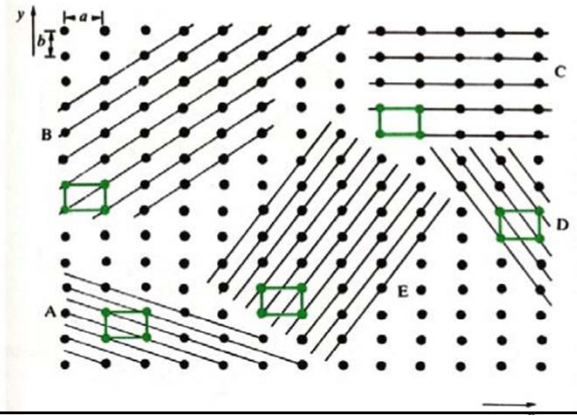
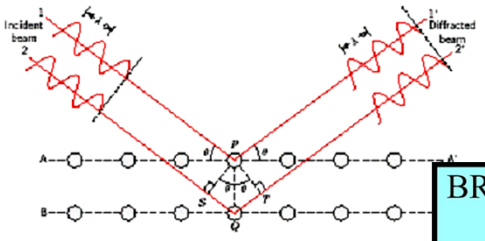
Lattice planes

- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of three integers referred to as Miller Indices



Powder diffraction



BRAGG LAW

$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal

θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays

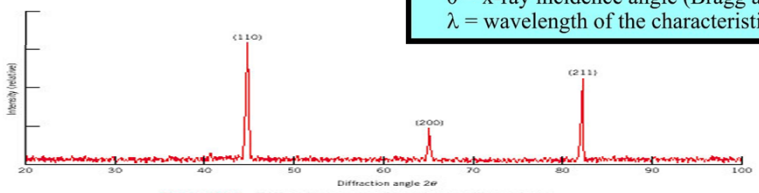
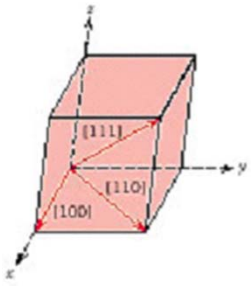


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

Crystallographic Directions And Planes



Lattice Directions

Individual directions: [uvw]

Symmetry-related directions: <uvw>

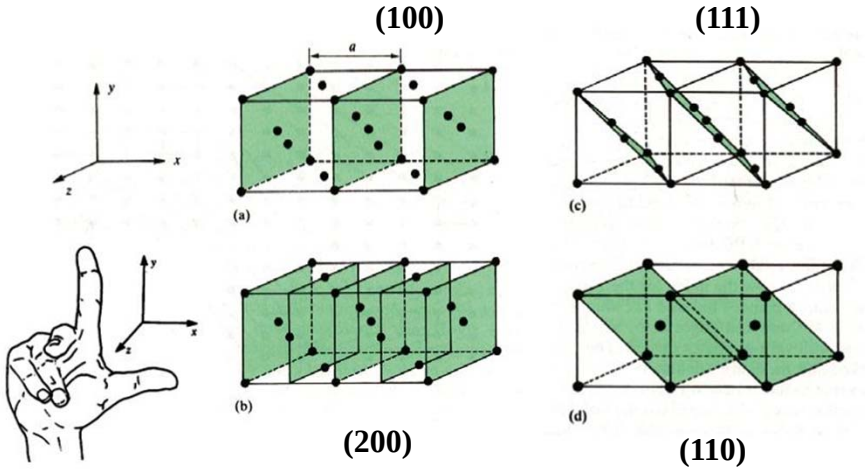
Miller Indices:

1. Find the intercepts on the axes in terms of the lattice constant a, b, c
2. Take the reciprocals of these numbers, reduce to the three integers having the same ratio

(hkl)

Set of symmetry-related planes: {hkl}

Examples of Miller indices

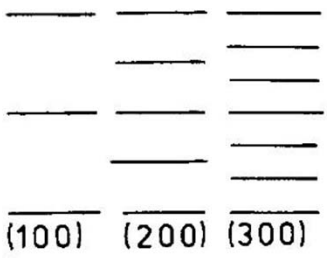


Families of planes

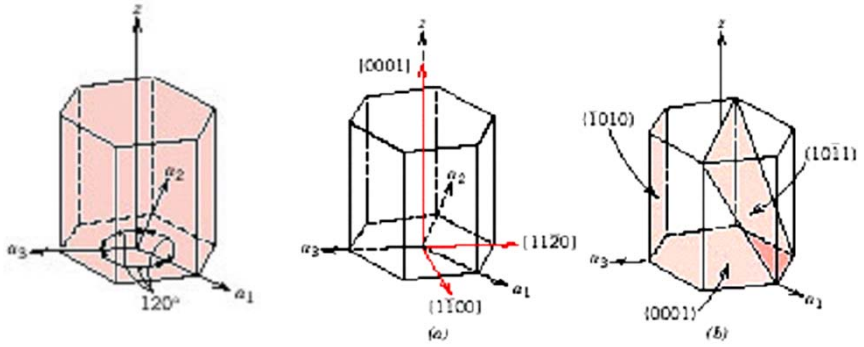
- Miller indices describe the orientation a spacing of a family of planes
  - The spacing between adjacent planes in a family is referred to as "d-spacing"

Three different families of planes

d-spacing between (300) planes is one third of the (100) spacing



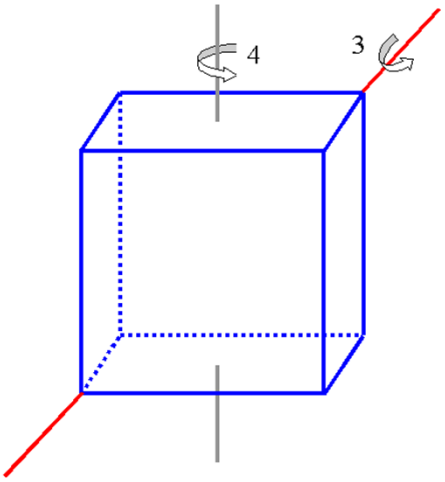
Crystallographic Directions And Planes



Miller-Bravais indices

[uvtw], (hkil)

t=-(u+v) *i=-(h+l)*



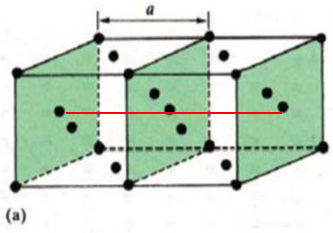
In cubic system,

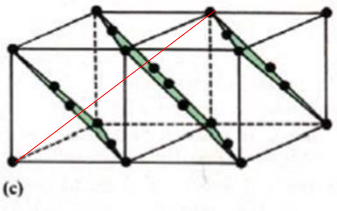
[hkl] direction perpendicular to (hkl) plane

