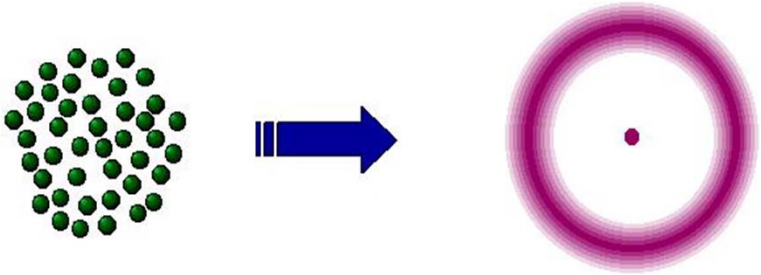
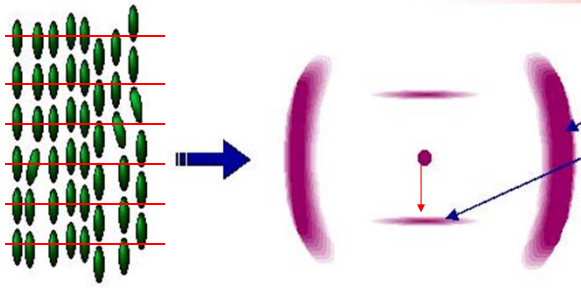
Diffraction from amorphous solids

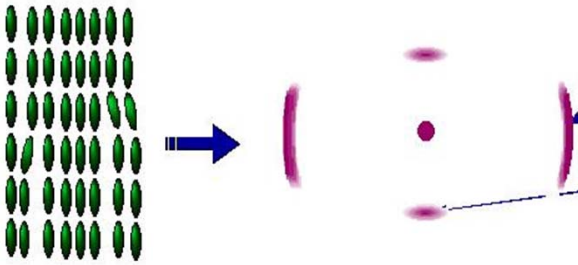
- **No long-range order**
  - Only significant order is nearest neighbour spacing
  - Diffraction pattern forms diffuse halo
  - Typical of colloidal suspensions and globular clusters
- **Diffraction is large or small angle depending on the size of the "particle"**



