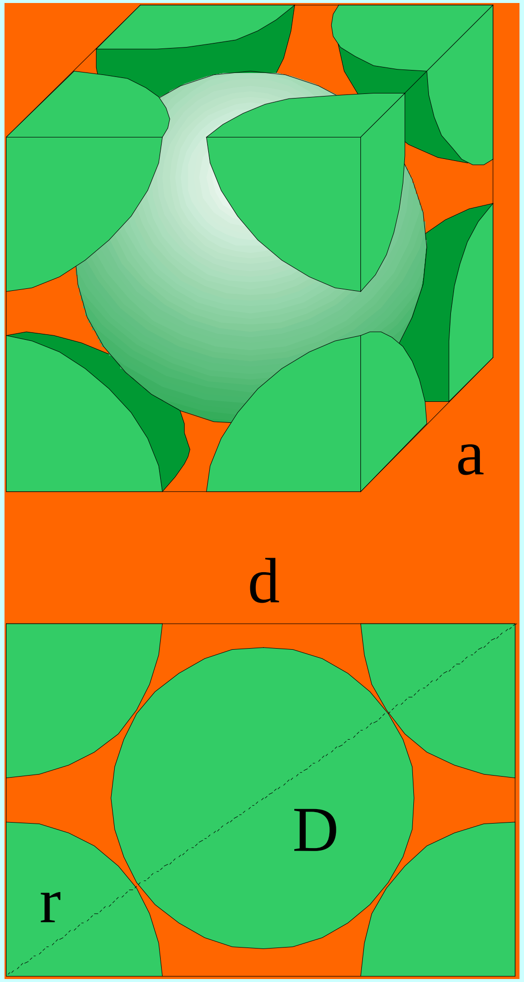
Z = 1



Space filling 52%

BCC = W, Tungsten



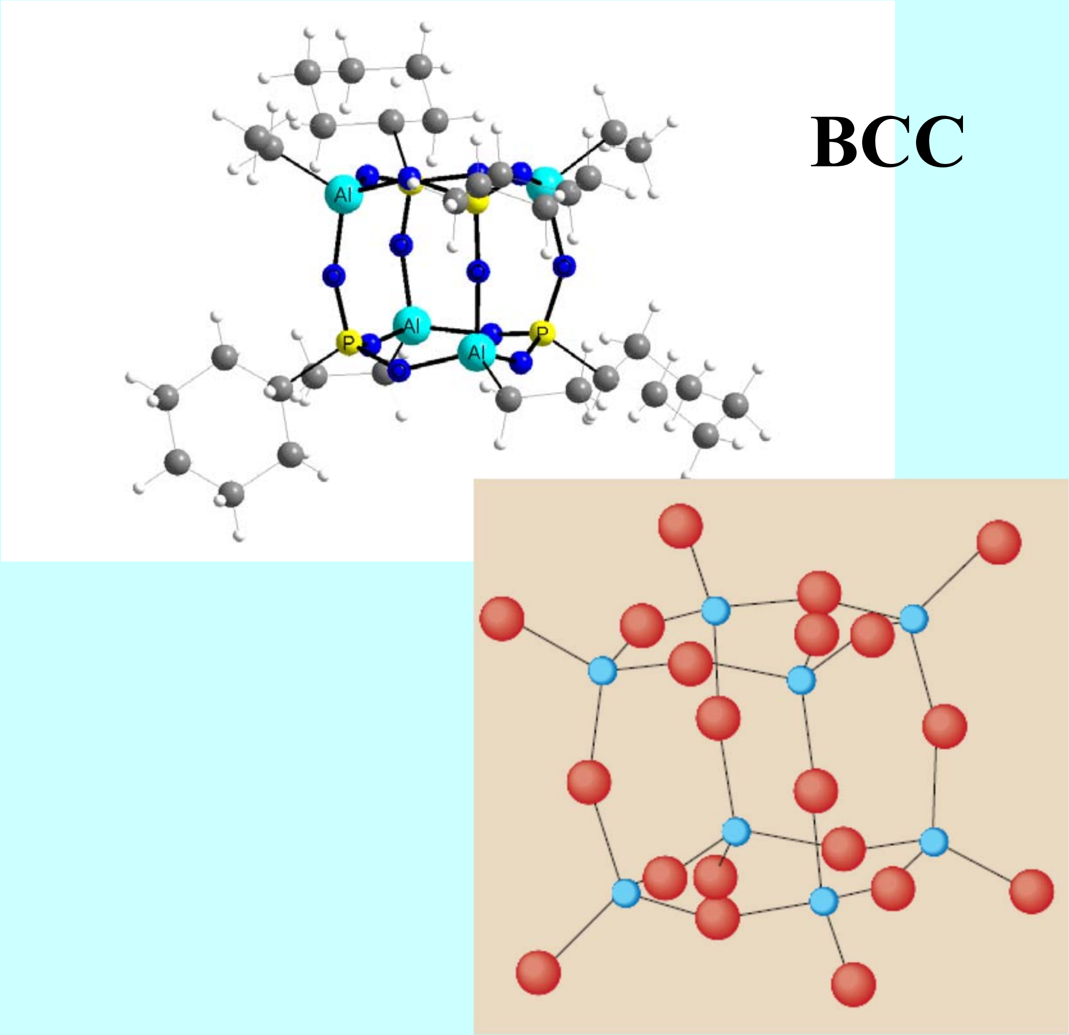


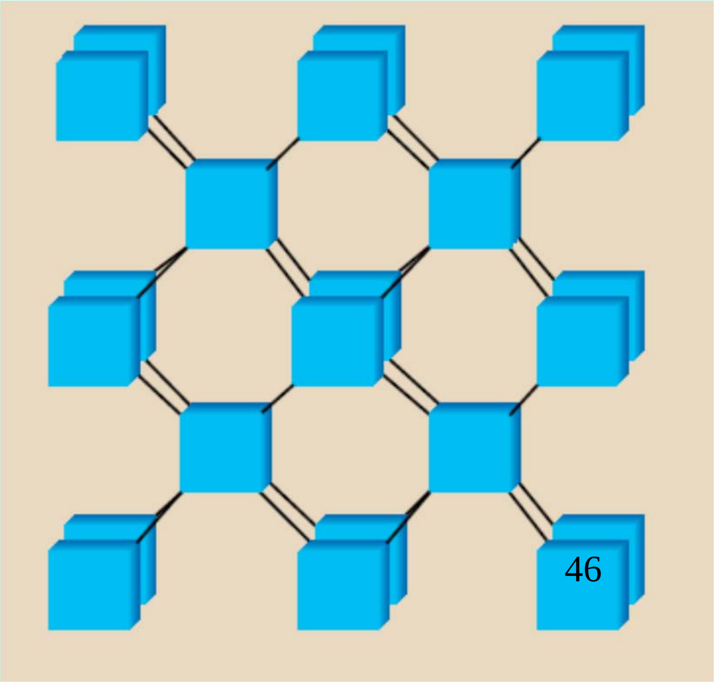
Space filling 68%

CN 8

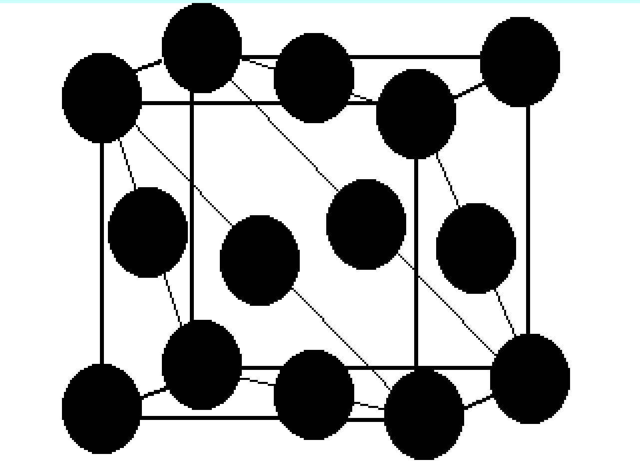
Fe, Cr, V, Li-Cs, Ba

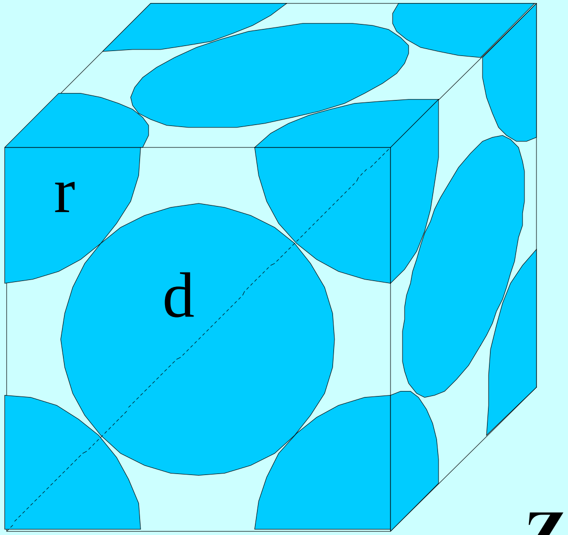
BCC



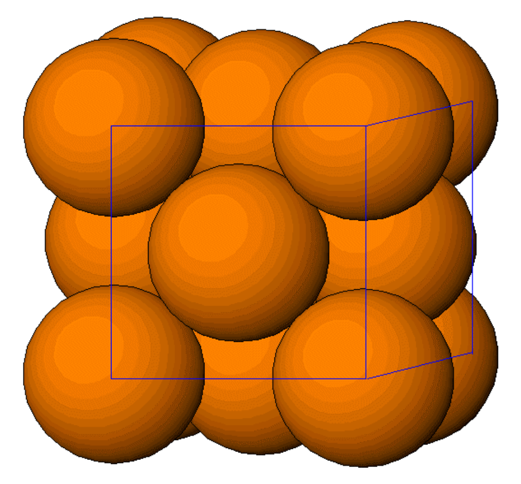


FCC = Copper, Cu = CCP





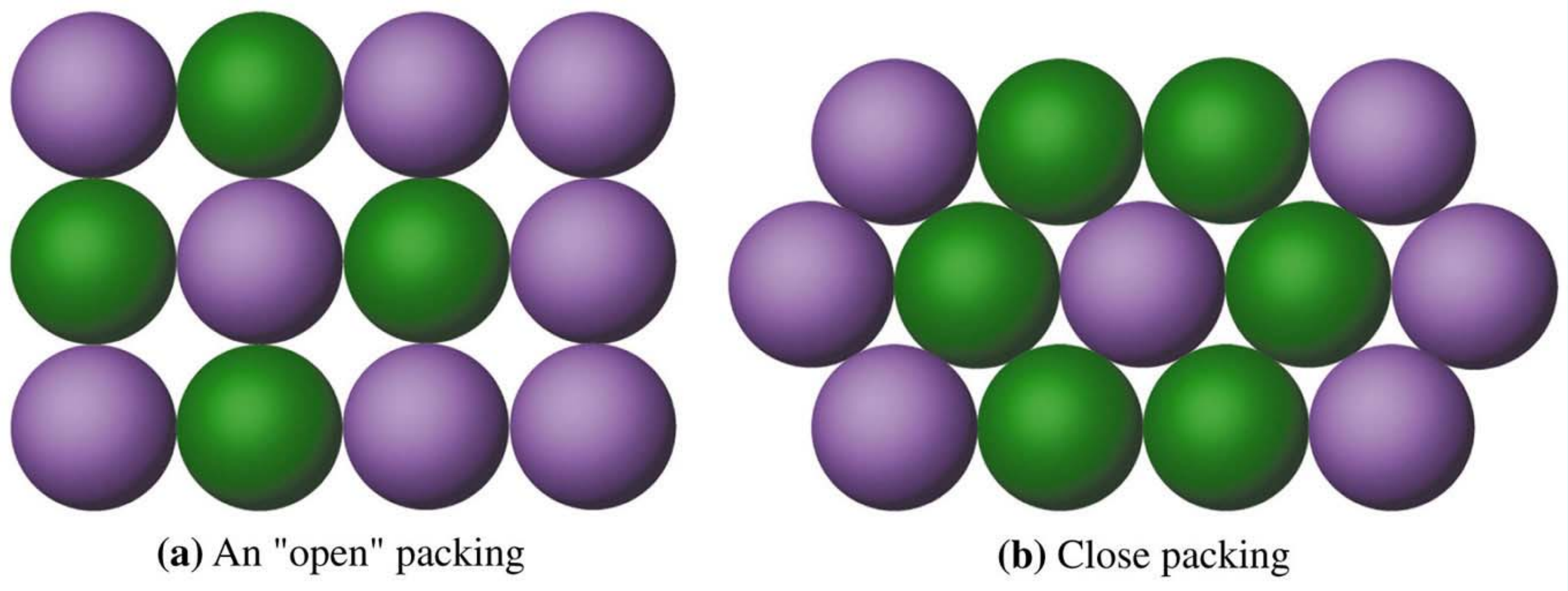
Z = 4



Space filling 74%

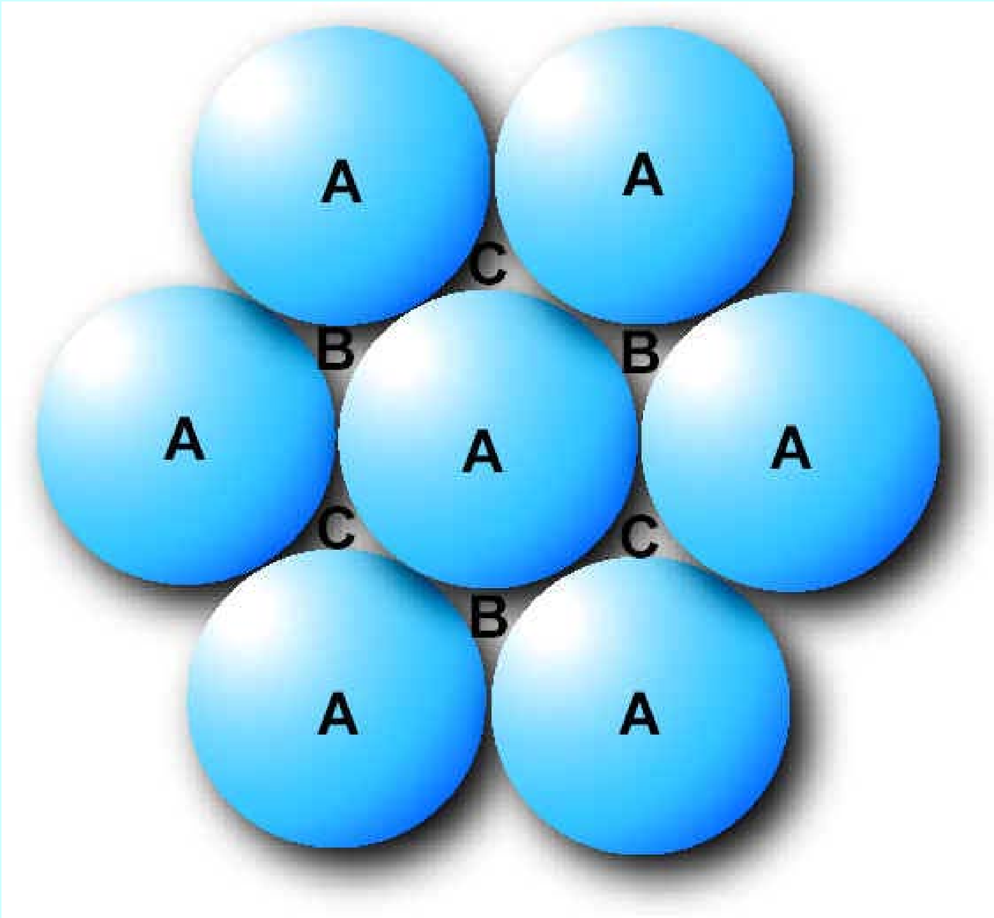
CN 12

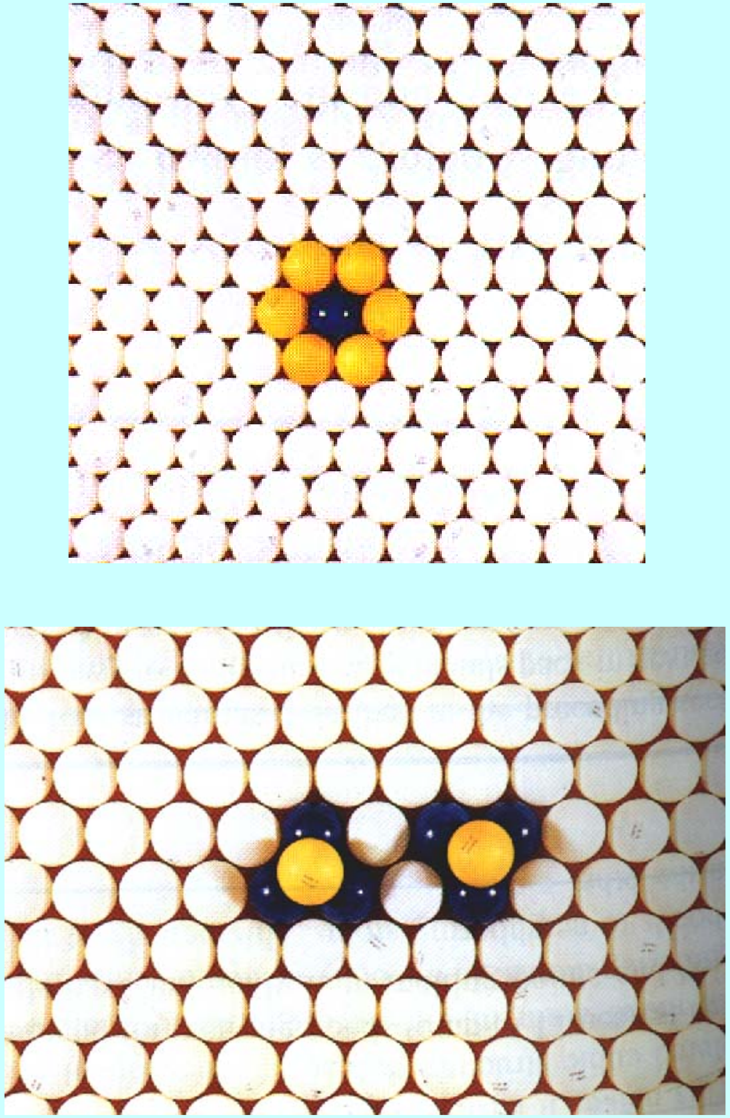
Close Packing in Plane 2D



(a) An "open" packing

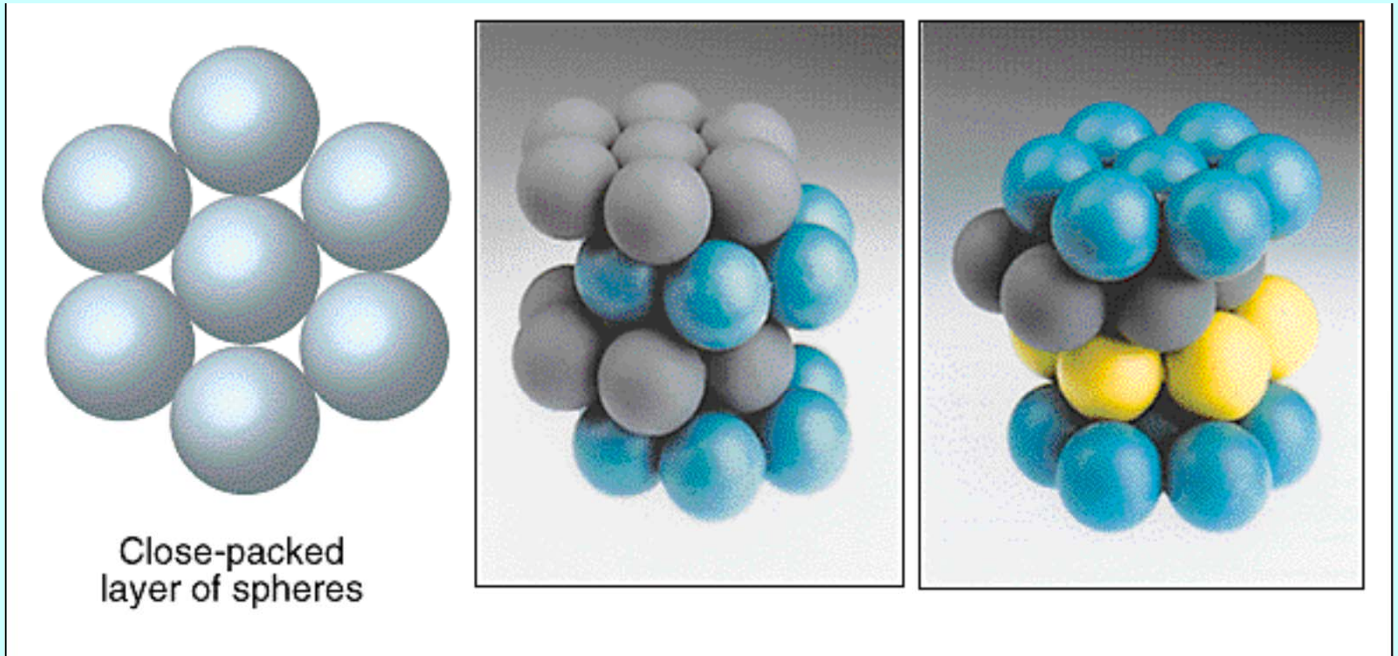
(b) Close packing





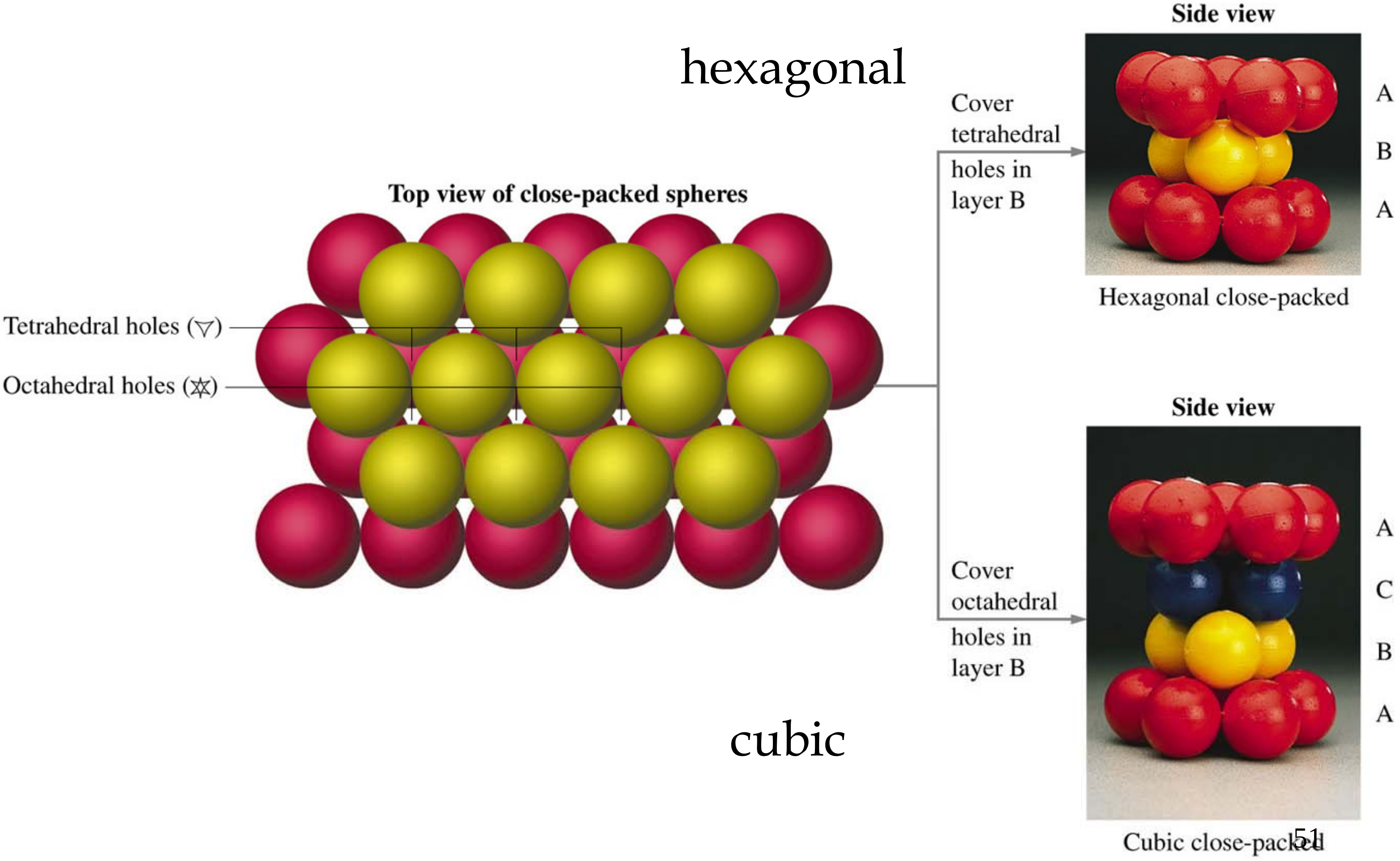
B and C holes cannot be occupied at the same time

Close Packing in Space 3D



Hexagonal
HCP

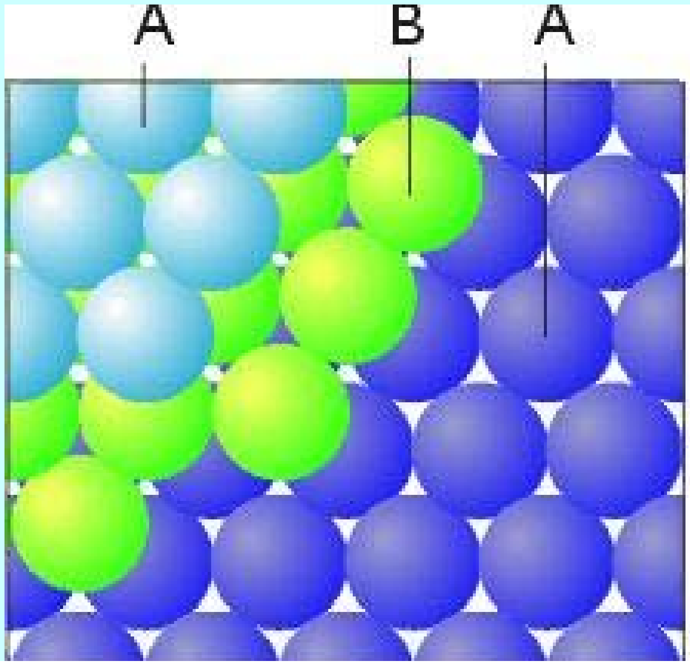
Cubic
CCP



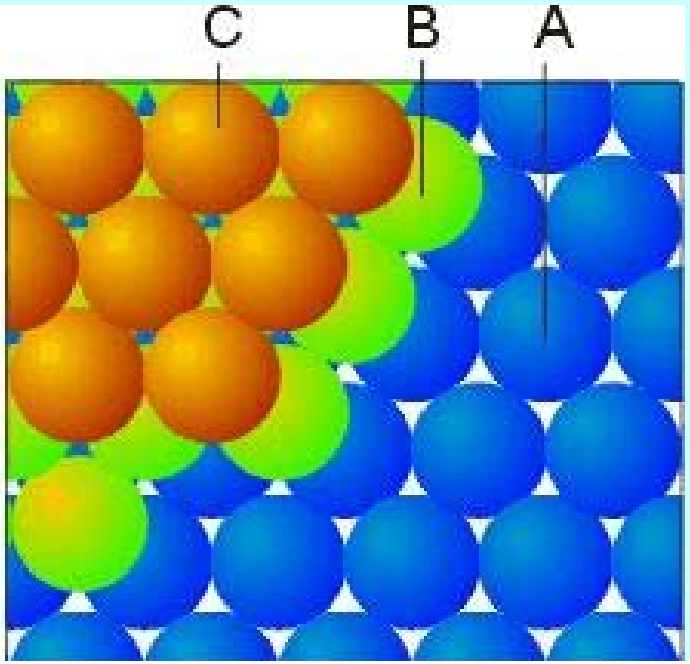
hexagonal

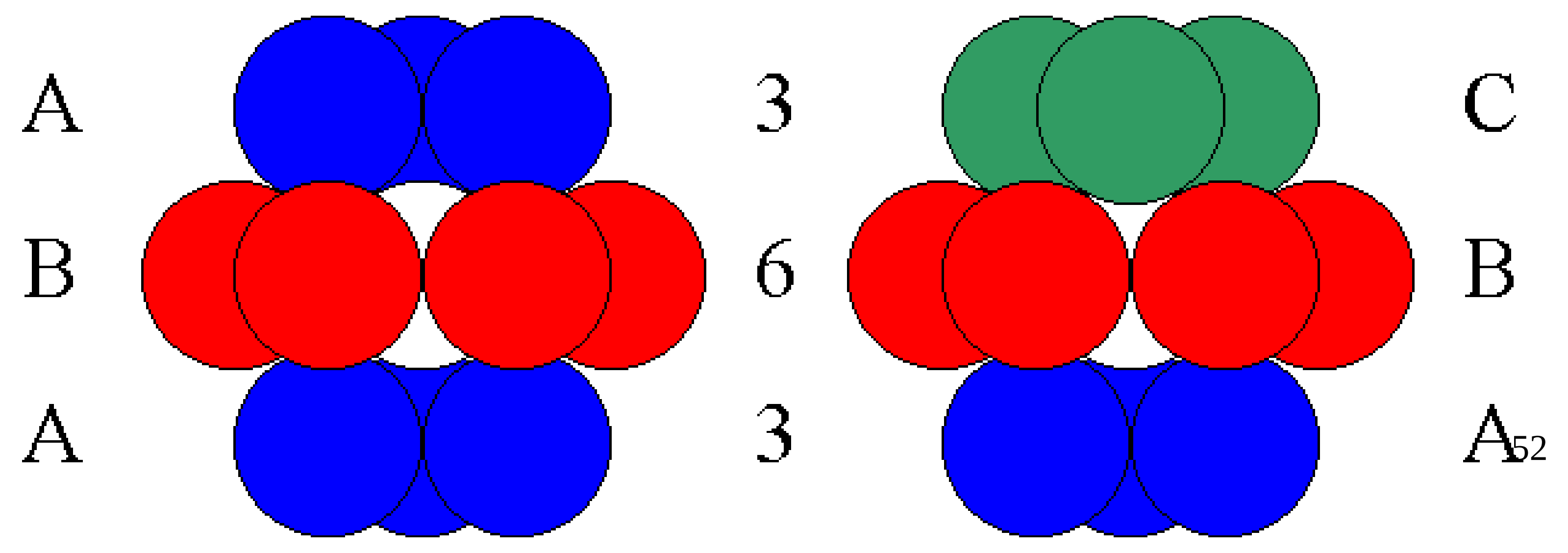
cubic

hexagonal



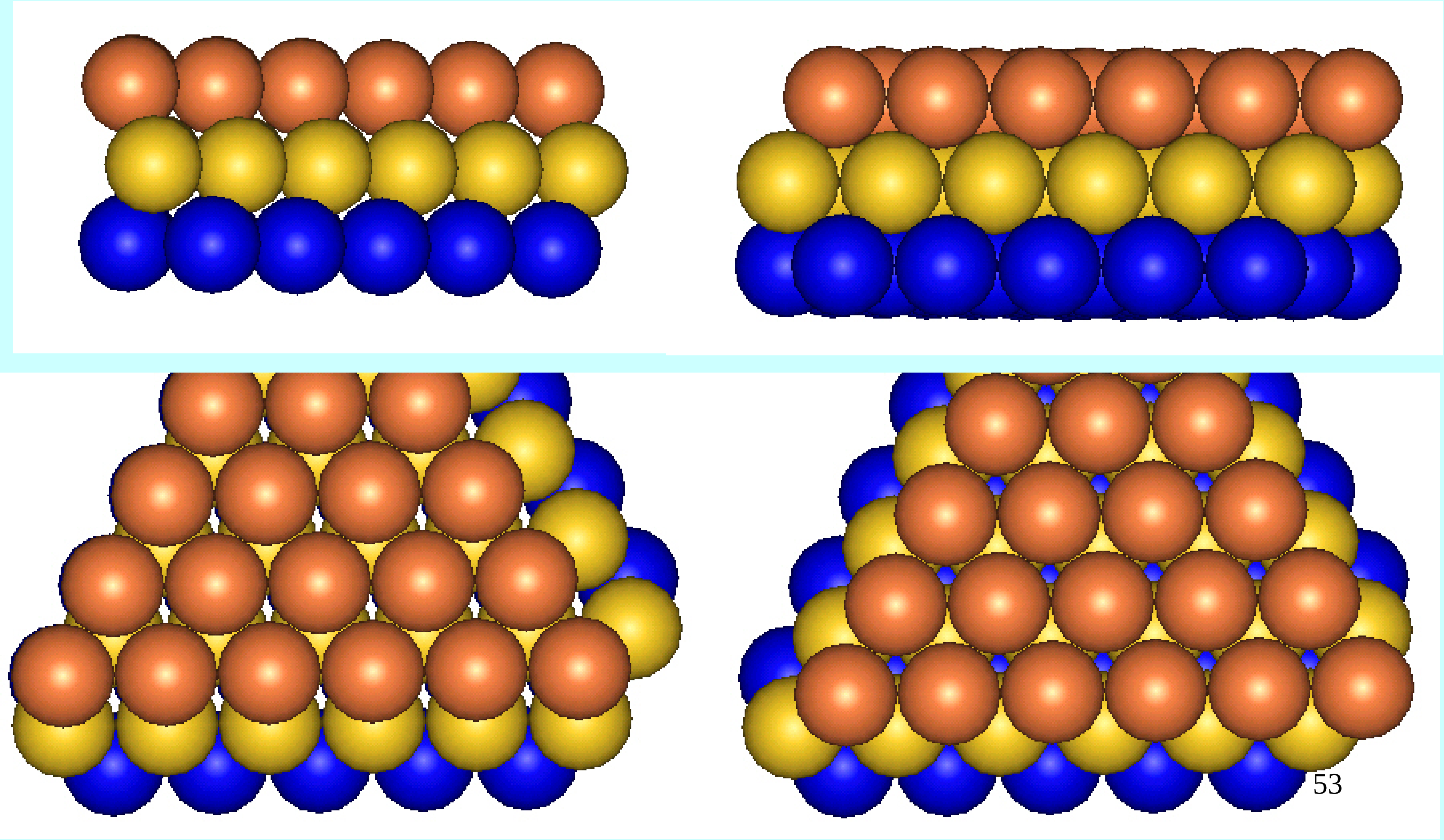
cubic



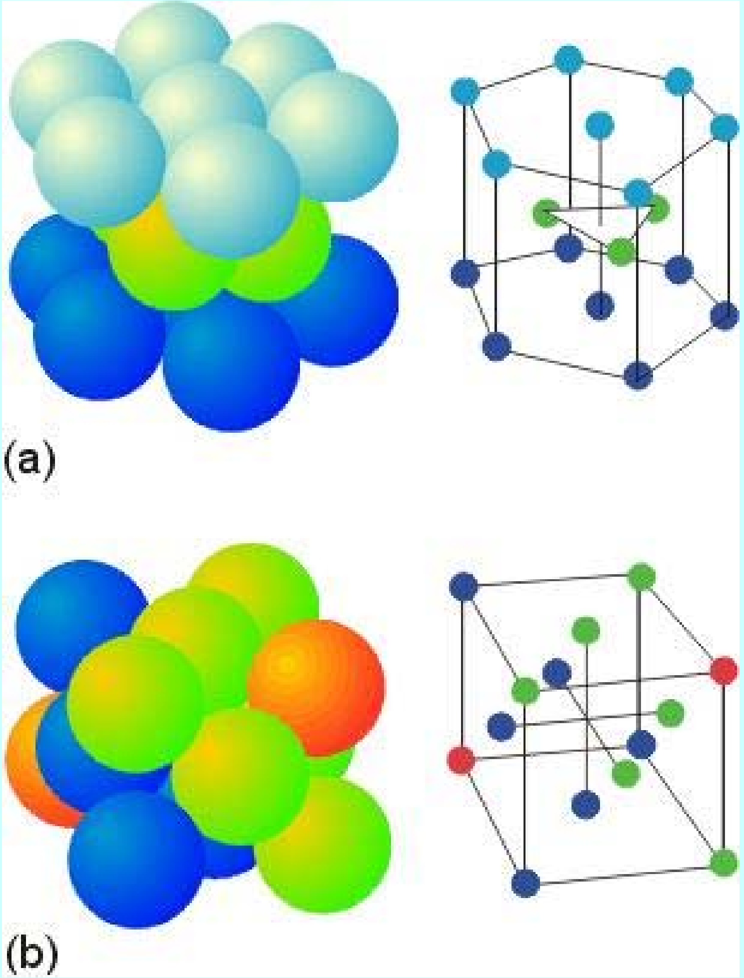


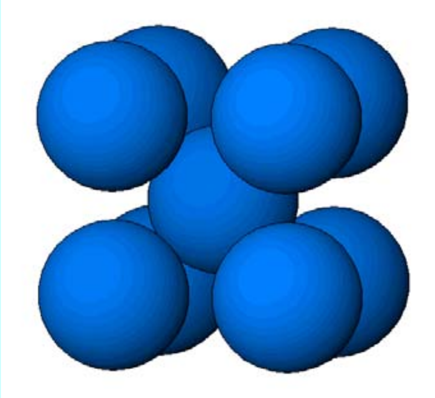
hexagonal

cubic

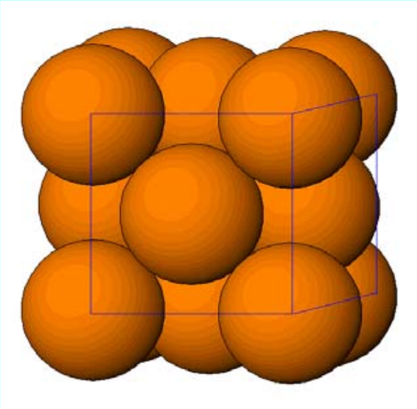


**Mg, Be, Zn, Ni, Li, Be, Os, He,
Sc, Ti, Co, Y, Ru**





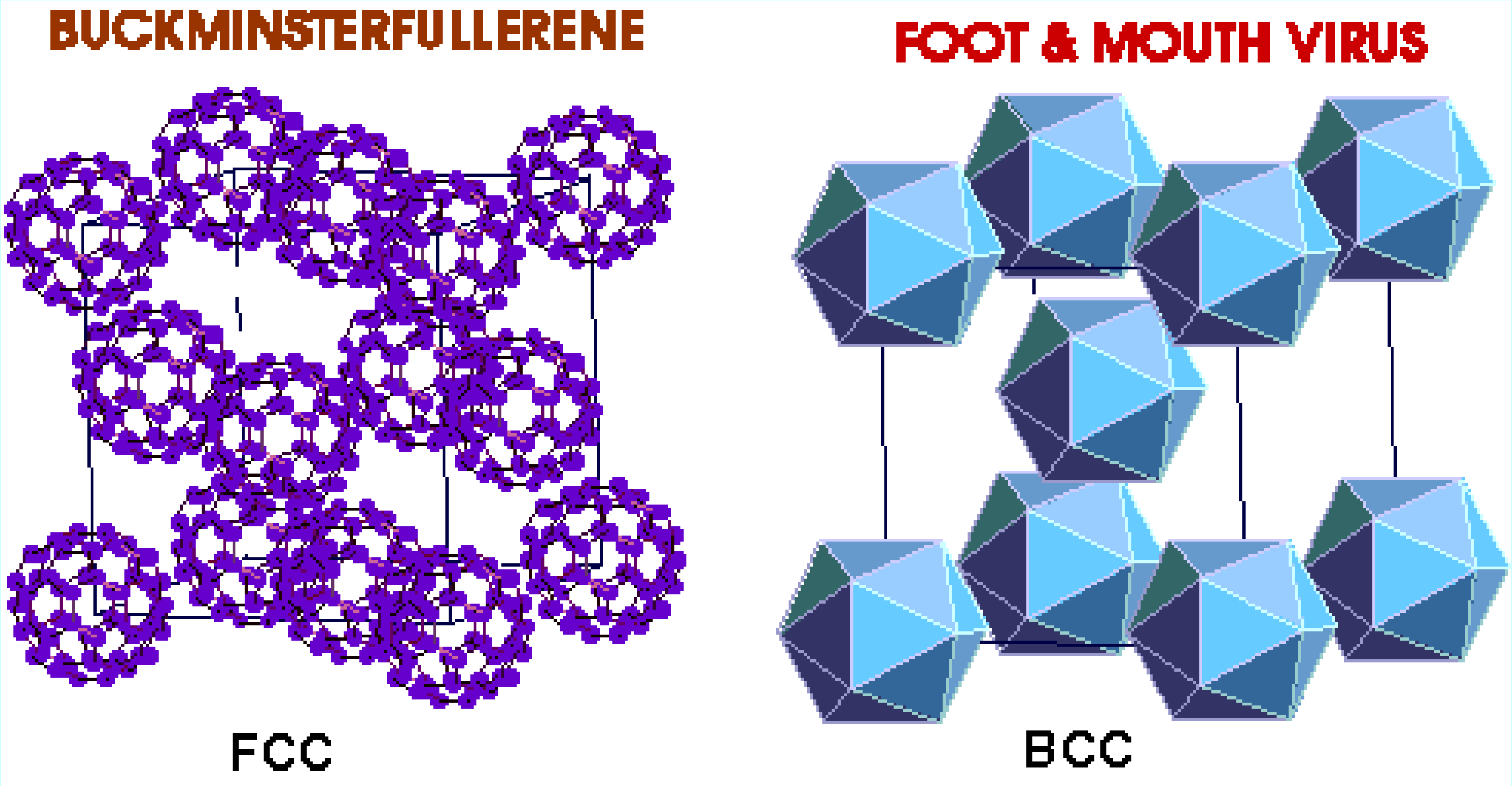
hexagonal



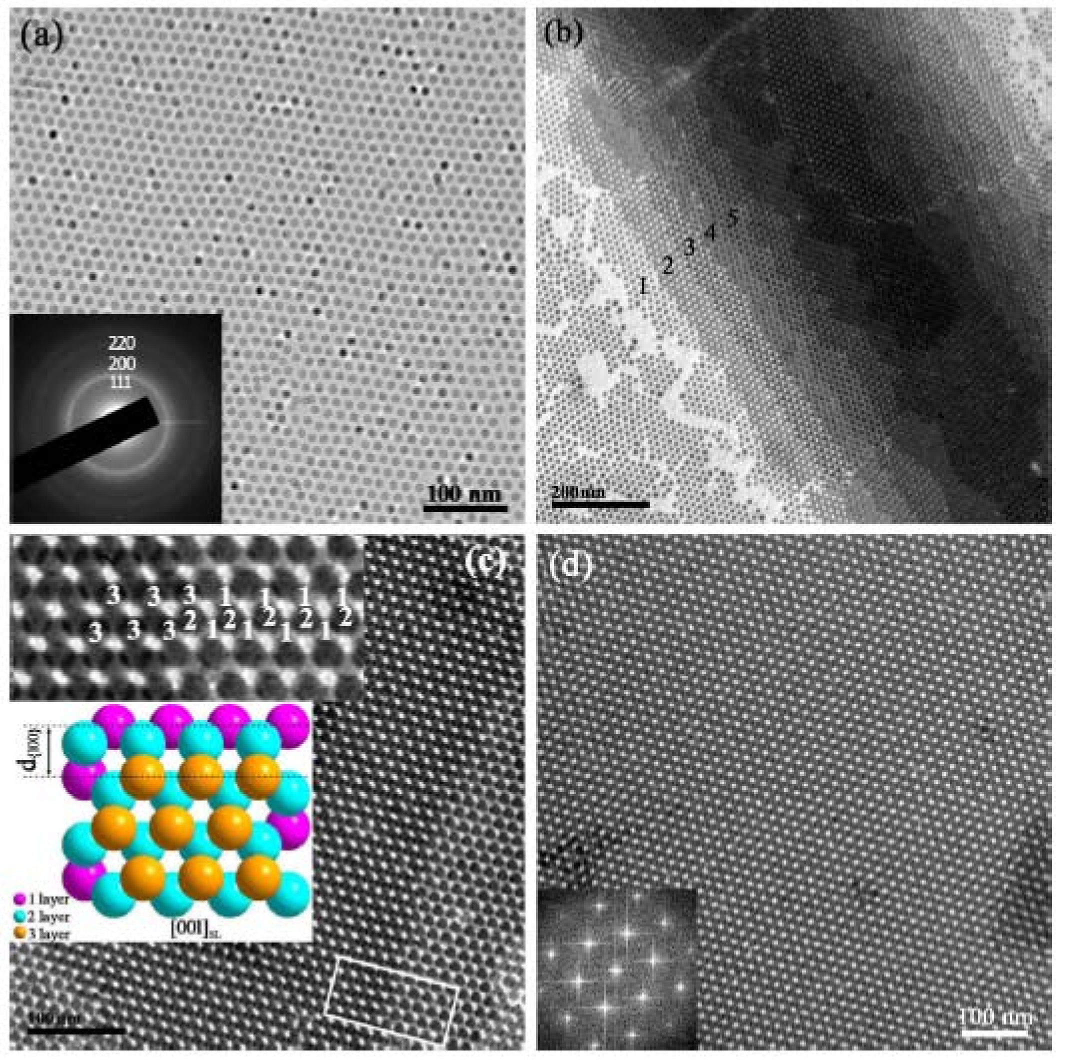
cubic

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

Structures with Larger Motifs

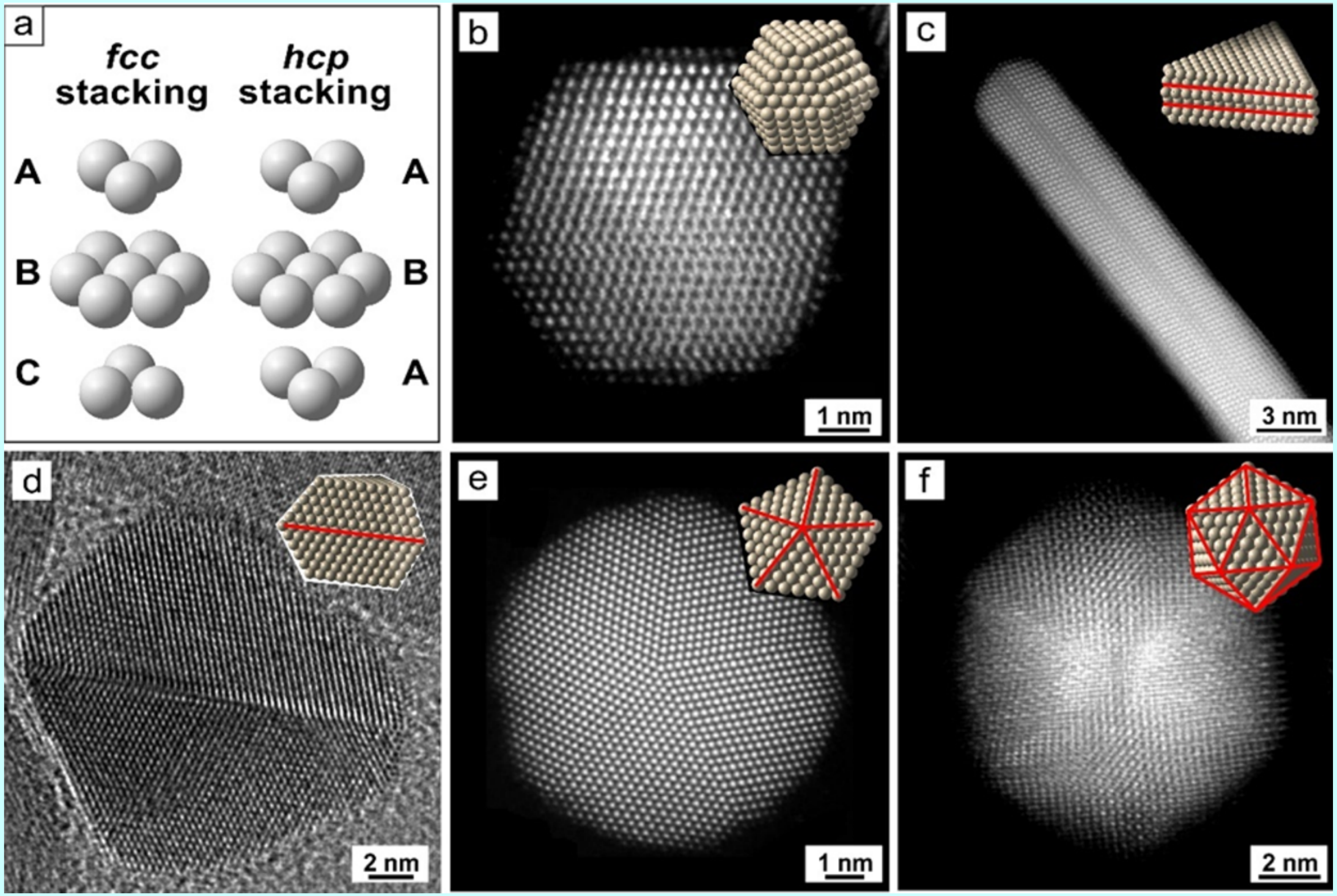


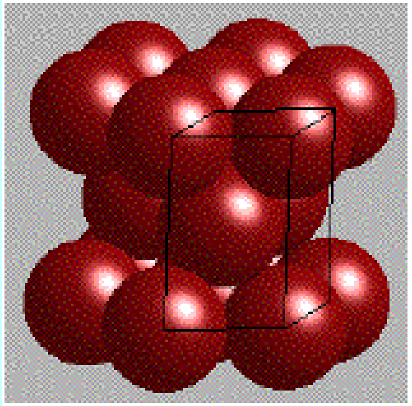
Structures with Larger Motifs



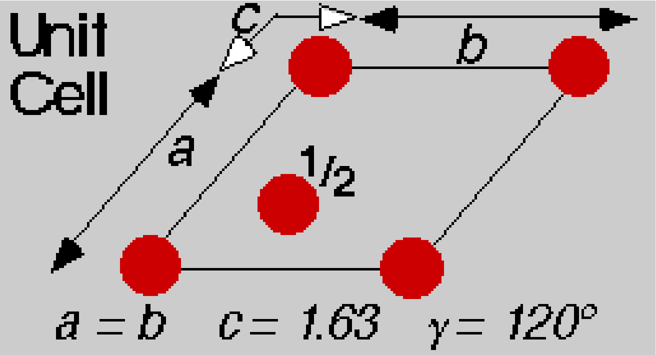
TEM images of superlattices composed of 11.3 nm Ni nanoparticles