Lattice spacing

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For cubic system





d-spacing formulae

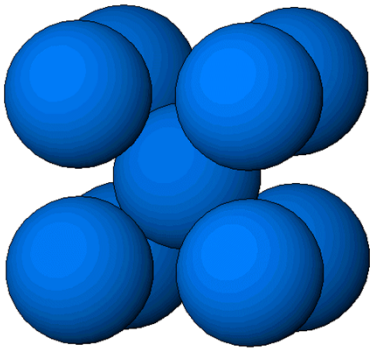
- For a unit cell with orthogonal axes
  - $(1 / d^2_{hkl}) = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$
- Hexagonal unit cells
  - $(1 / d^2_{hkl}) = (4/3)([h^2 + k^2 + hk]/ a^2) + (l^2/c^2)$

Powder diffraction

BRAGG LAW

$$2d(\sin\theta) = \lambda_o$$

where:
d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays



$$\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2}$$

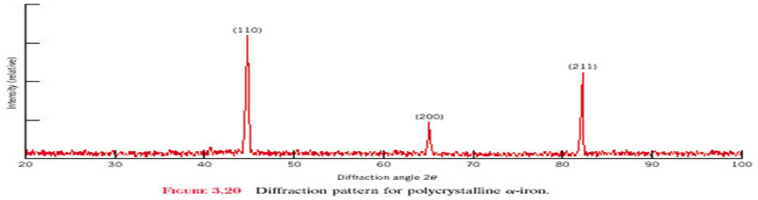
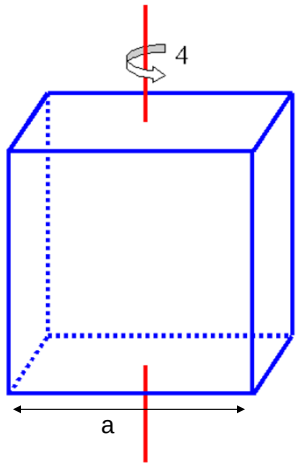


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

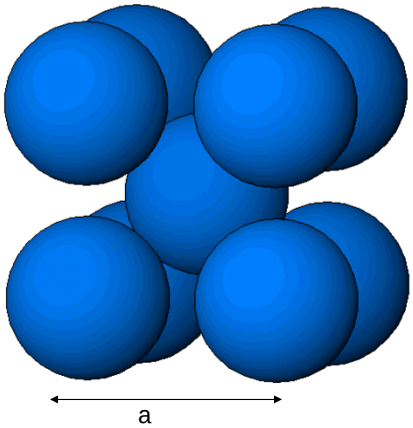
Unit cell symmetries - cubic



$$\% = \frac{\frac{4}{3}\pi(\frac{a}{2})^3}{a^3} = \frac{\pi}{6}$$

52.36%

BCC Lattice

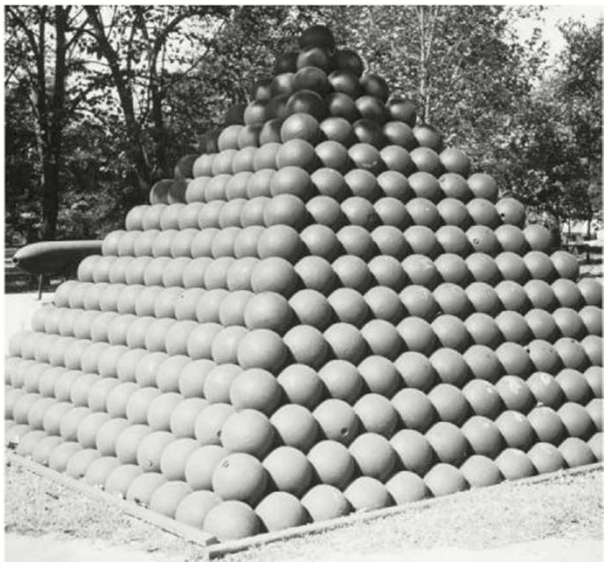


α-Iron is **body-centered cubic**

$$\% = 2 \times \frac{\frac{4}{3}\pi(\frac{\sqrt{3}a}{4})^3}{a^3} = \frac{3\sqrt{3}\pi}{24}$$

68%

What is the highest density for sphere packing?

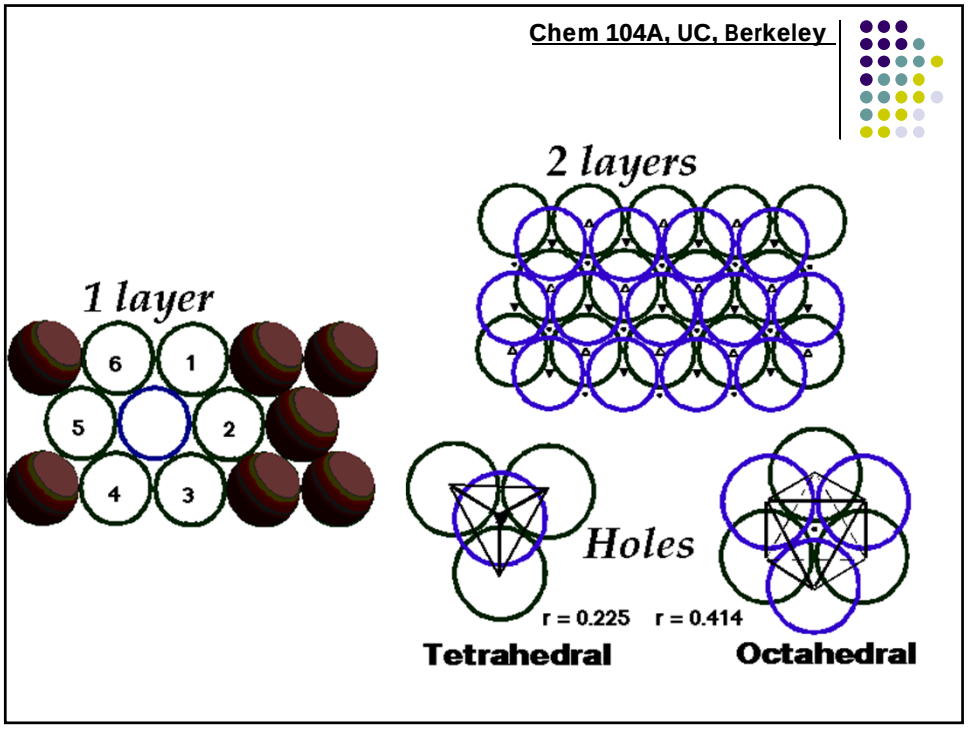


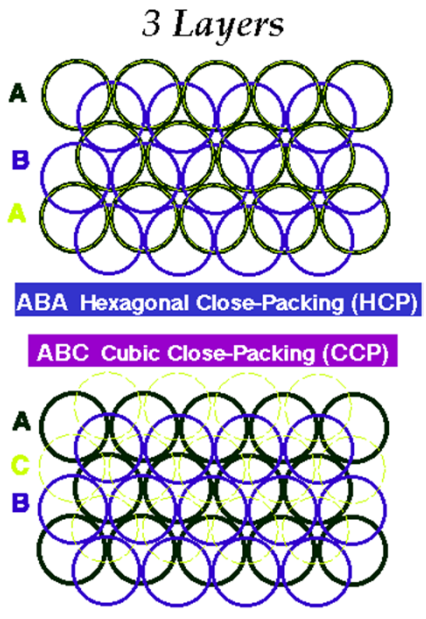
Kepler's Conjecture

In 1611 the German astronomer Johannes Kepler stated that no packing could be denser than that of the face-centred cubic (f.c.c.) lattice arrangement favored by grocers for stacking oranges, which fills about 0.7405 of the available space.