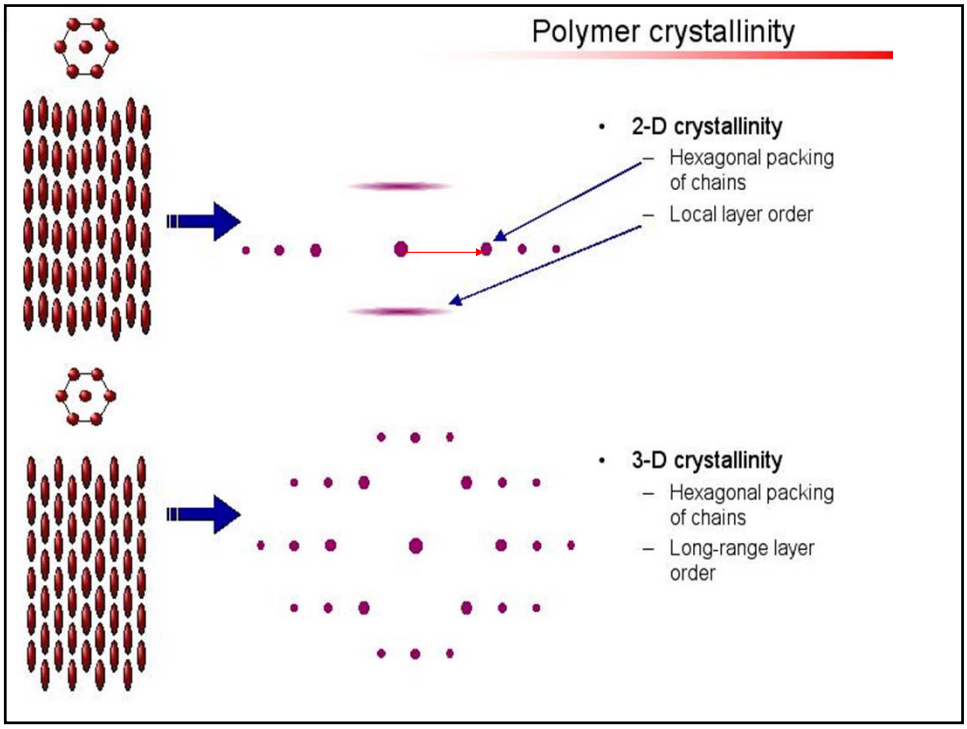
Polymer order

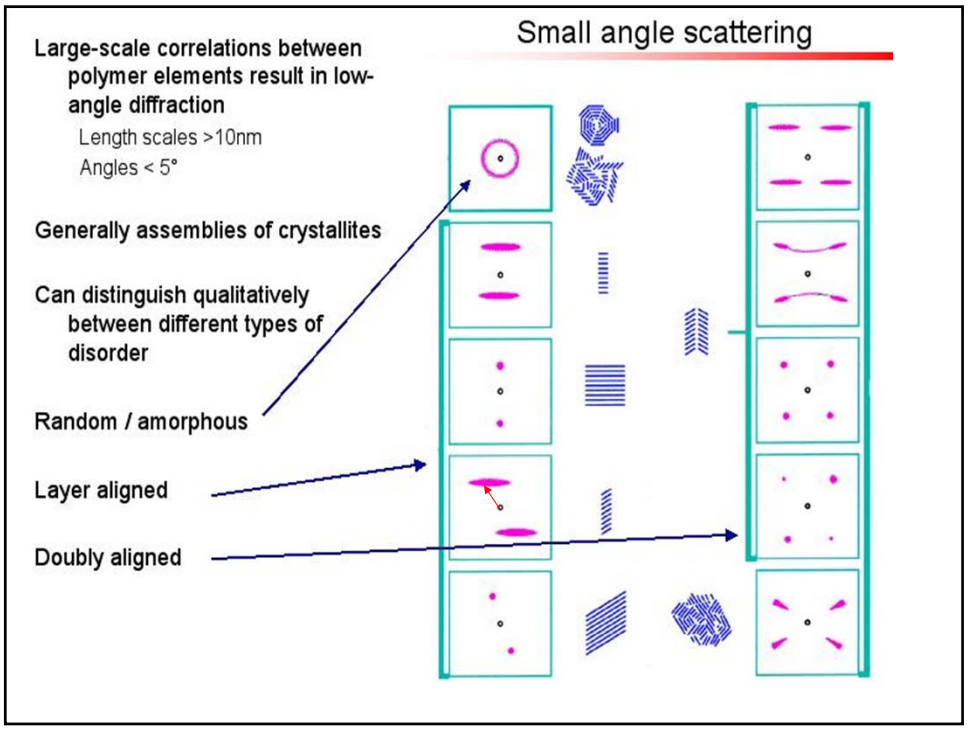


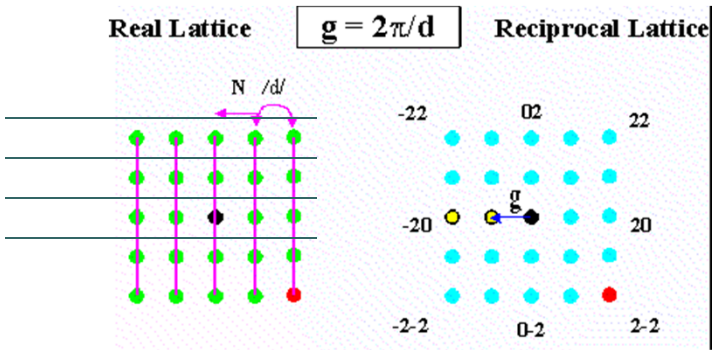
- **Oriented nematic**
  - Short-range inter-chain order
  - Local layering



- **Oriented smectic-A**
  - Short-range inter-chain order
  - Layering extended normal to chains
    - Diffraction spots


Polymer crystallinity
• 2-D crystallinity
– Hexagonal packing of chains
– Local layer order
• 3-D crystallinity
– Hexagonal packing of chains
– Long-range layer order


Small angle scattering
Large-scale correlations between polymer elements result in low-angle diffraction
Length scales >10nm
Angles < 5°
Generally assemblies of crystallites
Can distinguish qualitatively between different types of disorder
Random / amorphous
Layer aligned
Doubly aligned



Theorem:

For any family of lattice planes separated by distance d, there are reciprocal lattice vectors perpendicular to the planes, the shortest being 2π/d.

Orientation of plane is determined by a normal vector
The miller indices of a lattice plane are the coordination at the reciprocal lattice vector normal to the plane.