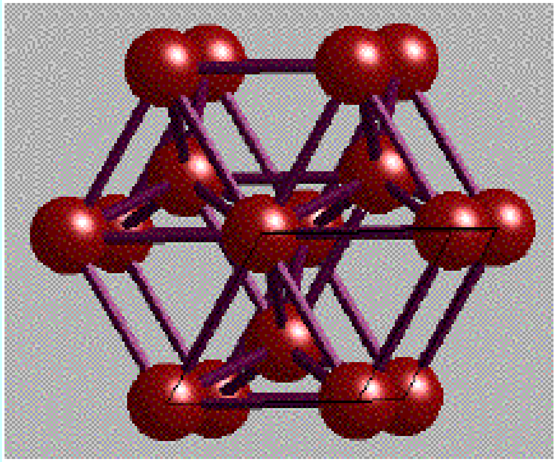
Structures with Larger Motifs

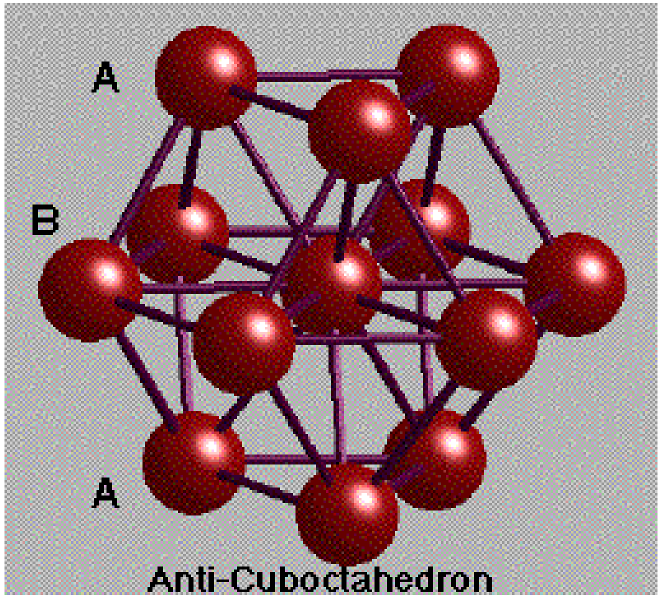


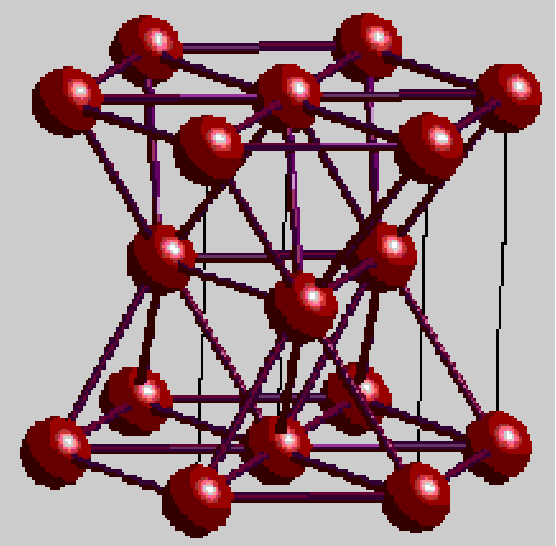


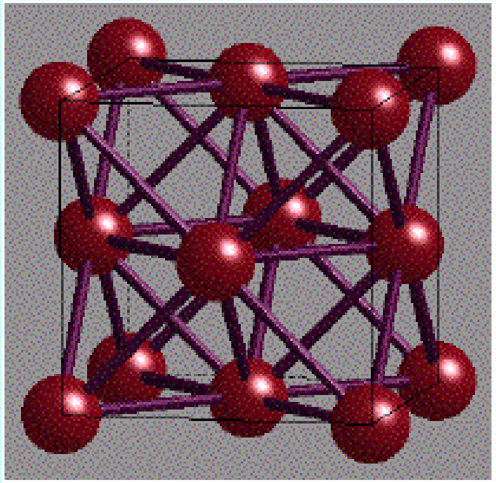
HEXAGONAL CLOSE-PACKING











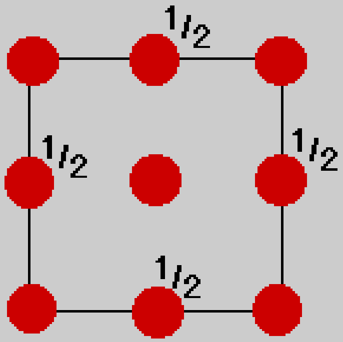
CUBIC CLOSE-PACKING

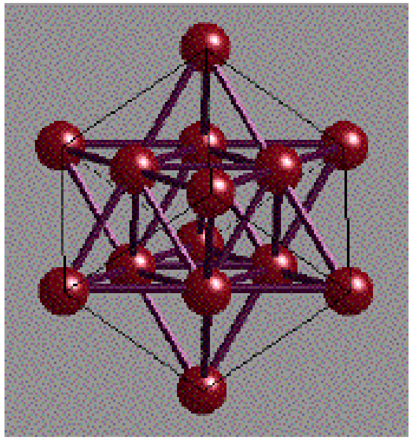
Face-Centred Cubic (FCC) Unit Cell

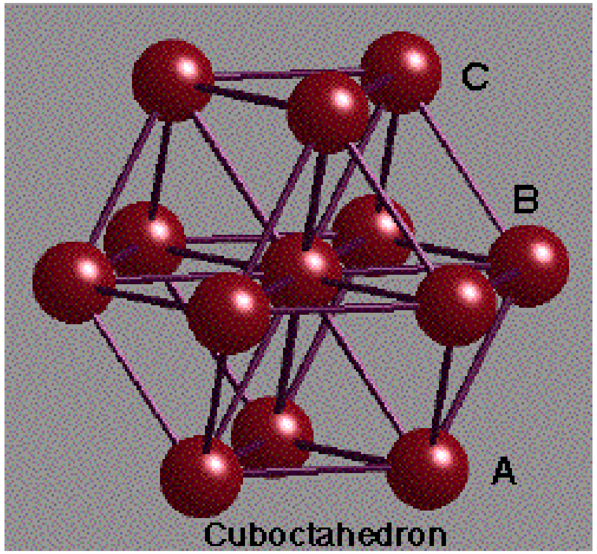
Unit Cell

$a=b=c$

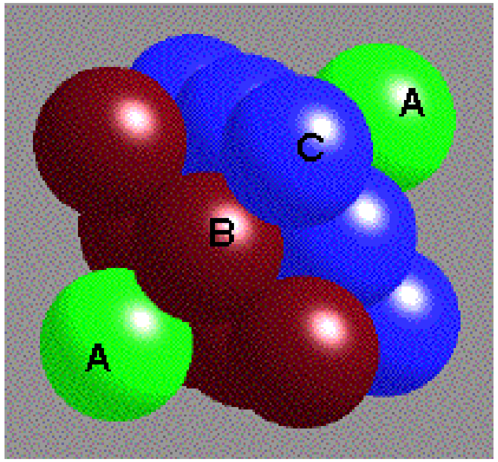
$\alpha=\beta=\gamma=90°$



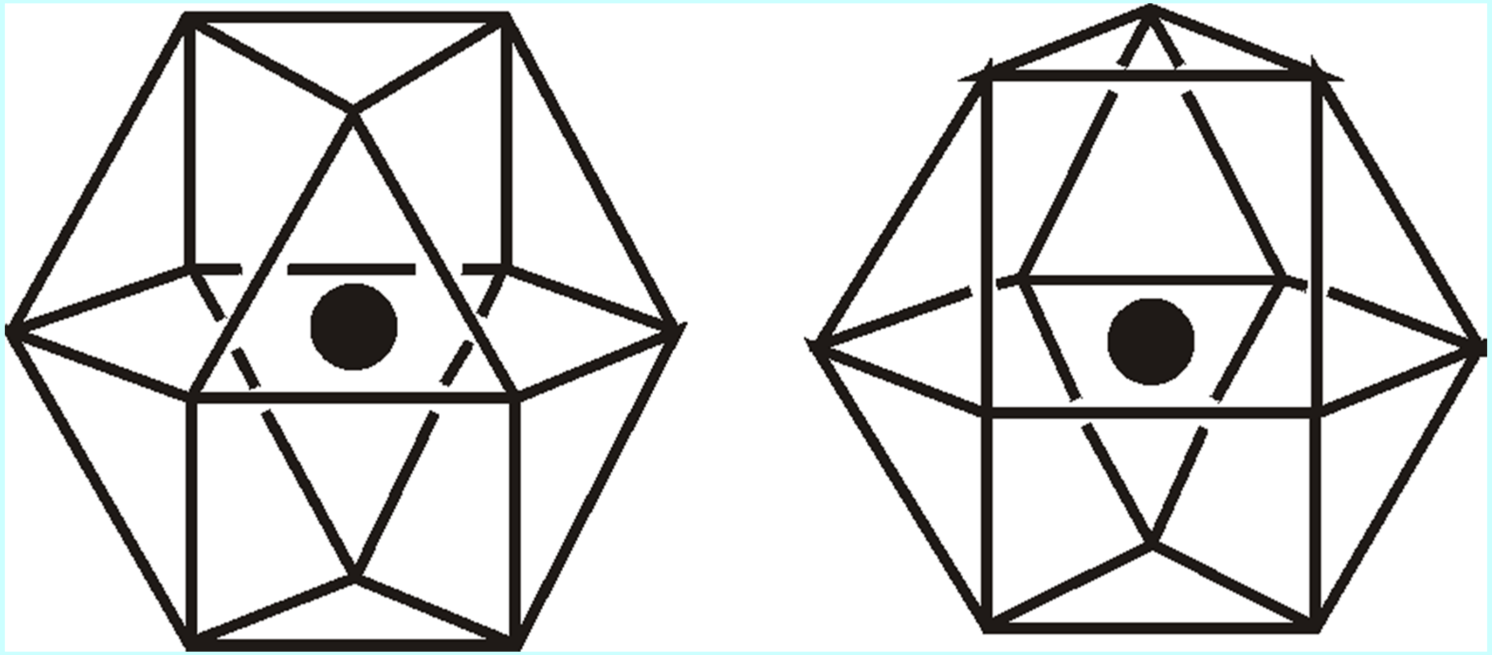




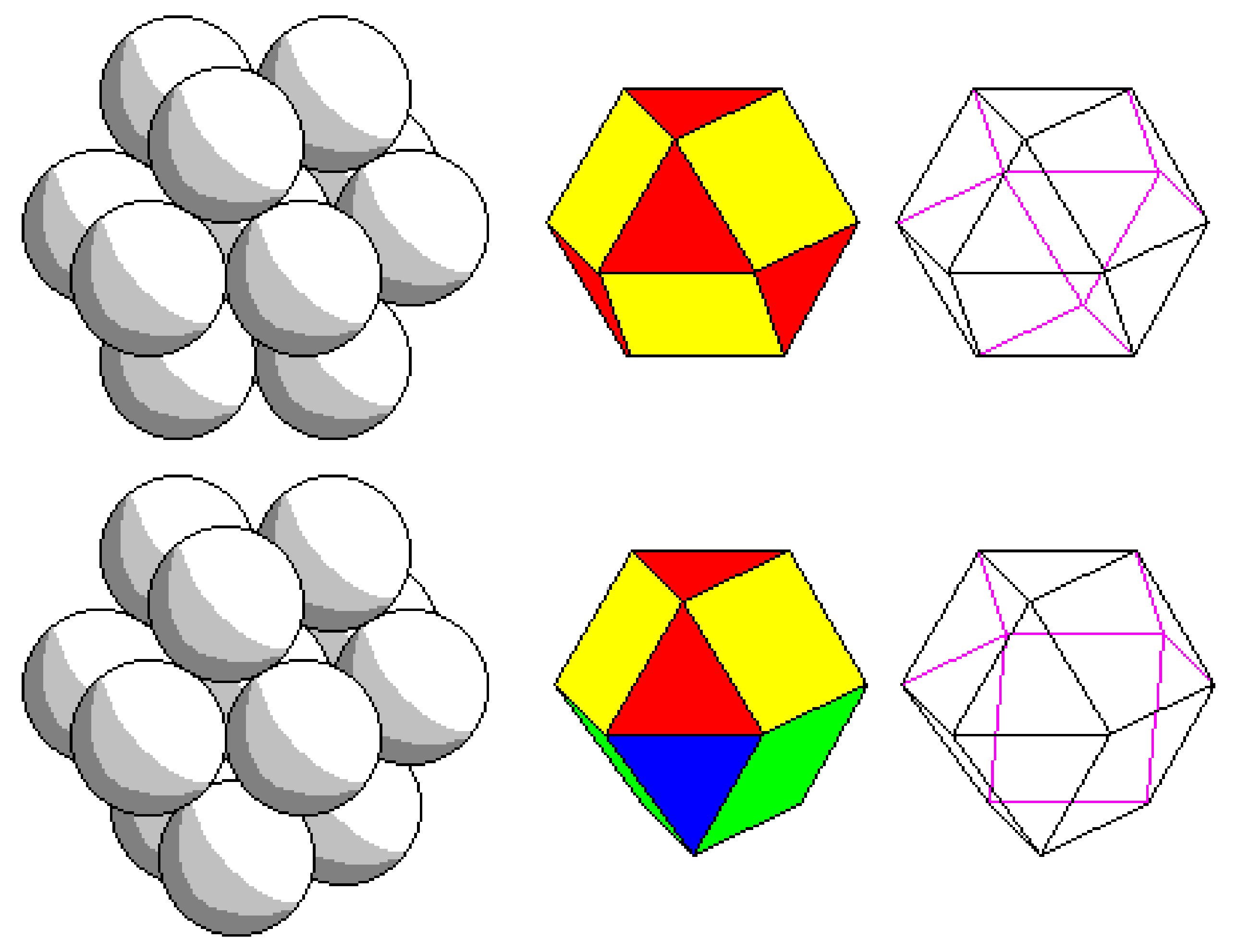
Cuboctahedron



Coordination Polyhedrons

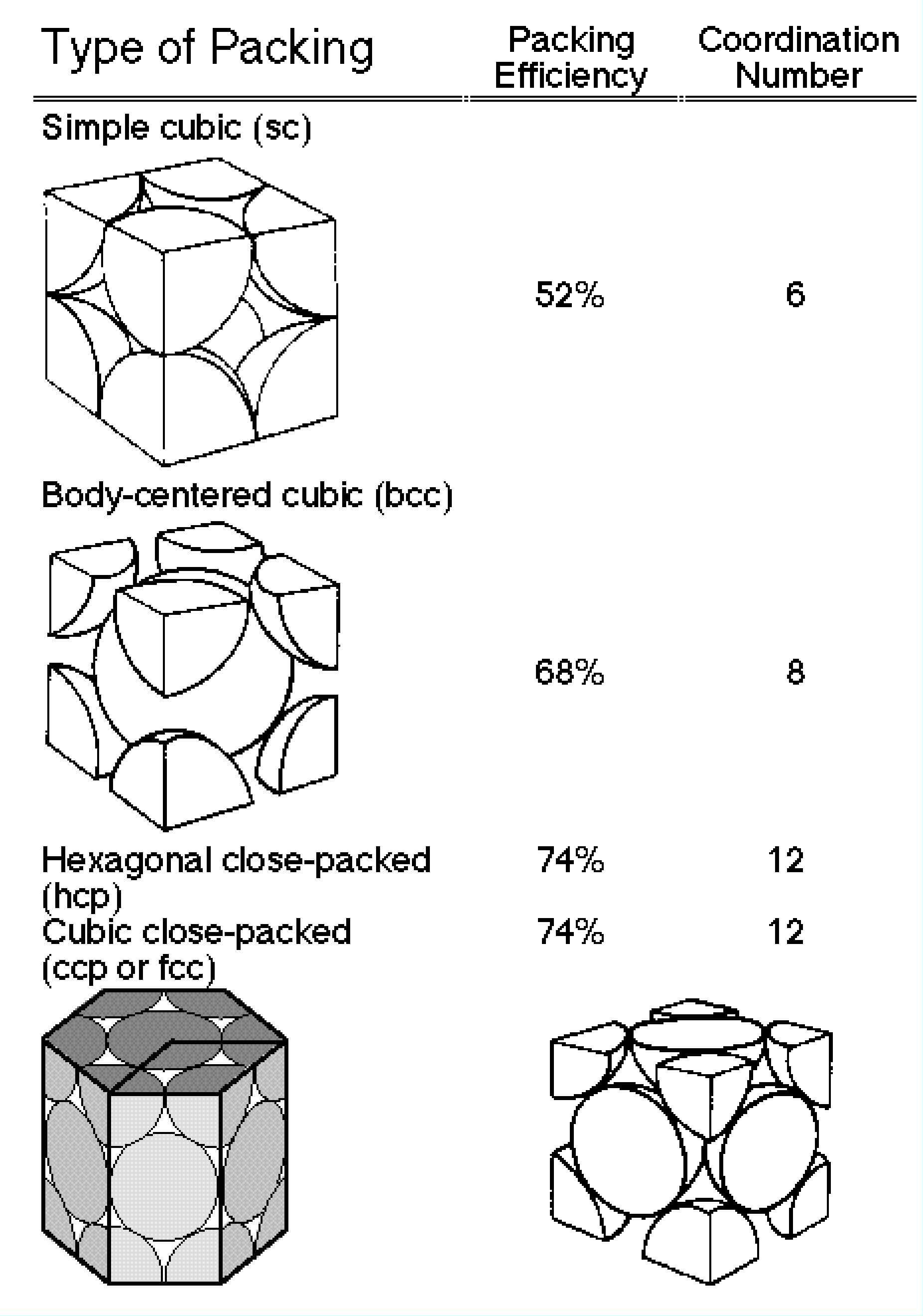


Coordination Polyhedrons



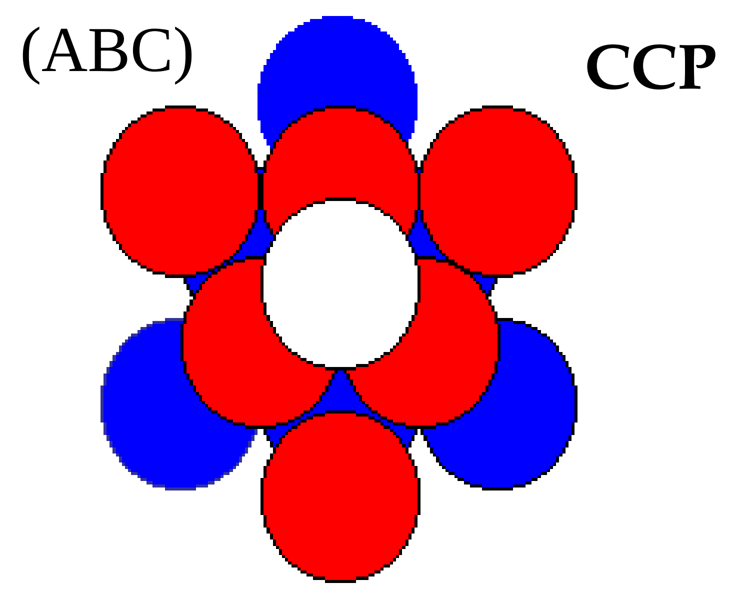
Space Filling

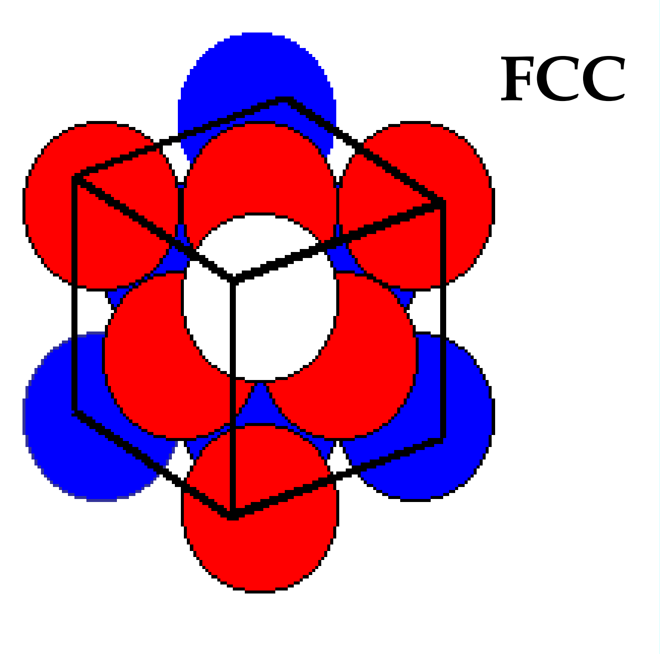
a = lattice parameter	Atom Radius, r	Number of Atoms (lattice points), Z	Space filling
SC	a/2	1	52%
BCC	√3a/4	2	68%
FCC	√2a/4	4	74%
Diamond	√3a/8	8	34%



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

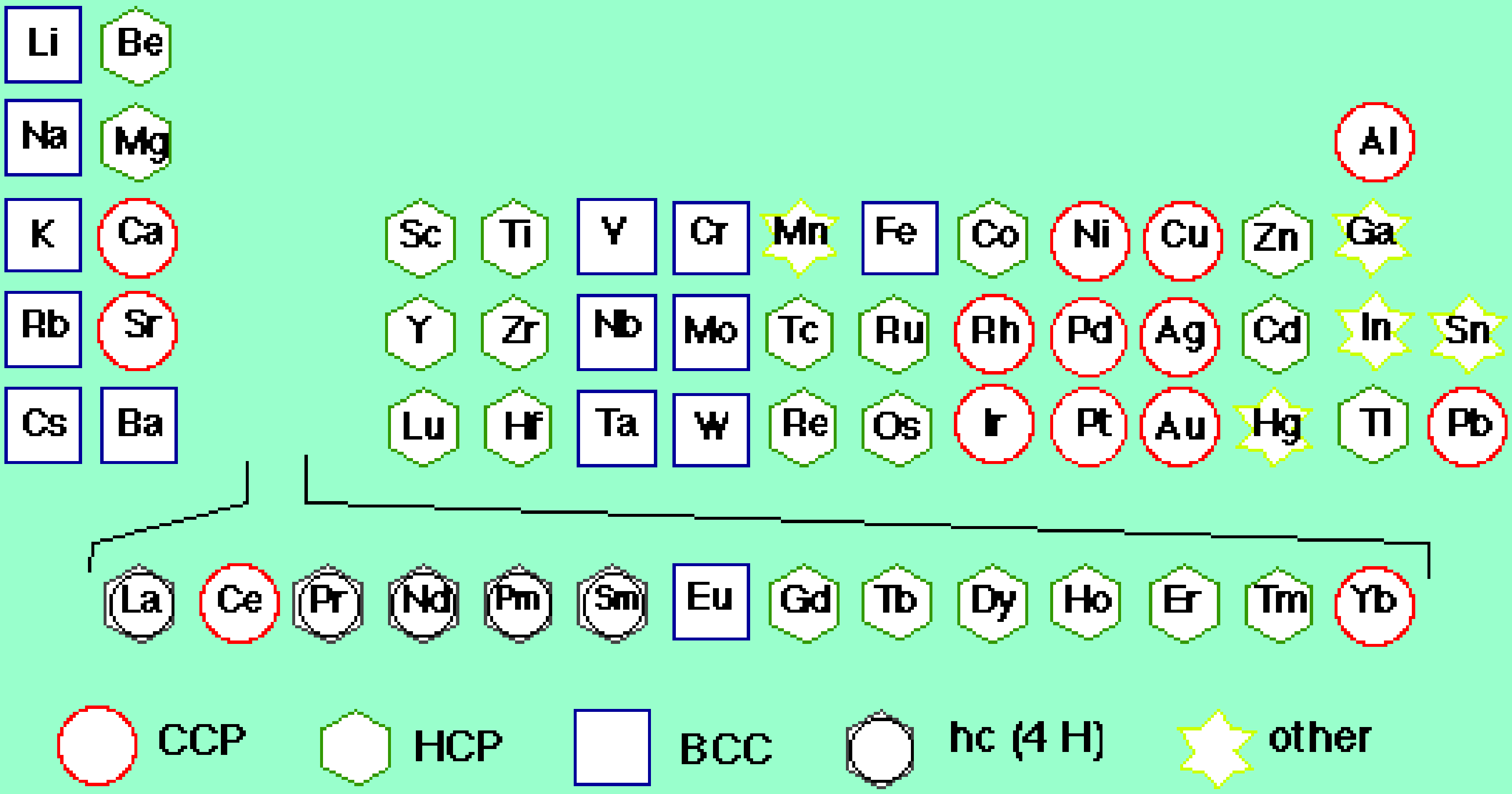
CCP = FCC



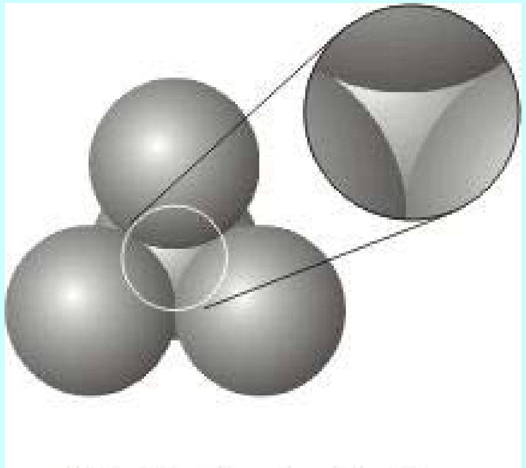


Close packed layers of CCP are oriented perpendicularly to the body diagonal of the cubic cell of FCC

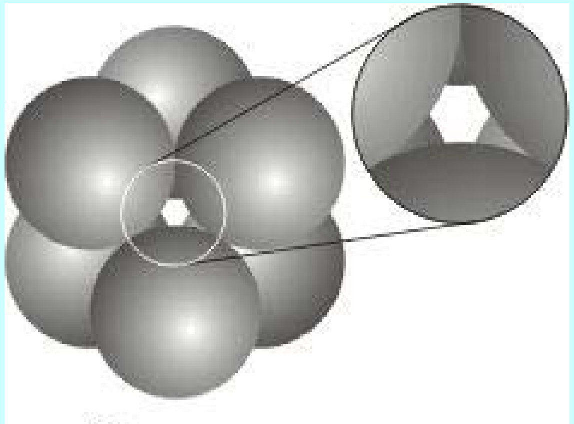
Periodic Table of Metal Structures



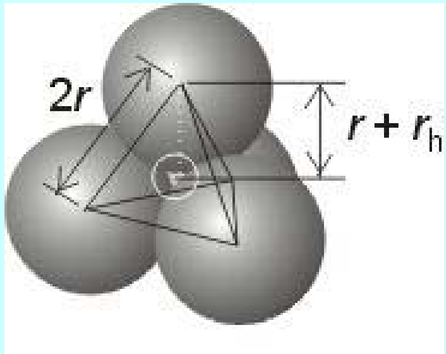
Two Types of Voids (Holes)

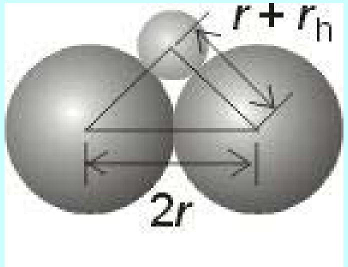


5 Tetrahedral hole

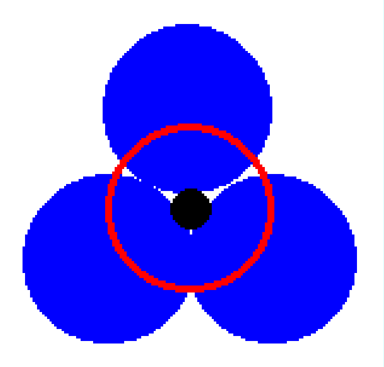


2 Octahedral hole

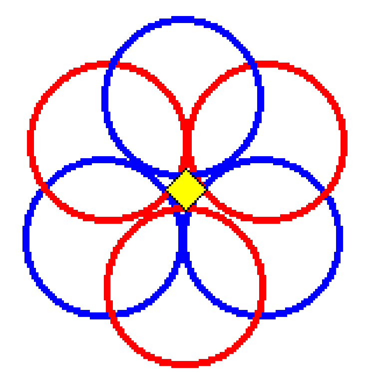




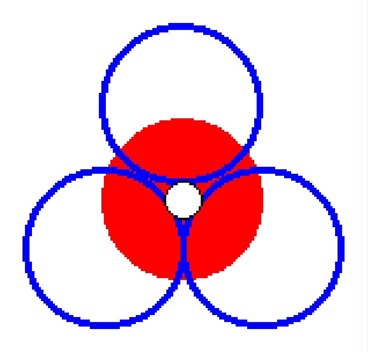
3



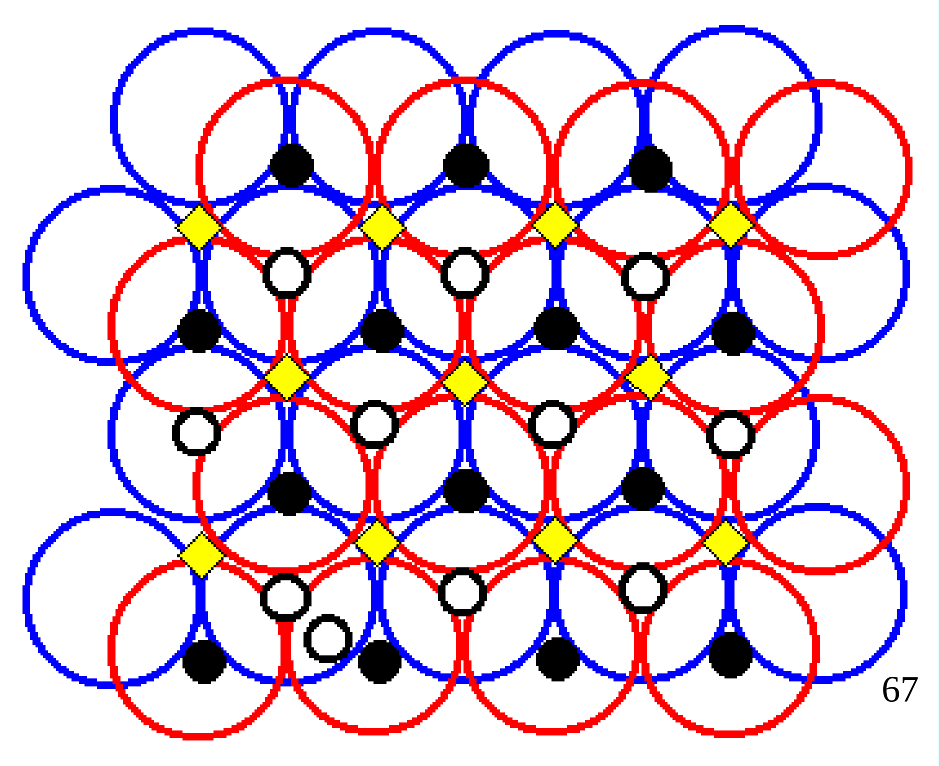
Tetrahedral Holes T+



Octahedral Holes



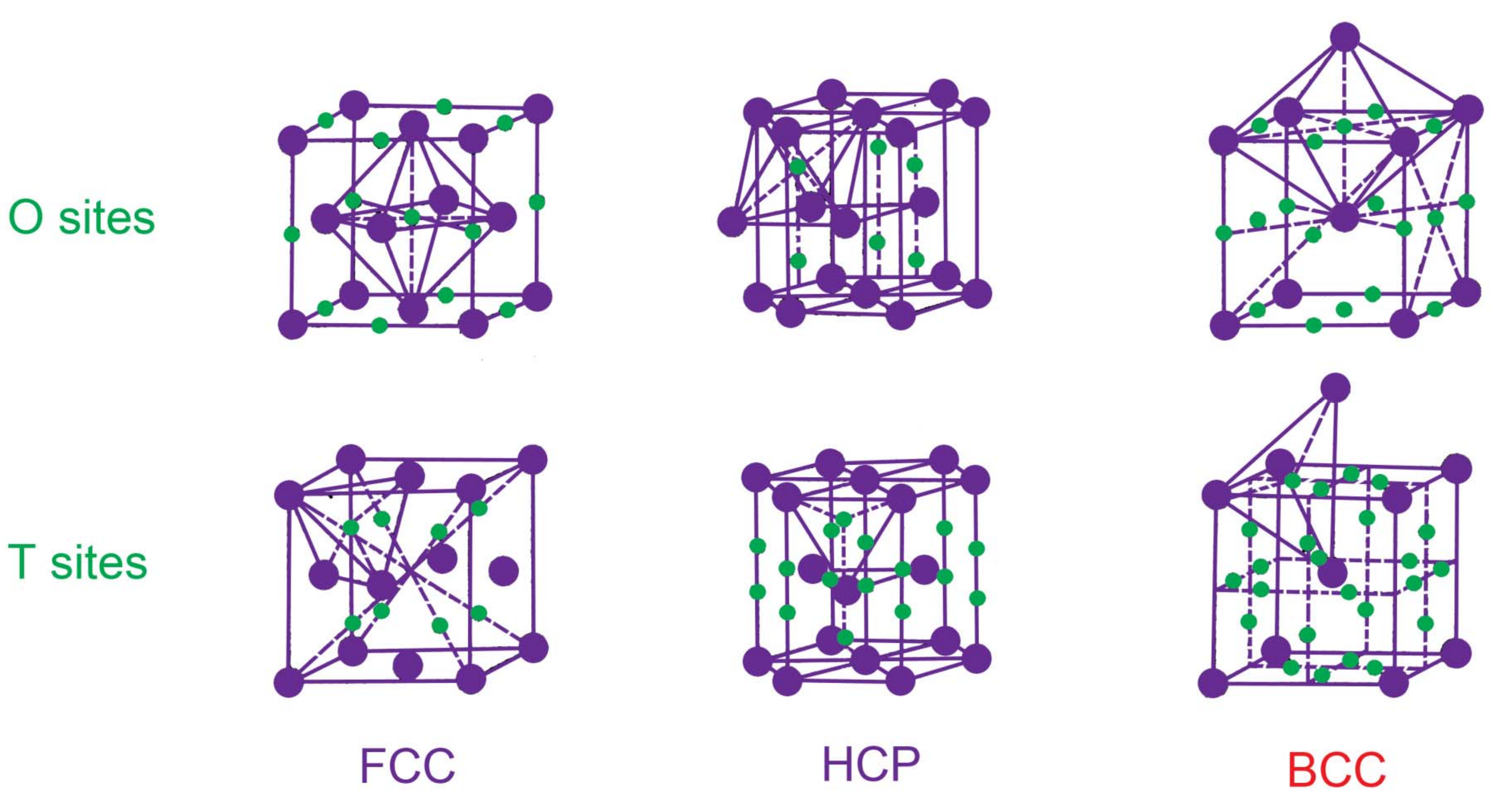
Tetrahedral Holes T-



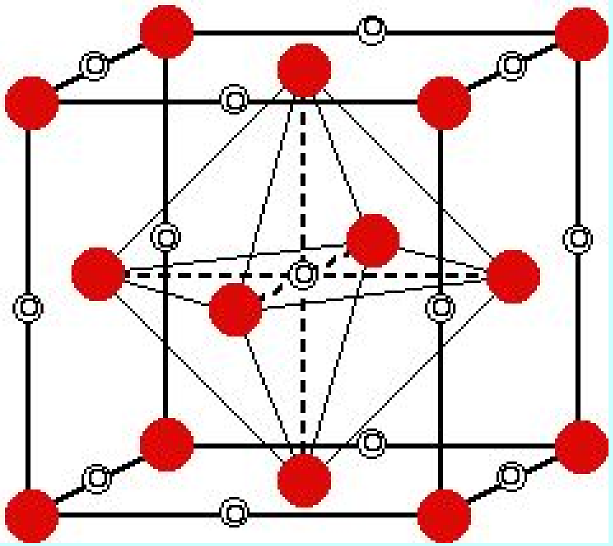
N cp atoms in lattice cell

N Octahedral Holes
2N Tetrahedral Holes

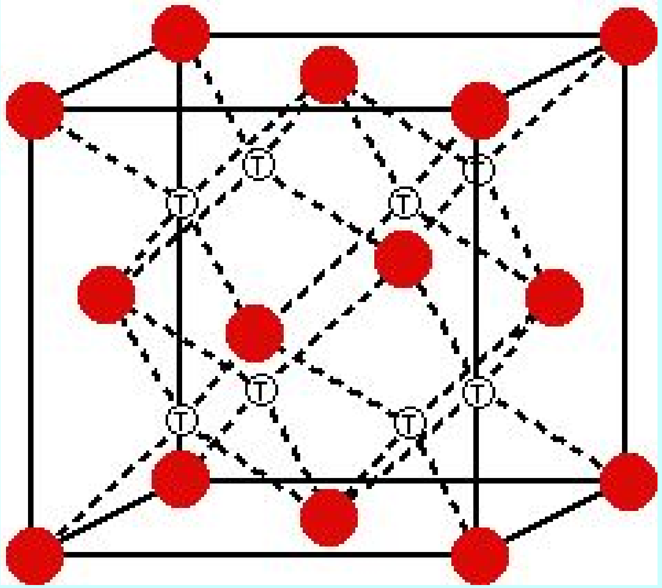
Two Types of Voids (Holes)



Two Types of Voids (Holes)