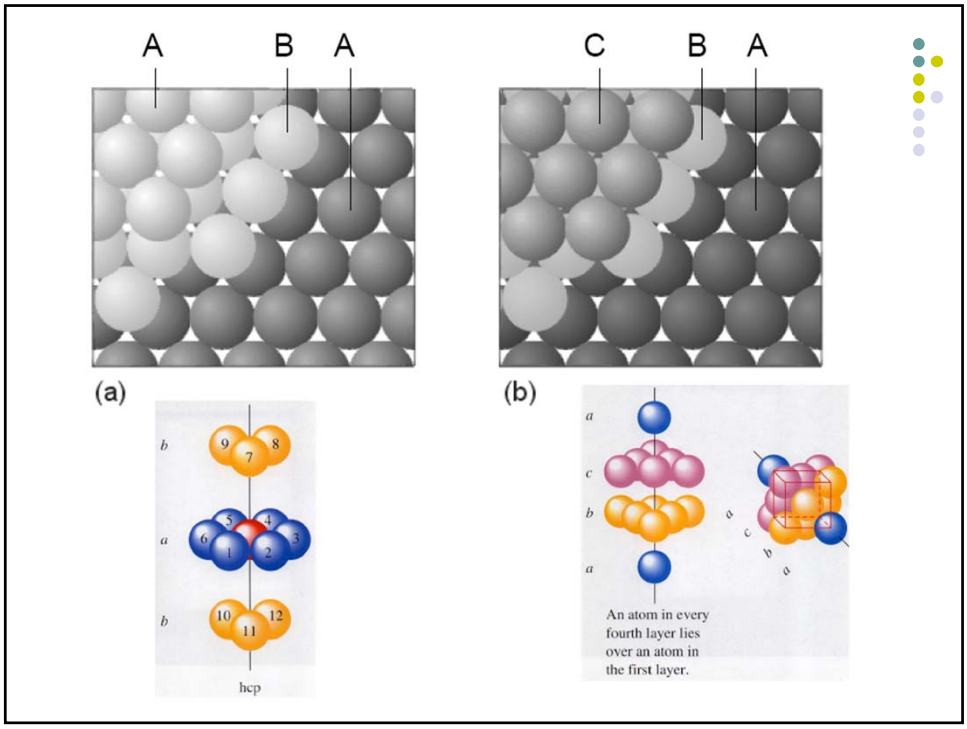
It took mathematicians some 400 years to prove him right.

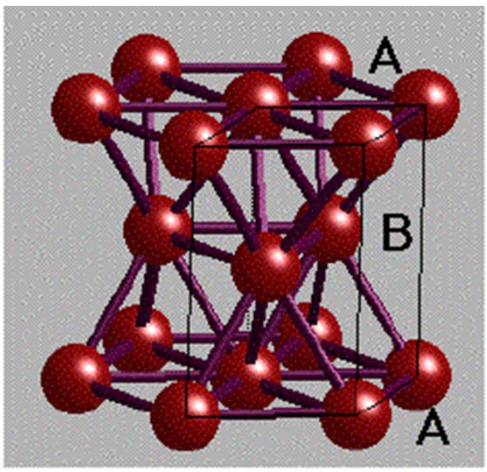
Hales, T. C. *Discrete Computational Geom.* 17, 1-51 (1997); 18, 135-149 (1997).





Close packing structures:
Cubic vs. Hexagonal



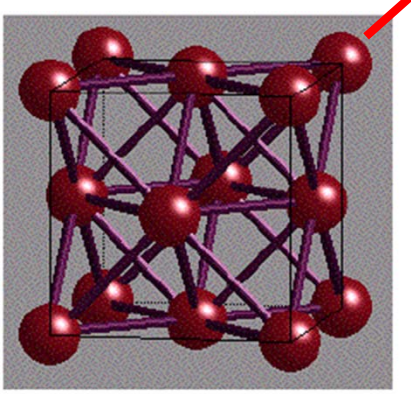


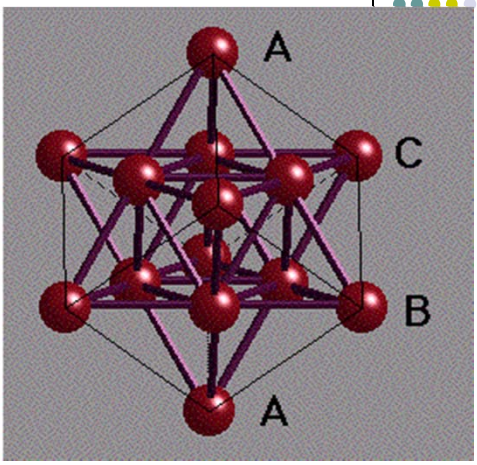
CN=12

(0,0,0)
(1/3,2/3,1/2)

HCP Hexagonal Close-Packing

CN=12





CCP Cubic Close-Packing

$$\% = \frac{4 \times 1.33\pi r^3}{(2\sqrt{2}r)^3} = 74.05\%$$

For BCC; 68.02%

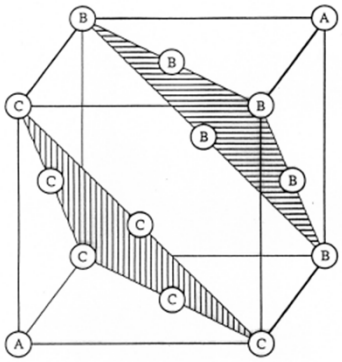
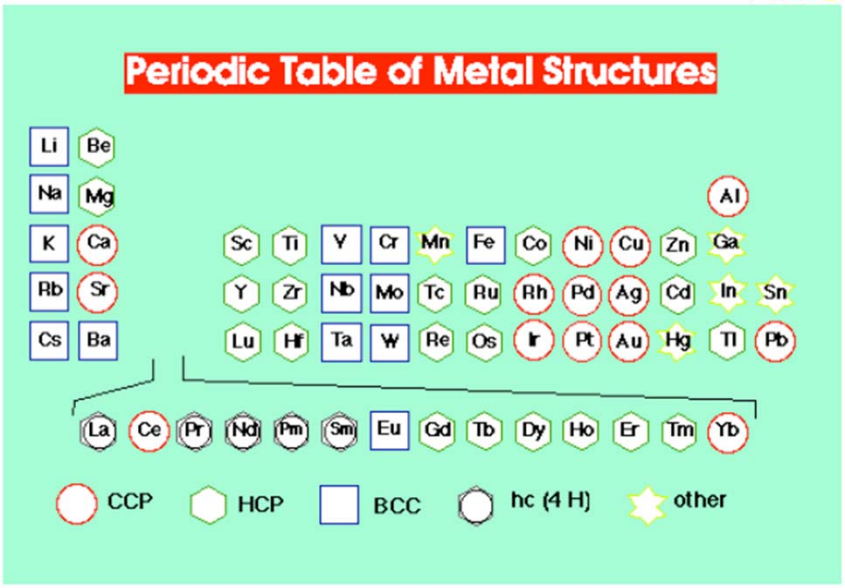


Figure 6.13 Cubic close-packed layers A, B, and C within a face-centered-cubic unit cell.

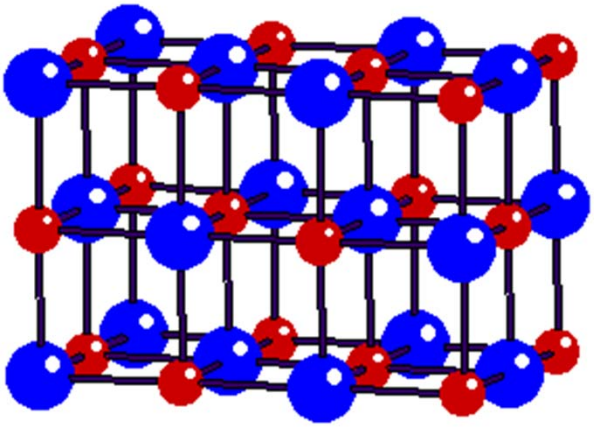


Rare Gas: Ne, He, Ar, Kr, Xe (**ccp; fcc**)

Metal: Cu, Ag, Au, Ni, Pd, Pt (**ccp**)

Mg, Zn, Cd, Ti (**hcp**)

Fe, Cr, Mo (**bcc**)



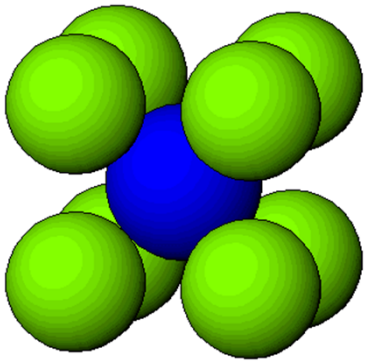
Simple Cubic Lattice

Caesium Chloride (CsCl) is **primitive cubic**

Different atoms at corners and body center. NOT body centered, therefore.

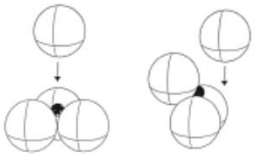
Lattice type P

Also CuZn, CsBr, LiAg

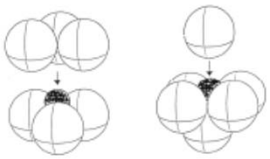


Lattice Holes

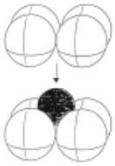
Tetrahedral (T_d)



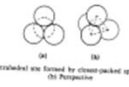
Octahedral (O_h)



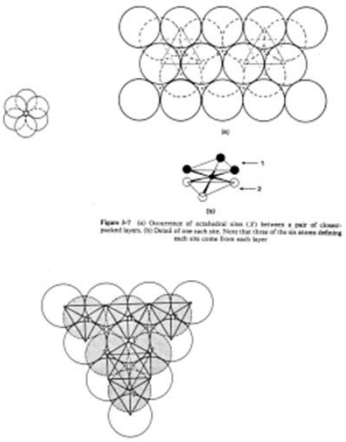
Cubic



tetrahedral holes:

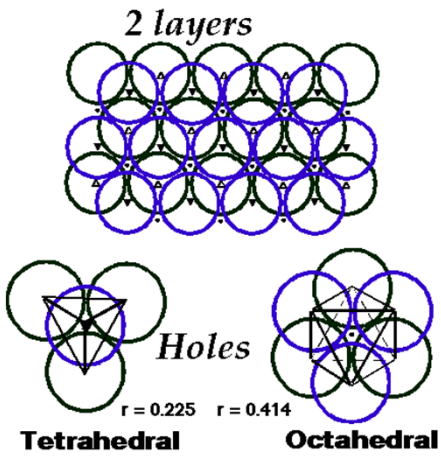


octahedral holes:



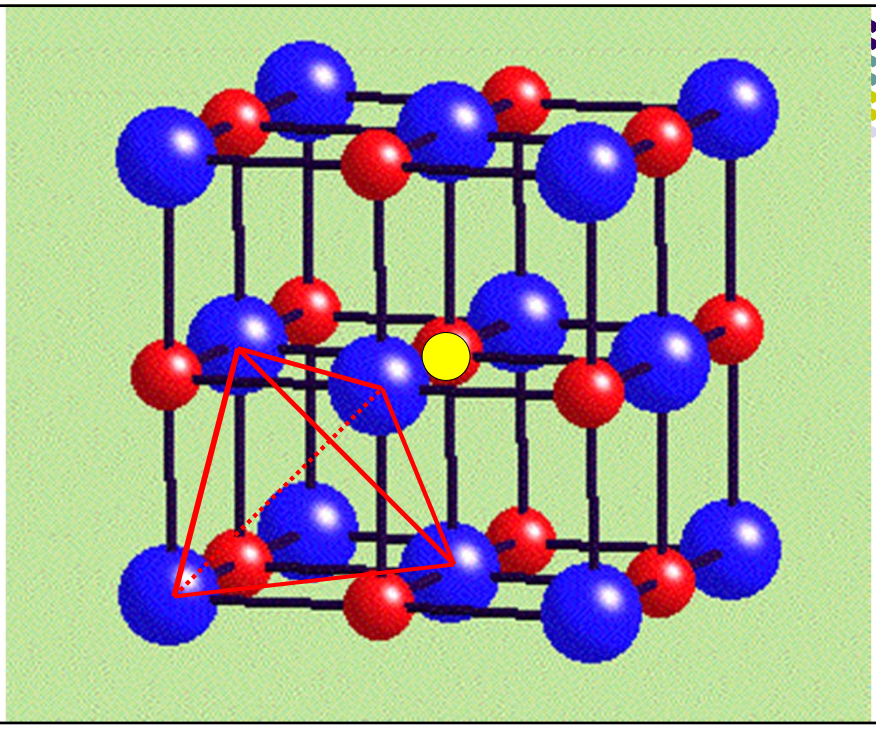
Ionic structures:

Can be considered as close packing of large anions with Cation filling in the interstitial sites.