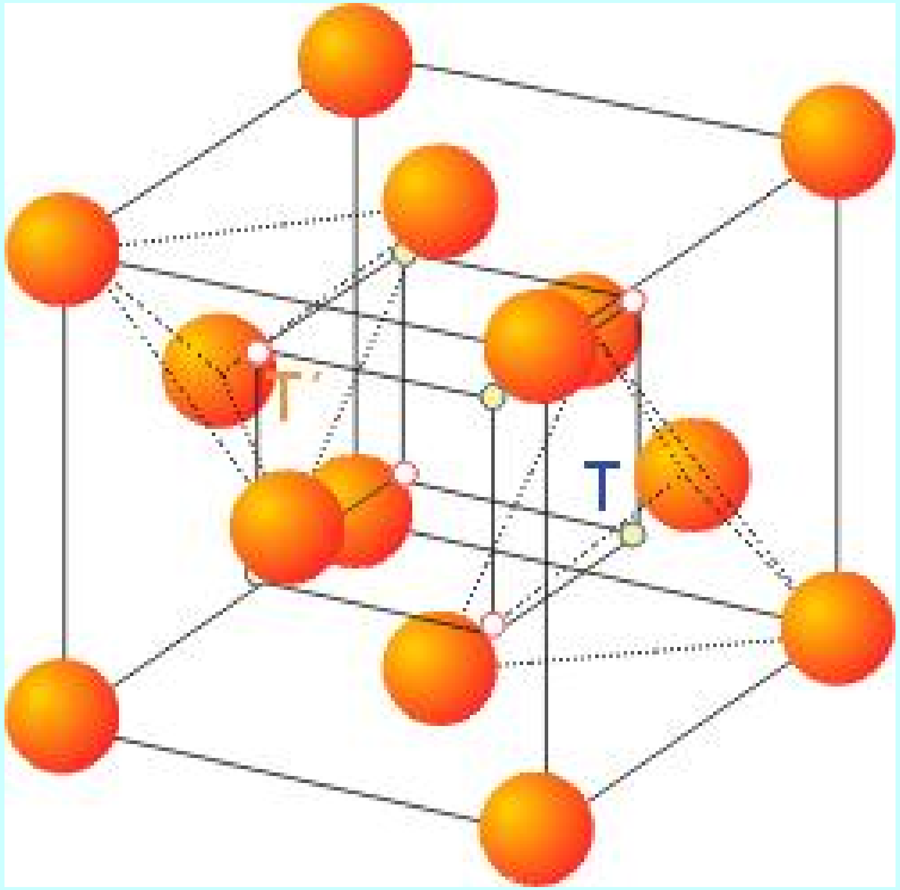


Octahedral Holes



Tetrahedral Holes

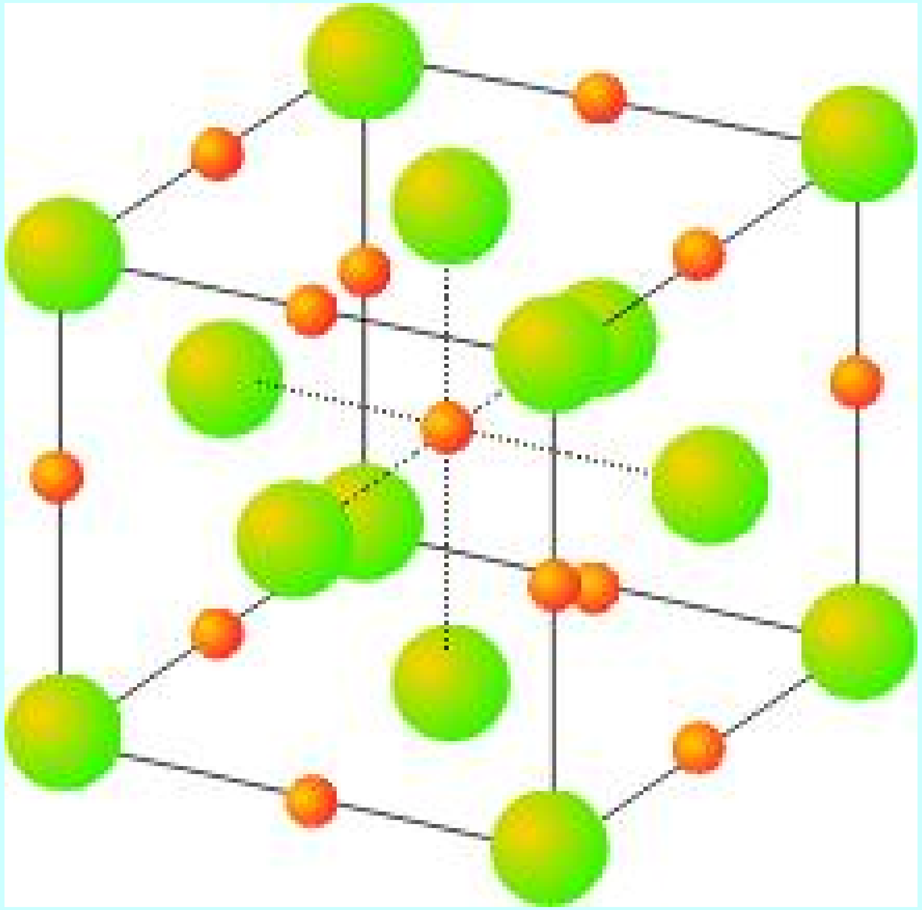
Tetrahedral Holes (2N)



Z = <u>4</u>
number of atoms in the
cell (N)

N = <u>8</u>
number of tetrahedral
holes (2N)

Octahedral Holes (N)



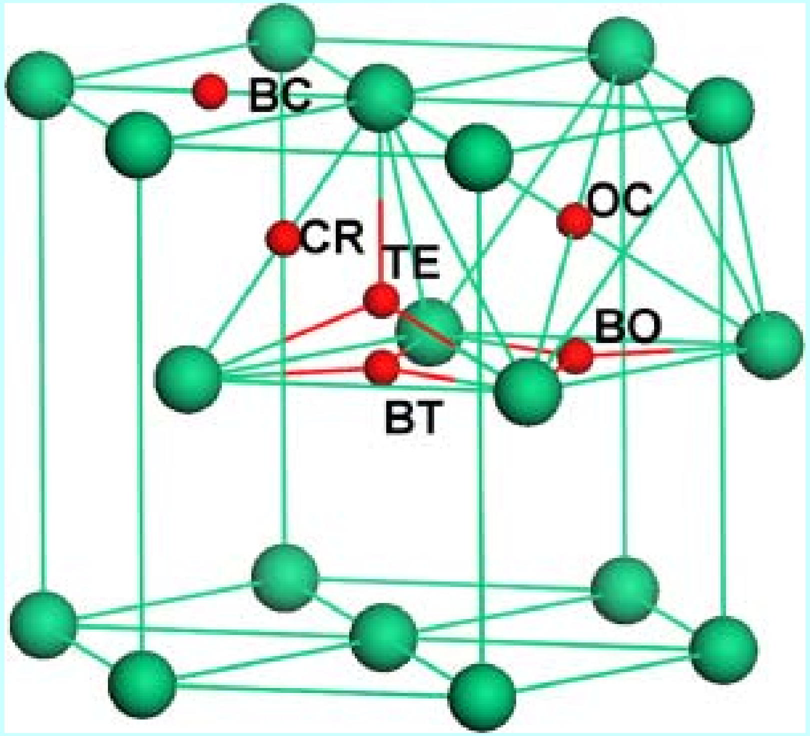
Z = <u>4</u>
number of atoms in the cell (N)

N = <u>4</u>
number of octahedral holes (N)

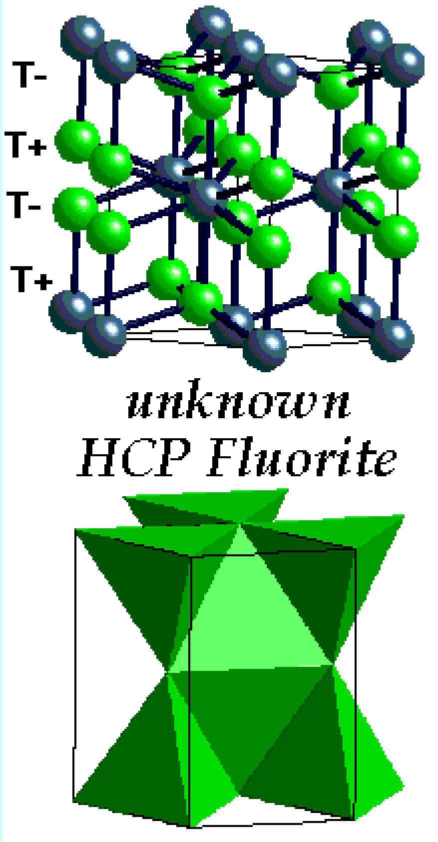
Two Types of Voids (Holes)

N cp atoms in lattice cell

N Octahedral Holes
2N Tetrahedral Holes



Tetrahedral Holes (2N)



Characteristic Structures of Solids = Structure Types

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

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

Lithium bismutide Li_3Bi

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

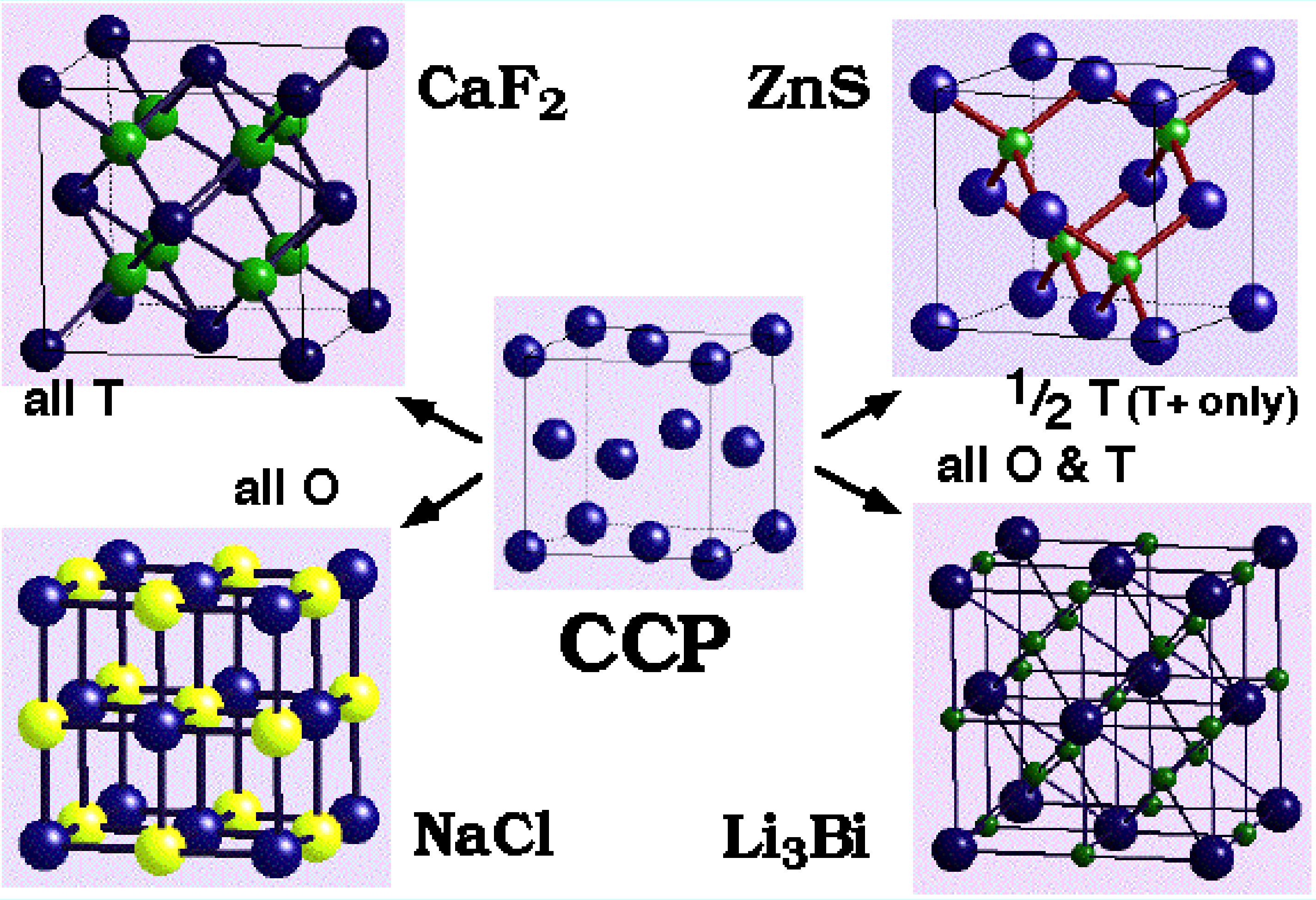
Nickel arsenide NiAs FeS, PtSn, CoS ...

Wurtzite ZnS ZnO, MnS, SiC

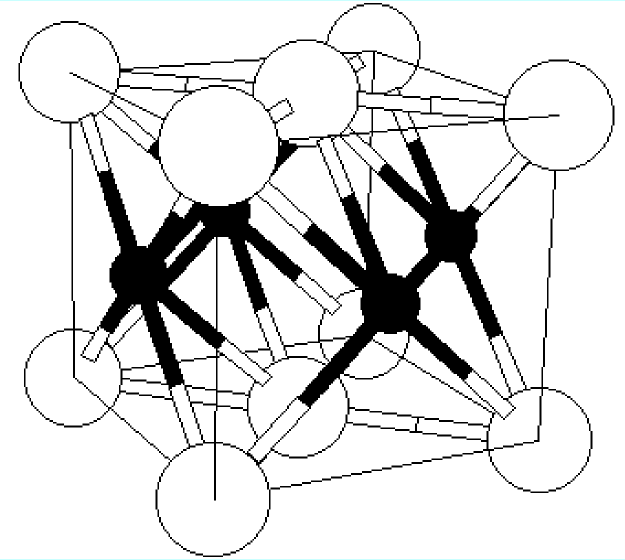
Rhenium diboride ReB_2

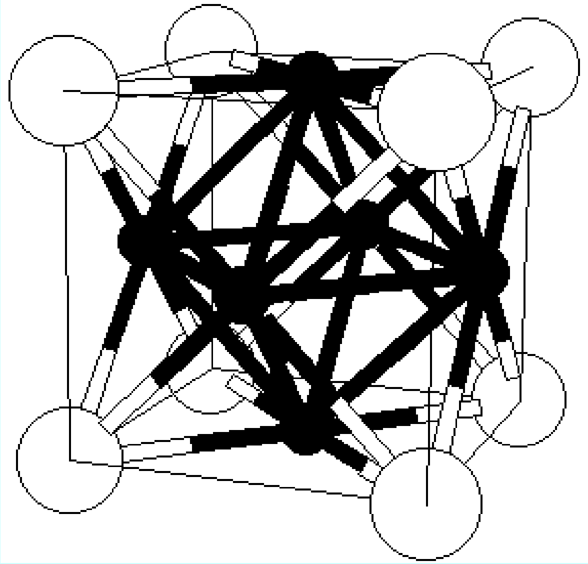
ICSD
3555 NaCl
3438 MgAl2O4
2628 GdFeO3

Structure Types Derived from CCP = FCC



Structure Types Derived from CCP = FCC





Structure Types Derived from CCP = FCC

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

Comparison between structures with filled octahedral and tetrahedral holes

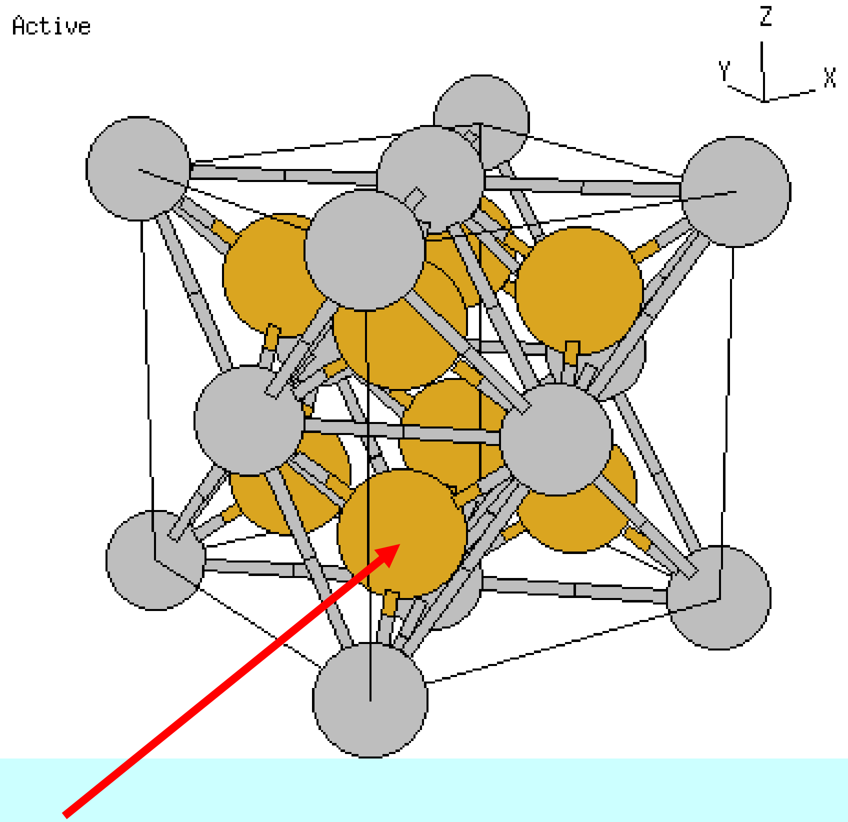
o/t	fcc(ccp)	hcp
all oct.	NaCl	NiAs
all tetr.	CaF_2	ReB_2
o/t (all)	Li_3Bi	(Na_3As) (!) problem
½ t	sphalerite (ZnS)	wurtzite (ZnS)
½ o	$CdCl_2$	CdI_2

Fluorite CaF_2 and antifluorite Li_2O

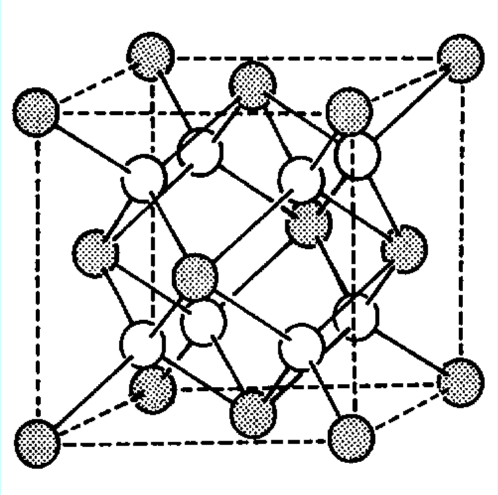
Fluorite structure = a face-centered cubic array (FCC) of **cations** = cubic close packing (CCP) of cations with all tetrahedral holes filled by anions = a simple cubic (SC) array of anions.

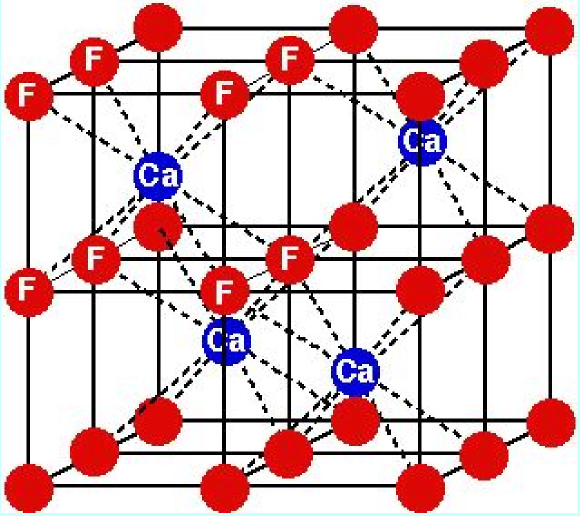
Antifluorite structure = a face-centred cubic (FCC) array of **anions** = cubic close packing (CCP) of anions, with cations in all of the tetrahedral holes (the reverse of the fluorite structure).

Fluorite (CaF_2, antifluorite Li_2O)



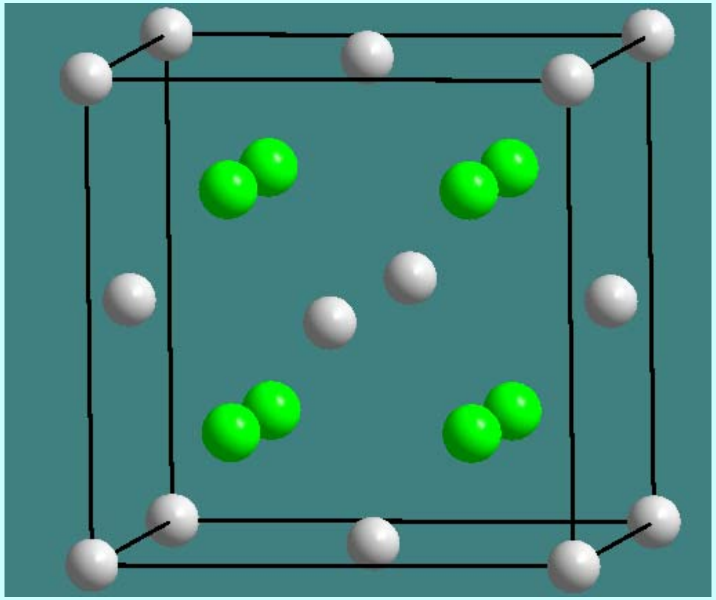
F / Li





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

Fluorite structures (CaF_2, antifluorite Li_2O)



Oxides: Na_2O, K_2O, UO_2, ZrO_2, ThO_2

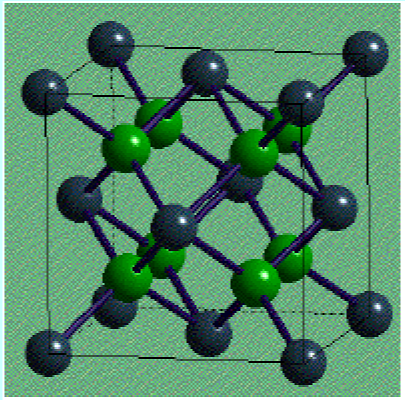
alkali metal sulfides, selenides and tellurides

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

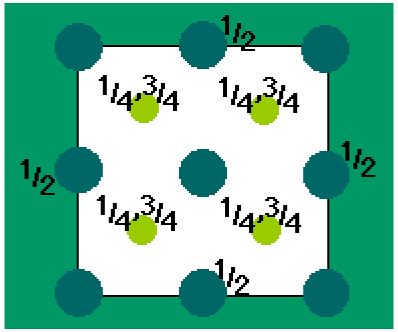
CaF_2, SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, CdF_2, HgF_2, EuF_2, β-PbF_2, PbO_2

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

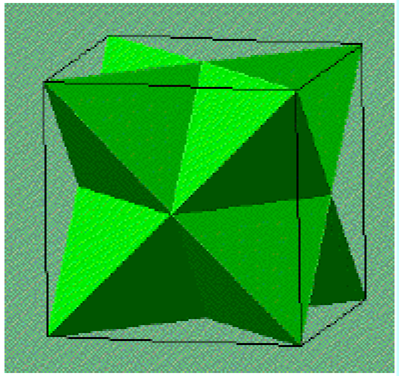
Fluorite structures (CaF_2, antifluorite Li_2O)



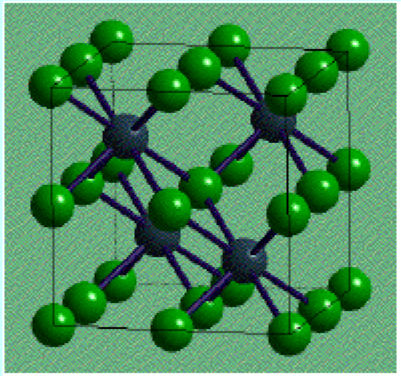
Fluorite A-cell



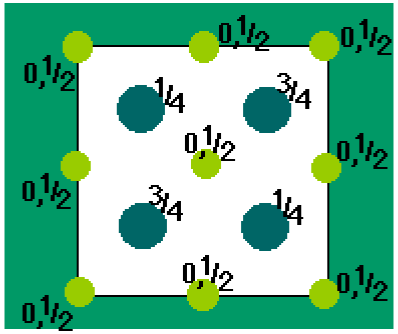
Plan view



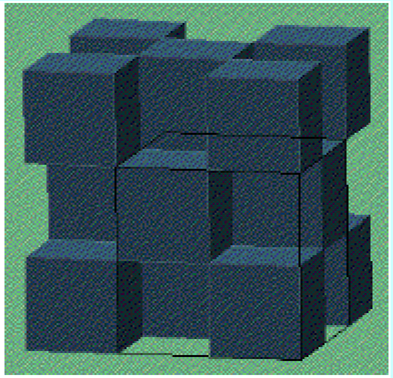
FCa_4 Tetrahedra



Fluorite B-cell

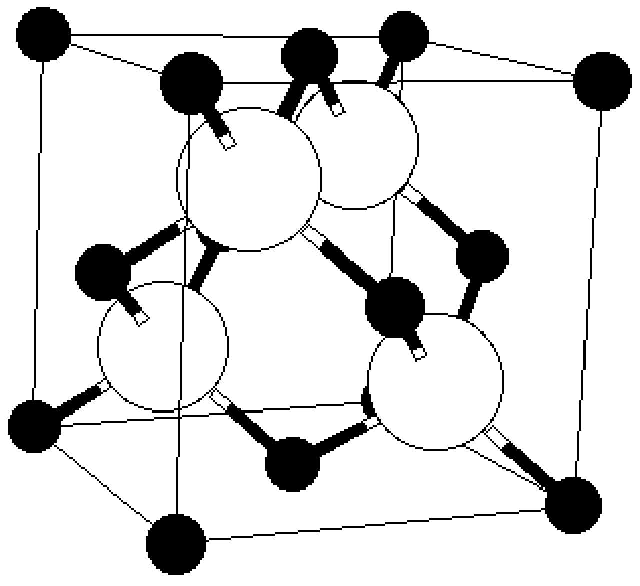


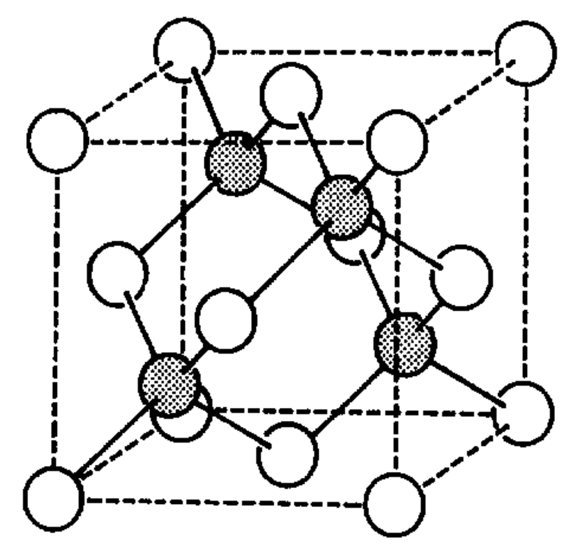
Plan view

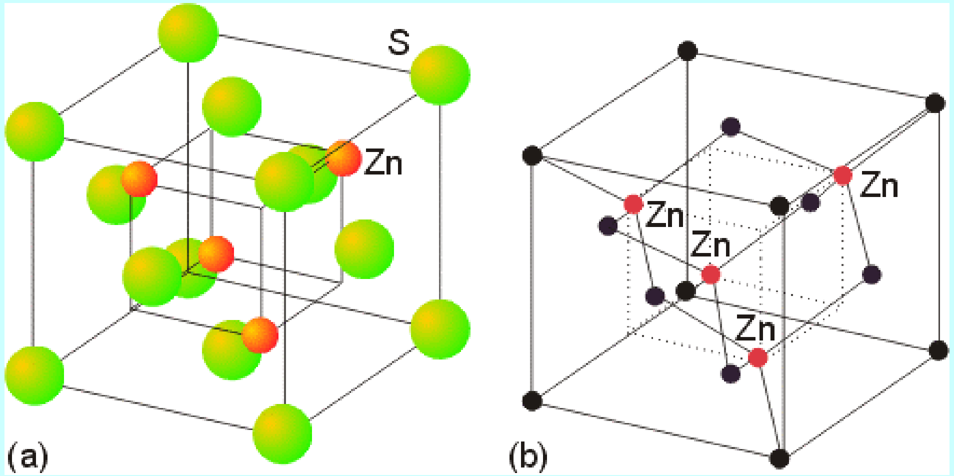


CaF_8 Cubes

Sphalerite (zincblende, ZnS)

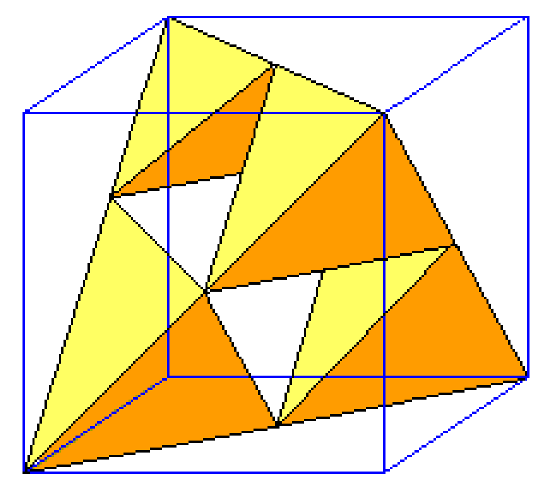


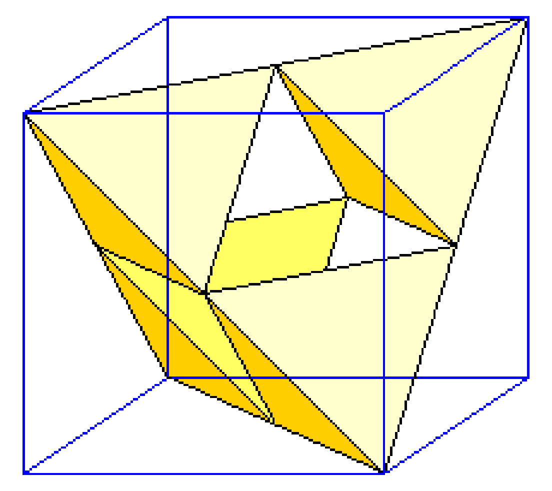


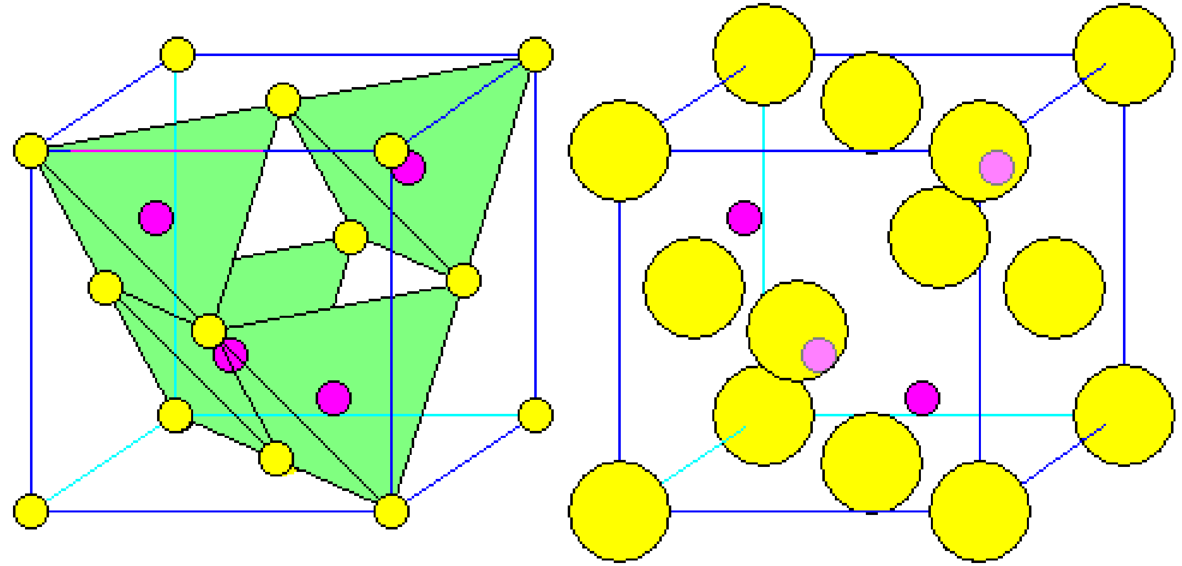


Cubic close packing of anions with 1/2 tetrahedral holes filled by cations

Sphalerite (zincblende, ZnS)

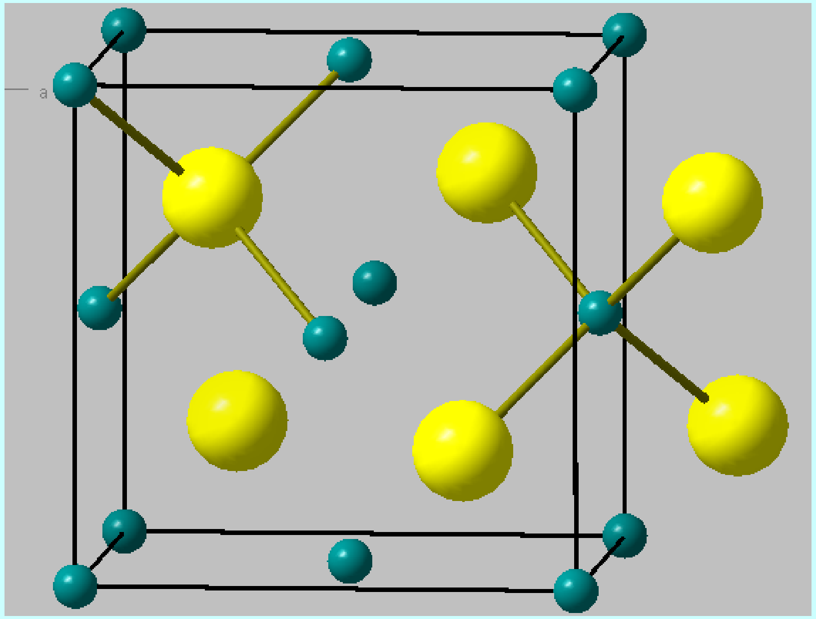






Sphalerite ZnS

Sphalerite (zincblende, ZnS)



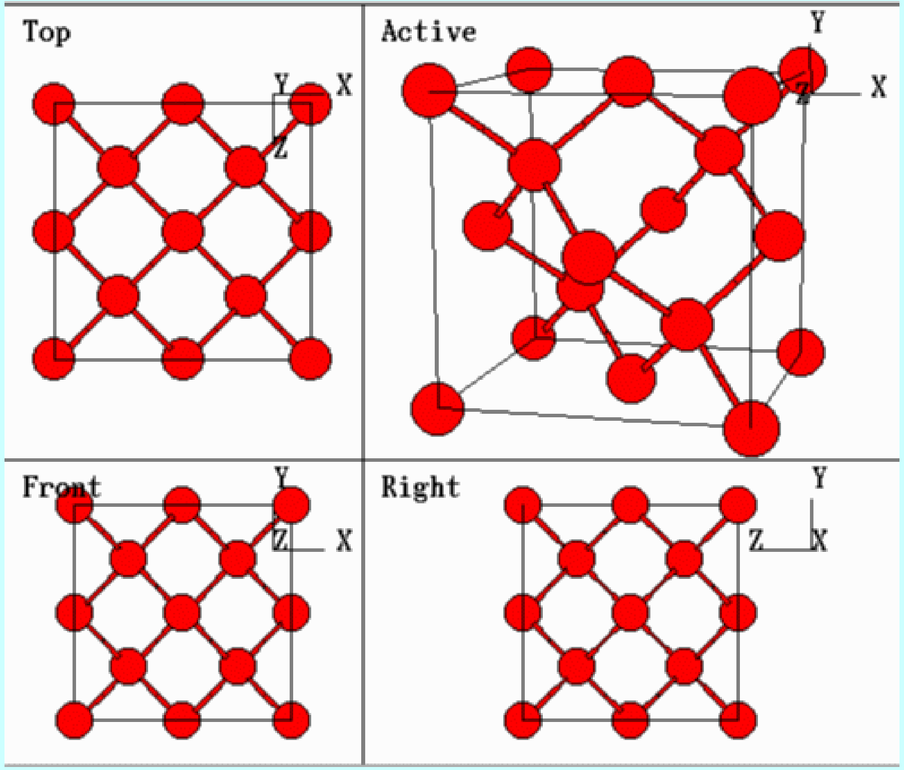
13-15 compounds: BP, BAs, AlP, AlAs, GaAs, GaP, GaSb, AlSb, InP, InAs, InSb

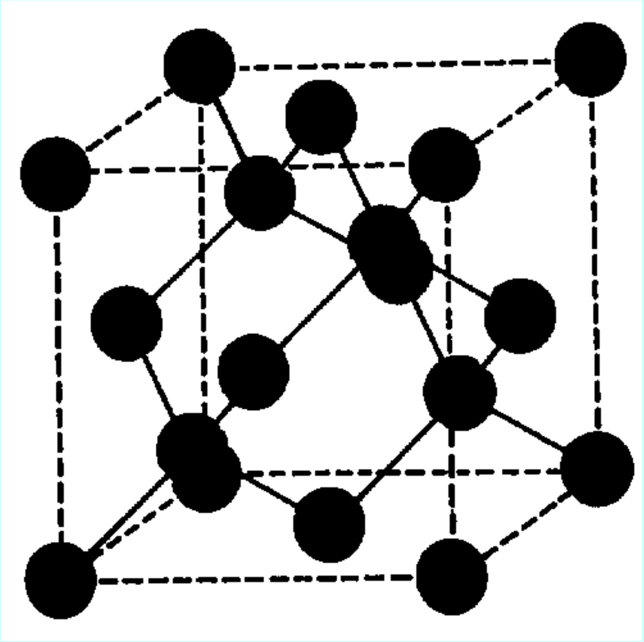
12-16 compounds: BeS, BeSe, BeTe, β-MnS (red), β-MnSe, β-CdS, CdSe, CdTe, HgS, HgSe, HgTe, ZnSe, ZnTe

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

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

Diamond

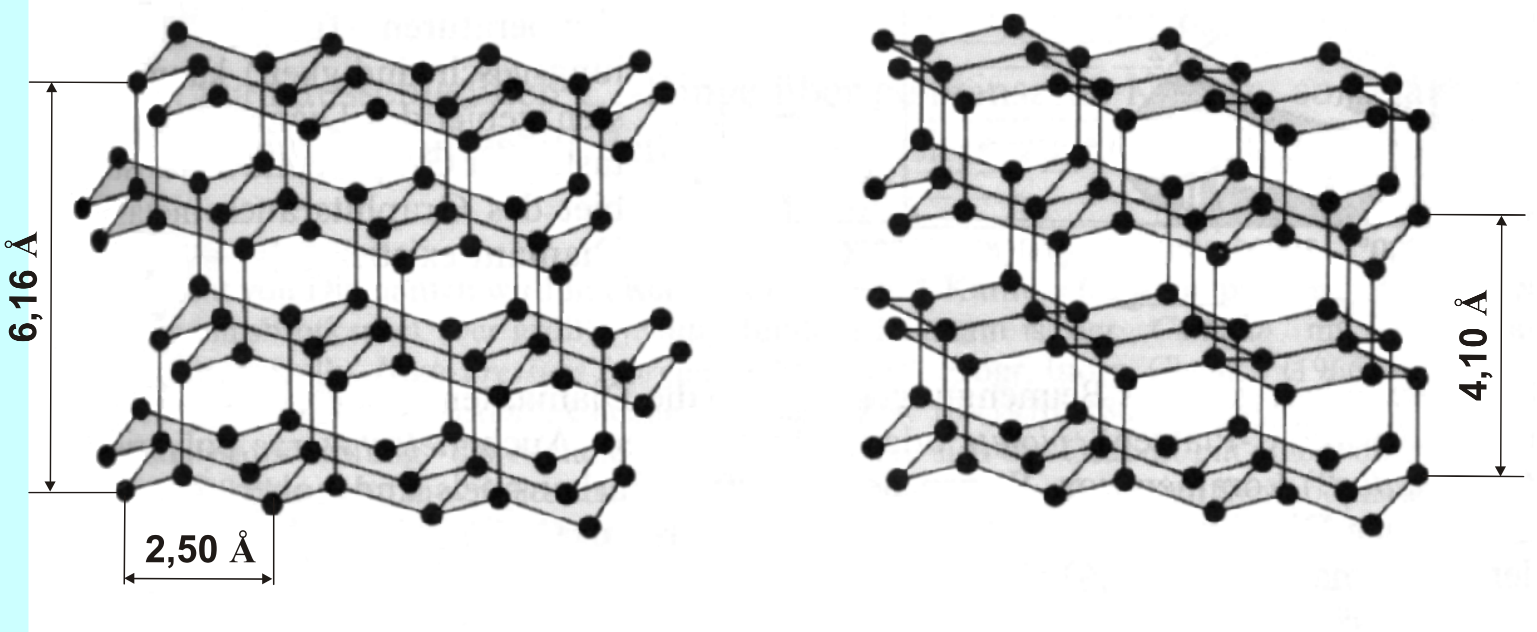




Diamond

cubic

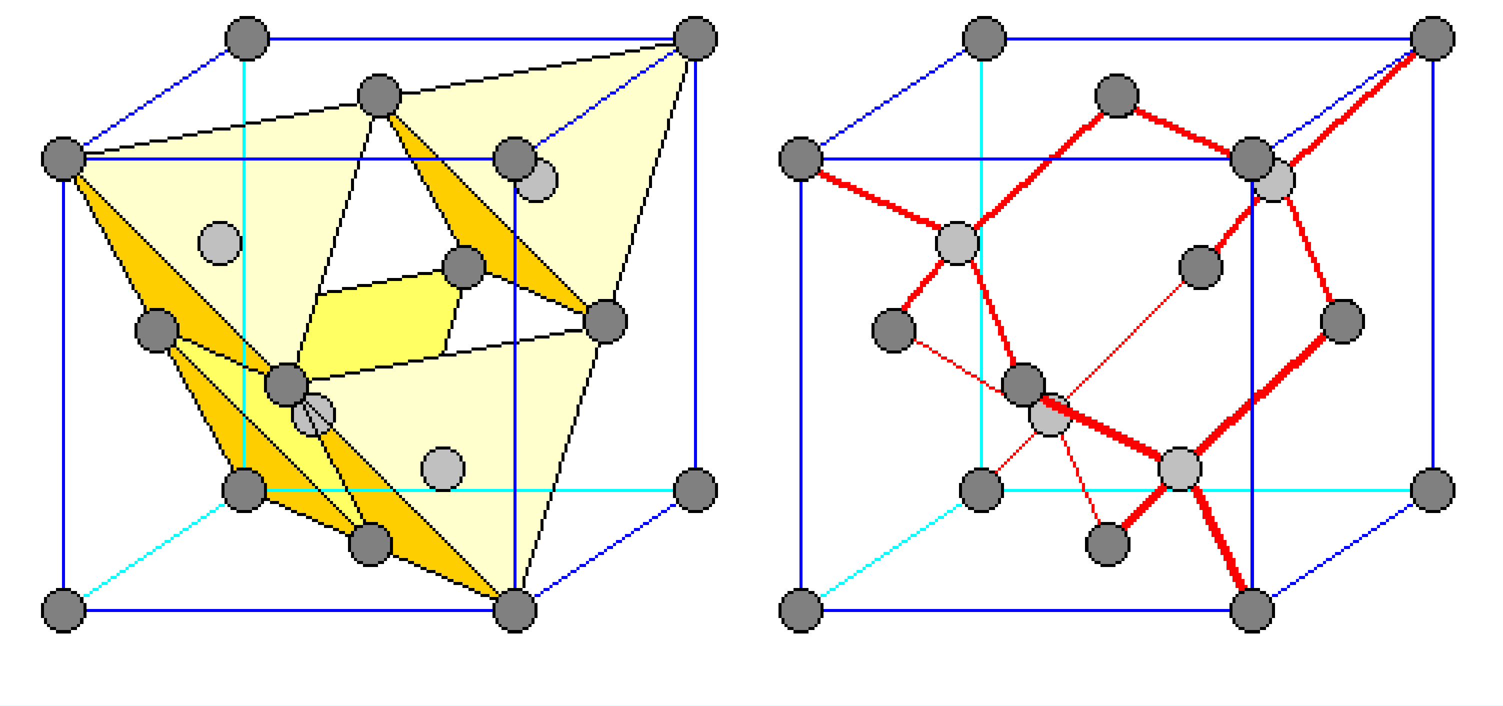
hexagonal



SiO_2 cristobalite

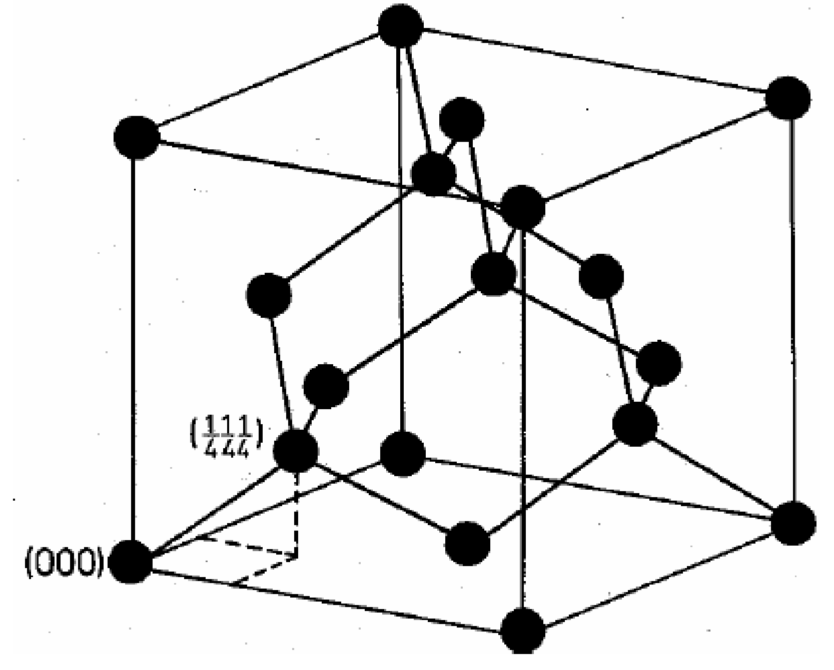
Lonsdaleite
SiO_2 tridymite
ice

Cubic Diamond



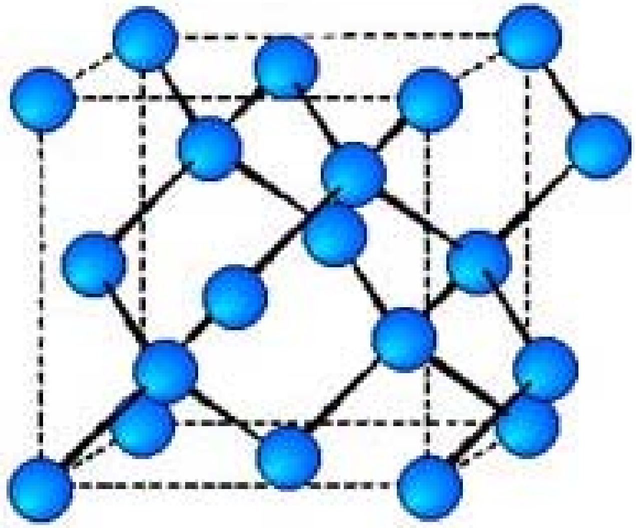
Diamond Structure

C, Si, Ge, grey-Sn



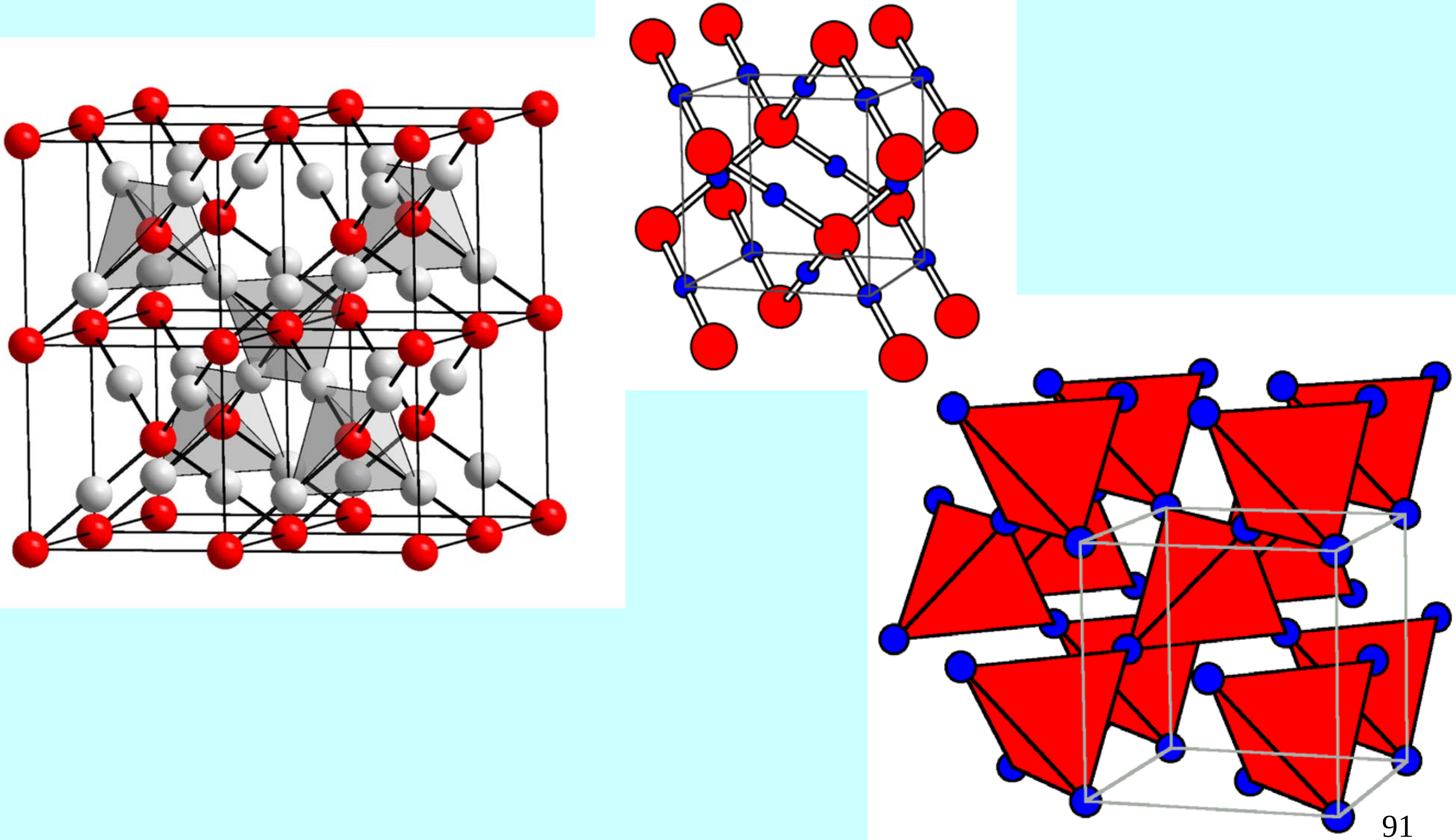
- Add 4 atoms to a FCC
- Tetrahedral bond arrangement
- Each atom has 4 nearest neighbors and 12 next nearest neighbors

Elements of the 14th Group

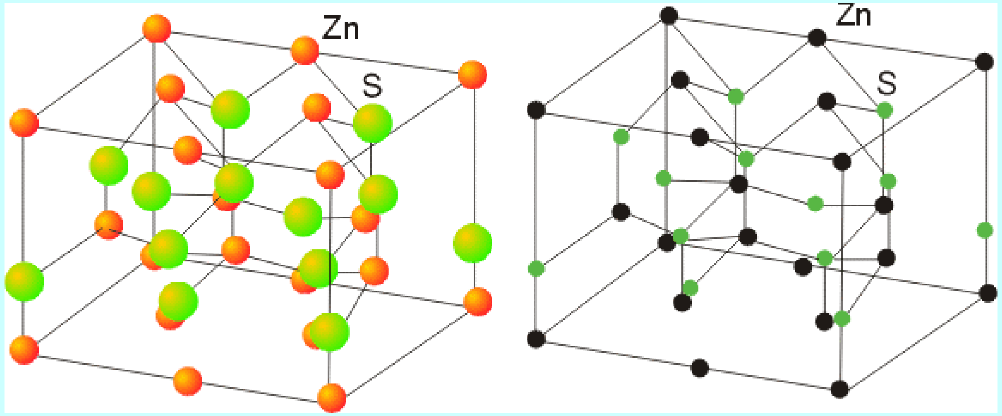


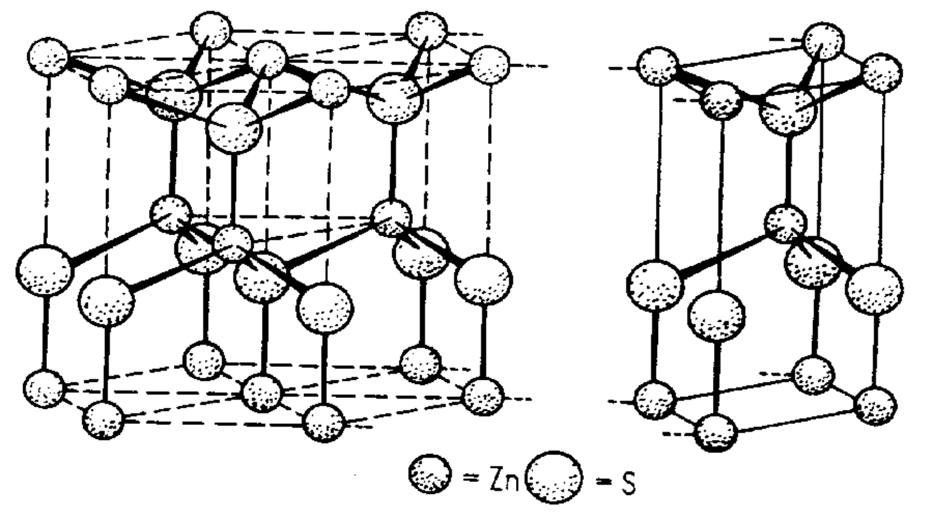
	a (Å)	d (g.cm $^{-3}$)
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
a-Sn	6.489	7.285

Cuprite Cu_2O Cubic Lattice



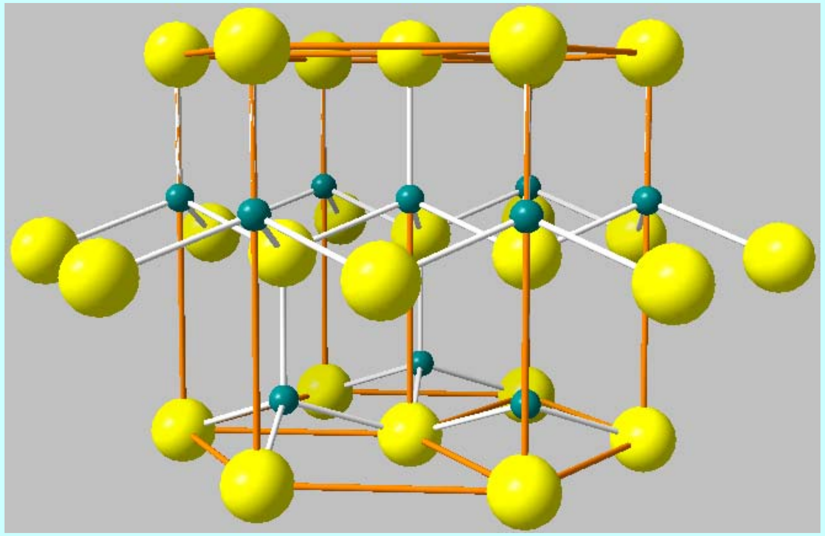
Wurzite, ZnS

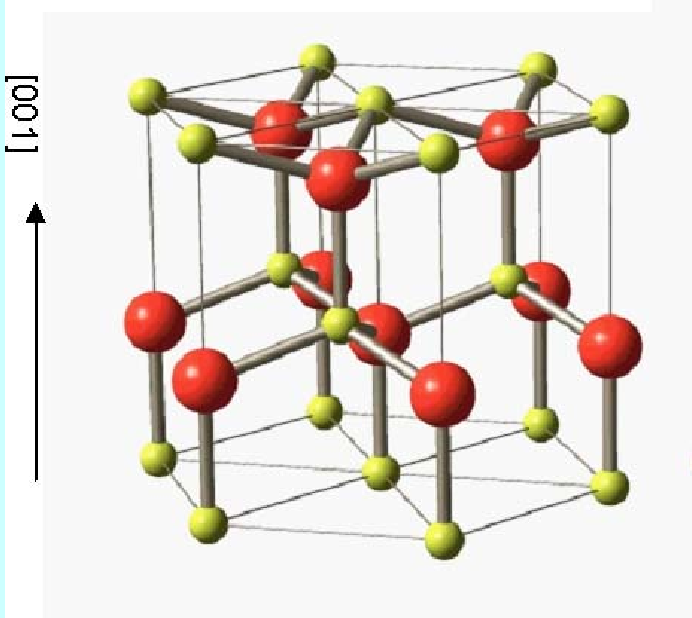




Hexagonal close packing of anions with 1/2 tetrahedral holes filled by cations

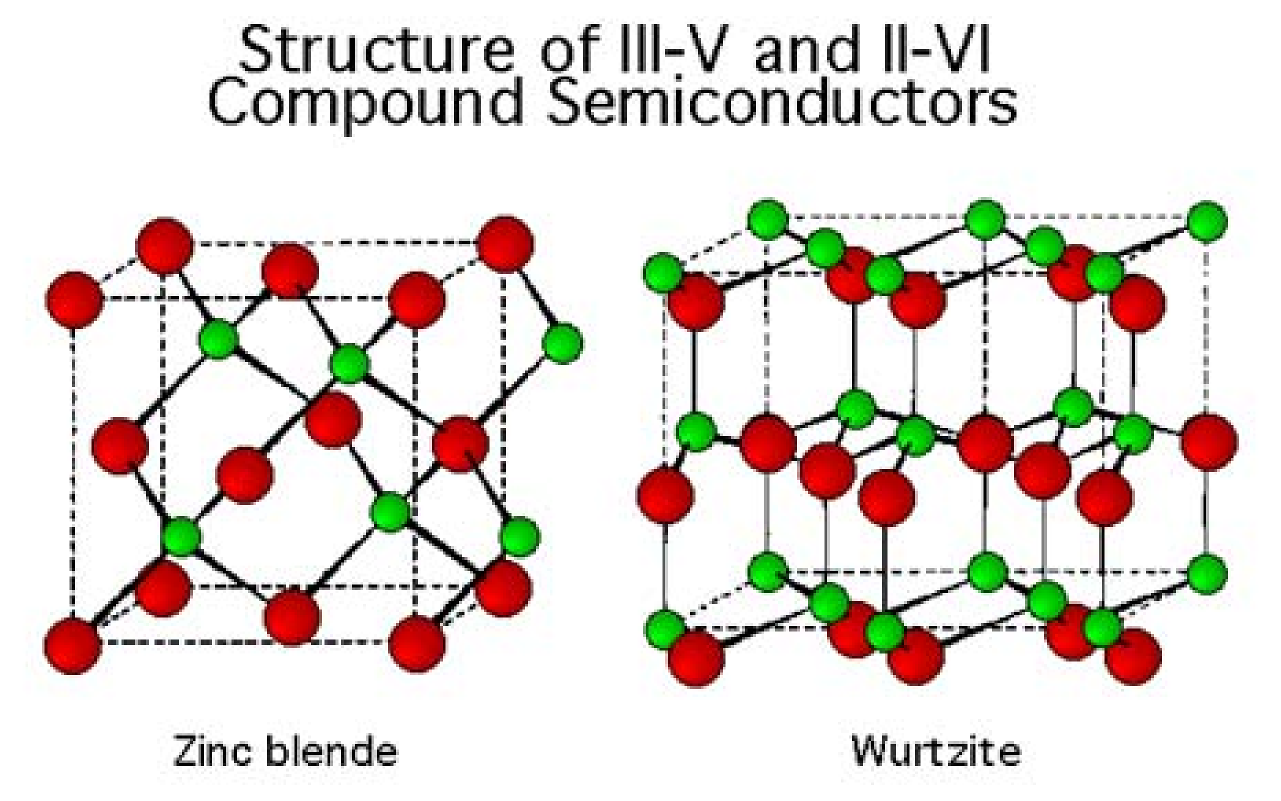
Wurzite, ZnS



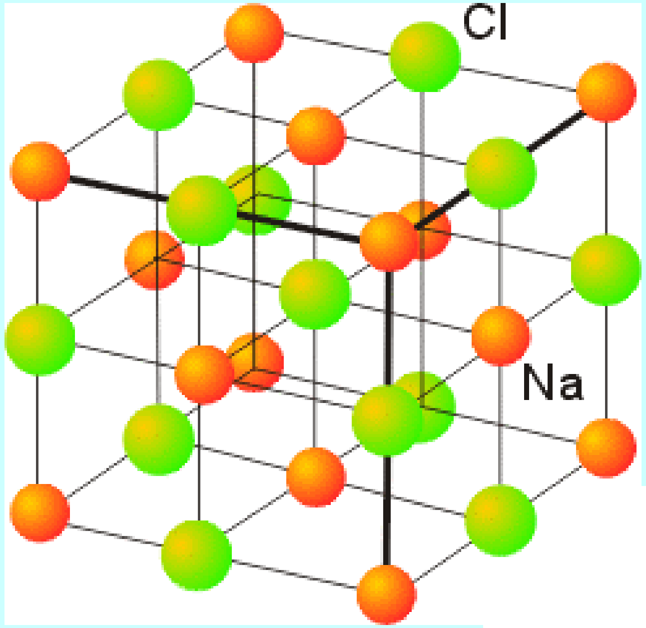


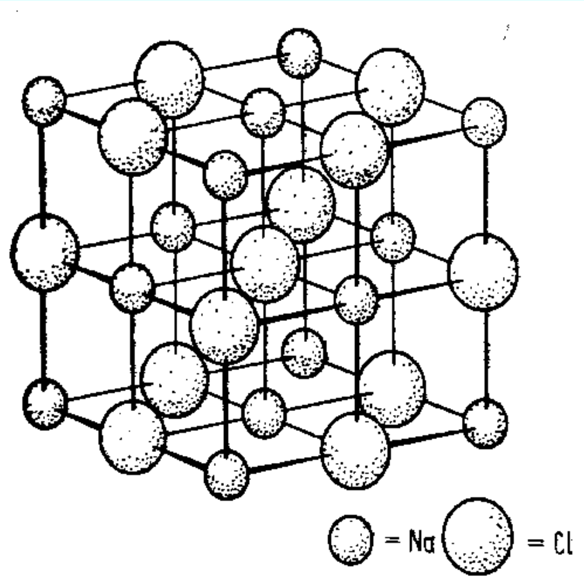
ZnO, ZnS, ZnSe, ZnTe, BeO, CdS, CdSe, MnS, AgI, AlN

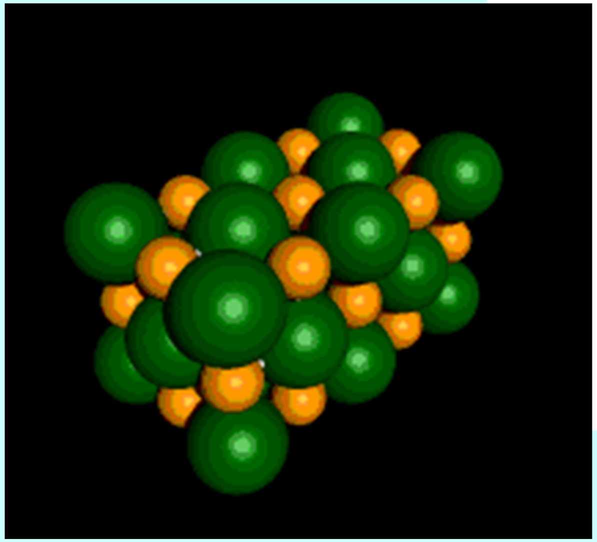
Semiconductors of 13-15 and 12-16 type

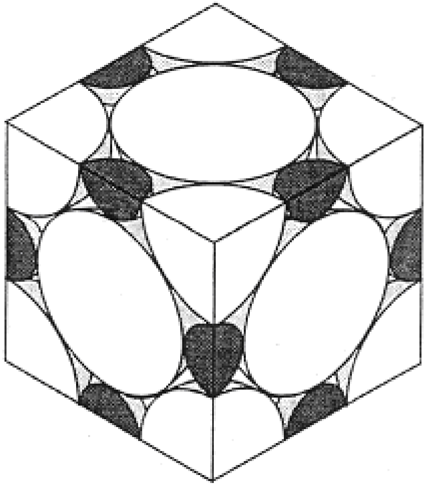


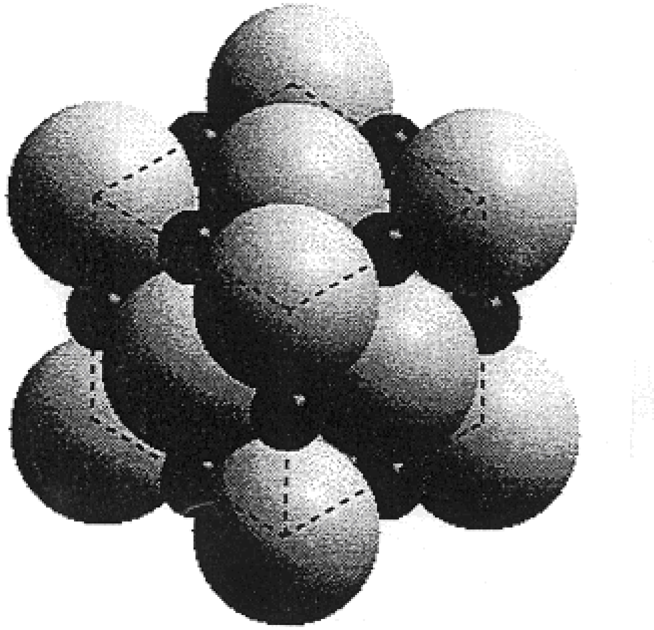
Rock Salt, NaCl





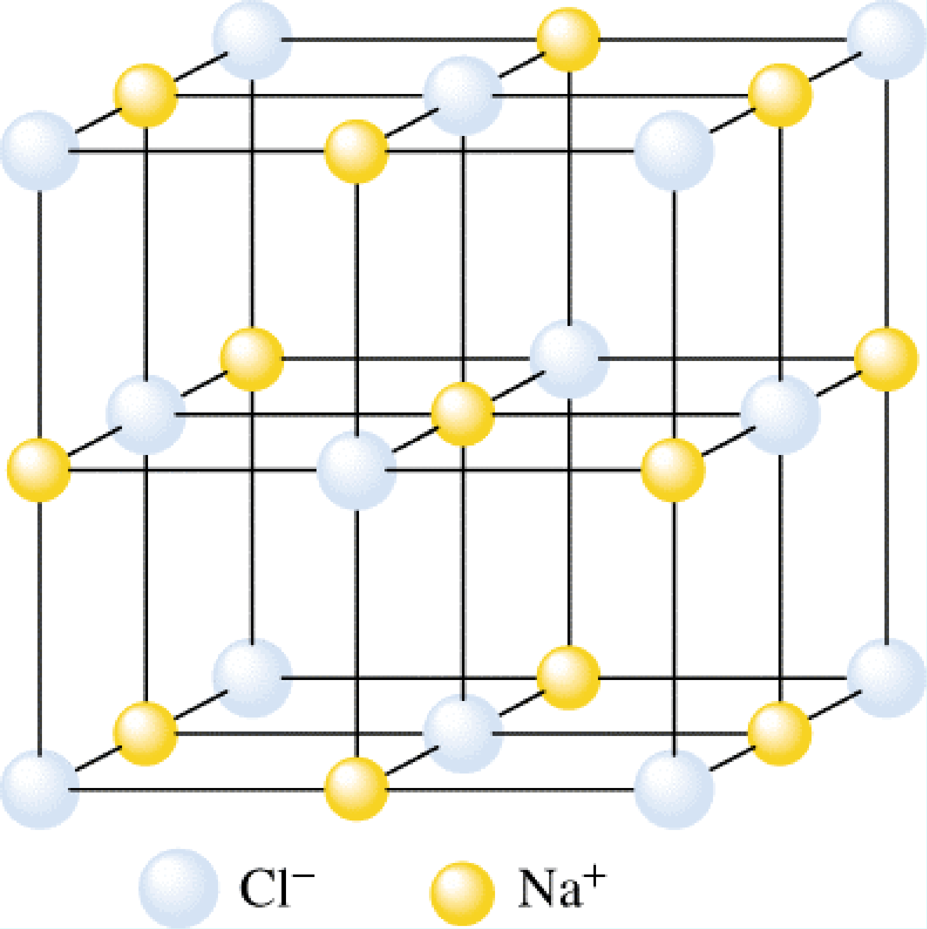


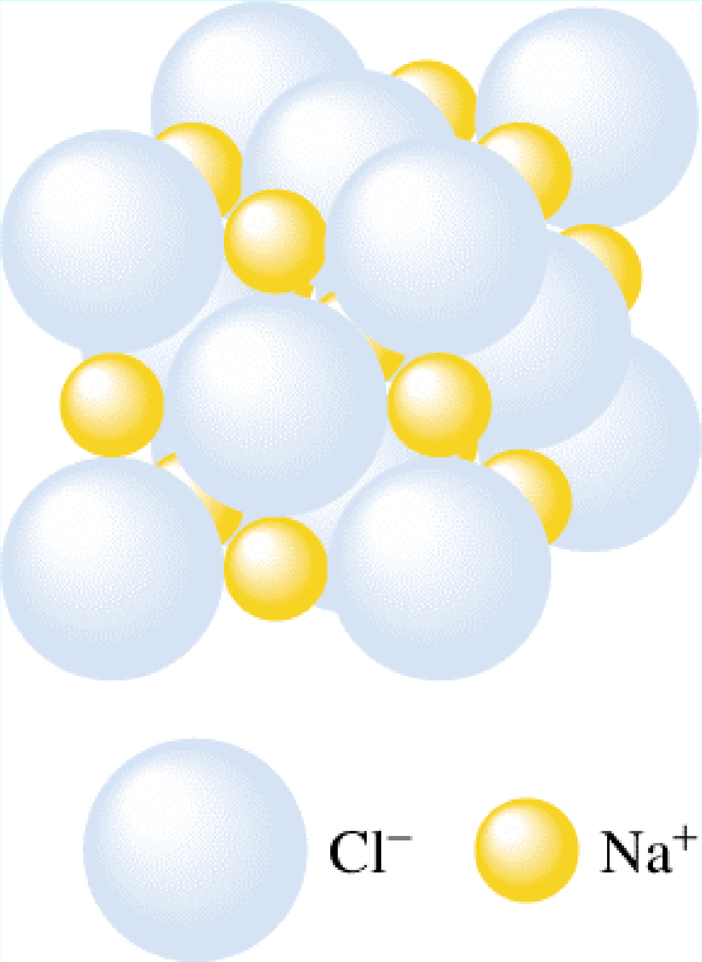




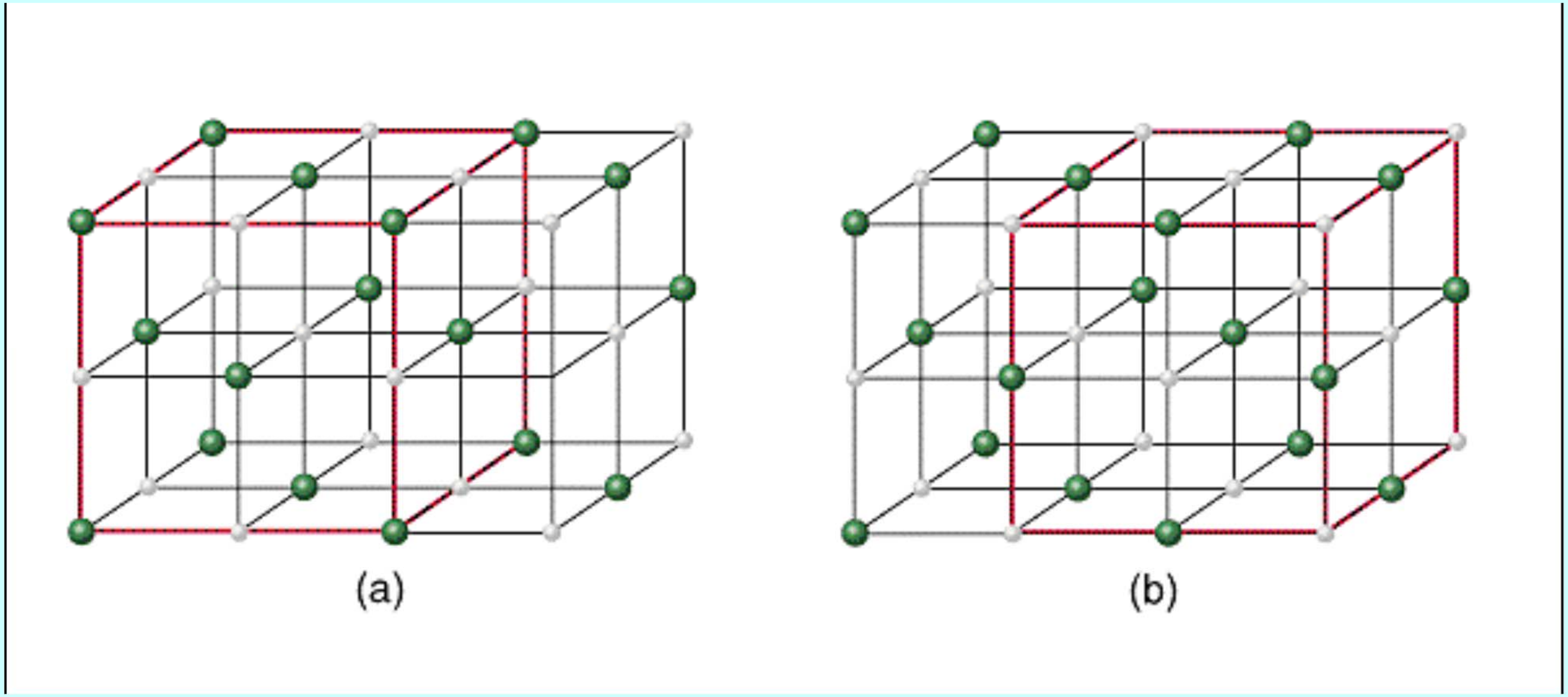
Cubic close packing of anions with all octahedral holes filled by cations

Rock Salt, NaCl



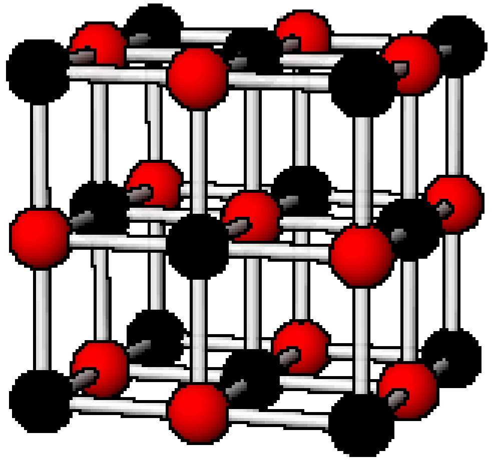


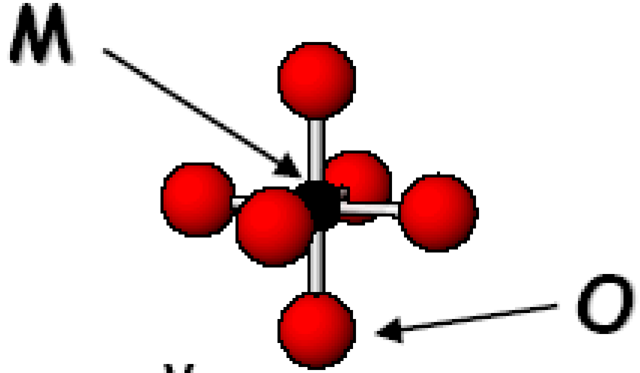
Rock Salt, NaCl

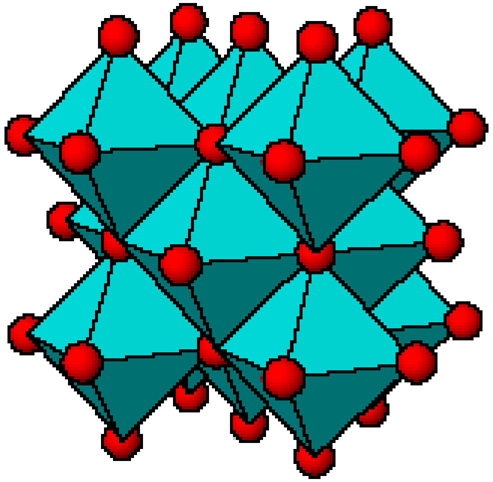


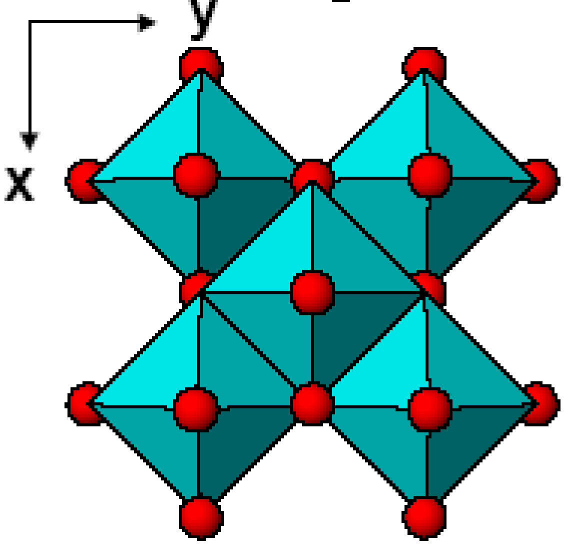
Anion and cation sublattices

Rock Salt Crystal Structure

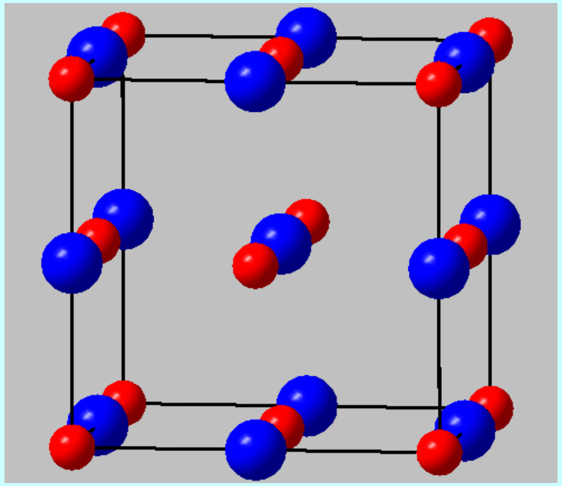








Rock salt structures (NaCl)

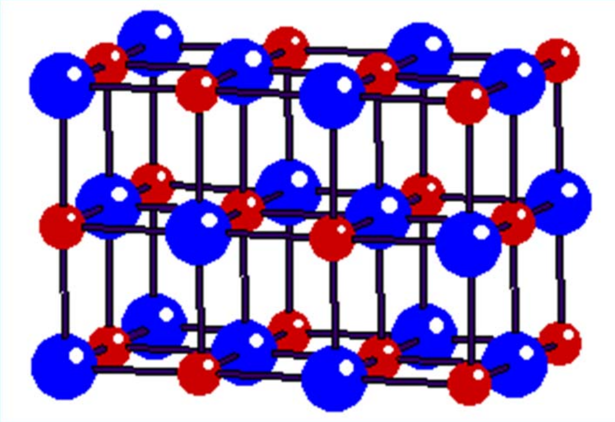


Hydrides: LiH, NaH, KH,
NH_4BH_4 – H_2 storage material
Pd(H)
Borides: ZrB, HfB

Carbides: TiC, ZrC, VC, UC

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

Oxides: MgO, CaO, SrO, BaO, TiO, VO, MnO, FeO, CoO, NiO
Chalcogenides: MgS, CaS, SrS, BaS, 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

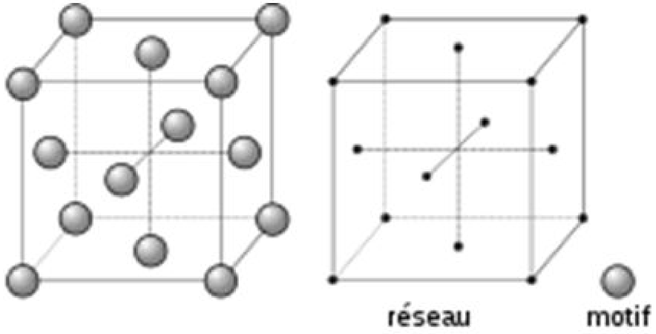
Rock salt structures (NaCl)

Palladium-Hydrogen system

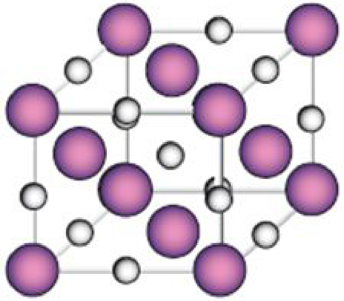
palladium

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

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



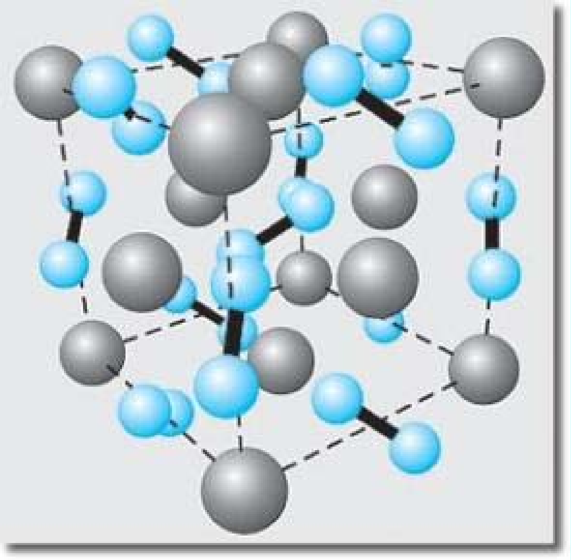
fcc structure

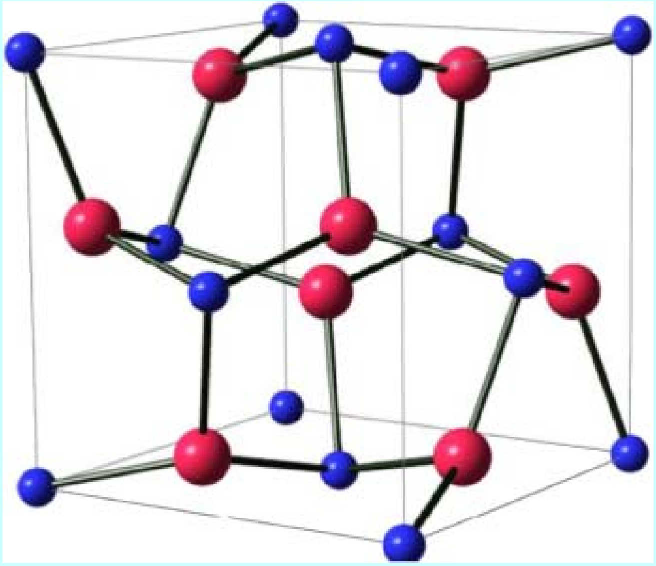


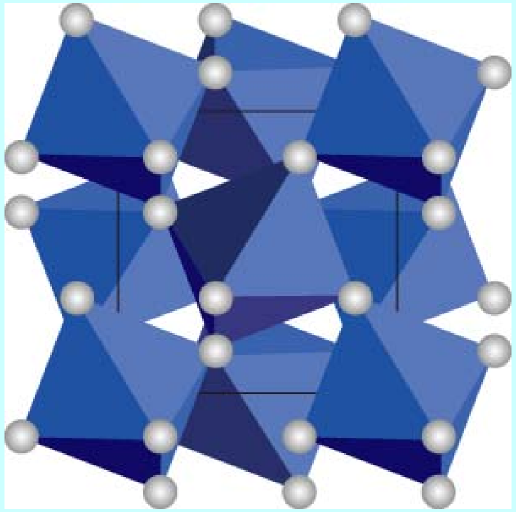
PdH(D)x
(x:hydrogen concentration H(D)/Pd)

Rock salt structures (NaCl)

FeS_2 (pyrite), CaC_2, NaO_2

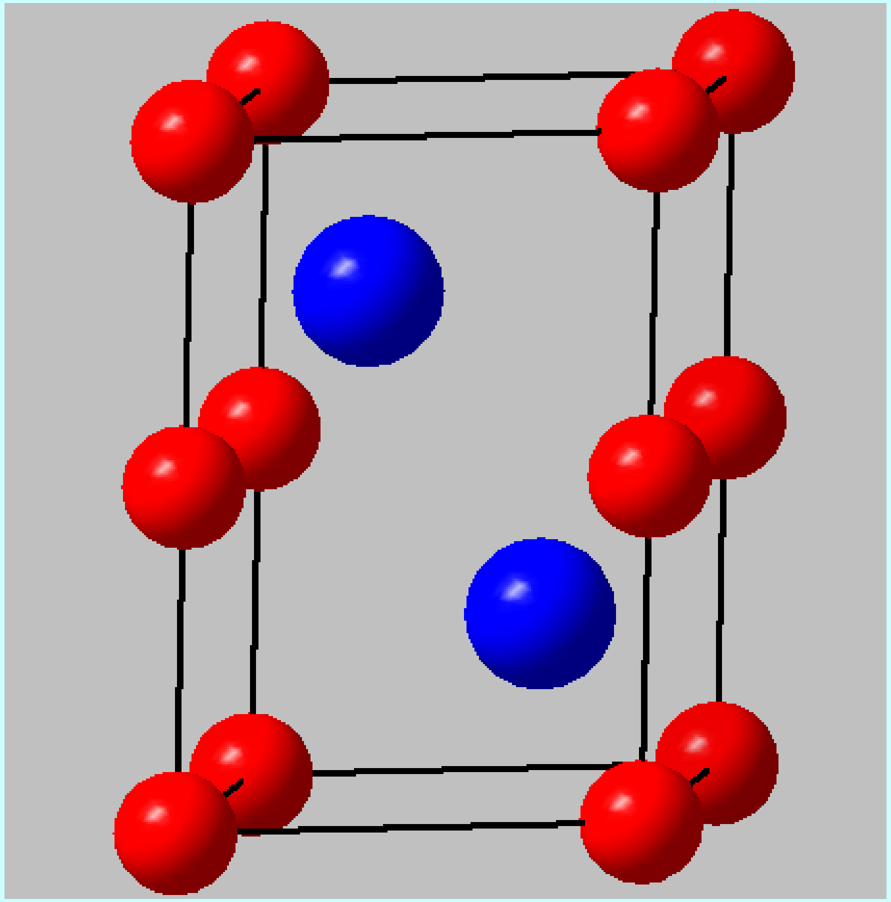






SiO_2 (pyrite - high pressure polymorph, Uranus and Neptune core)

NiAs - type



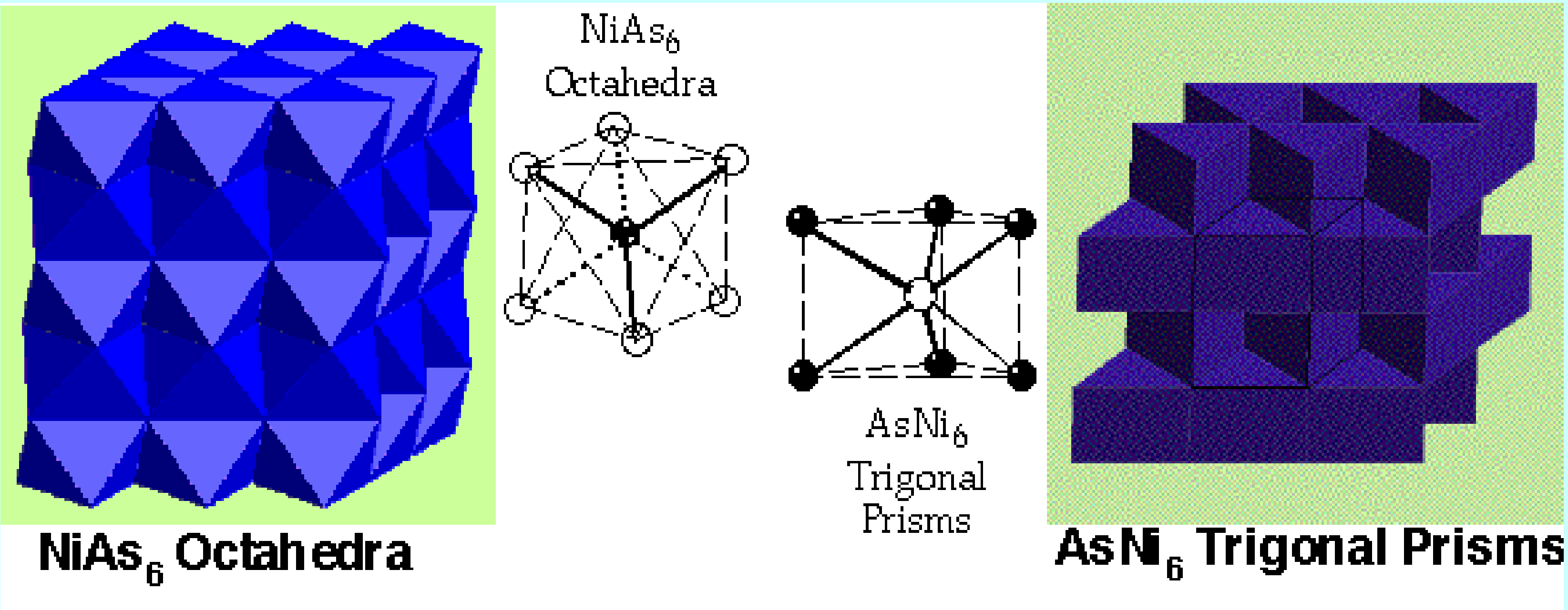
Hexagonal close packing of anions with all octahedral holes filled by cations