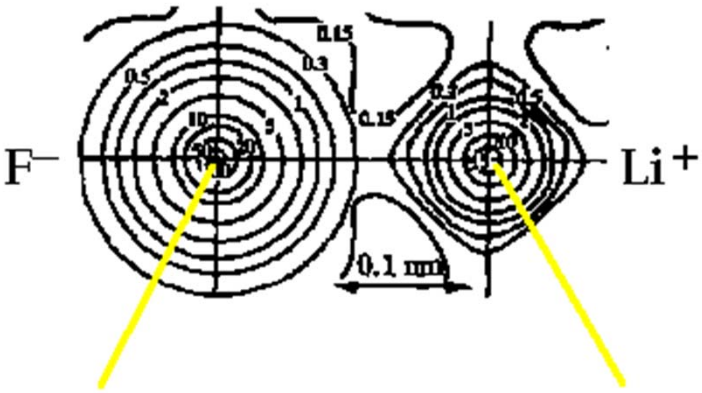


For every anion, there are

1 Octahedral site
2 tetrahedral sites.



What's the Numerical Value of a specific Ionic Radius?

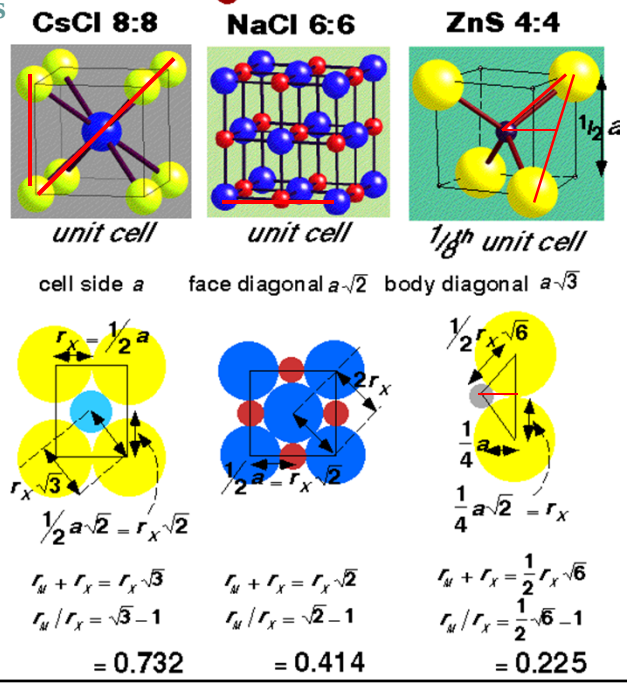


High resolution X-Ray Diffraction

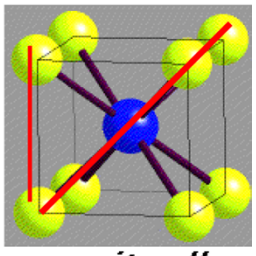
Limiting Radius Ratios

Radius Ratio Rule

Red line: Contacting

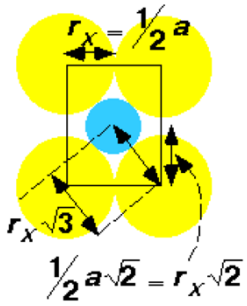


CsCl 8:8



unit cell

cell side a



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

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

$$= 0.732$$

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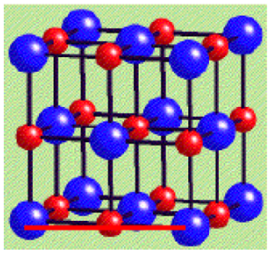
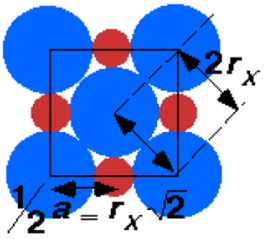
NaCl 6:6



unit cell

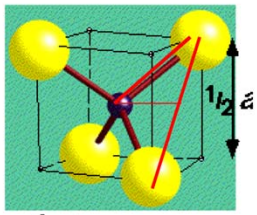
face diagonal $a\sqrt{2}$

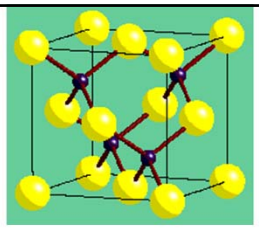


$$r_M + r_X = r_X\sqrt{2}$$

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

$$= 0.414$$

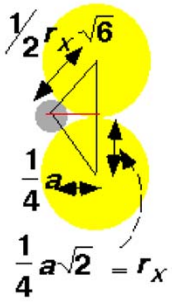




Zinc Blende
ZnS

The diamond network with alternate Zn & S atoms

body diagonal $a\sqrt{3}$



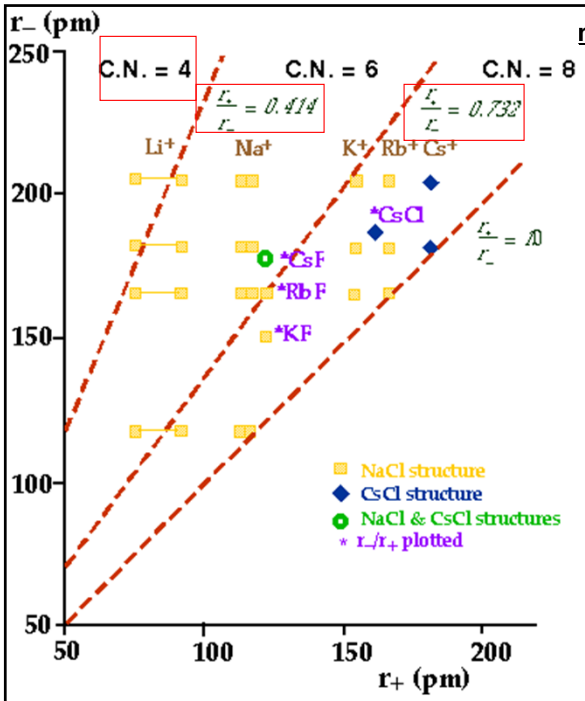
$$r_M + r_X = \frac{1}{2} r_X \sqrt{6}$$

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

$$= 0.225$$

Limiting Radius Ratios - anions in the coordination polyhedron of cation are in contact with the cation and with each other

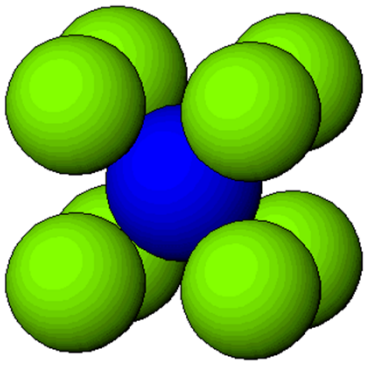
Radius Ratio	Coordination no.	Binary (AB) Structure-type
$r_+/r_- = 1$	12	none known
$1 > r_+/r_- > 0.732$	8	CsCl
$0.732 > r_+/r_- > 0.414$	6	NaCl
$0.414 > r_+/r_- > 0.225$	4	ZnS



Applicable to ionic solid
Not covalent solid

Many exceptions!