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

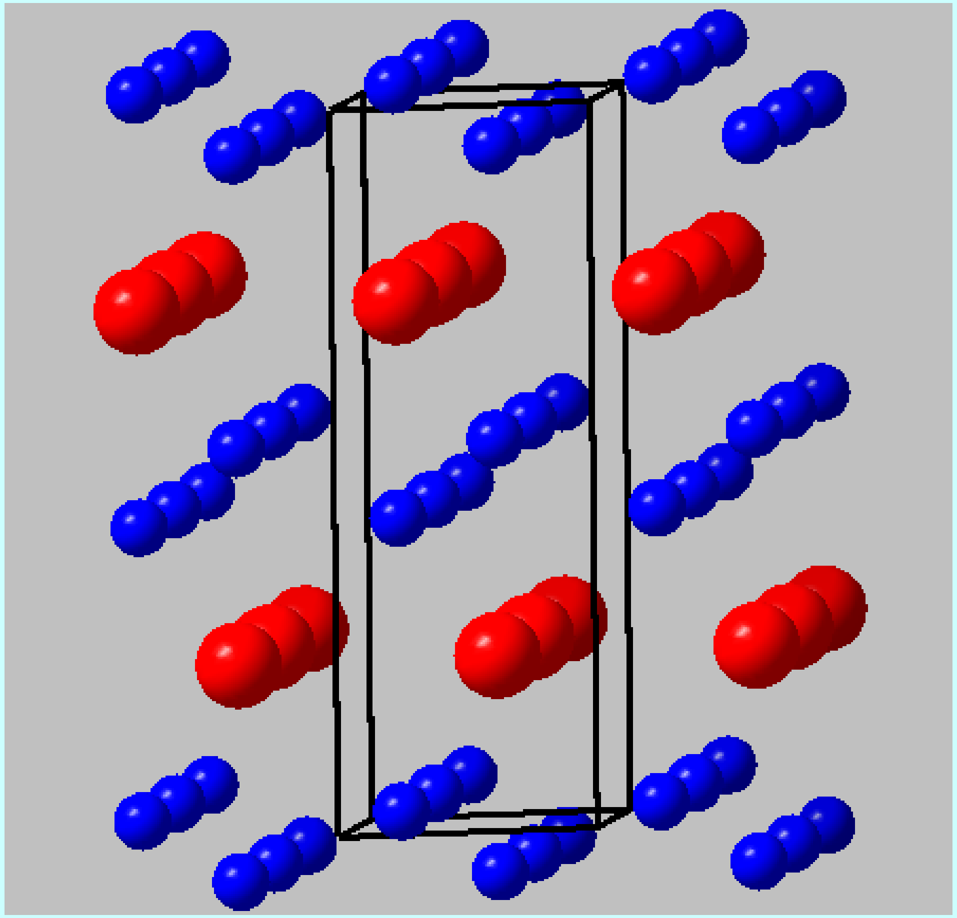
PtB (anti-NiAs structure)

NiAs - type

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

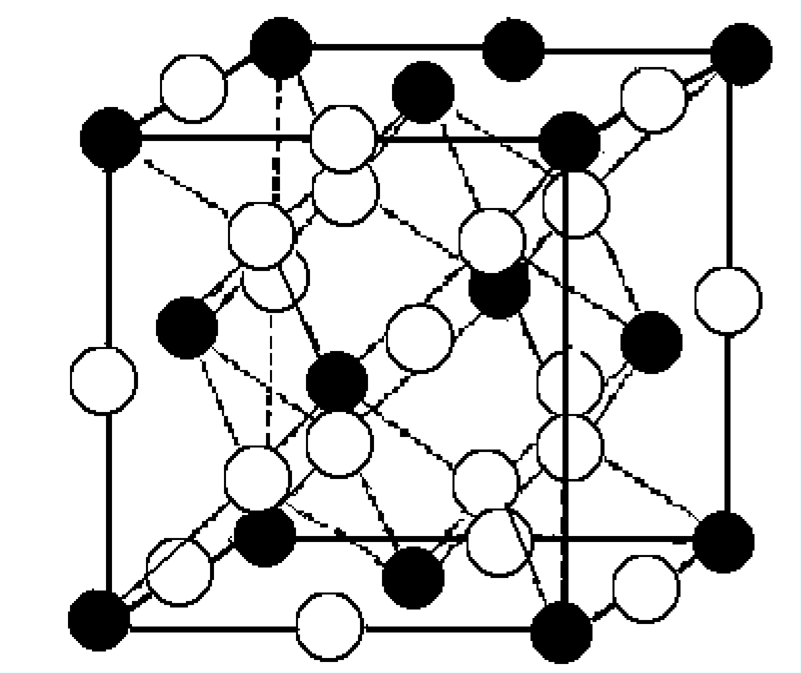


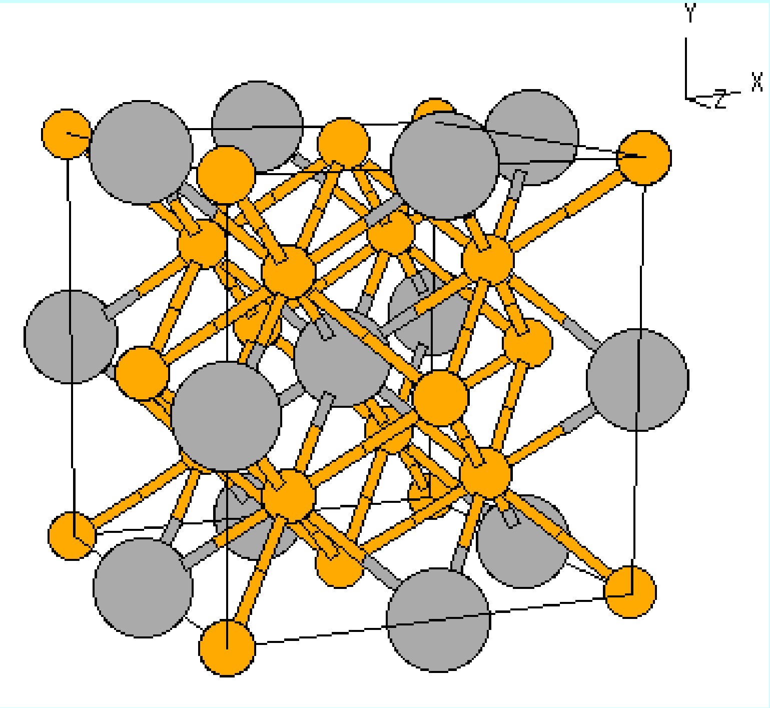
ReB_2 - type



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

Li_3Bi - type (anti BiF_3)

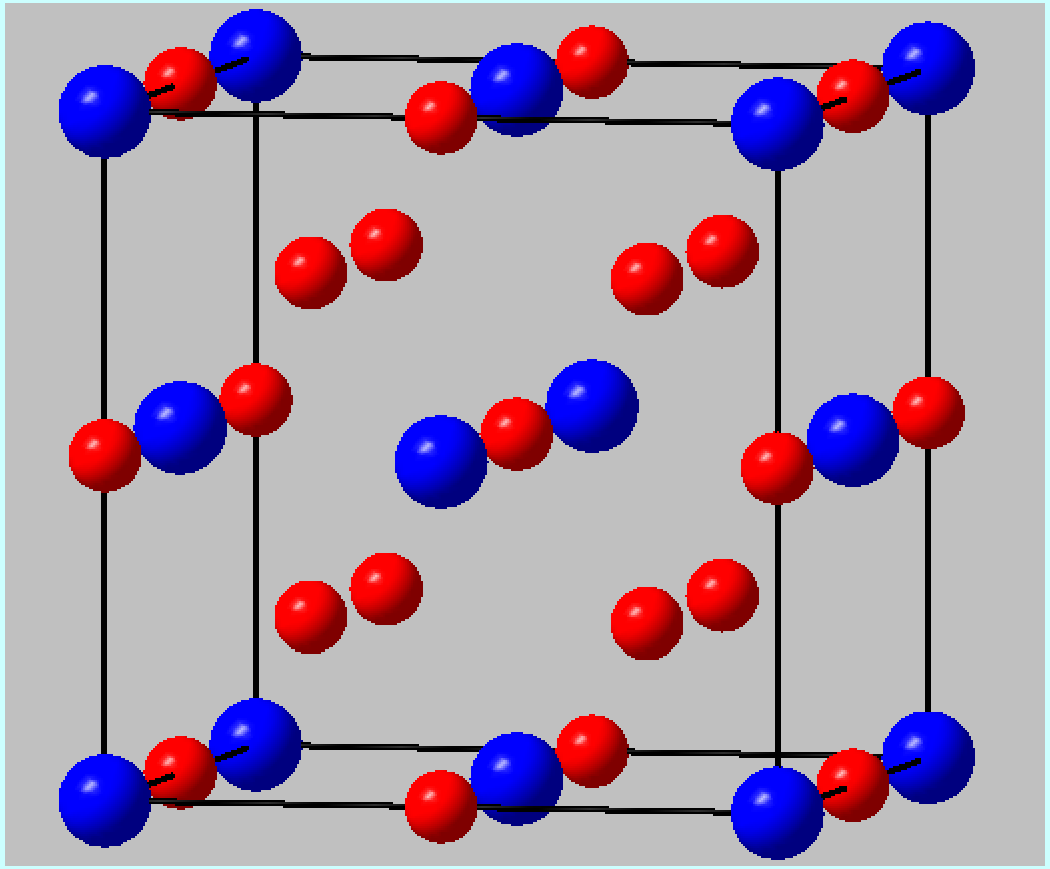




$[Cr(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$

bcc

Li_3Bi - type (anti BiF_3)



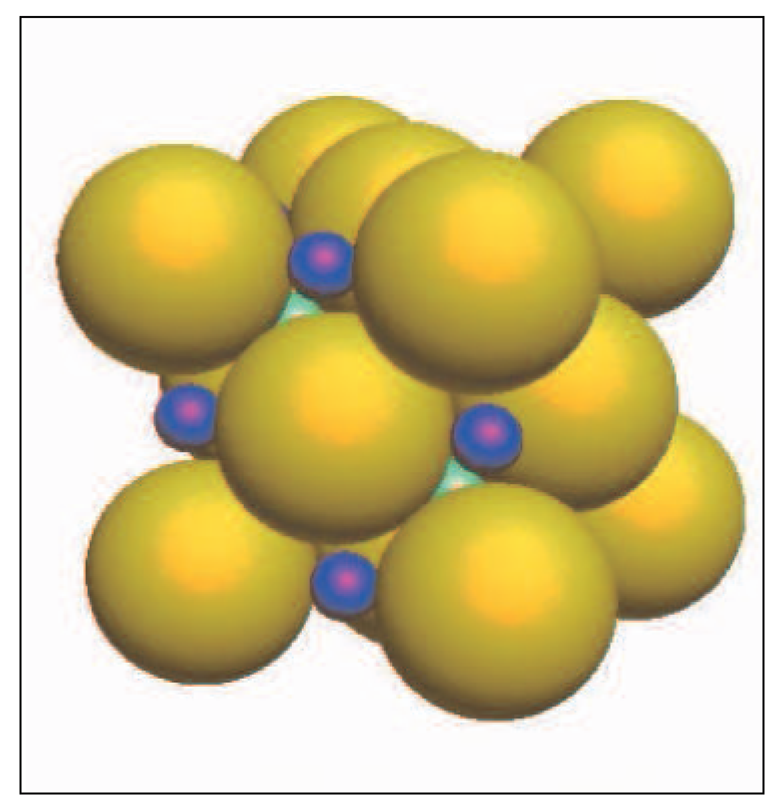
Fe_3Al

$[Cr(NH_3)_6]Cl_3$

$K_3[Fe(CN)_6]$

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

Li_3Bi - type (anti BiF_3)

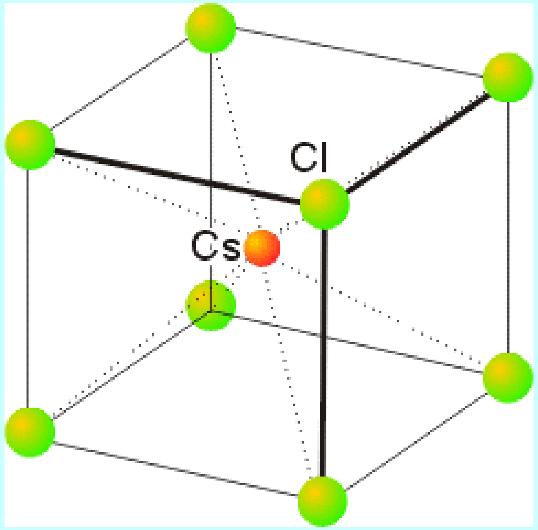


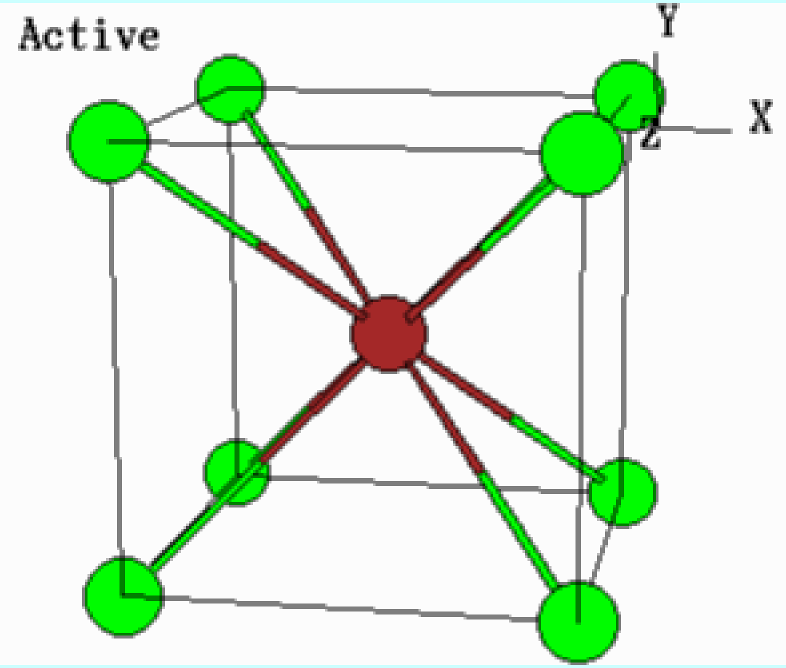
M_3C_{60}

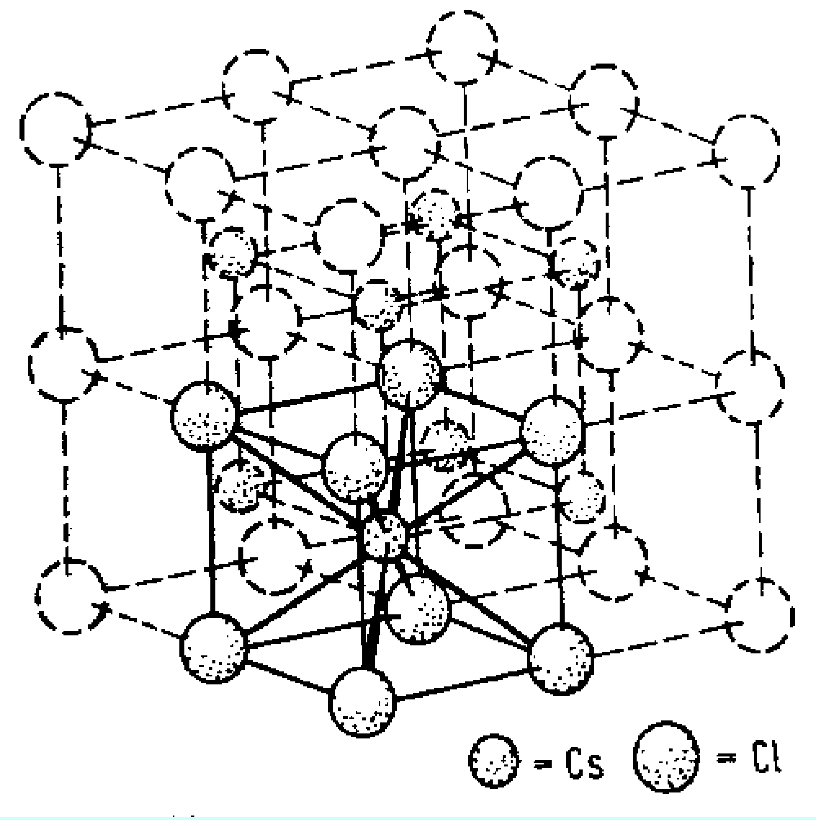
Cubic close packing of C_{60}^{3-} anions with all tetrahedral and octahedral holes filled by cations

CsCl

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

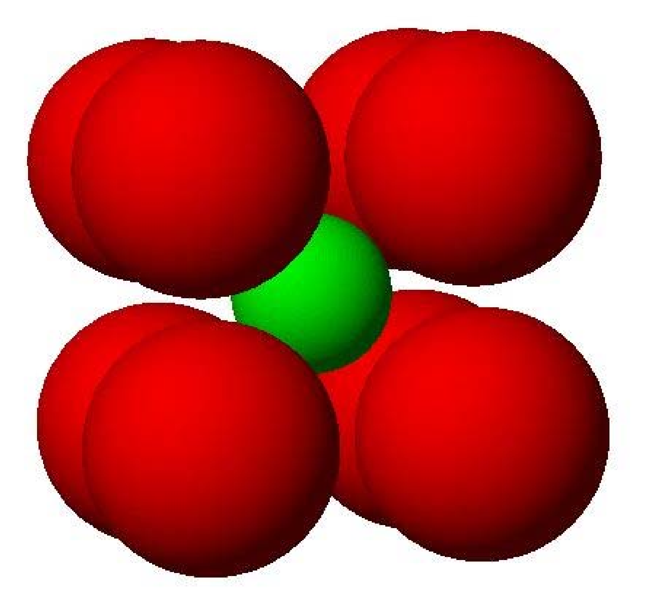




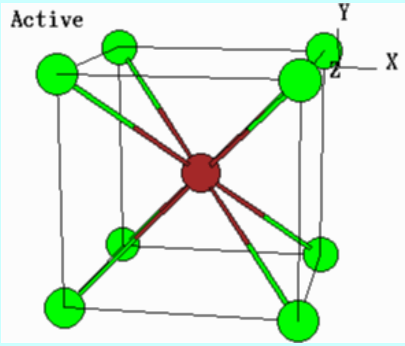


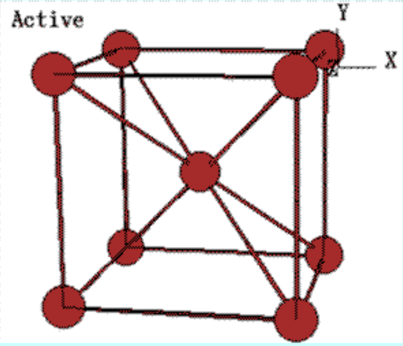
Primitive cubic packing of $CsCl_8$ cubes sharing all faces

CsCl



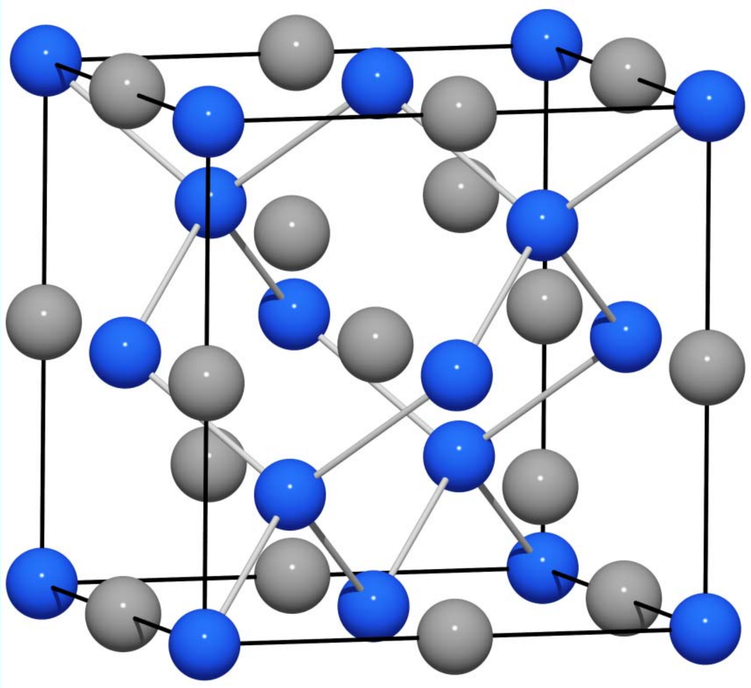
CsCl is not BCC

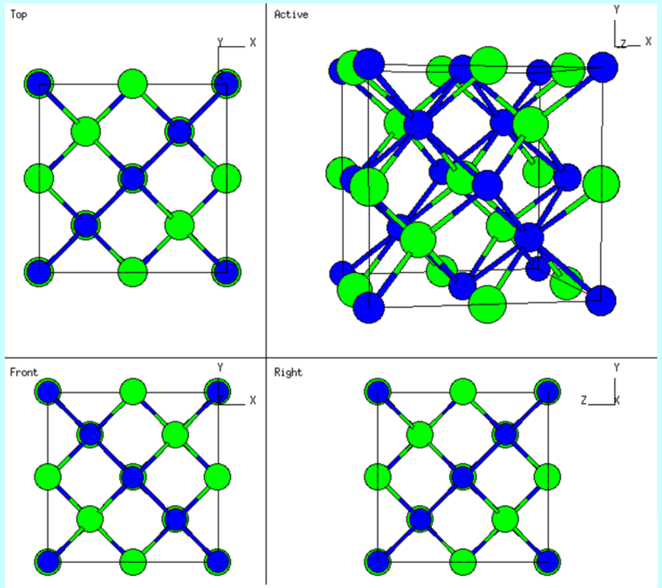


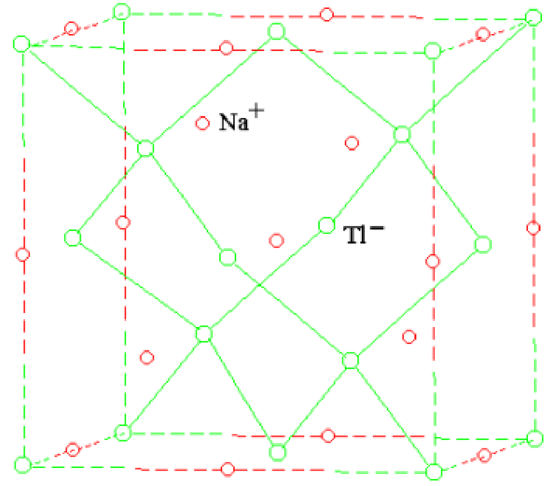


CsBr, CsI, CsCN, NH_4Cl, NH_4Br, TlCl, TlBr, TlI, CuZn, CuPd, LiHg

NaTl





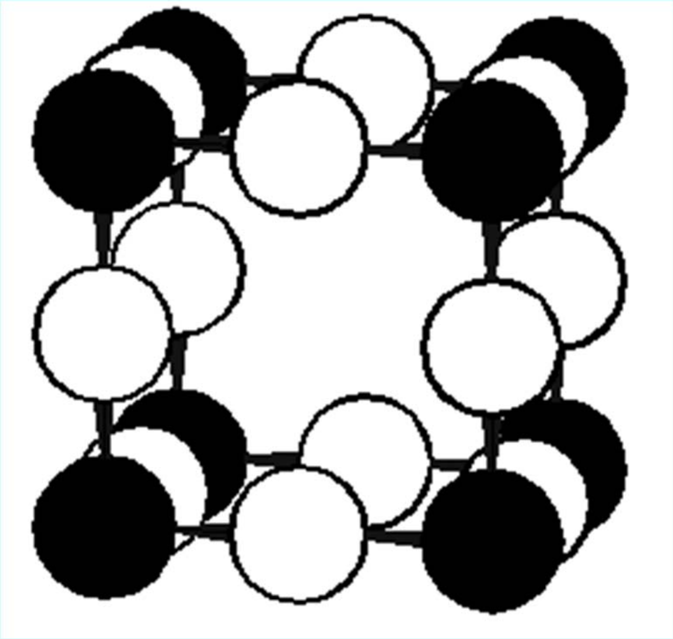


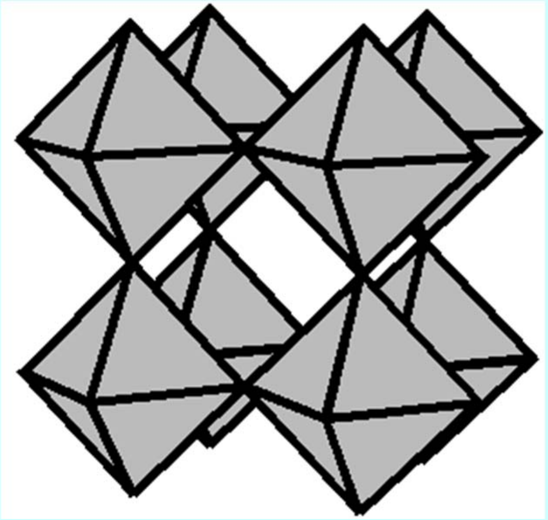
U. Müller , Inorganic Structural Chemistry , John Wiley , Chichester (UK) , 1993 ; Figure 65 , p. 123 .

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

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

ReO_3





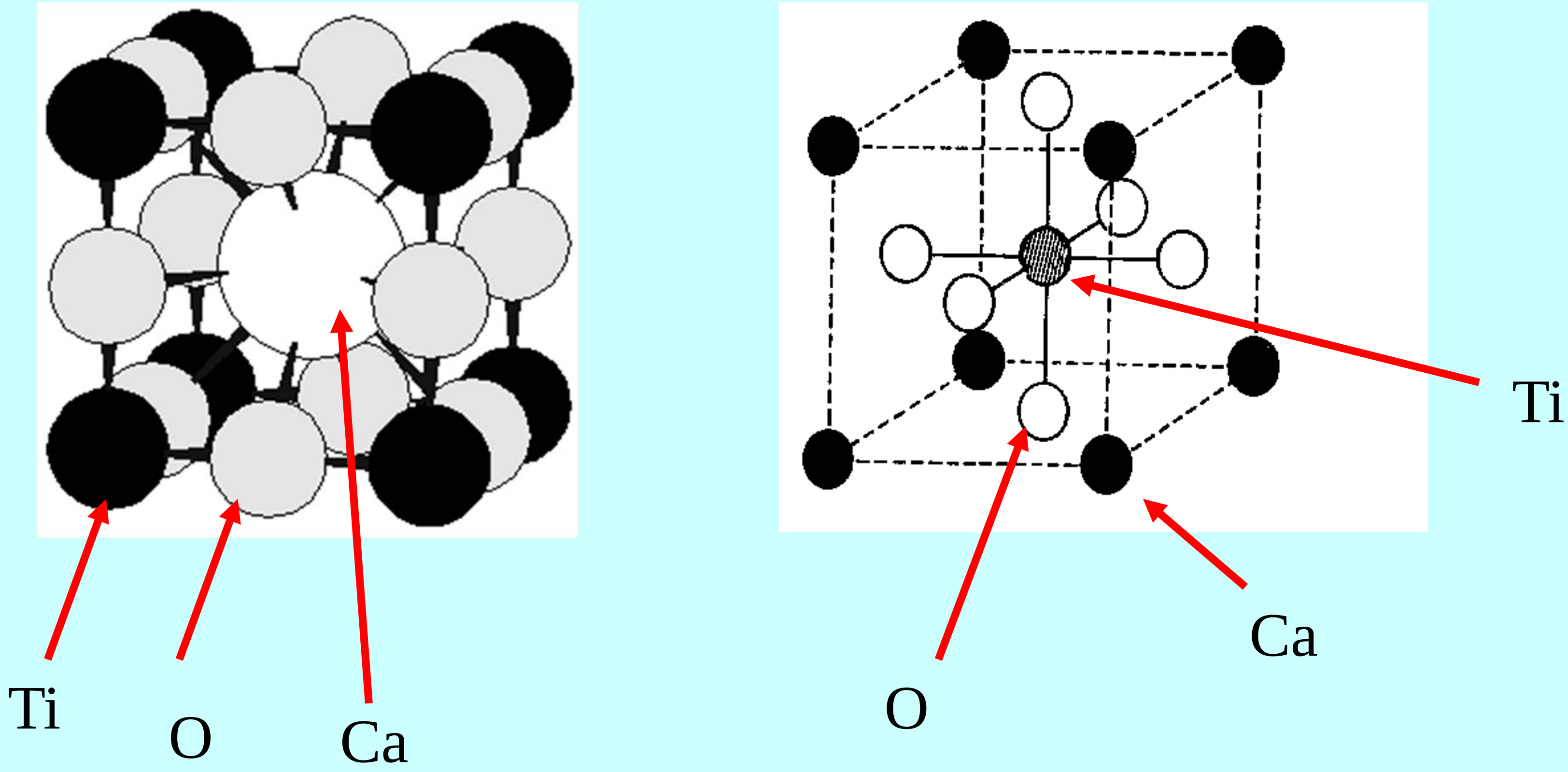
SC of ReO_6 octahedra

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

UO_3, MoF_3, NbF_3, TaF_3, Cu_3N

Perovskite, $CaTiO_3$

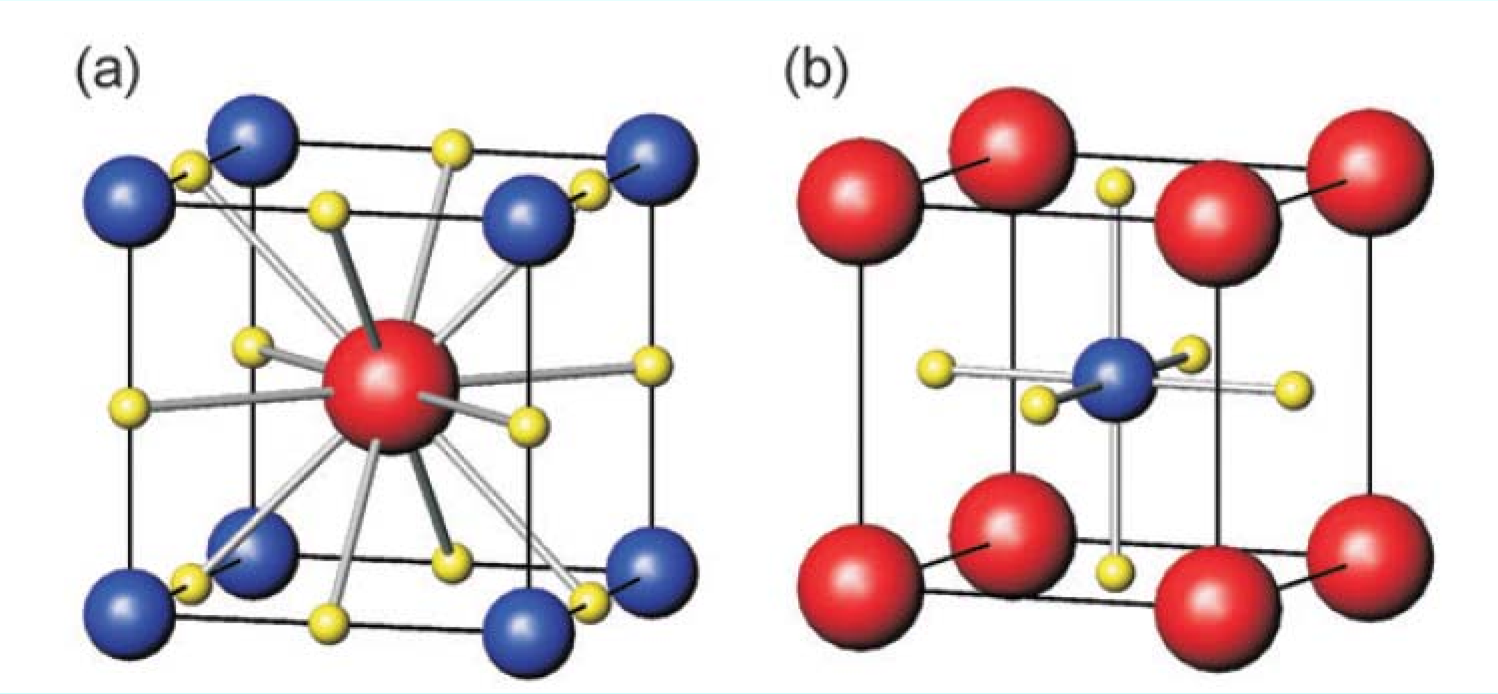
Two equvivalent views of the unit cell of perovskite



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

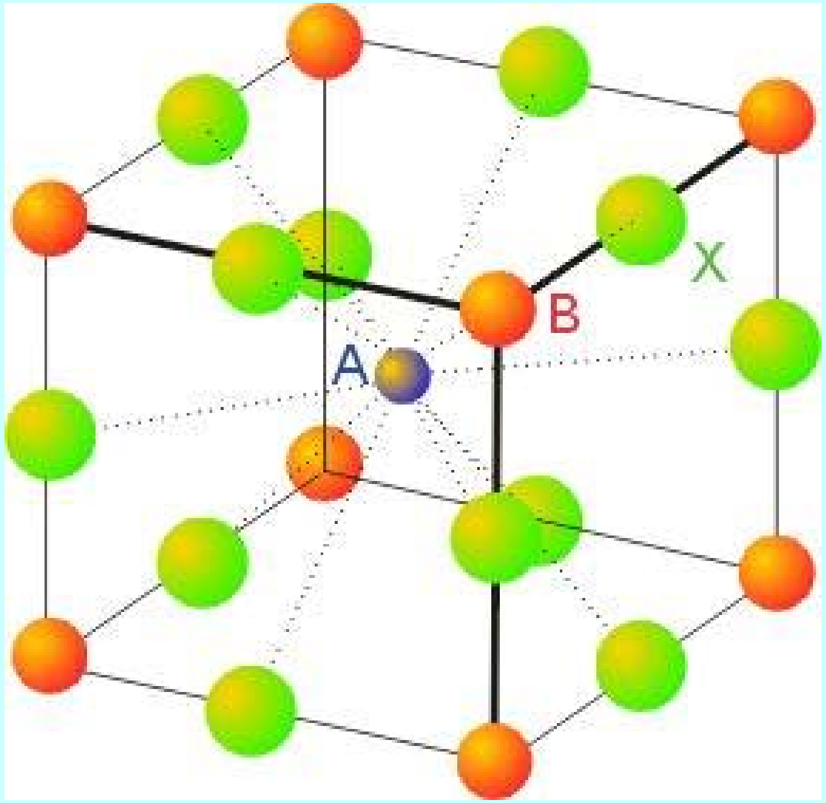
Perovskite, $CaTiO_3$

Two equvivalent views of the unit cell of perovskite



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

Perovskite structure $CaTiO_3$



TiO_6 – octahedra

CaO_{12} – cuboctahedra

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

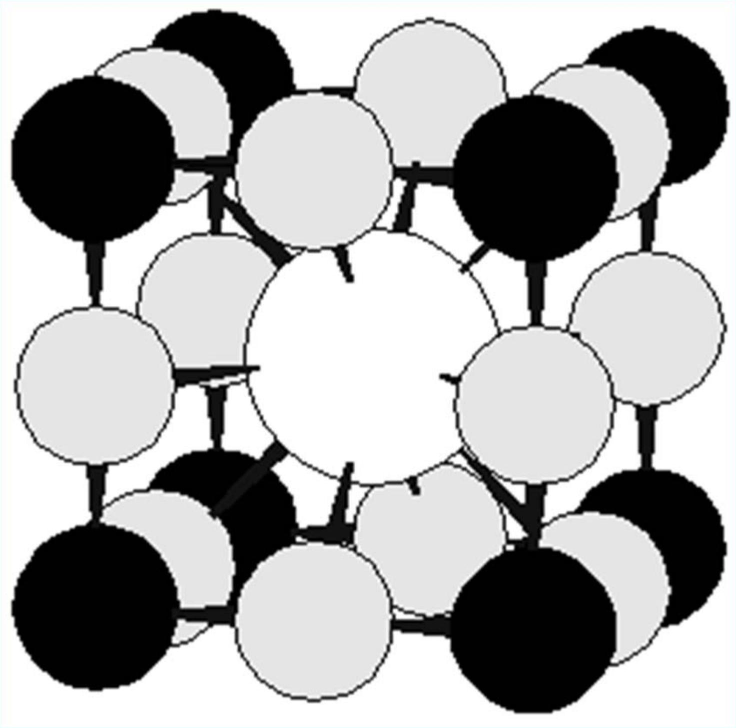
preferred structure of piezoelectric, ferroelectric and superconducting materials

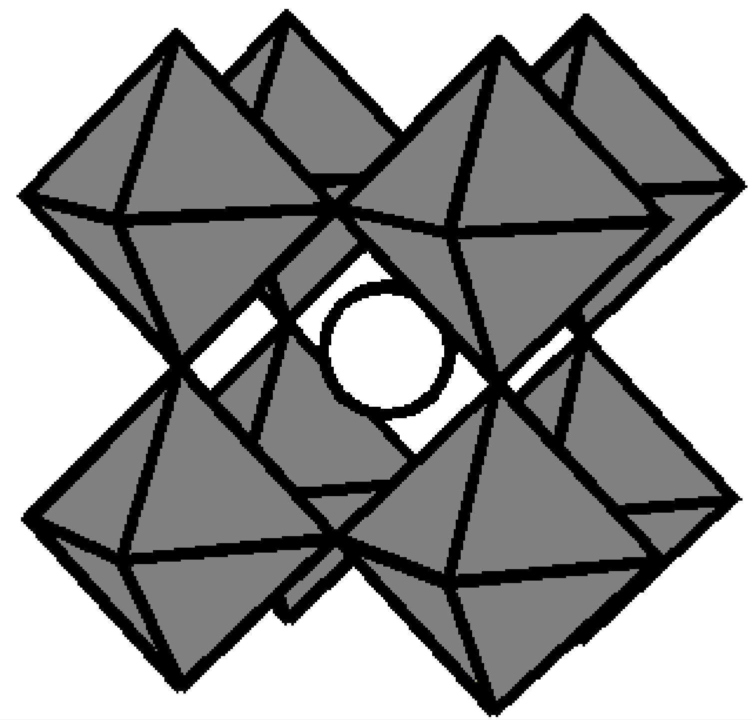
$$t = \frac{r_{A\text{-}X}}{\sqrt{2}\, r_{B\text{-}X}} = \frac{r_A + r_X}{\sqrt{2}\,(r_B + r_X)}$$

Goldschmidt’s tolerance factor

Perovskite, $CaTiO_3$

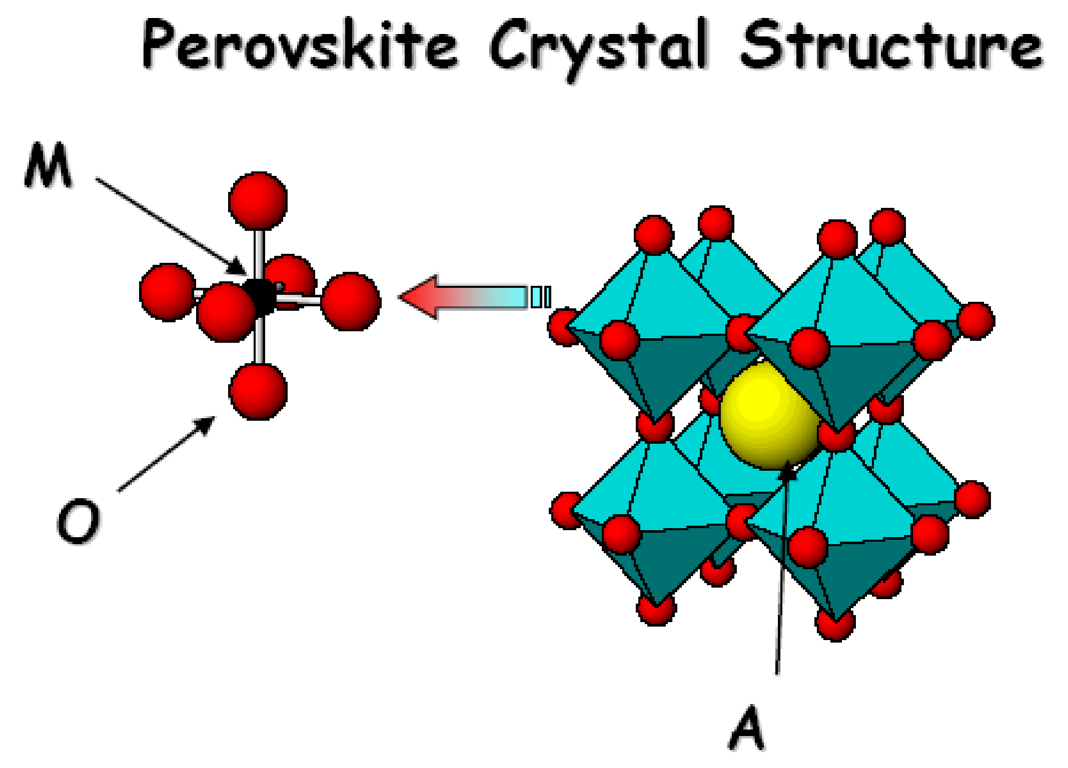
Cubic "close packing" of A and X with 1/4 octahedral holes filled by B cations