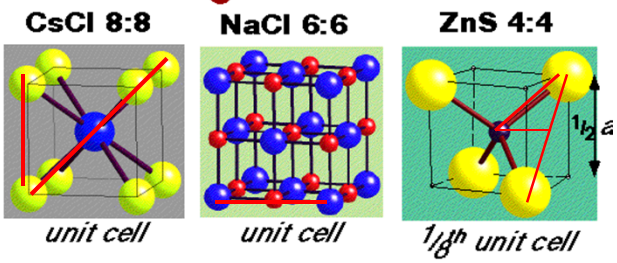
ZnS:
r+/r-=0.88/1.70=0.5
Expect CN=6



Cs (0,0,0)
Cl (½, ½, ½)

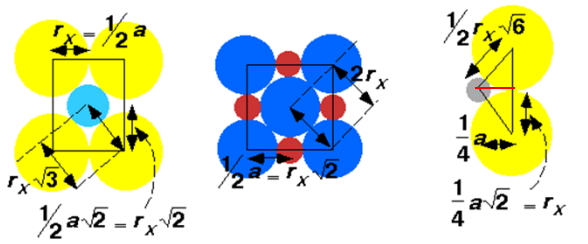
Limiting Radius Ratios

Radius Ratio Rule



Red line: Contacting

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



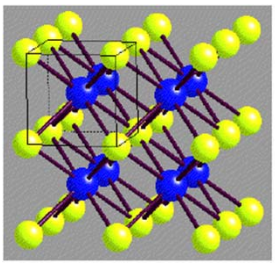
$r_M + r_X = r_X\sqrt{3}$ $r_M / r_X = \sqrt{3} - 1$ = 0.732

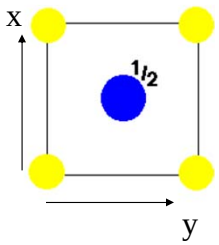
$r_M + r_X = r_X\sqrt{2}$ $r_M / r_X = \sqrt{2} - 1$ = 0.414

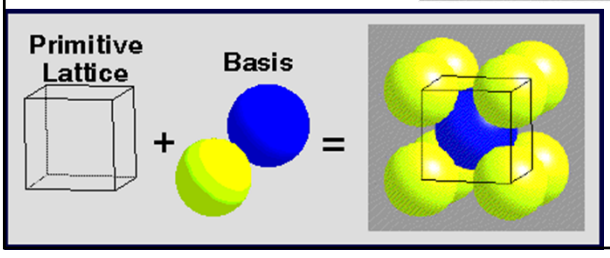
$r_M + r_X = \frac{1}{2} r_X\sqrt{6}$ $r_M / r_X = \frac{1}{2}\sqrt{6} - 1$ = 0.225

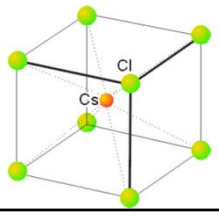
Chem 104A, UC, Berkeley

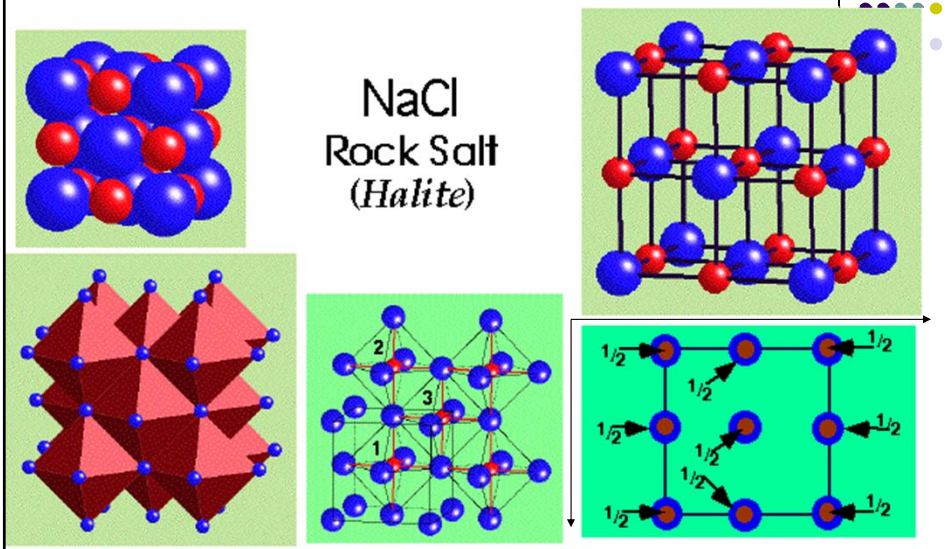
- ***Motif*: Cl at (0,0,0); Cs at ($^1/_2$,$^1/_2$,$^1/_2$)**
- **1 CsCl in unit cell**
- ***Coordination*: 8:8 (cubic)**
- **Adoption by chlorides, bromides and iodides of larger cations,**
- ***e.g.* Cs^+, Tl^+, NH_4^+**





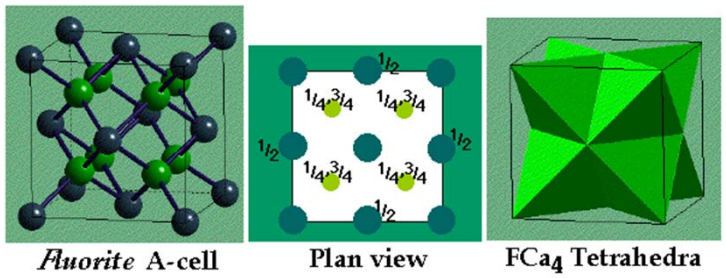




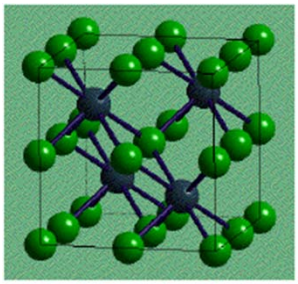


NaCl; ccp, O sites: 100%

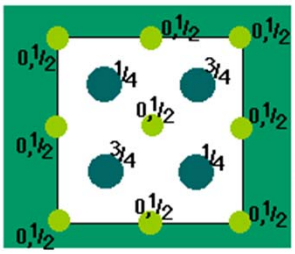
CaF_2



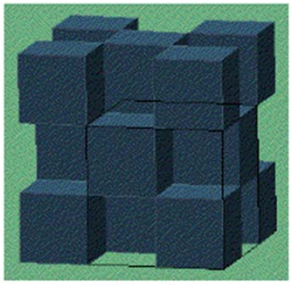
- **CCP Ca^{2+} with F^- in all Tetrahedral holes**
- ***Lattice*: fcc**
- ***Motif*: Ca^{2+} at (0,0,0); $2F^-$ at ($^1/_4$,$^1/_4$,$^1/_4$) & ($^3/_4$,$^3/_4$,$^3/_4$)**
- **4 CaF_2 in unit cell**
- ***Coordination*: Ca^{2+} 8 (cubic) : F^- 4 (tetrahedral)**
- **In the related Anti-Fluorite structure Cation and Anion positions are reversed**