Similarity to CsCl

Perovskite, $CaTiO_3$

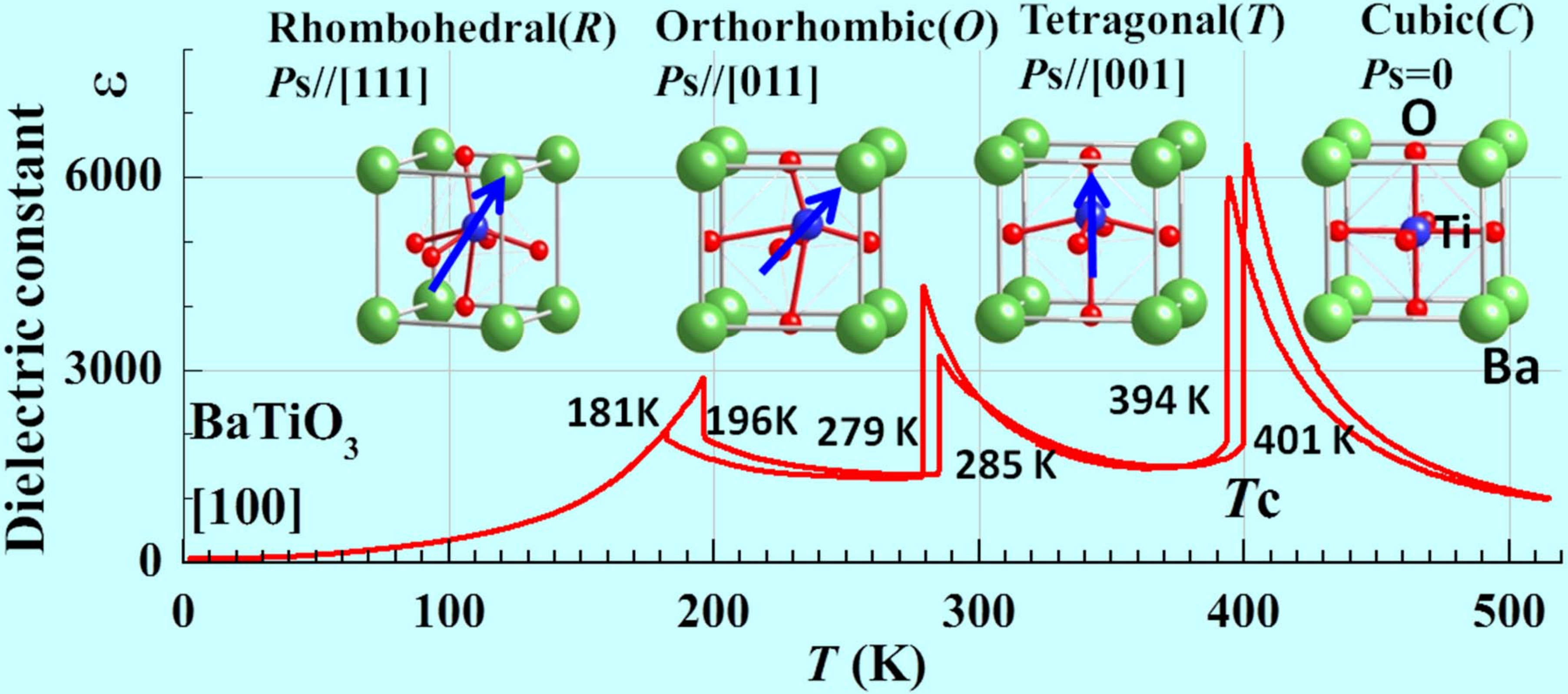


$MgSiO_3$, $CaSiO_3$

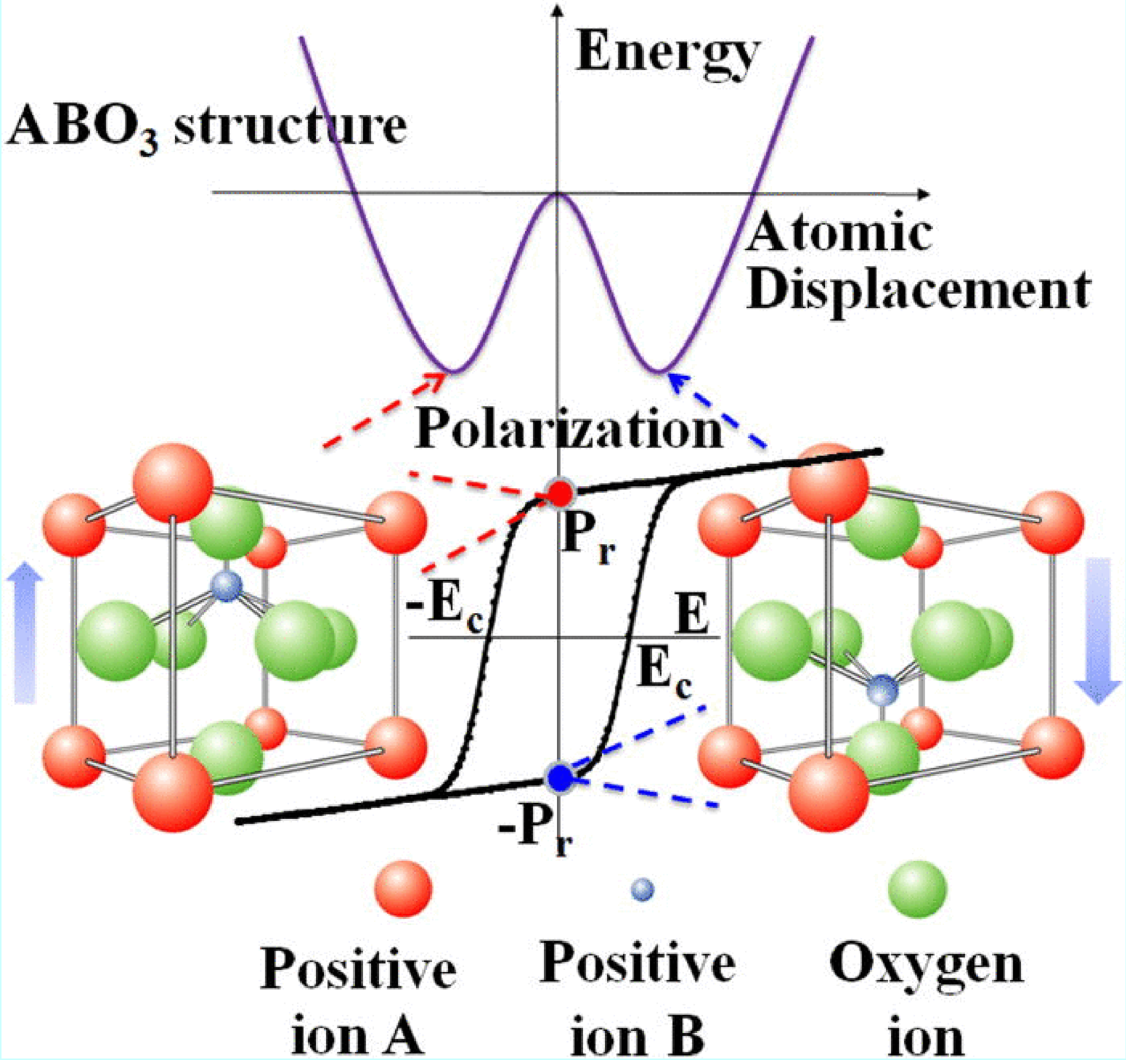
$KNbO_3$, $KTaO_3$, KIO_3, $NaNbO_3$, $NaWO_3$, $LaCoO_3$, $LaCrO_3$, $LaFeO_3$, $LaGaO_3$, $LaVO_3$, $SrTiO_3$, $SrZrO_3$, $SrFeO_3$

$ThTaN_3$, $BaTaO_2N$

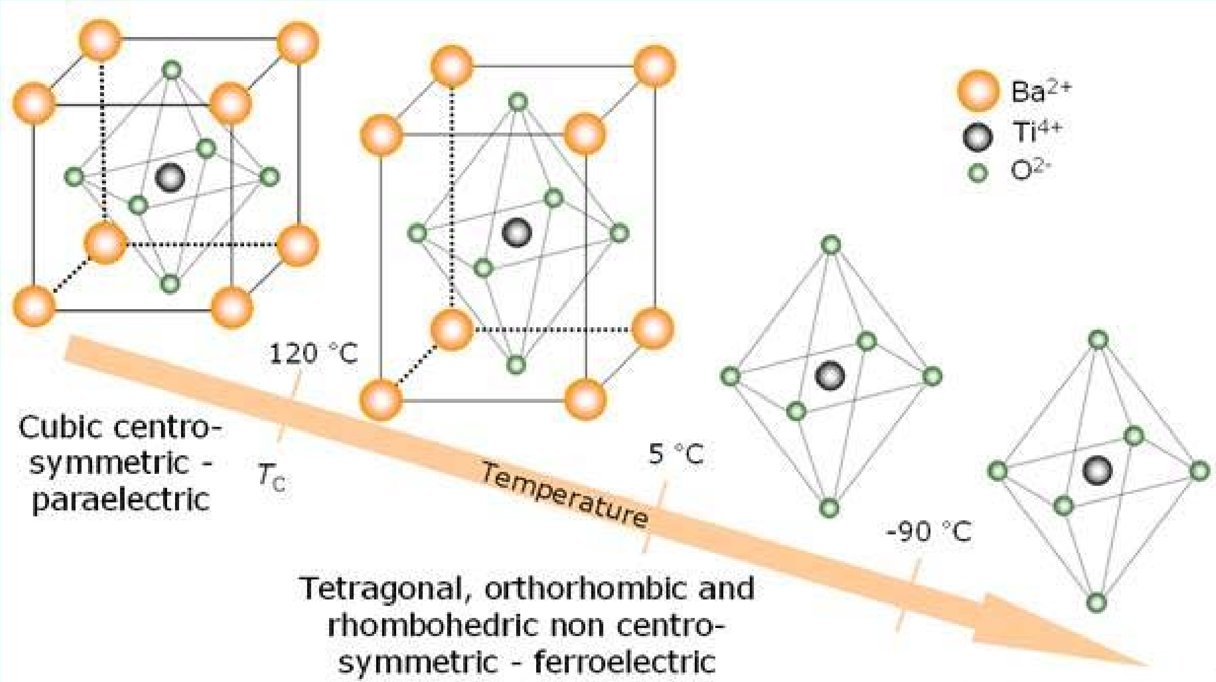
Perovskite, $BaTiO_3$

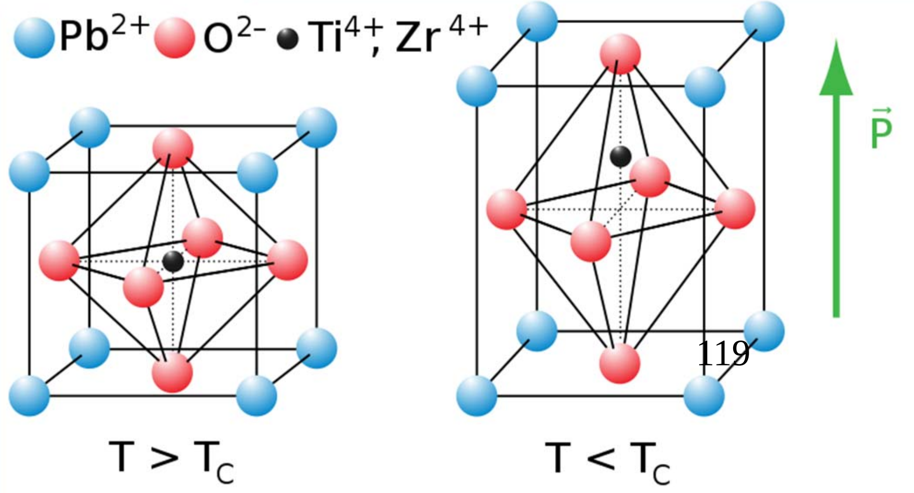


Perovskite - ferroelectric $BaTiO_3$

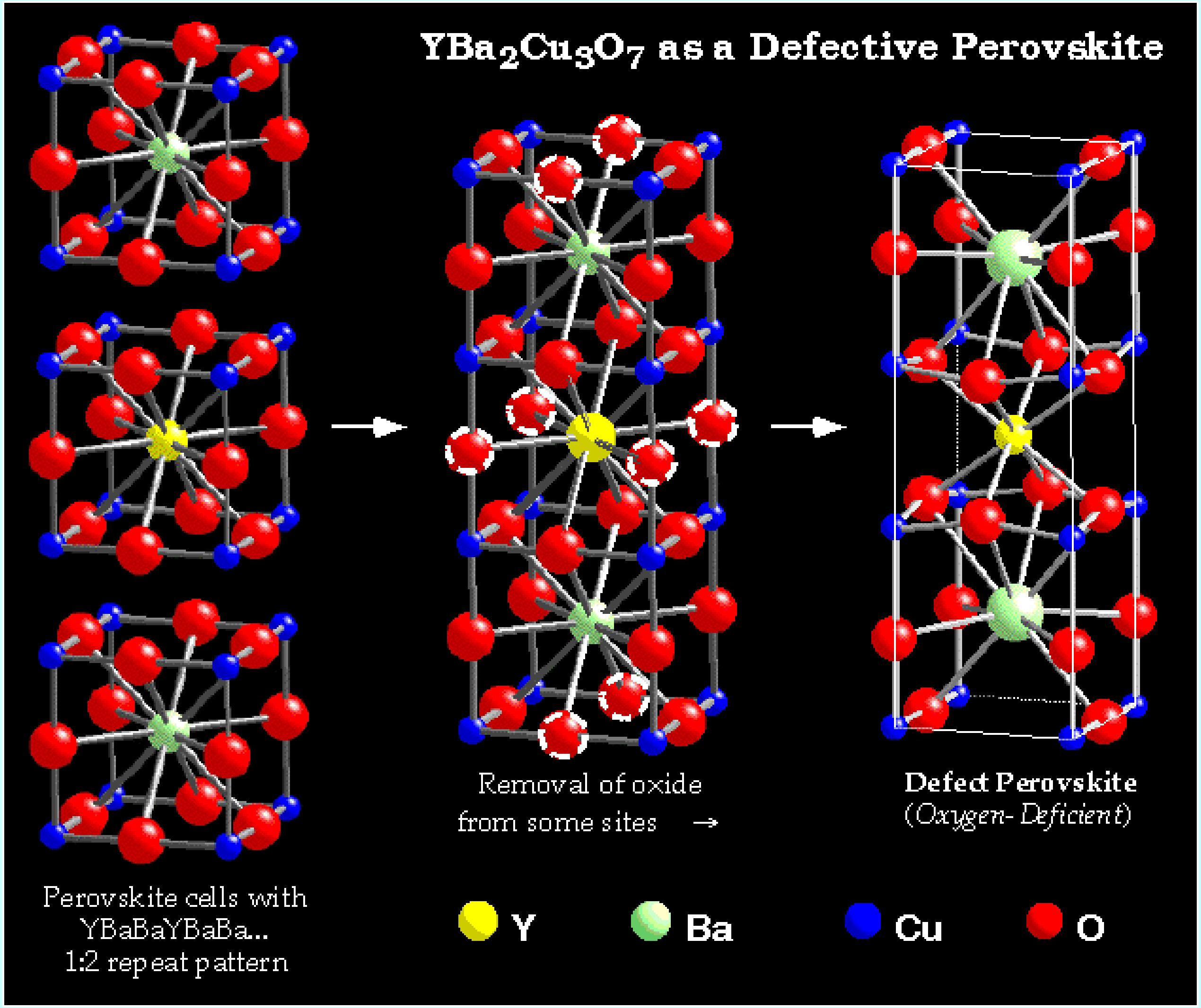


Perovskite - ferroelectric $BaTiO_3$

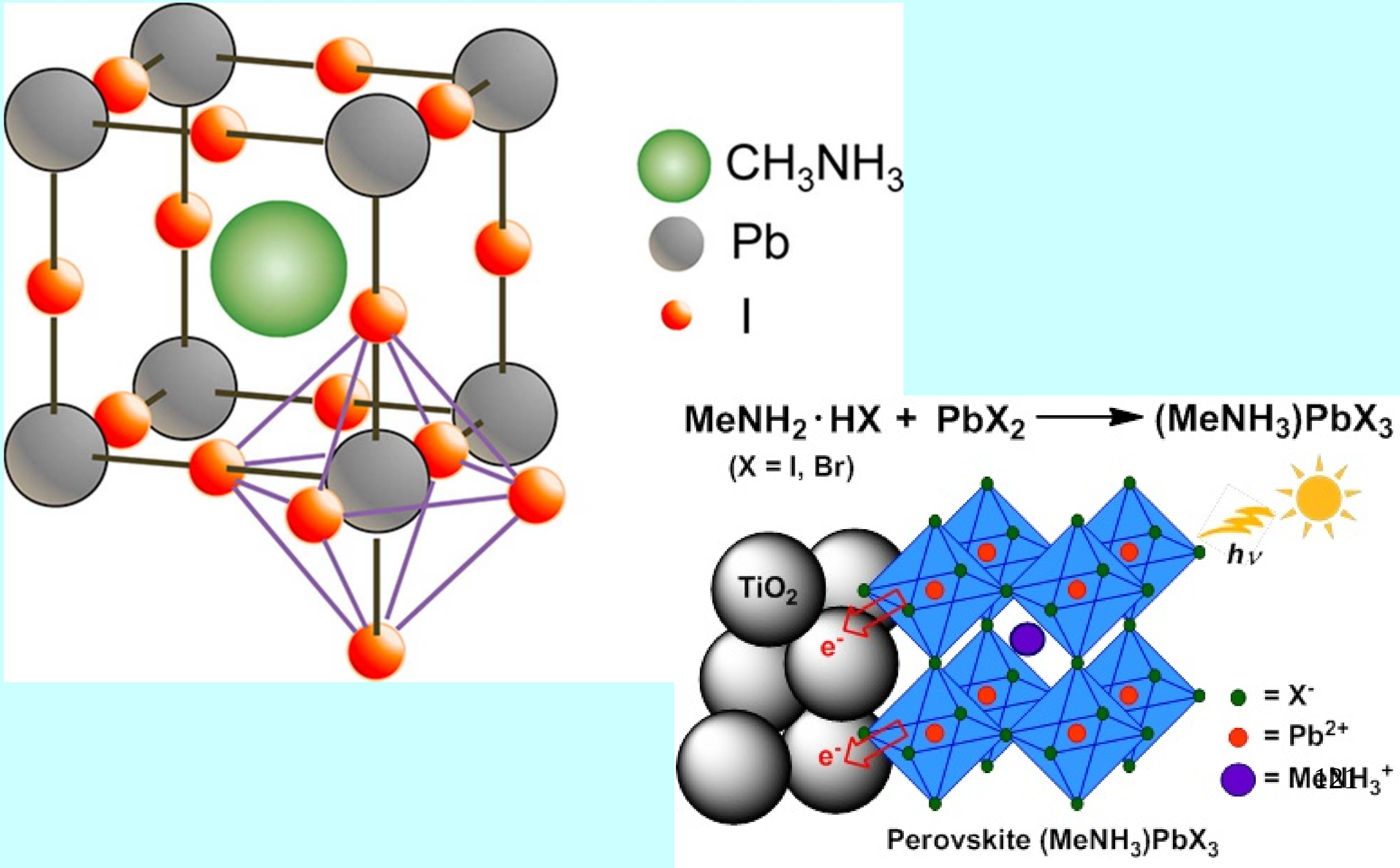




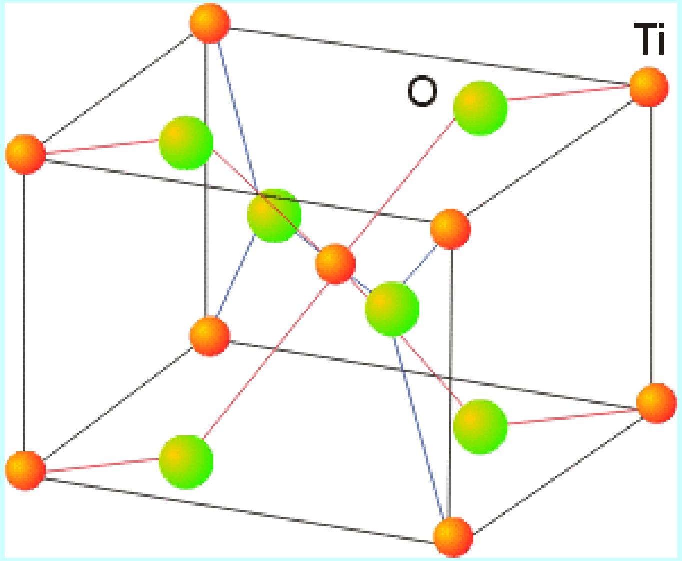
Perovskite structure of YBCO

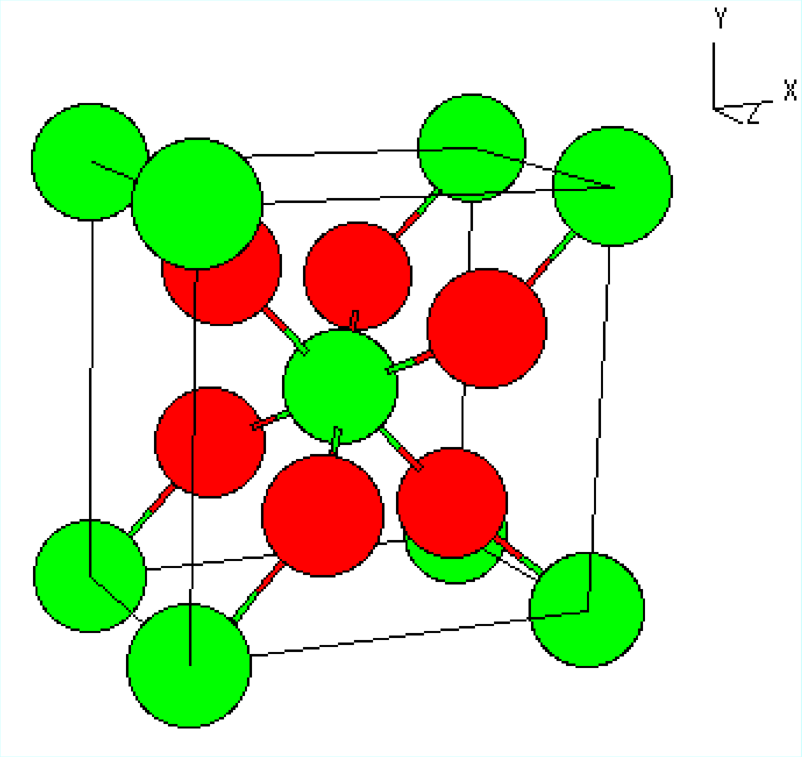


Perovskite structure of $CH_3NH_3PbI_3$



Rutile, TiO_2





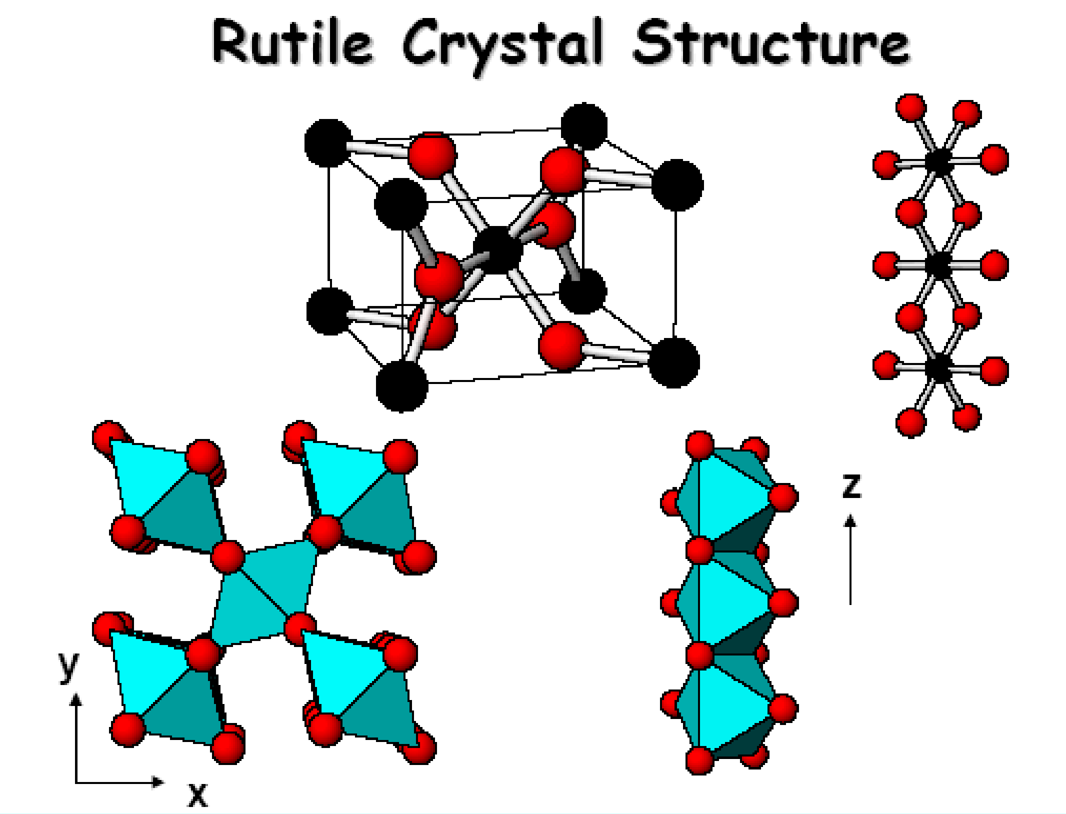
CN – stoichiometry Rule

A_xB_y

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

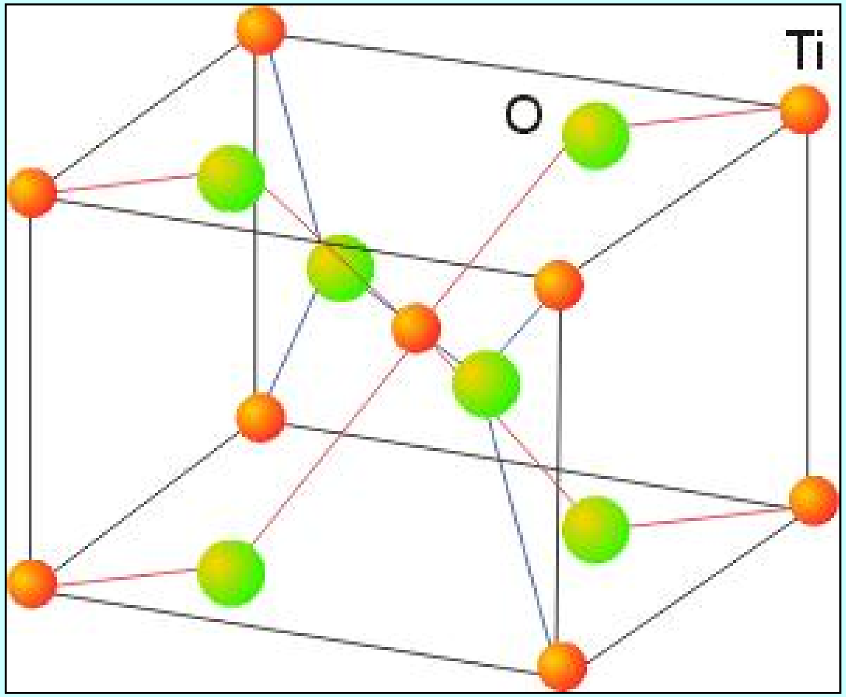
Distorted hexagonal close packing of anions with 1/2 octahedral holes filled by cations (giving a tetragonal lattice)

Rutile, TiO_2



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

The rutile structure: TiO_2

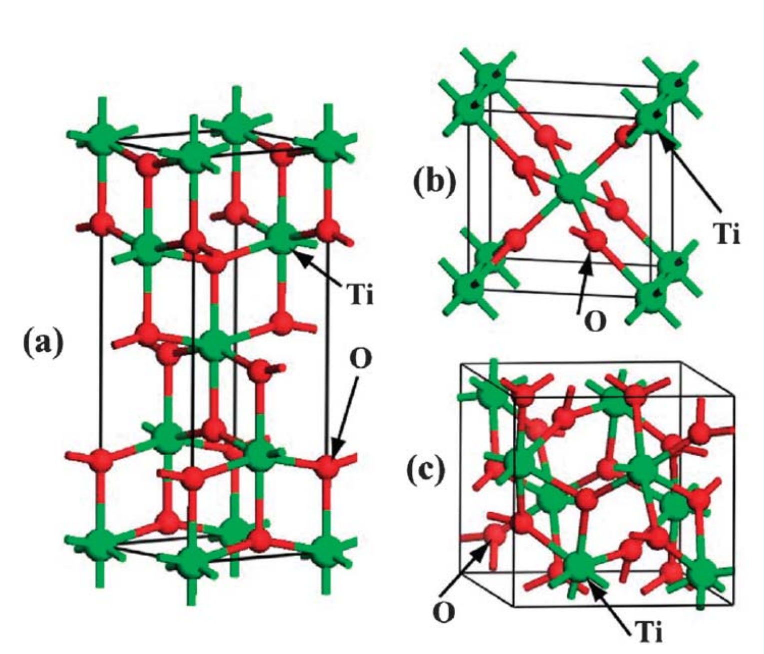


TiO_6 – octahedra

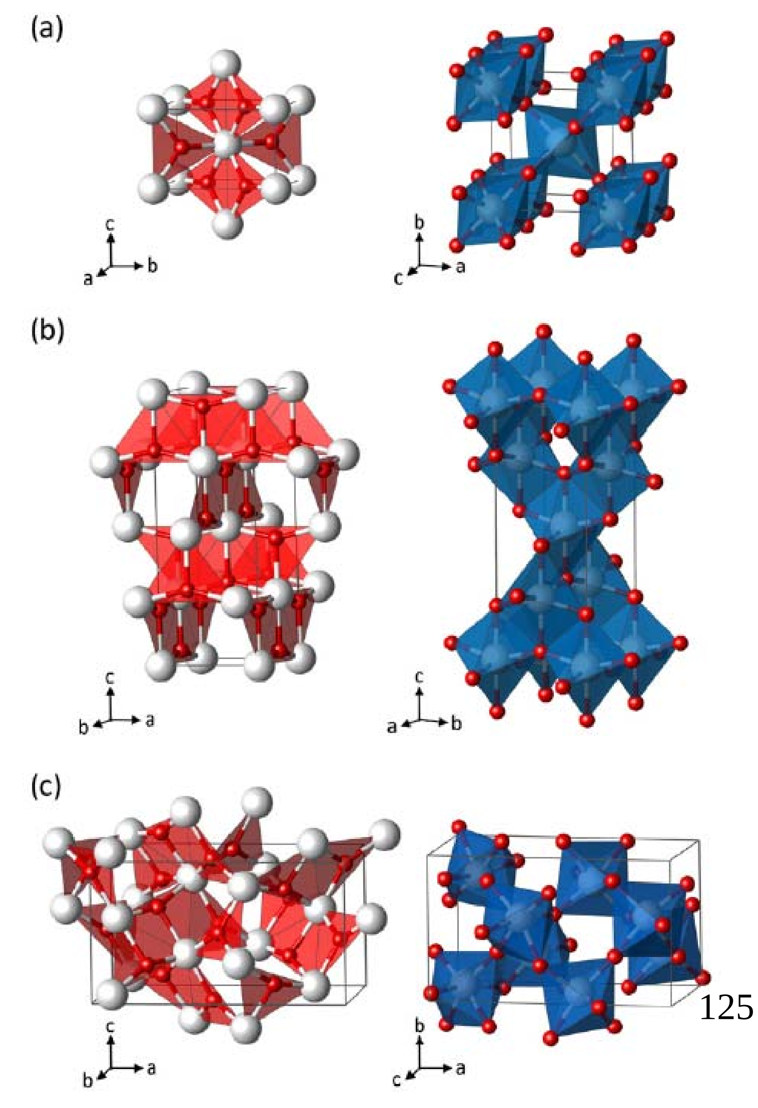
OTi_3 – trigonal planar

(alternative to CaF_2 for highly charged smaller cations)

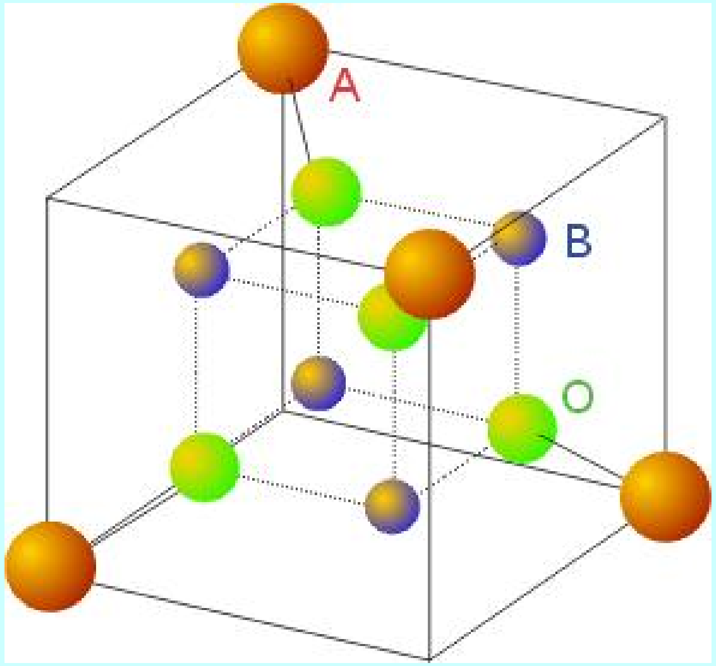
Three polymorphs of TiO_2



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



The spinel structure: $MgAl_2O_4$



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

→ normal spinel:

AB_2O_4

→ inverse spinel:

$B[AB]O_4$

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

→ basis structure for several magnetic materials

Spinel

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

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

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

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

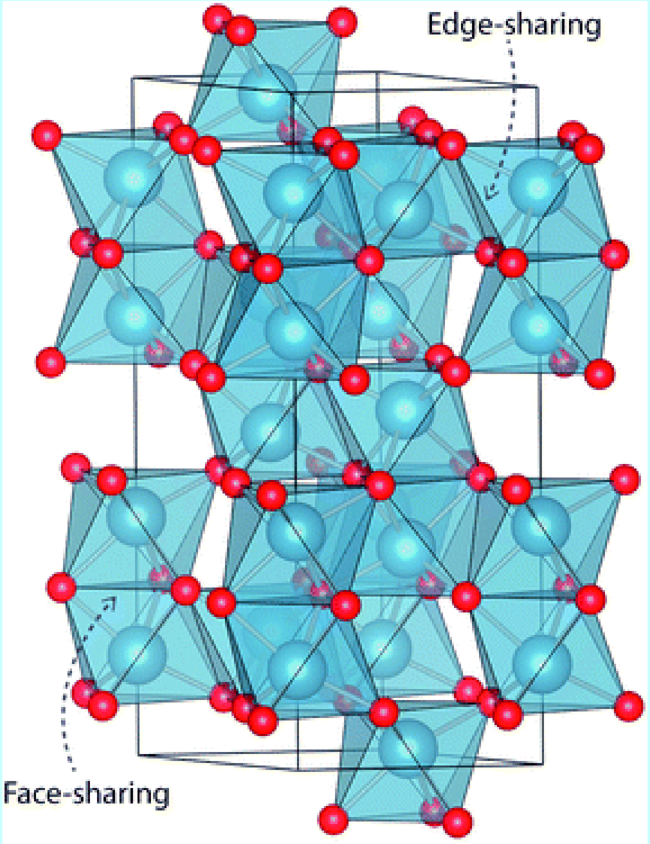
δ = the inversion parameter

$(A_\delta B_{1-\delta})_A[A_{1-\delta}B_{1+\delta}]_BO_4$

Values from $\delta = 1$ (normal) to $\delta = 0$ (inverse)

May depend on synthesis conditions

Corundum



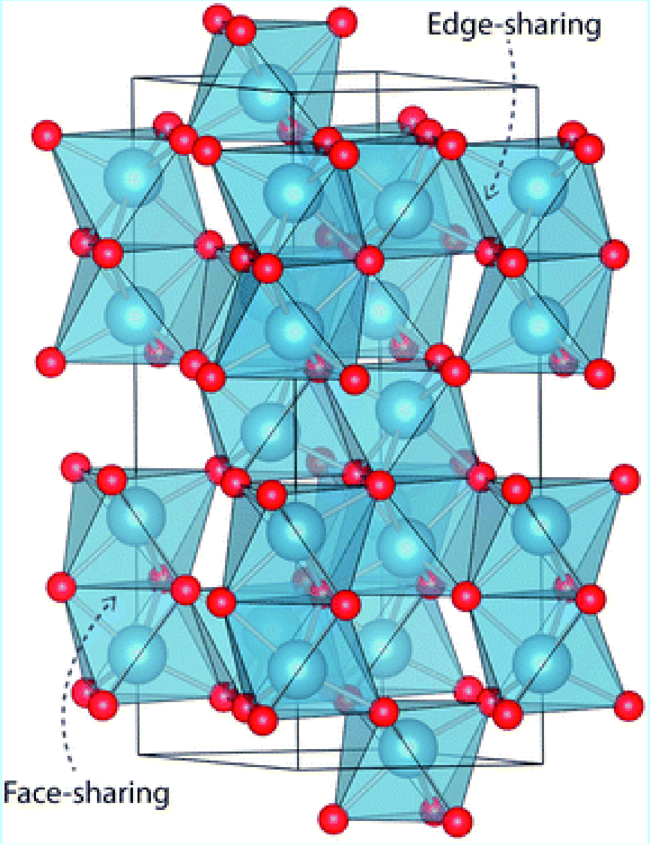
Al_2O_3 consists of hcp O^{2-} ions

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

The Al centres are surrounded by ……. oxides

Oxide ligands are ……………coordinated by Al

Corundum



AlO_6 octahedral units are linked in both face-sharing and edge-sharing orientations as parallel and perpendicular to the c-axis, respectively. The relative orientation of the metal centres causes a pseudo Peierls distortion, resulting in neighbouring metal centres that are rotated at an angle of 64.3° away from each other. Elongation in pairs of the surrounding oxide ligands results in a pentagonal bi-pyramidal geometry belonging to the space group R-3c. The material is largely ionic in nature with a wide band gap of 9.25 eV.

Garnets

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

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

Synthetic garnets $A_3B_5O_{12}$

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

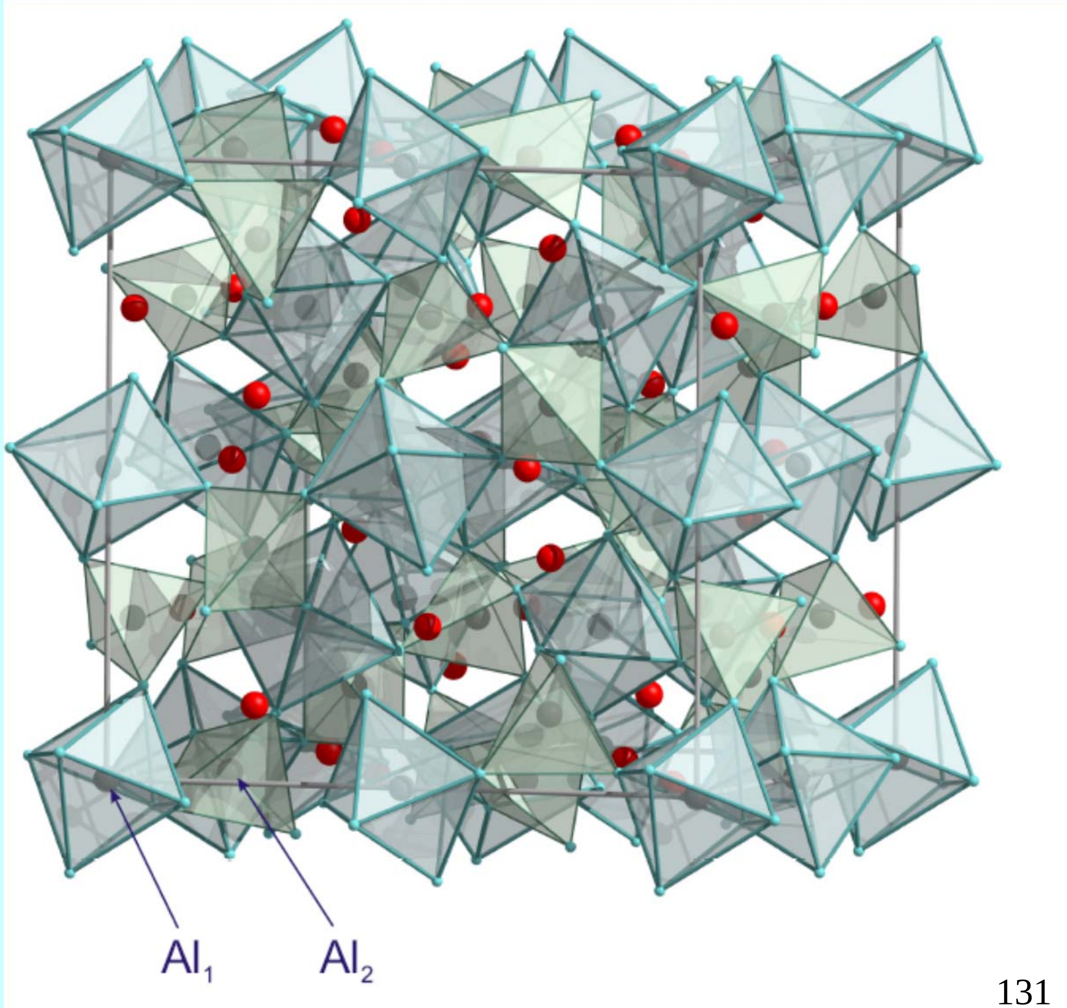
Garnets

Garnet $Y_3Al_5O_{12}$

Y_3 = red - dodecahedral trivalent cations, large size

Al_5 = blue
2 octahedral
3 tetrahedral

O_{12}



Fullerides

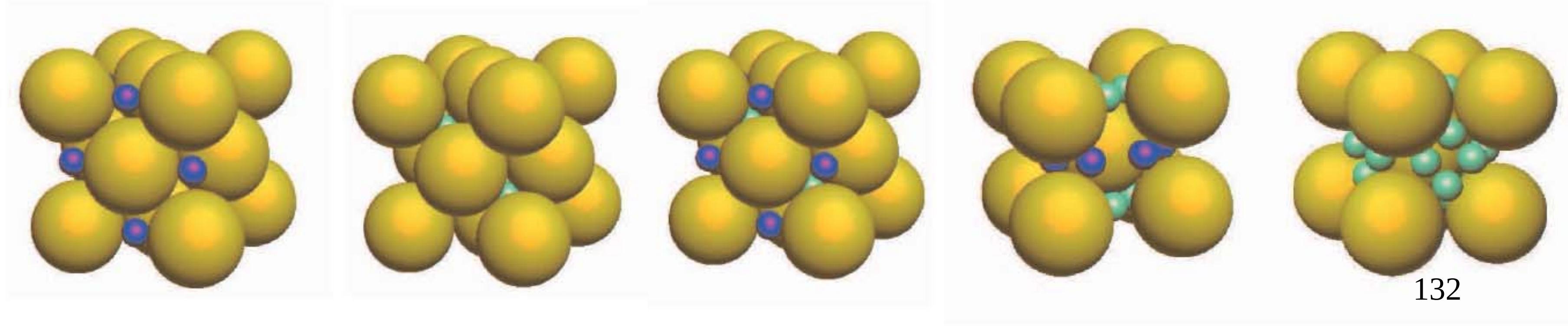
M_1C_{60} all the octahedral (O) sites (dark blue) are occupied (NaCl)

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

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

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

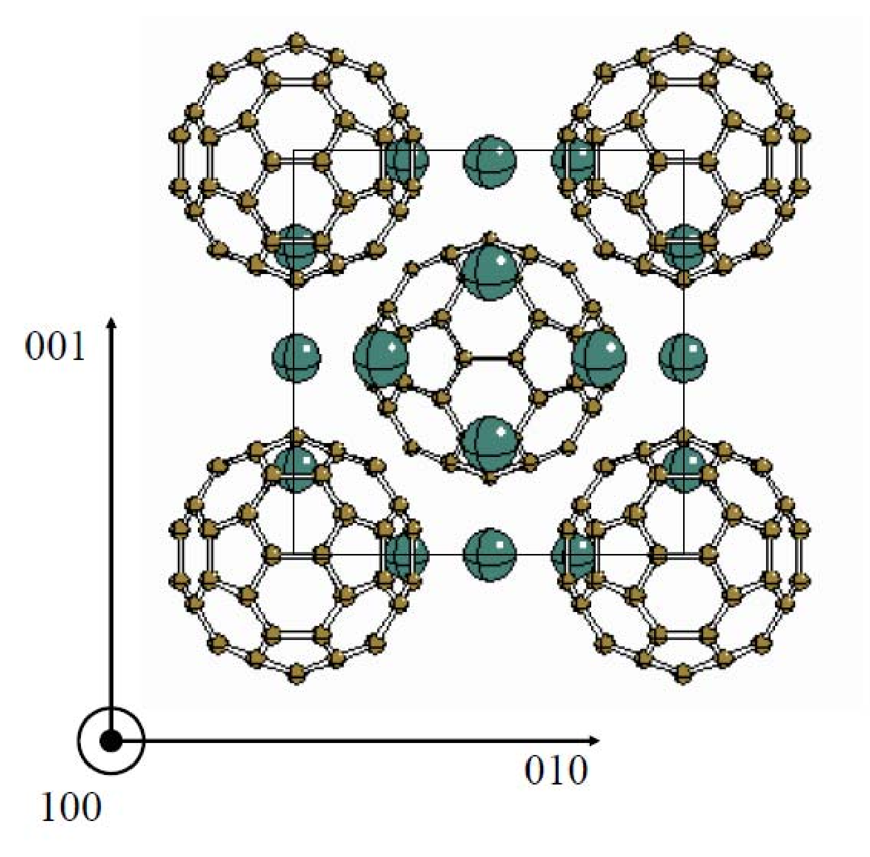
M_6C_{60} a bcc lattice and all its T sites are occupied



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

Fullerides

BCC unit cell of Rb_6C_{60} and Cs_6C_{60}



Layered Structures

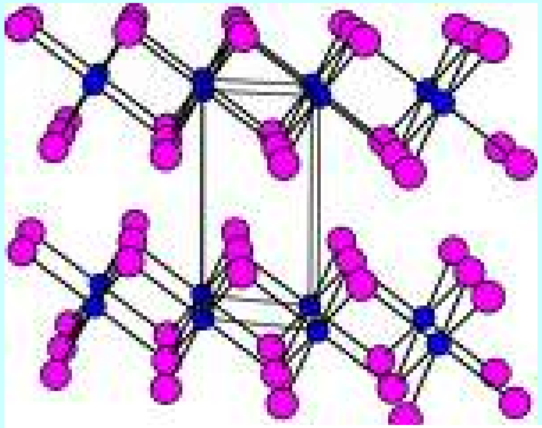
CdI_2 Hexagonal close packing of anions with 1/2 octahedral holes filled by cations

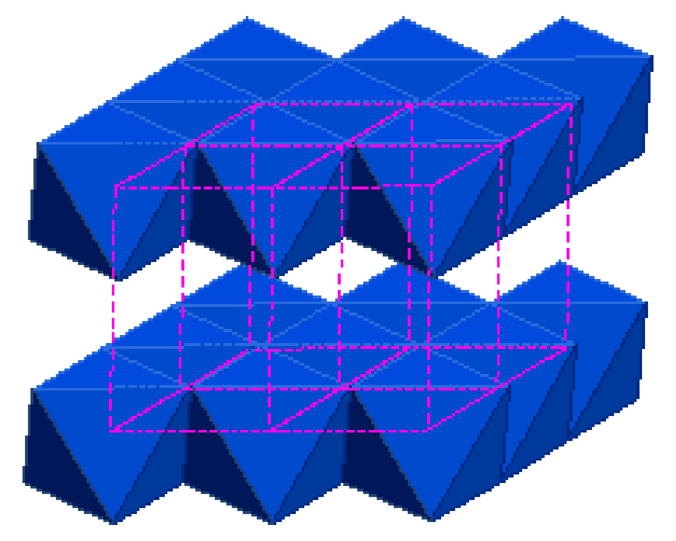
CoI_2, FeI_2, MgI_2, MnI_2, PbI_2, ThI_2, TiI_2, TmI_2, VI_2, YbI_2, ZnI_2, VBr_2, $TiBr_2$, $MnBr_2$, $FeBr_2$, $CoBr_2$, $TiCl_2$, TiS_2., TaS_2.

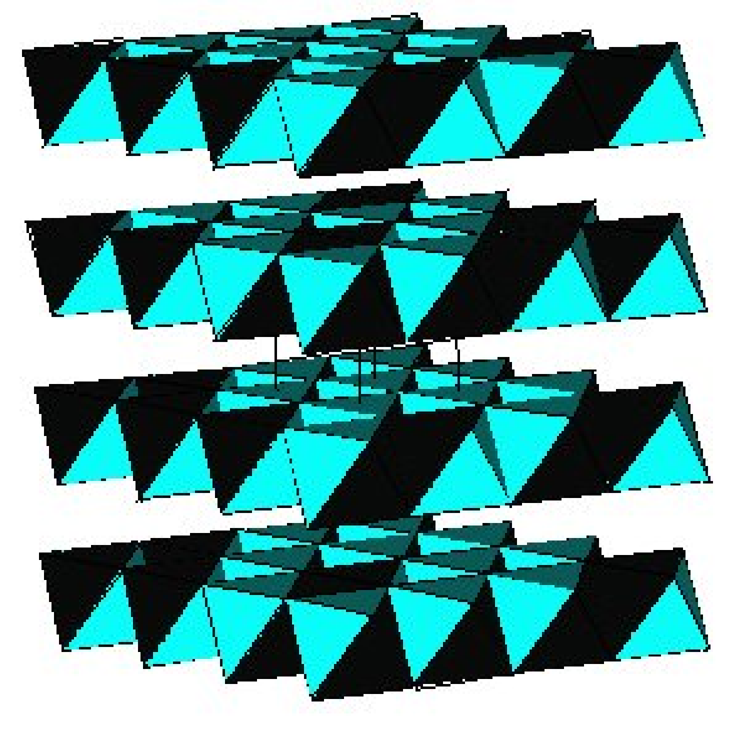
$CdCl_2$ Cubic close packing of anions with 1/2 octahedral holes filled by cations

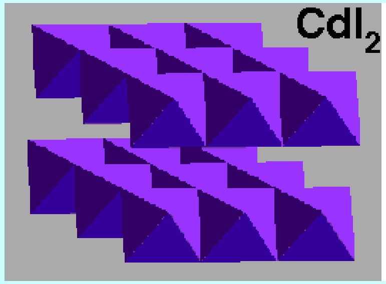
$CdCl_2$, $CdBr_2$, $CoCl_2$, $FeCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$, NiI_2, $ZnBr_2$, ZnI_2, Cs_2O* (anti-$CdCl_2$ structure)

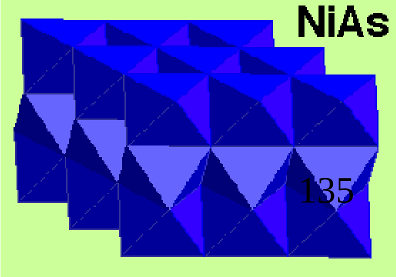
CdI_2 Hexagonal Close Packing



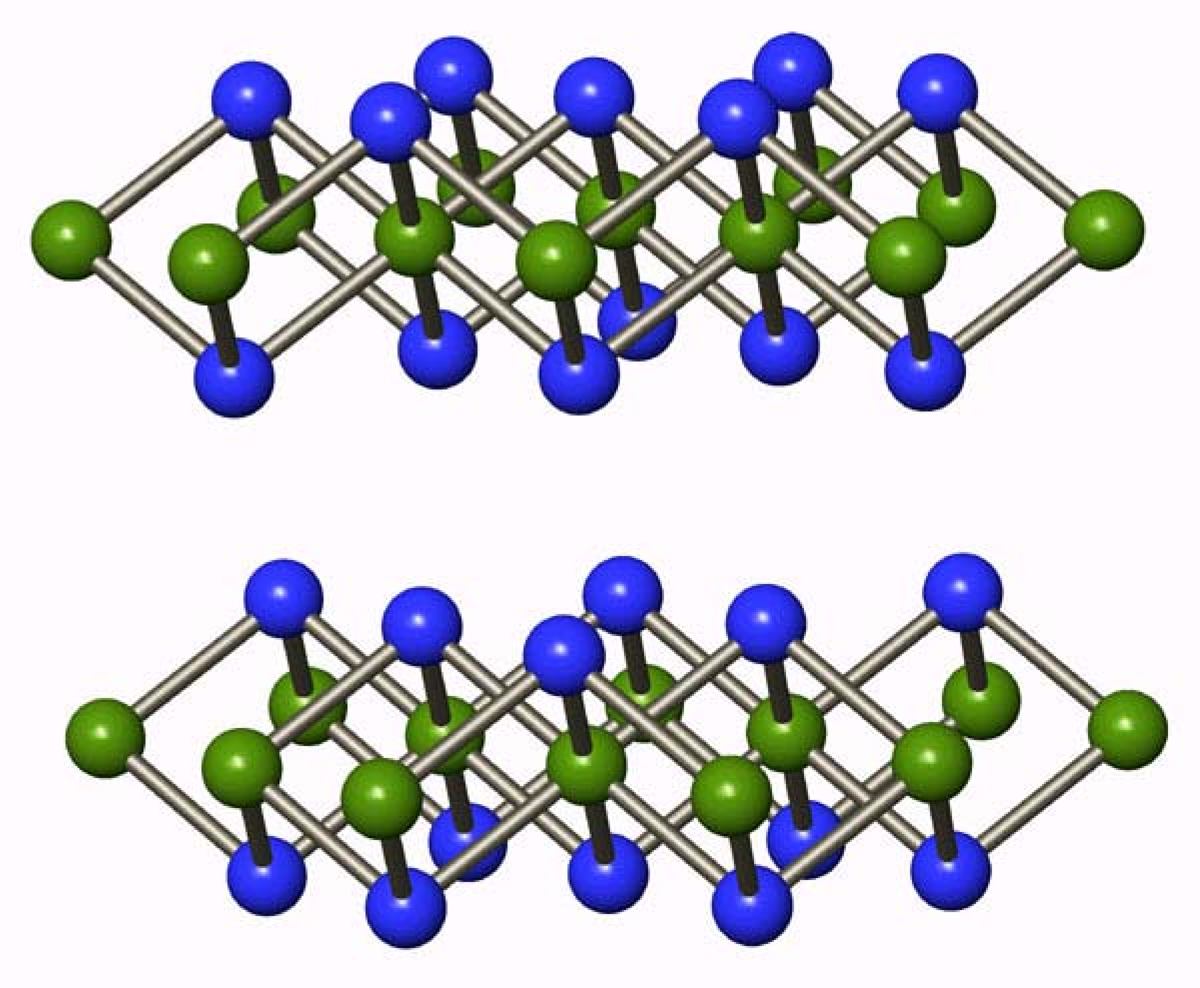




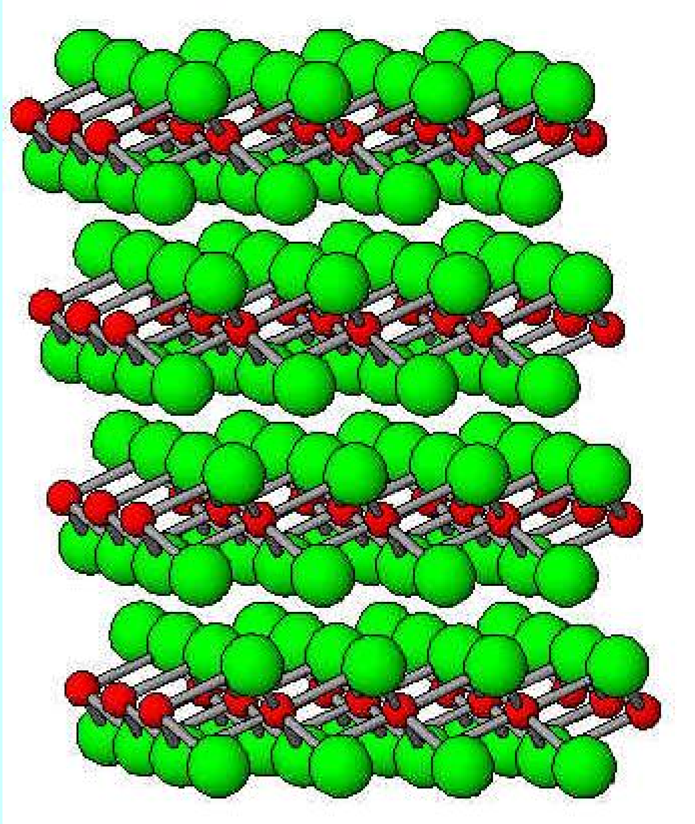


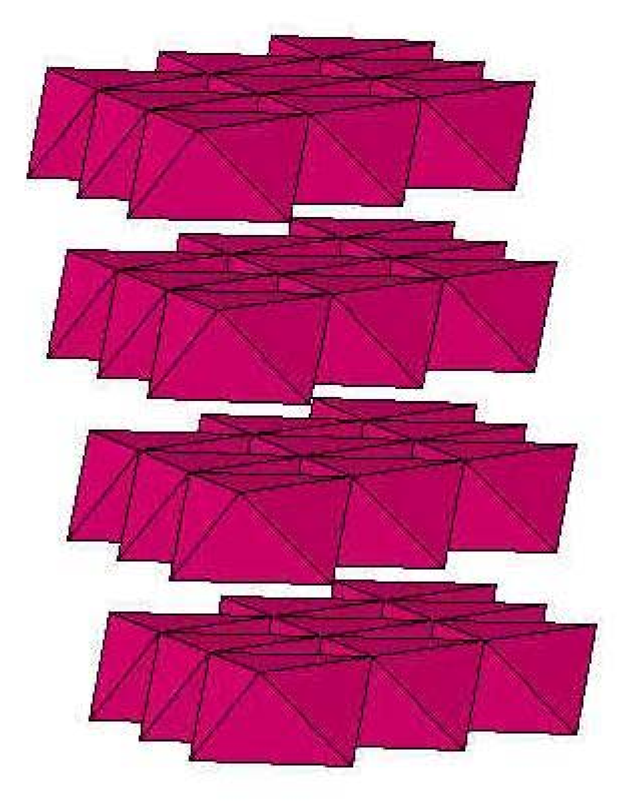


$CdCl_2$ Cubic Close Packing



$CdCl_2$ Cubic Close Packing





Strukturbericht Symbols

A partly systematic method for specifying the structure of a crystal
A - monatomic (elements), **B** - diatomic with equal numbers of atoms of each type (AB), **C** - a 2-1 abundance ratio (AB_2), **D**0 - 3-1, etc.

Structure type	Struktur bericht	Space group (S.G. No.)	Lattice
Cu	**A1**	Fm-3m (225)	fcc
W, Fe	**A2**	Im-3m (229)	bcc
Mg	**A3**	$P6_3$/mmc (194)	hcp
C - diamond	**A4**	Fd-3m (227)	diamond
NaCl	**B1**	Fm-3m (225)	
CsCl	**B2**	Pm-3m (221)	
ZnS	**B3**	F43m (216)	Zincblende
ZnS	**B4**	$P6_3$/mc (186)	Wurtzite
CaF_2	**C1**	Fm-3m (225)	Fluorite

Pearson Symbols

Indicate the crystal symmetry and the number of atoms in the unit cell
e.g.: NaCl - a face-centered (**F**) cubic (**c**) structure with 8 atoms in the unit cell = cF8
monoclinic (**m**), hexagonal (**h**), orthorhombic (**o**), asymmetric (**a**), primitive (**P**)
the Pearson symbol does not necessarily specify a unique structure (see cF8)

Structure type	Pearson Symbol	Struktur bericht	Space group (S.G. No.)
Cu	**cF4**	**A1**	Fm-3m (225)
W, Fe	**cI2**	**A2**	Im-3m (229)
Mg	**hP2**	**A3**	$P6_3/mmc$ (194)
C - diamond	**cF8**	**A4**	Fd-3m (227)
NaCl	**cF8**	**B1**	Fm-3m (225)
CsCl	**cP2**	**B2**	Pm-3m (221)
ZnS (zb)	**cF8**	**B3**	F43m (216)
ZnS (w)	**hP4**	**B4**	$P6_3/mc$ (186)
CaF_2	**cF12**	**C1**	Fm-3m (225)

Space Group Symbols

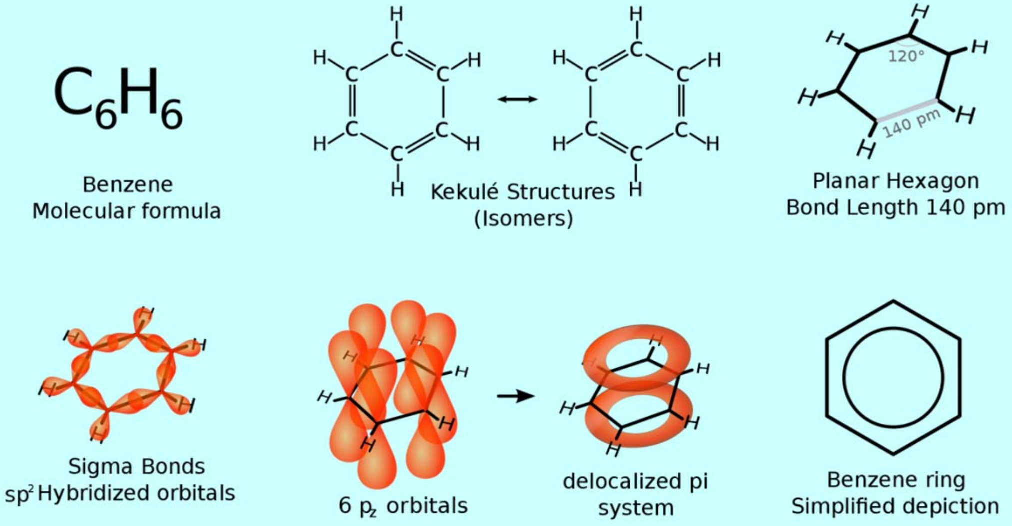
primitive (**P**), face-centered (**F**), body-centered (**I**), base-centered (**A**, **B**, **C**), rhombohedral (**R**)

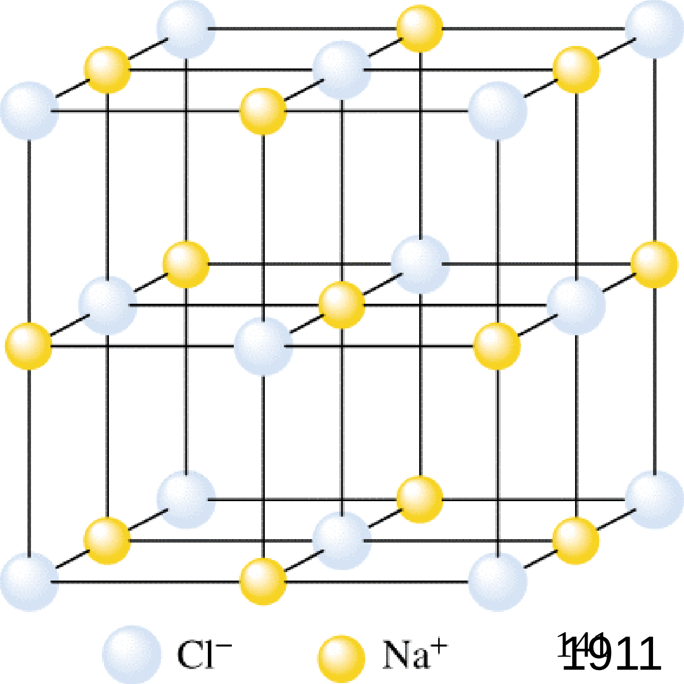
S. G. Class	**Centering**	**Symbol syntax (examples)**
Triclinic	P	P1, P-1
Monoclinic	P, C, B	Paxis, Pplane, Paxis/plane (**$P2_1$, Cm**, **$P2_1$/c)**
Orthorhombic	P, F, I, C, A	Paxisaxisaxis, Pplaneplaneplane (**Pmmm, $Cmc2_1$**)
Tetragonal	P, I	P**4**, P4axisaxisaxis, P4planeplaneplane (**I4/m, P4mm**)
Trigonal	P, R	P**3**axis, P3plane (**R-3m)**
Hexagonal	P	P**6**, P6axisplane (**$P6_3$/mmc)**
Cubic	P, F, I	Paxis**3**plane, Pplane3plane (**Pm-3m, Fm-3m)**

Bonding models for covalent and ionic compounds

G. N. Lewis 1923
Electron pair sharing
Orbital overlap
Chemical bond
Number of bonds = atomic valence

Born, Lande, Magelung, Meyer 1918
Electrostatic attraction (Coulomb)
Repulsion





1911

Organic vs inorganic bonding

Lattice Enthalpy, L

The **lattice enthalpy** change, L, is the standard molar enthalpy change ΔH_L^0 for the process:

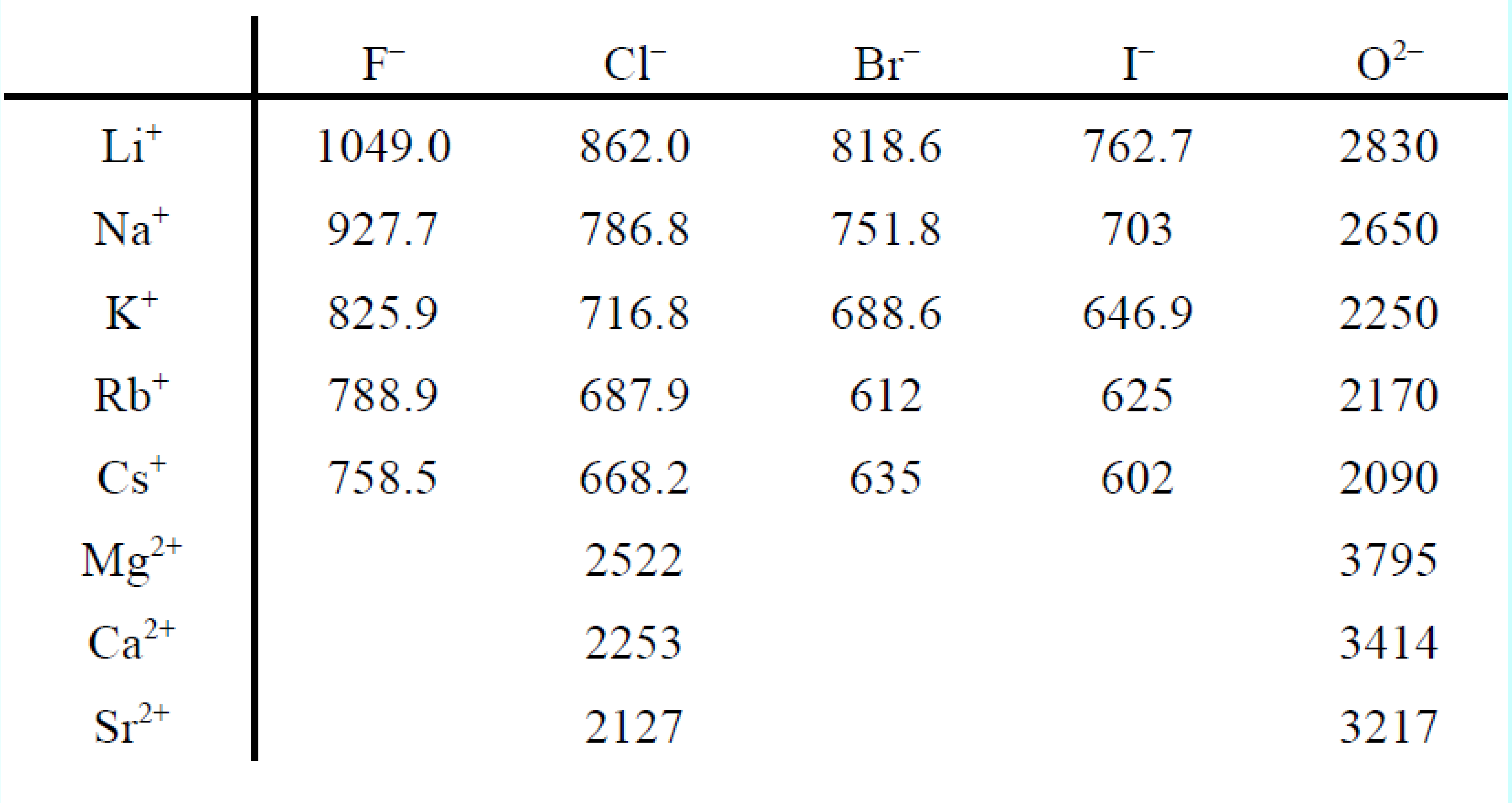
$$M^+_{(gas)} + X^-_{(gas)} \rightarrow MX_{(solid)} \quad (L)$$

The formation of a solid from ions in the gas phase is always **exothermic**
Lattice enthalpies are usually **negative**

The most stable crystal structure of a given compound is the one with the highest (**most negative**) lattice enthalpy.

(entropy considerations neglected)

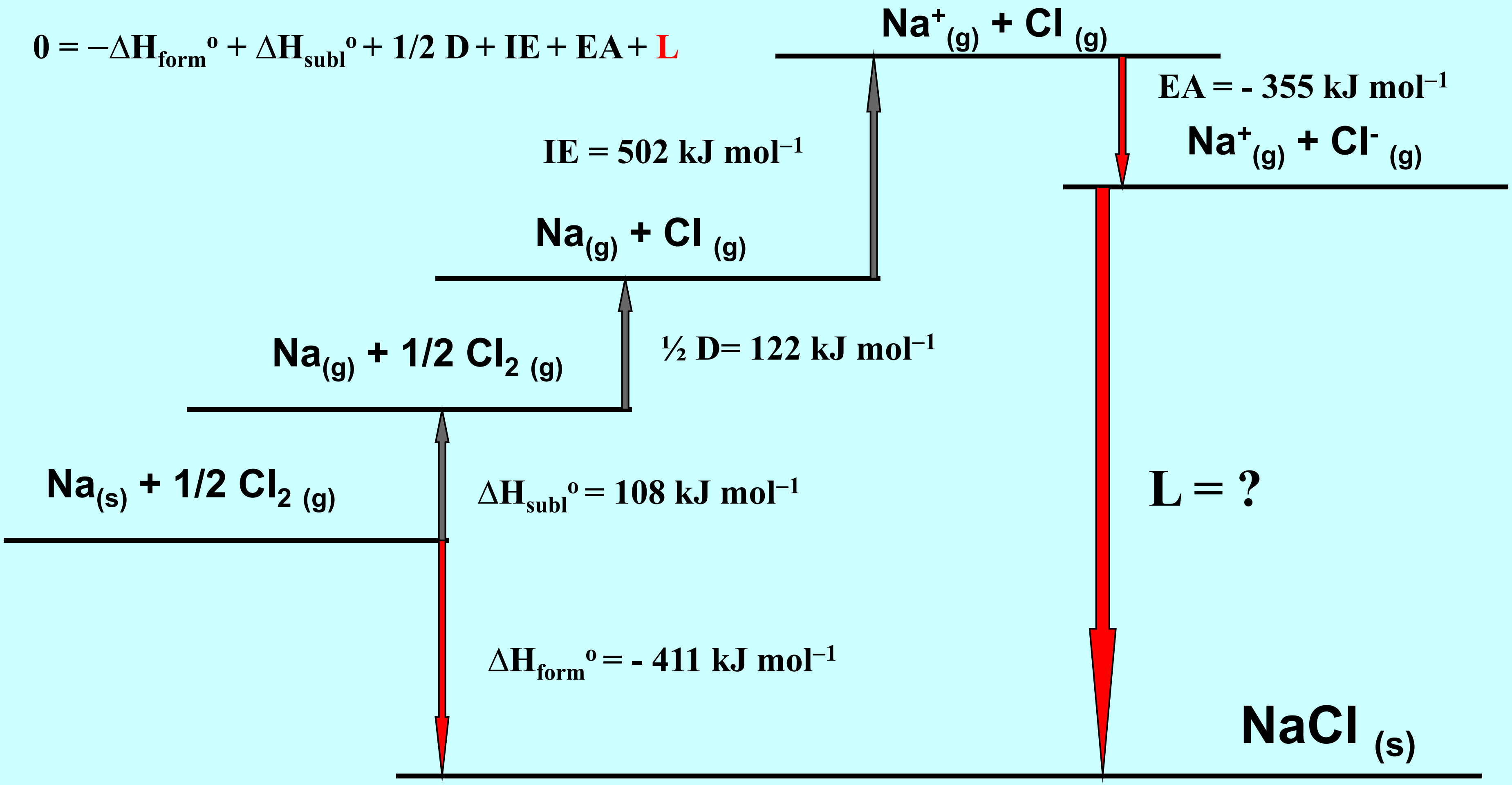
Lattice Enthalpy, L, kJ/mol



	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1049.0	862.0	818.6	762.7	2830
Na^+	927.7	786.8	751.8	703	2650
K^+	825.9	716.8	688.6	646.9	2250
Rb^+	788.9	687.9	612	625	2170
Cs^+	758.5	668.2	635	602	2090
Mg^{2+}		2522			3795
Ca^{2+}		2253			3414
Sr^{2+}		2127			3217

Born-Haber cycle

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



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

EA = - 355 kJ mol^{-1}

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

IE = 502 kJ mol^{-1}

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

½ D= 122 kJ mol^{-1}

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

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

ΔH_{subl}^{o} = 108 kJ mol^{-1}

L = ?

ΔH_{form}^{o} = - 411 kJ mol^{-1}

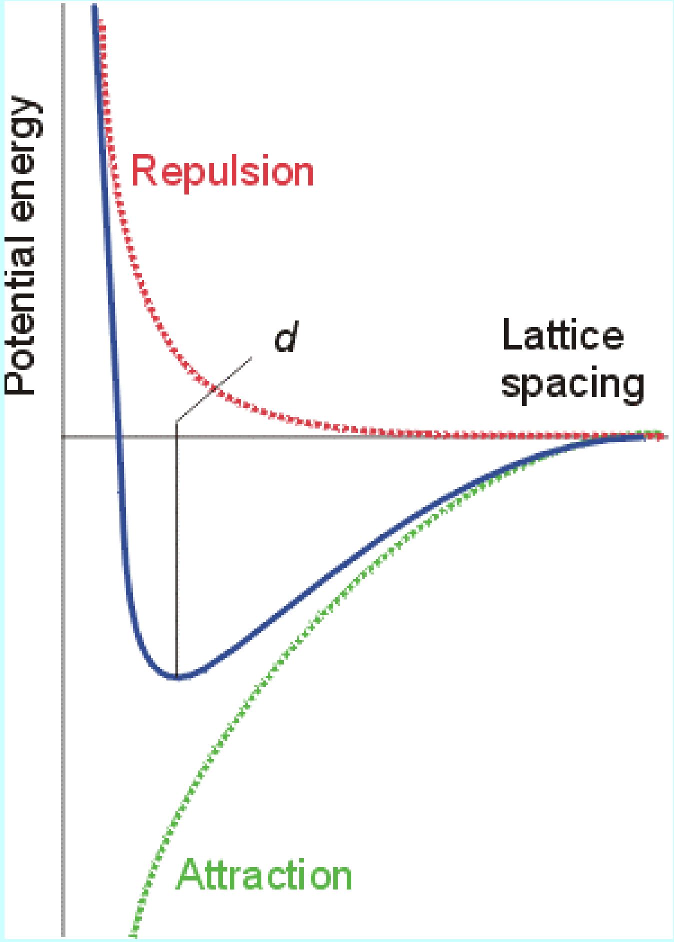
$NaCl_{(s)}$

$0 = 411 + 108 + 122 + 502 + (-355) + L$

L = – 788 kJ mol^{-1}

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

Lattice Enthalpy



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

One ion pair

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

$E_{rep} = B / d^n$
(modelled empirically)
n = Born exponent
(experimental measurement of compressibilty)
B = a constant

Lattice Enthalpy

1 mol of ions

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

A = Madelung constant - a single ion interacts with all other ions

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

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

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

Find minimum dL/d(d) = 0

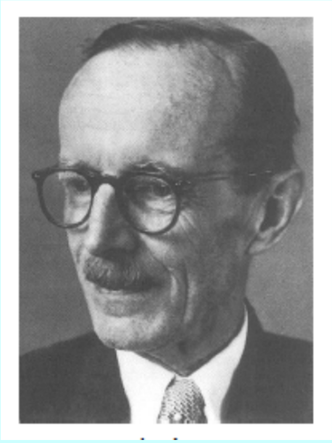
Calculation of Lattice Enthalpies

Coulombic contributions to lattice enthalpies

$$E_{Coul} = -N_A A \boxed{\frac{z_+ z_- e^2}{4\pi\varepsilon_0 d}}$$

Coulomb potential of an ion pair

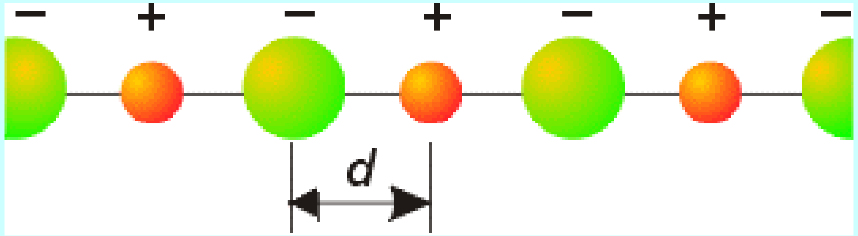
E_{Coul} : Coulomb potential (electrostatic potential)
A : Madelung constant (depends on structure type)
N_A: Avogadro constant
z : charge number
e : elementary charge
ε_o: dielectric constant (vacuum permittivity)
d : shortest distance between cation and anion



Madelung Constant

Count all interactions in the crystal lattice

The simplest example : 1D lattice

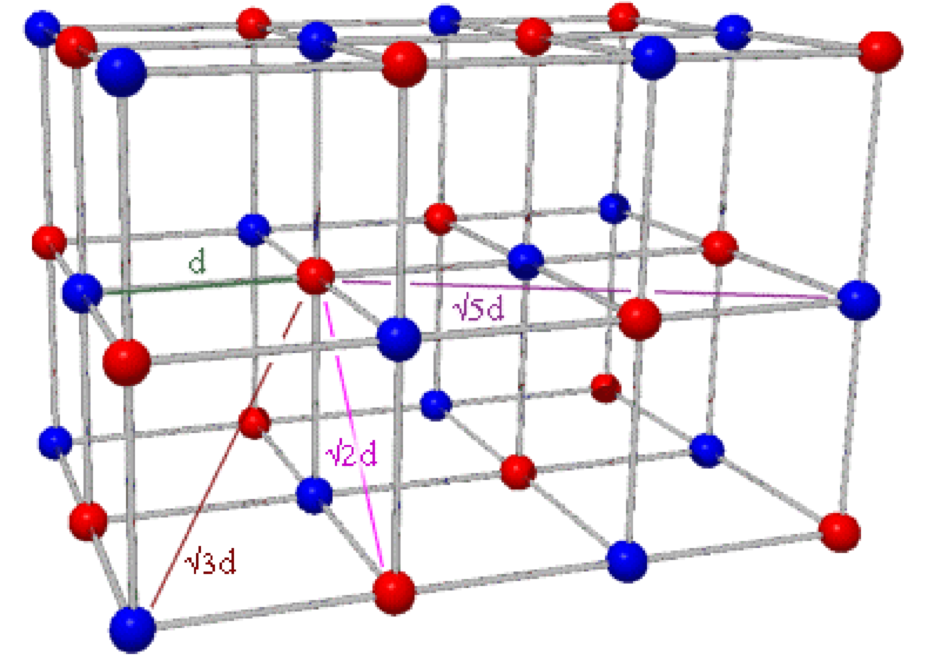


$E_{coul} = (e^2 / 4 \pi \varepsilon_0)*(z_A z_B / d)*[+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + ...]$

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

Madelung constant A = 1.3863…
for an infinite linear chain of ions
= sum of convergent series

Madelung Constant for NaCl



3D ionic solids:
Coulomb attraction and
repulsion

a single ion interacts with all
other ions

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

convergent series

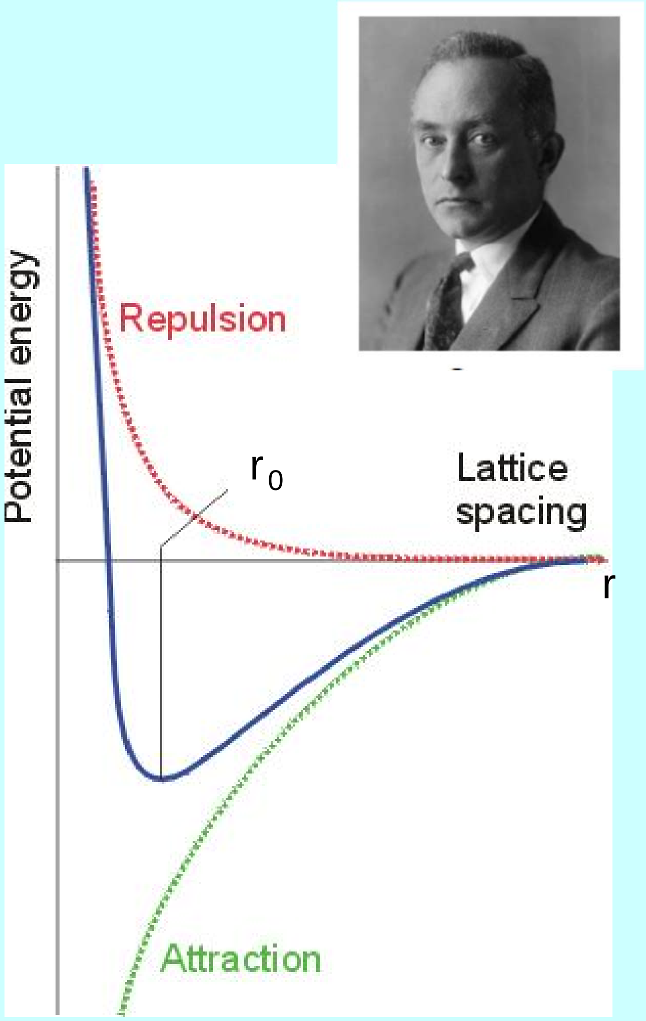
$E_{coul} = (e^2 / 4 \pi \varepsilon_0) * (z_A z_B / d) * A$

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \ldots. = 1.74756$$

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
Linear Lattice	1.38629
Ion Pair	?

Born repulsion E_{rep}



Repulsion arising from overlap of electron clouds

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

approximation:

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

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

$$\Delta \mathrm{H}_L^0 = \min\left(E_{Coul} + E_{rep}\right)$$

(set first derivative of the sum to zero)

$$\boxed{\Delta \mathrm{H}_L^0 = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 d} N_A \left(1 - \frac{1}{n}\right)}$$

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

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

$$L = K \times v \times \frac{Z_A Z_B}{r_+ + r_-} \times \left(1 - \frac{G}{r_+ + r_-}\right)$$

K, G = constants

Kapustinski

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

v = the number of ions in one formula unit

Most important advantage of the Kapustinski equation

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

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

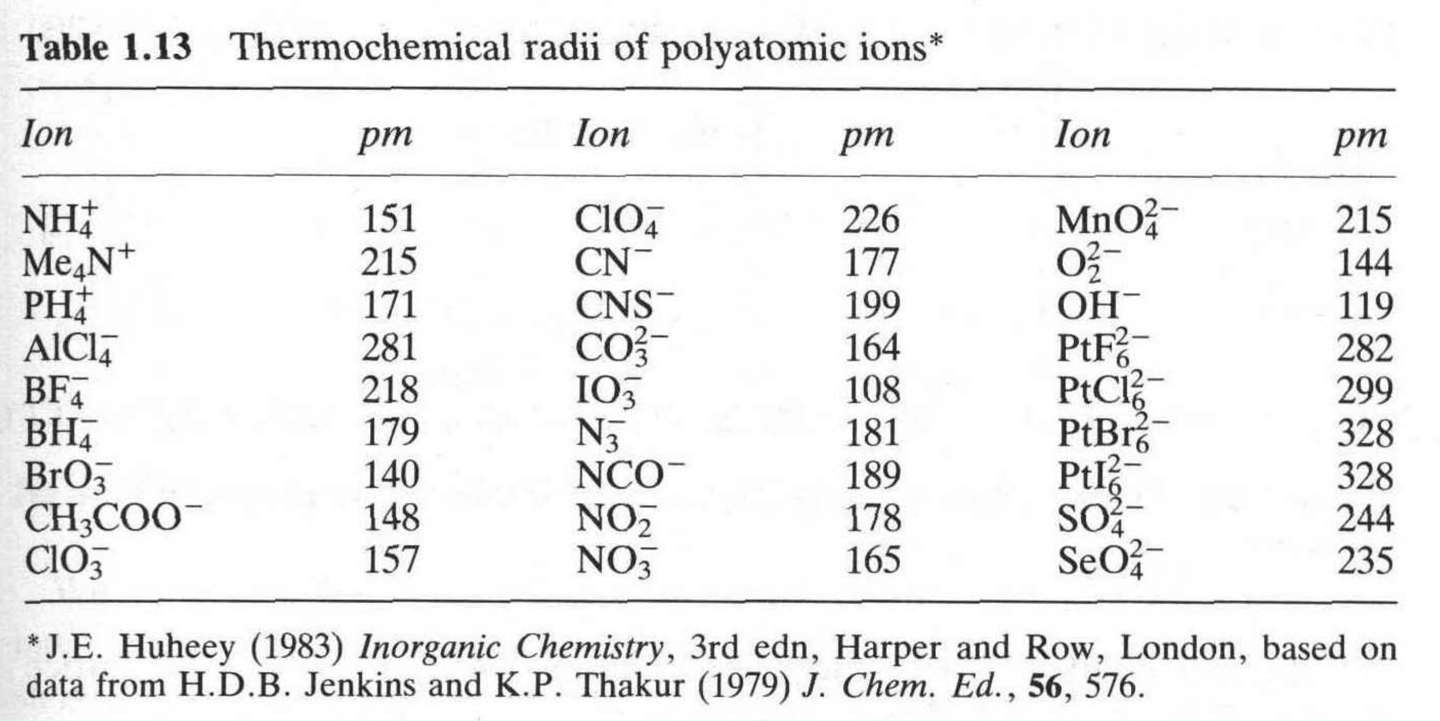


Table 1.13 Thermochemical radii of polyatomic ions*

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

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

Lattice Enthalpy

Born–Lande

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

El. config.	n	Example
He-He	5	LiH
Ne-Ne	7	NaF, MgO
Ar-Ar	9	KCl, CaS, CuCl, Zn^{2+}, Ga^{3+}
Kr-Kr	10	RbBr, AgBr, Cd^{2+}, In^{3+}
Xe-Xe	12	CsI, Au^{+}, Tl^{3+}

For compounds of mixed ion types, use the average value (e.g., for NaCl, n = 8).

Born–Mayer

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

$d^* = 0.345$ Å

Lattice Enthalpy of NaCl

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

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

Lattice Enthalpy consists of ionic and covalent contribution

Applications of lattice enthalpy calculations:

→ thermal stabilities of ionic solids

→ stabilities of oxidation states of cations

→ solubility of salts in water

→ calculations of electron affinity data

→ lattice enthalpies and stabilities of „non existent“ compounds

Pauling's Rules

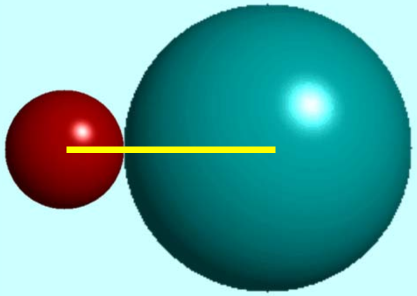
Five principles which could be used to determine the structures of complex ionic/covalent crystals

Pauling's Rule no. 1 Coordination Polyhedra

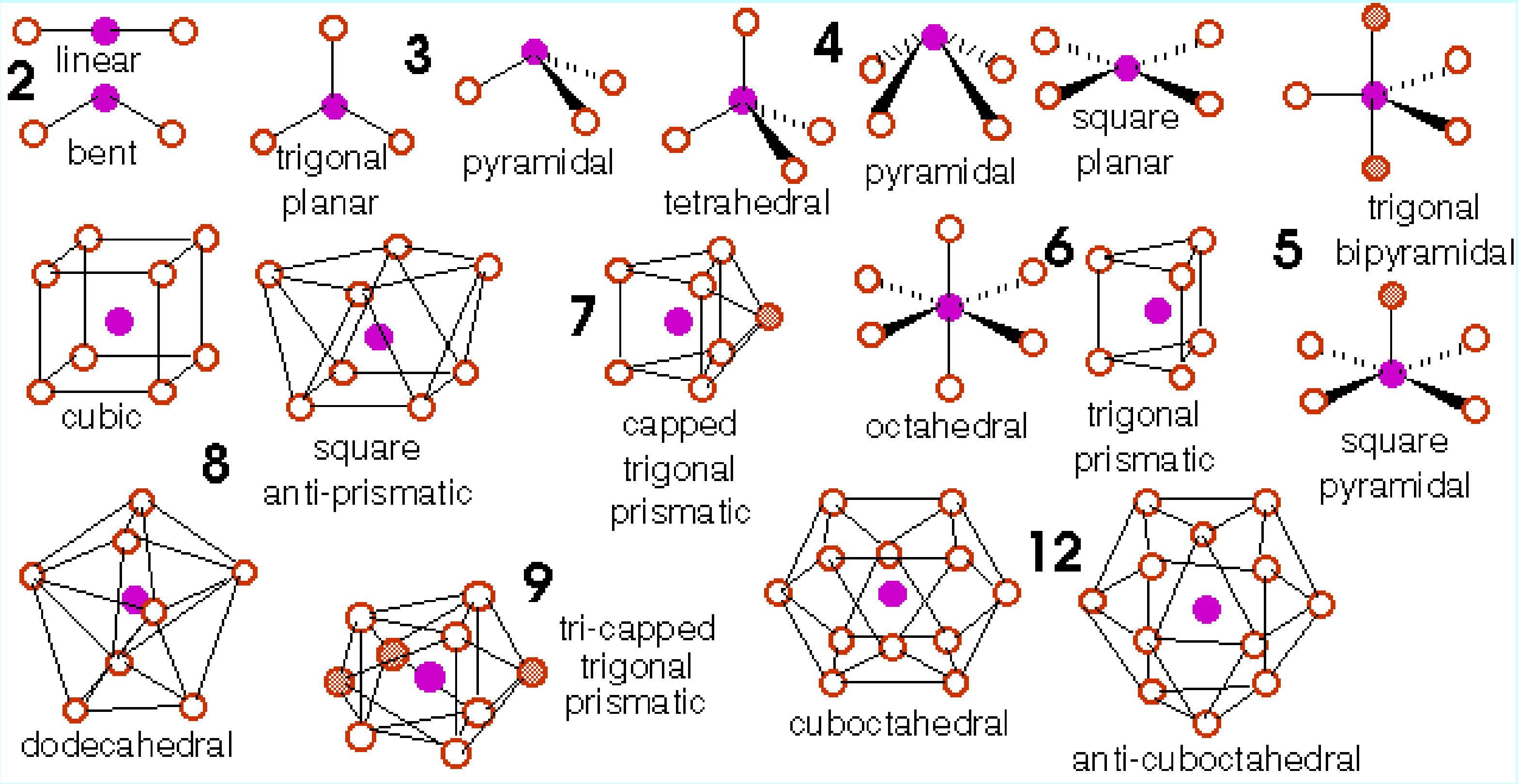
A coordinated polyhedron of anions is formed about each cation.