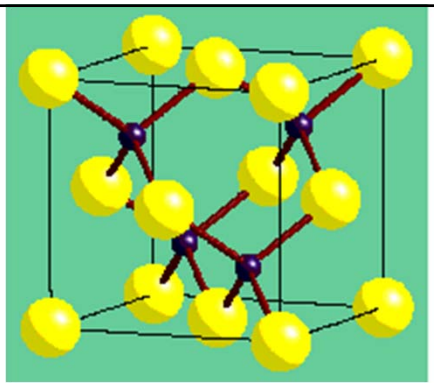
Fluorite B-cell



Plan view

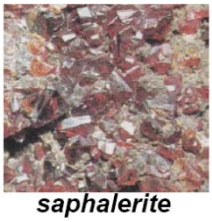


CaF_8 Cubes

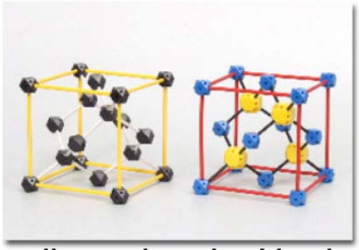


Zinc Blende
ZnS

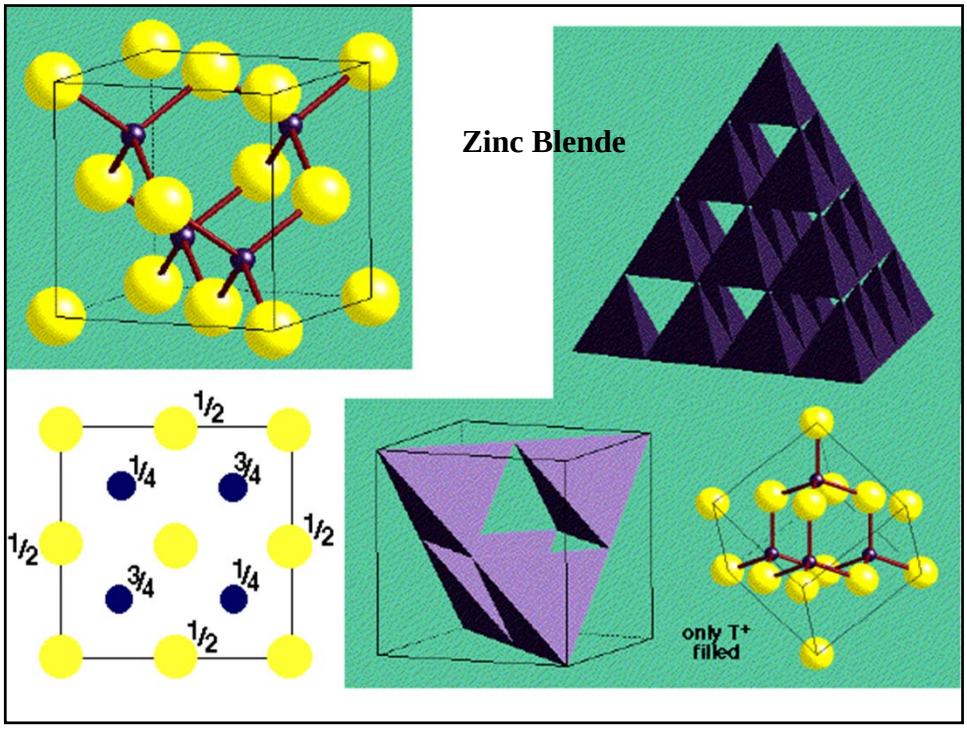
The diamond network with alternate Zn & S atoms



saphalerite

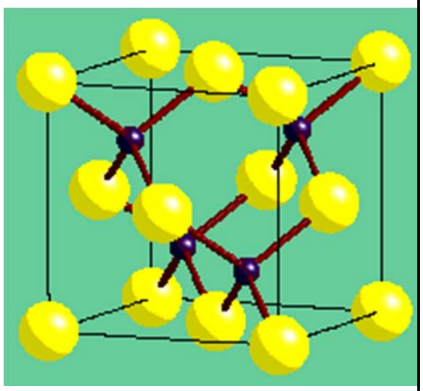


diamond *zinc blende*



Zinc Blende: ZnS

- CCP S^{2-} with Zn^{2+} in half Tetrahedral holes (only T+ {or T-} filled)
- ***Lattice***: fcc
- 4 ZnS in unit cell
- ***Motif***: S at (0,0,0); Zn at ($^1/_4$,$^1/_4$,$^1/_4$)
- ***Coordination***: 4:4 (tetrahedral)



NaCl

- Very common (inc. 'ionics', 'covalents' & 'intermetallics')
- Most alkali halides (CsCl, CsBr, CsI excepted)
- Most oxides / chalcogenides of alkaline earths
- Many nitrides, carbides, hydrides (e.g. ZrN, TiC, NaH)

CaF_2 (*Fluorite*)

- Fluorides of large divalent cations, chlorides of Sr, Ba
- Oxides of large quadrivalent cations (Zr, Hf, Ce, Th, U)

Na_2O (*Anti-Fluorite*)

- Oxides /chalcogenides of alkali metals

ZnS (*Zinc Blende/Sphalerite*)

- Formed from Polarizing Cations (Cu^+, Ag^+, Cd^{2+}, Ga^{3+}...) and Polarizable Anions (I^-, S^{2-}, P^{3-}, ...);
- *e.g.* Cu(F,Cl,Br,I), AgI, Zn(S,Se,Te), Ga(P,As), Hg(S,Se,Te)