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

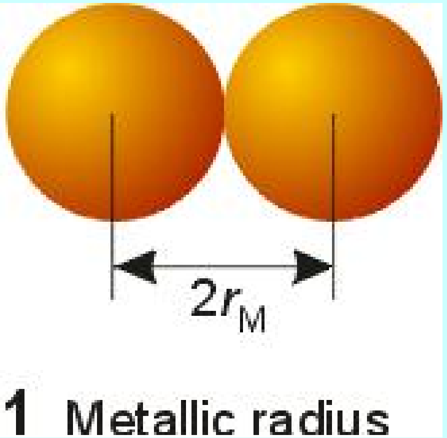
Cation coordination environment is determined by radius ratio.



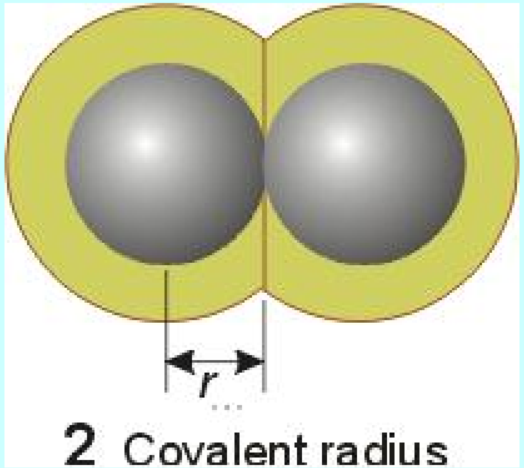
Coordination Polyhedra



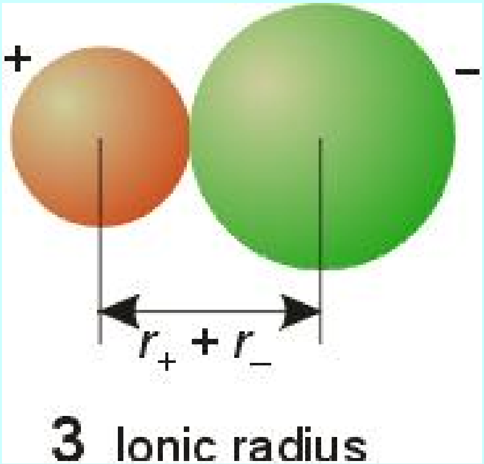
Different Types of Radii



1 Metallic radius



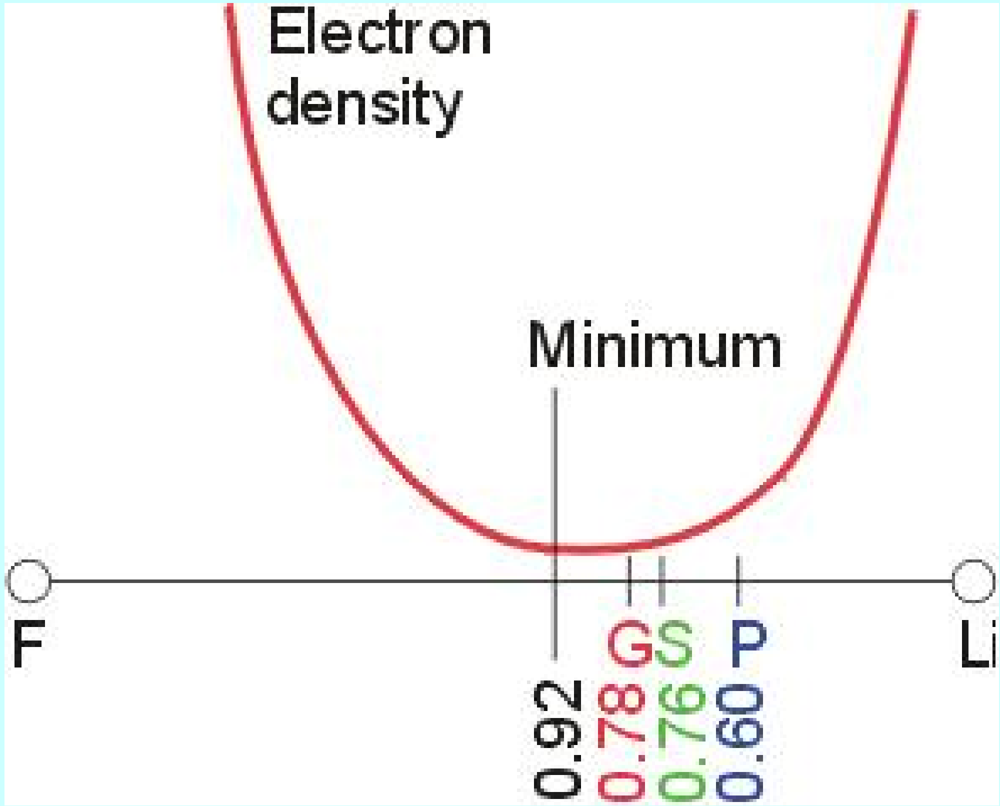
2 Covalent radius



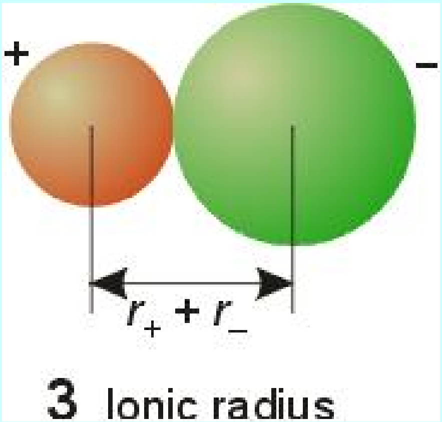
3 Ionic radius

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

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



Variation of ionic radii with coordination number

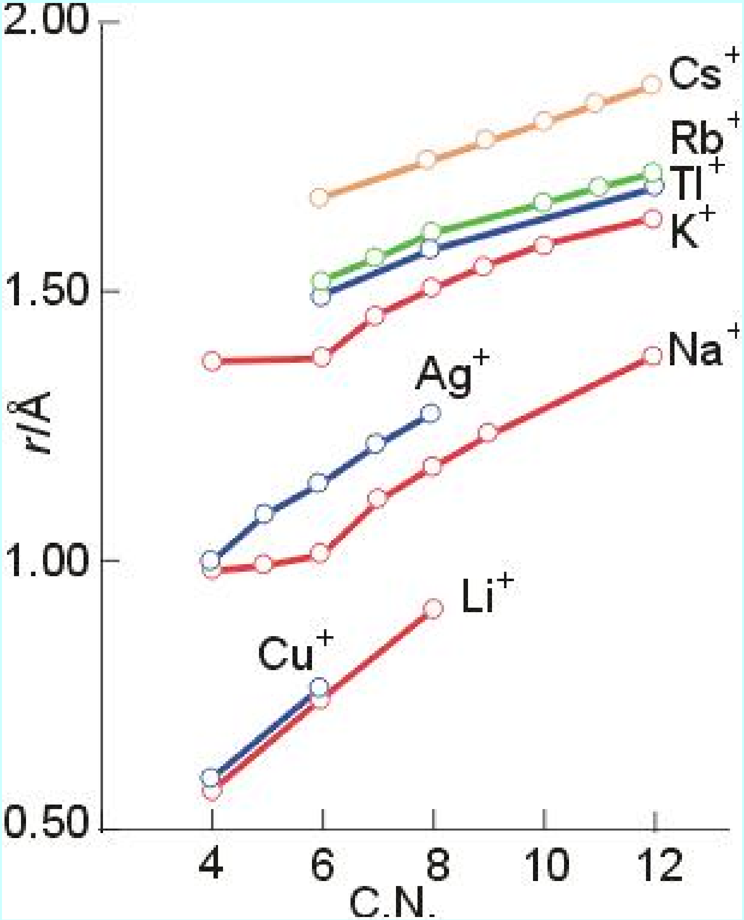


3 Ionic radius

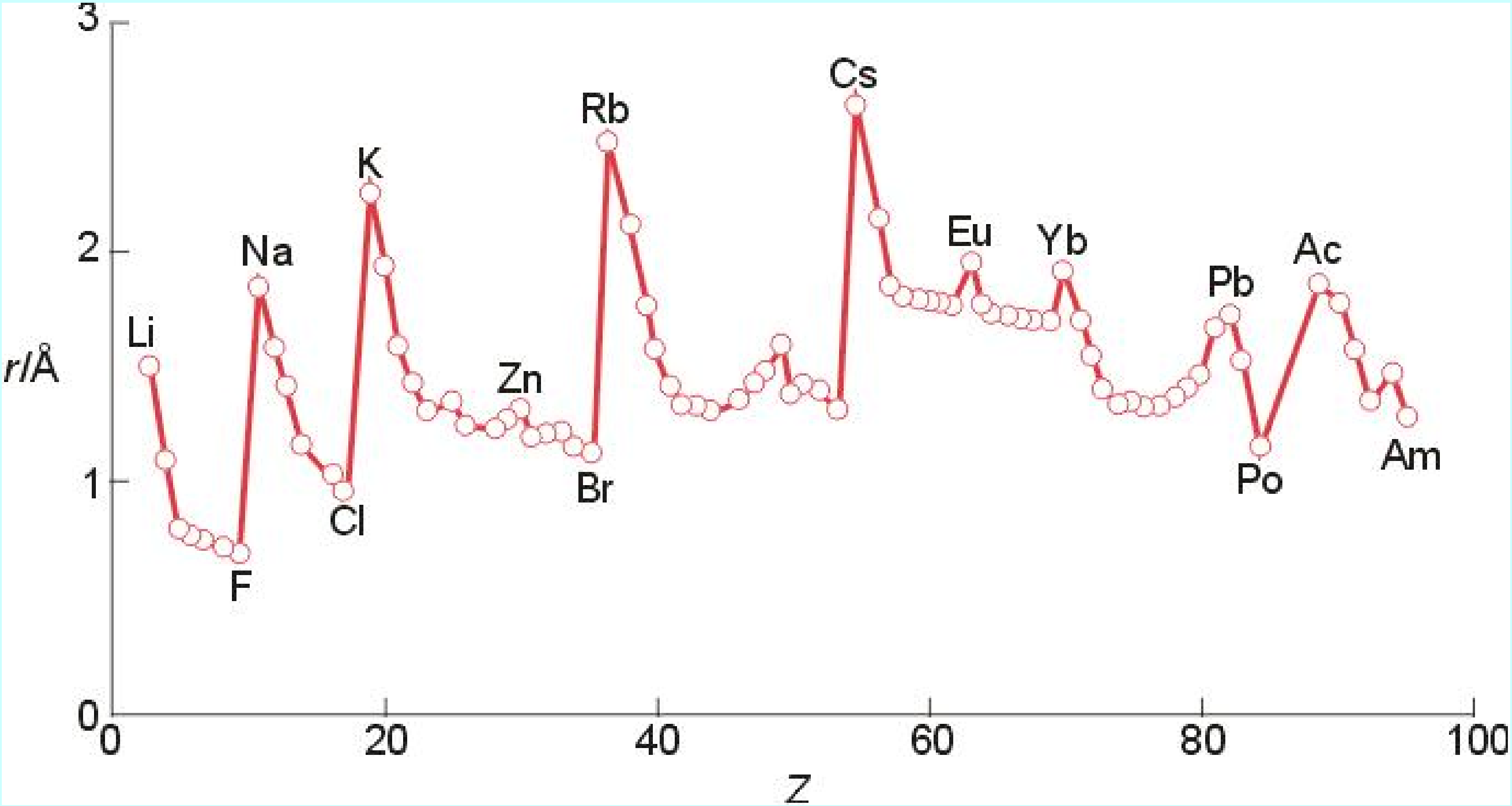
The radius of one ion was fixed to a reasonable value

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

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



Variation of atomic radii through the Periodic table



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

Sr^{2+}

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)

Al^{3+}	0.675
Ga^{3+}	0.760
In^{3+}	0.940
Tl^{3+}	1.025
Ti^{4+}	0.745
Zr^{4+}	0.86
Hf^{4+}	0.85

Right to left across the periodic table the radius decreases.

(6 coordinate radii, in Å)

La^{3+}	1.172
Nd^{3+}	1.123
Gd^{3+}	1.078
Lu^{3+}	1.001

General trends for ionic radii

1. Ionic radii increase down a group.

(Lanthanide contraction restricts the increase of heavy ions)

2. Radii of equal charge ions decrease across a period

3. Ionic radii increase with increasing coordination number

the higher the CN the bigger the ion

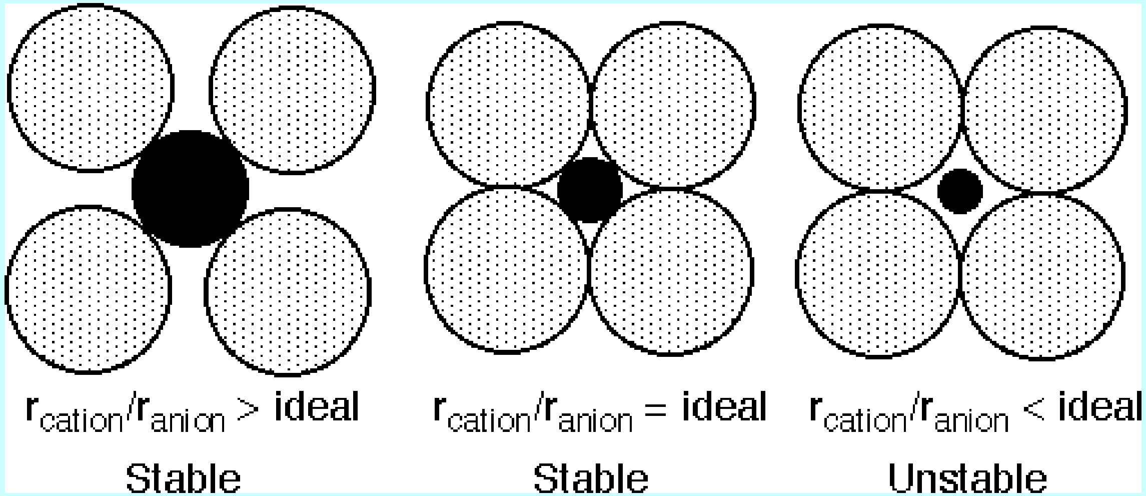
4. The ionic radius of a given atom decreases with increasing charge (r(Fe^{2+}) > r(Fe^{3+}))

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

6. Frequently used for rationalization of structures:

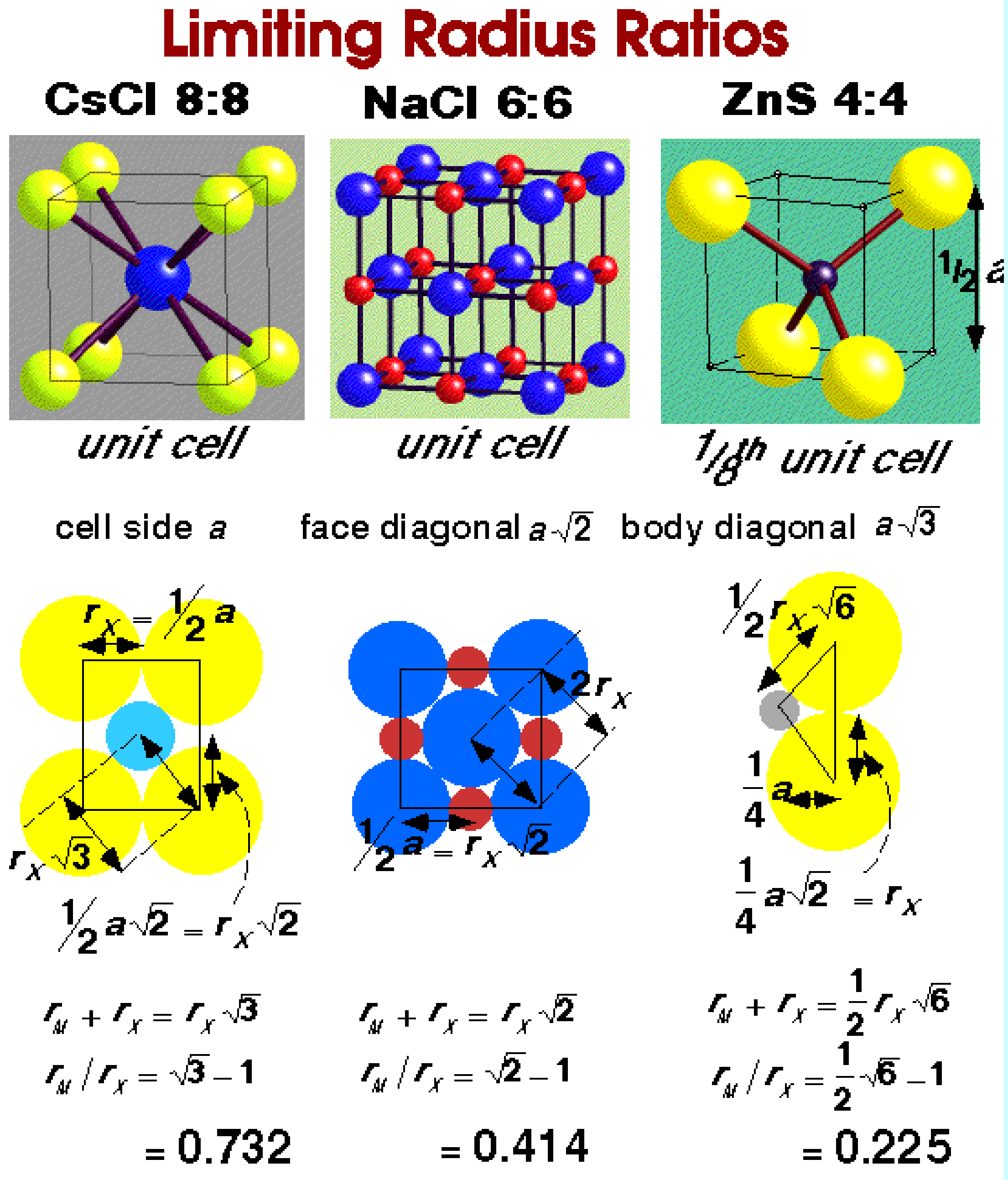
„radius ratio“ r(cation)/r(anion) (< 1)

Cation/anion Radius Ratio



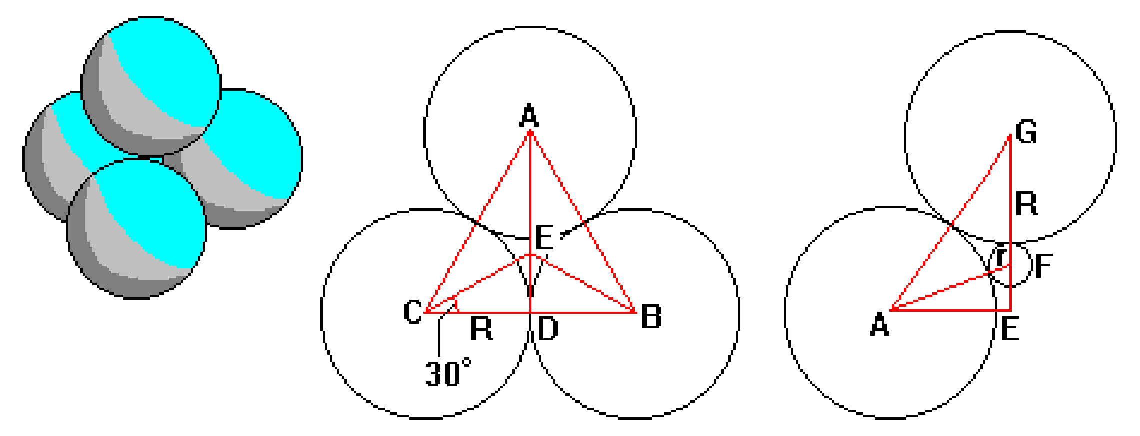
CN	r/R
12 – hcp/ccp	**1.00 (substitution)**
8 – cubic	**0.732 – 1.00**
6 – octahedral	**0.414 – 0.732**
4 – tetrahedral	**0.225 – 0.414**

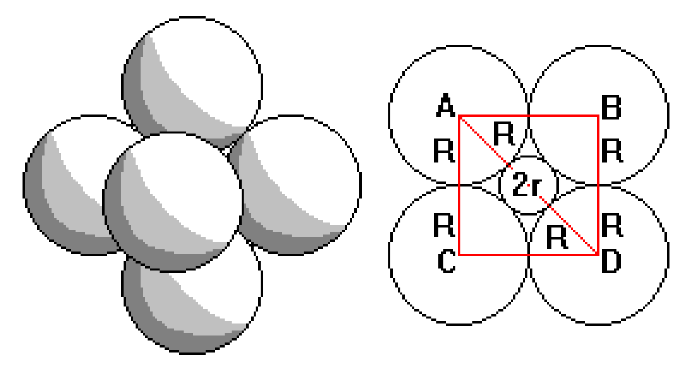
optimal radius ratio for given CN ions are in touch

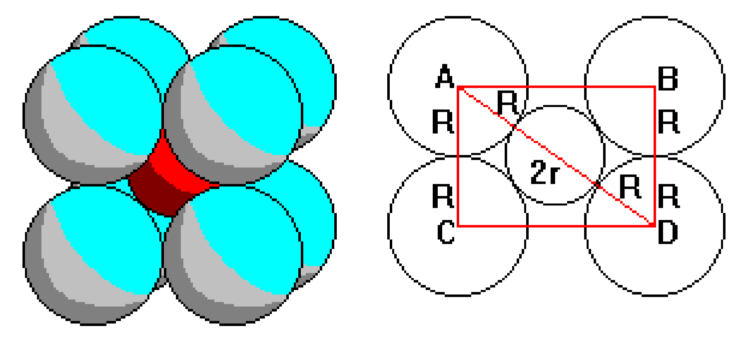


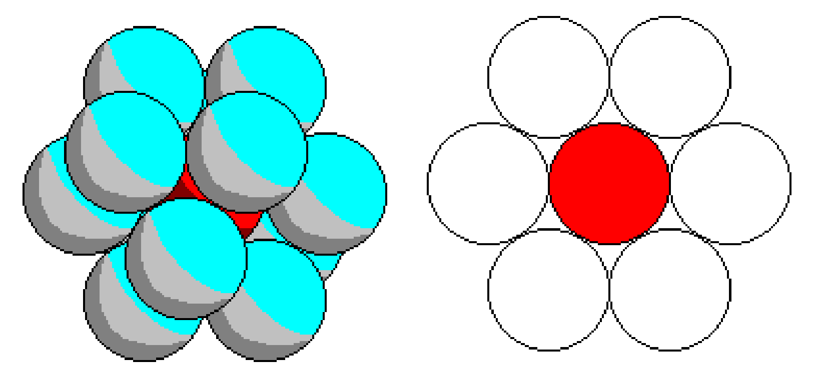
Limiting Radius Ratios

CsCl 8:8	**NaCl 6:6**	**ZnS 4:4**
unit cell	*unit cell*	*1/8th unit cell*
cell side a	face diagonal $a\sqrt{2}$	body diagonal $a\sqrt{3}$
$r_X = \frac{1}{2}a$	$2r_X$	$\frac{1}{2}r_X\sqrt{6}$
$r_X\sqrt{3}$	$\frac{1}{2}a = r_X\sqrt{2}$	$\frac{1}{4}a$
$\frac{1}{2}a\sqrt{2} = r_X\sqrt{2}$		$\frac{1}{4}a\sqrt{2} = r_X$
$r_M + r_X = r_X\sqrt{3}$	$r_M + r_X = r_X\sqrt{2}$	$r_M + r_X = \frac{1}{2}r_X\sqrt{6}$
$r_M / r_X = \sqrt{3} - 1$	$r_M / r_X = \sqrt{2} - 1$	$r_M / r_X = \frac{1}{2}\sqrt{6} - 1$
$= 0.732$	$= 0.414$	$= 0.225$


A
E
C
R
D
B
30°
G
R
r
F
A
E

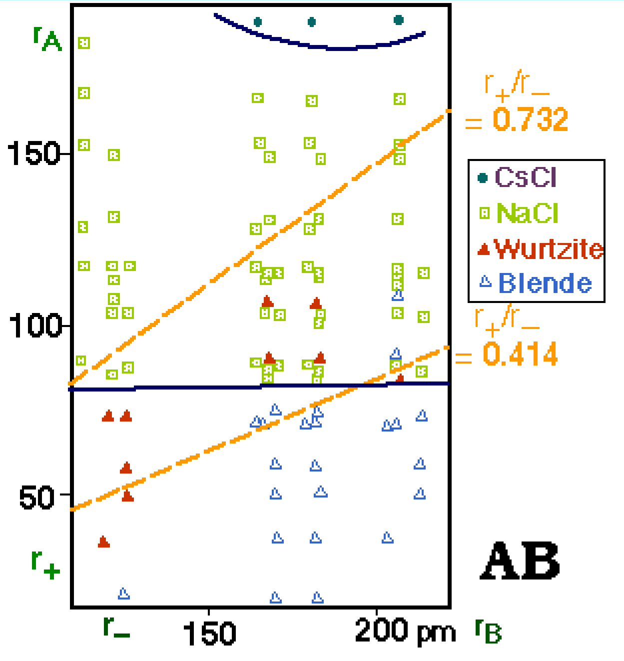

A
B
R
R
R
2r
R
R
R
C
D


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

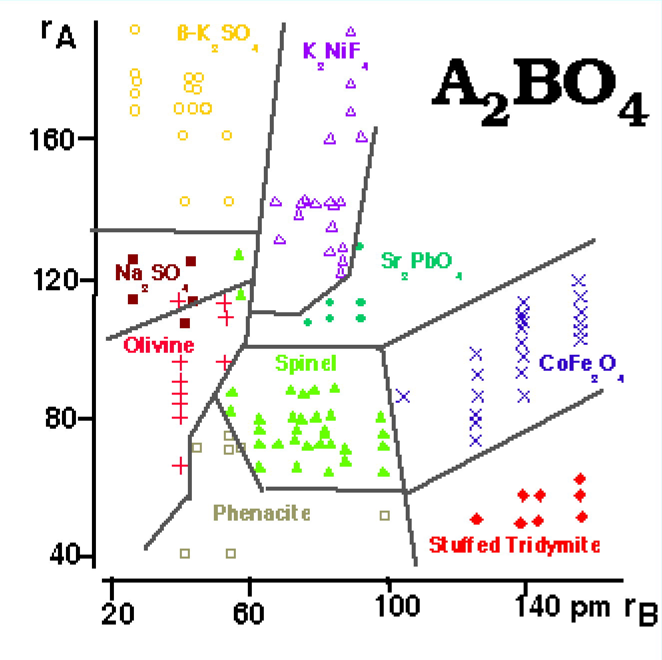


Structure Map

Dependence of the structure type on parameters, such as ionic radii, ionicity, electronegativity etc.



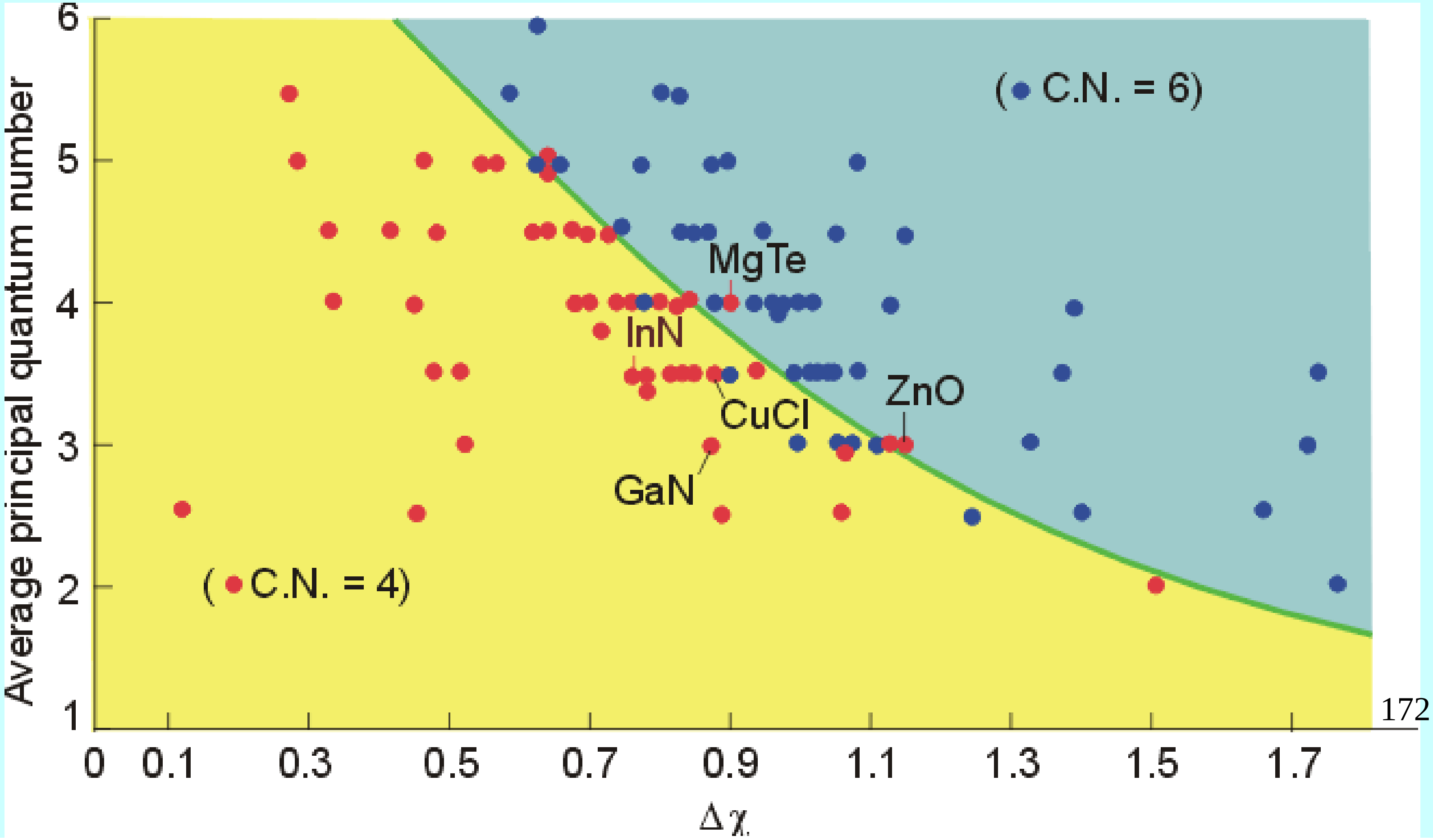
Structural map as function of radius ratios for AB compounds.



Structural map as function of radius ratios for A_2BO_4 compounds.

Structure Map

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



Pauling's Rules

Pauling's Rule no. 2 Bond Strength

The strength of an electrostatic bond = valence / CN
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.

TiO_2 (Rutile) Ti - oxidation state of +4, coordinated to 6 oxygens.
$V_{Ti} = +4 = 6\ (s_{ij}) \qquad s_{ij} = +2/3$

The bond valence of oxygen, coordinated by 3 Ti atoms
$Vo = 3\ (s_{ij}) = 3\ (-2/3) = -2$

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

Bond Strength

Brown, Shannon, Donnay, Allmann:
Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}.

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

R_{ij} = standard single bond length - determined empirically from (many) 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.

A constant $b = 0.37$

$R = d \qquad s = e^0 = 1$
$R < d \qquad s = e^{-1} < 1$
$R > d \qquad s = e^1 > 1$

Bond Strength

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

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

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

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^{-}

Bond Strength

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

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

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

$FeTiO_3$ (mineral Ilmenite) possesses the **corundum** structure – an hcp array of oxides with cations filling 2/3 of octahedral holes.
Decide which oxidation states are present: Fe(II) Ti(IV) or Fe(III) Ti(III)

Bond Distances (d_{exp}, Å)	Tabulated R_{ij} values	Constants
Fe–O = 3×2.07 and 3×2.20	R_0(Fe–O) = 1.795 Å	b = 0.30
Ti–O = 3×1.88 and 3×2.09	R_0(Ti–O) = 1.815 Å	b = 0.37

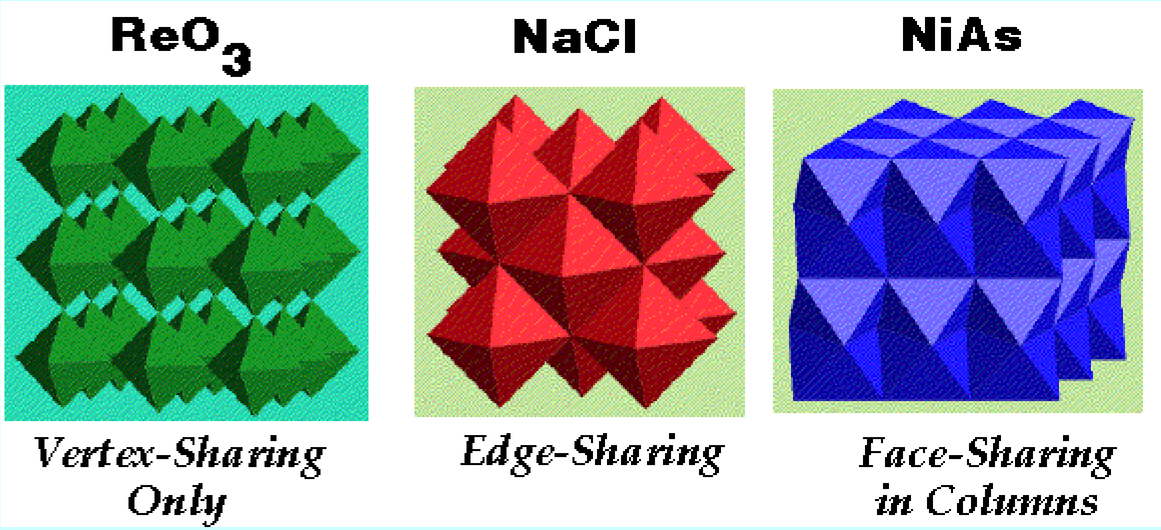
Oxygen valence and coordination number O?
Each oxygen is bound to Fe and Ti with both bond distances.

Pauling’s Rules

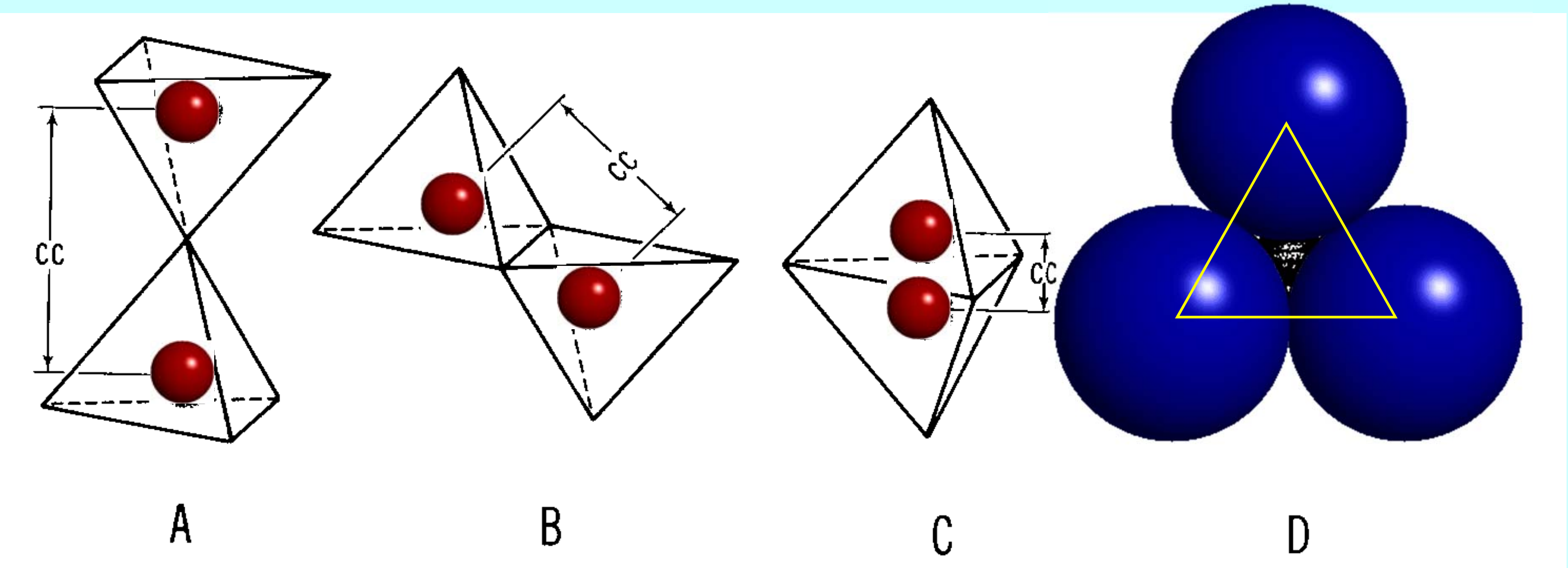
Pauling’s Rule no. 3   Polyhedral Linking

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.

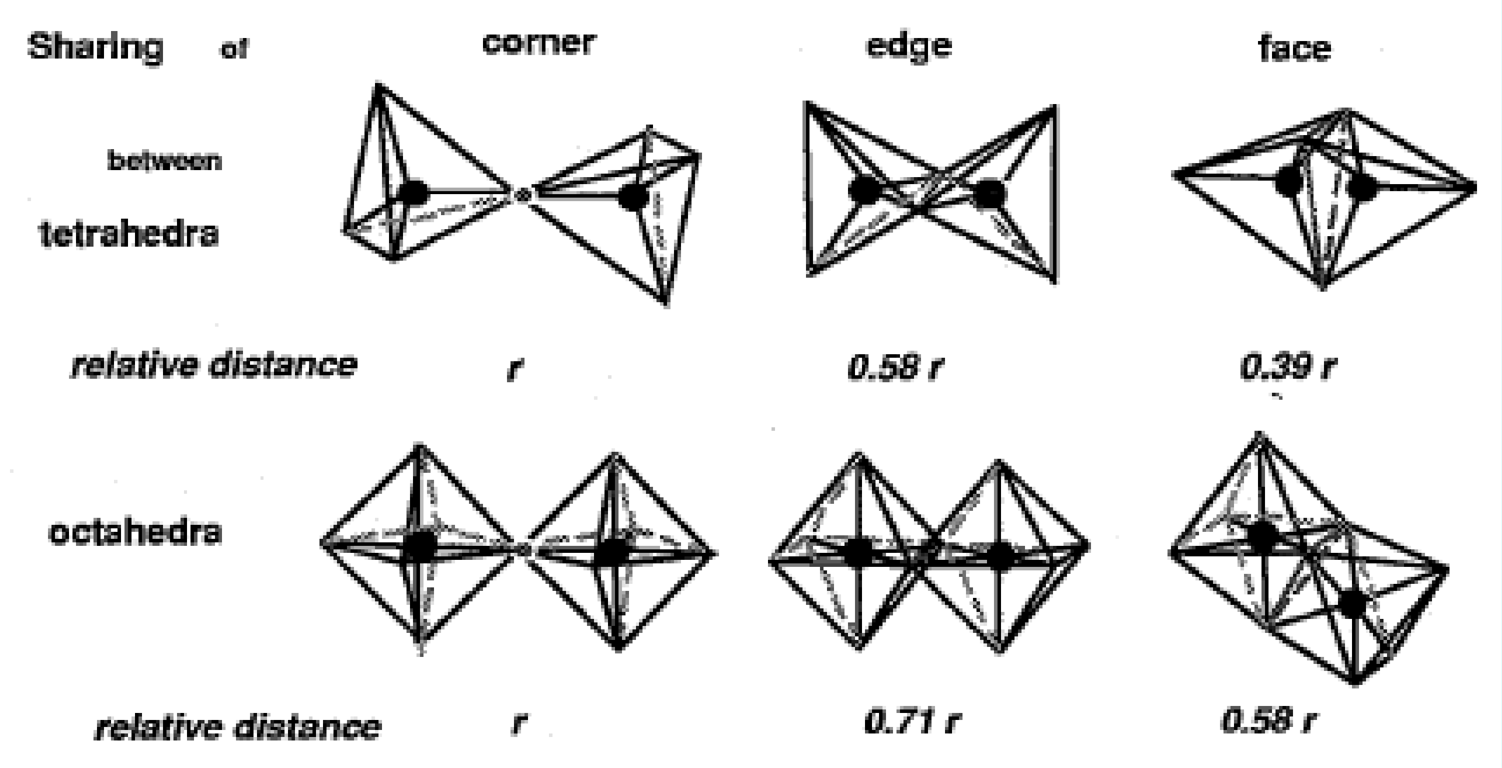
Avoid shared polyhedral edges and/or faces.



Polyhedral Linking



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

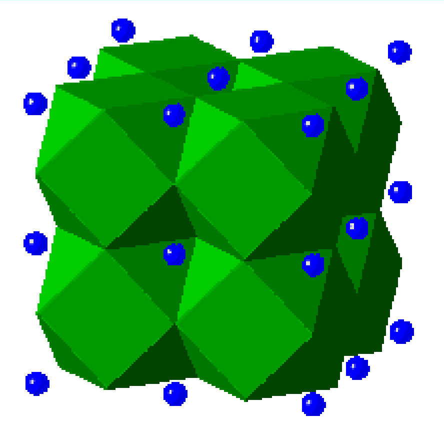
•degree of sharing increases (corner < edge < face)
•CN decreases (cubic < octahedral < tetrahedral)
•cation oxidation state increases (this leads to a stronger Coulomb repulsion)

Pauling’s Rules

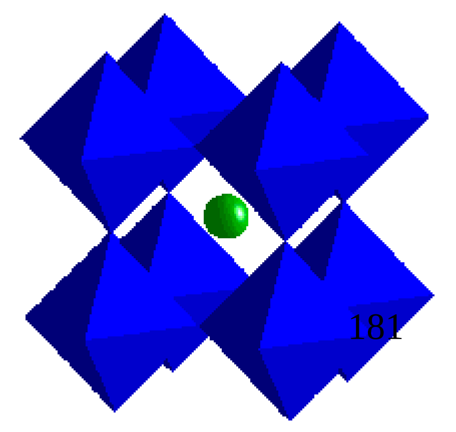
Pauling’s Rule no. 4 Cation Evasion

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

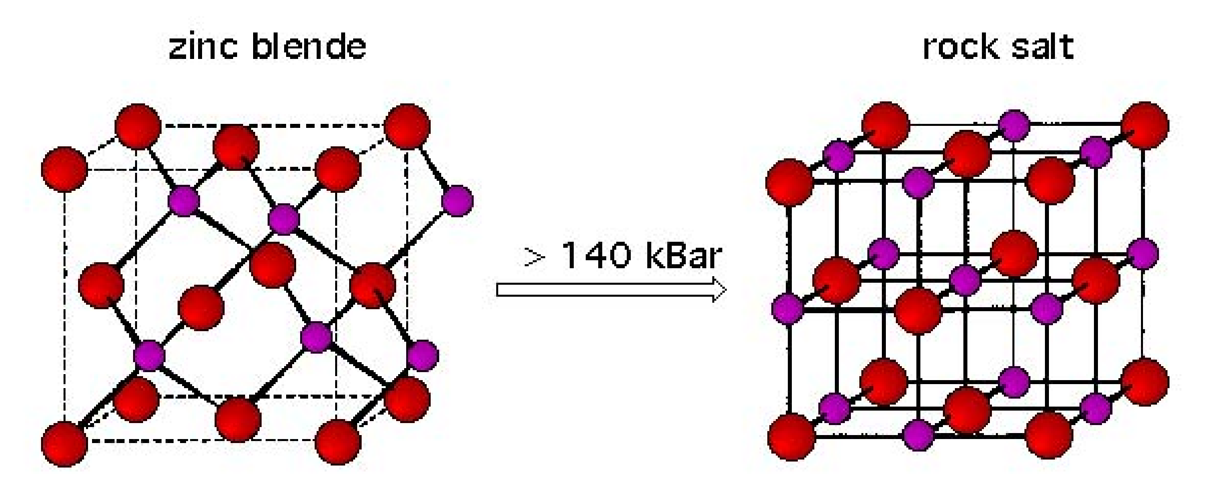
Pauling’s Rule no. 5 Environmental Homogeneity

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.

High Pressure Transformations



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

Pressure/Coordination Number Rule: increasing pressure – higher CN

Pressure/Distance Paradox: increasing pressure – longer bonds