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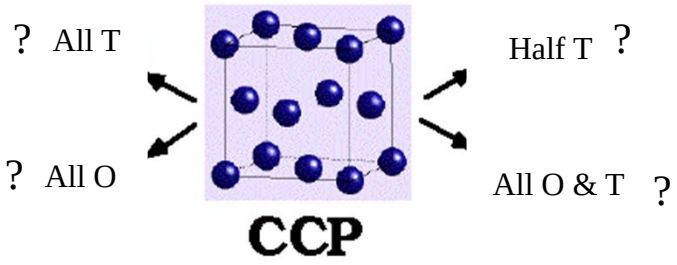
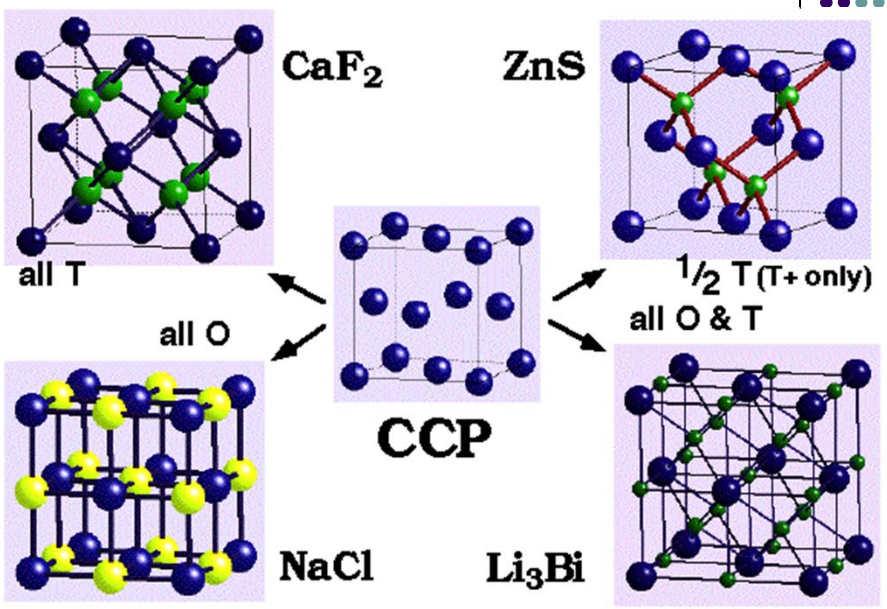
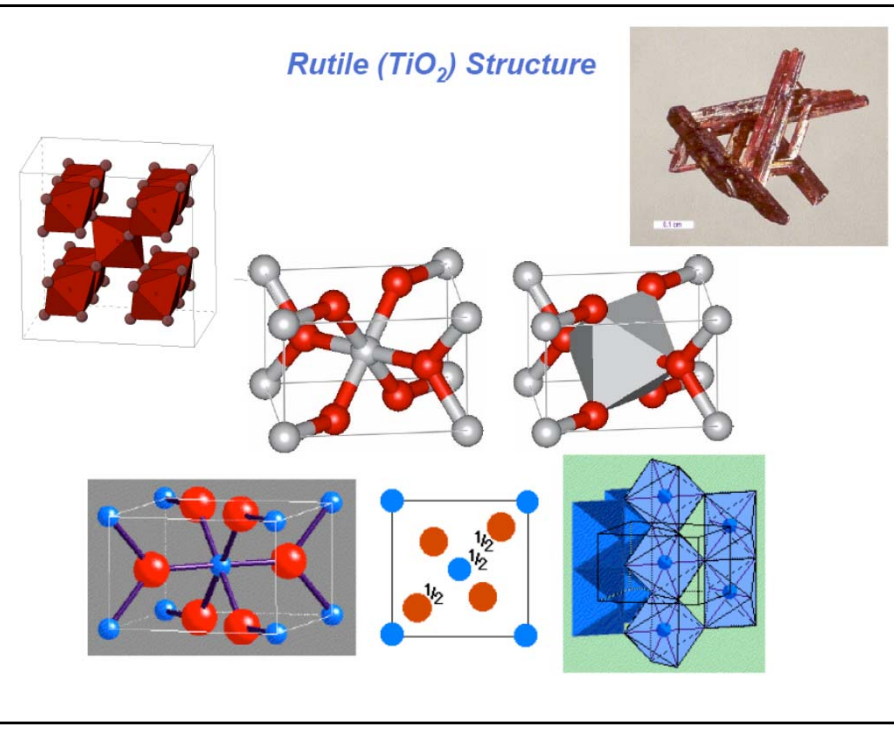
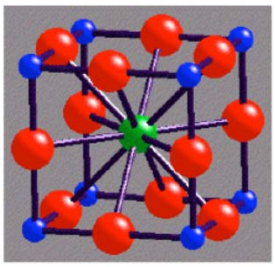
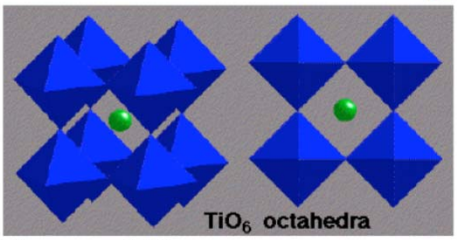



CaF2
ZnS
all T
1/2 T (T+ only)
all O
all O & T
CCP
NaCl
Li3Bi


Rutile (TiO2) Structure
1/2
1/2
1/2

Perovskite ($CaTiO_3$) Structure

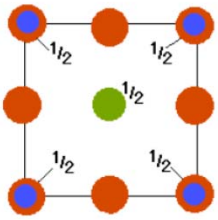


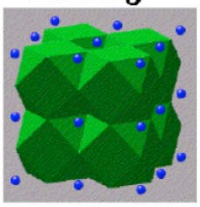


A-Cell

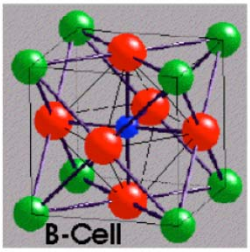
Perovskite
$CaTiO_3$

Ca Ti O

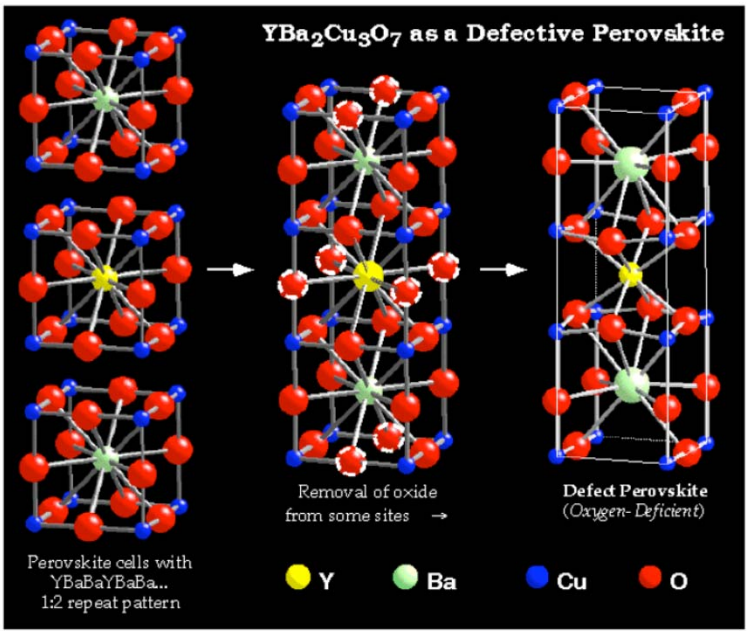




CaO_{12} cuboctahedra



Superconductor Structure ($YBa_2Cu_3O_{7-x}$)



Superconductor Structure ($YBa_2Cu_3O_{7-x}$) -Polyhedral Representation