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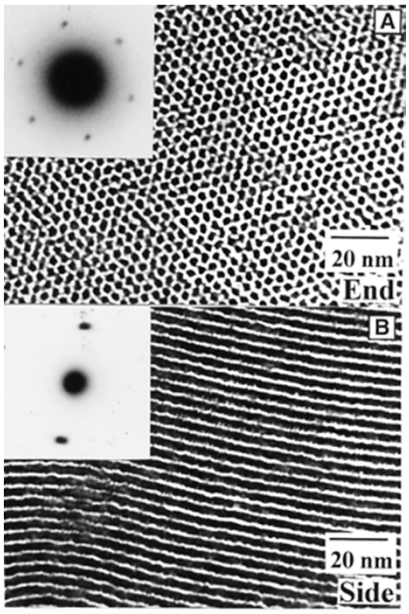
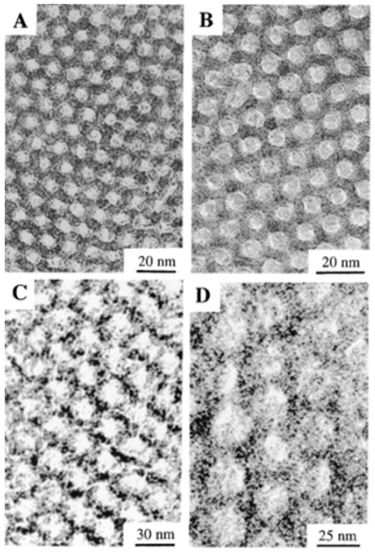
Small Angle X-ray Diffraction



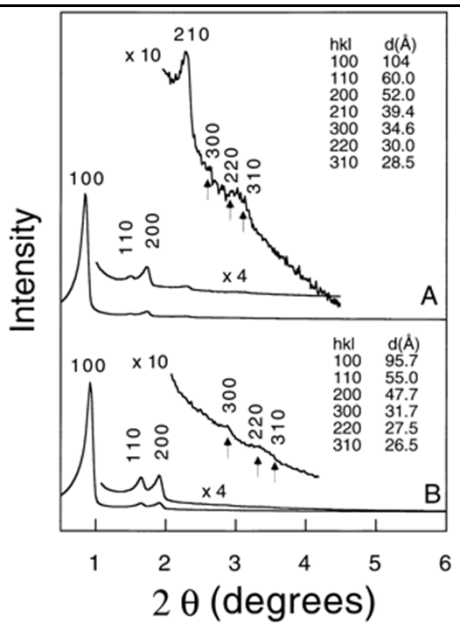
Direct Visualization of Individual Cylindrical and Spherical Supramolecular Dendrimers
Science 17 October 1997; 278: 449-452

Small Angle X-ray Diffraction



Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores Science, Vol 279, Issue 5350, 548-552 , 23 January 1998

Chem 253, UC, Berkeley



Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores Science, Vol 279, Issue 5350, 548-552 , 23 January 1998

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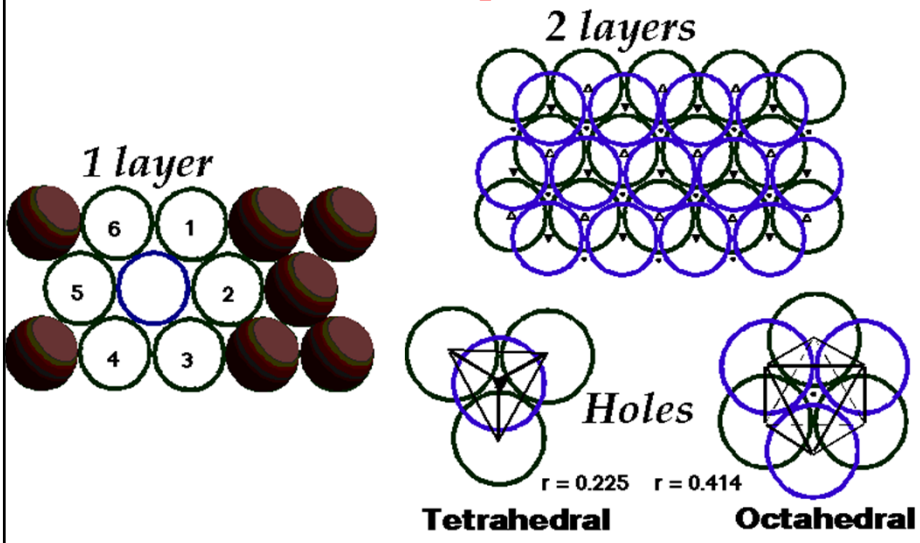
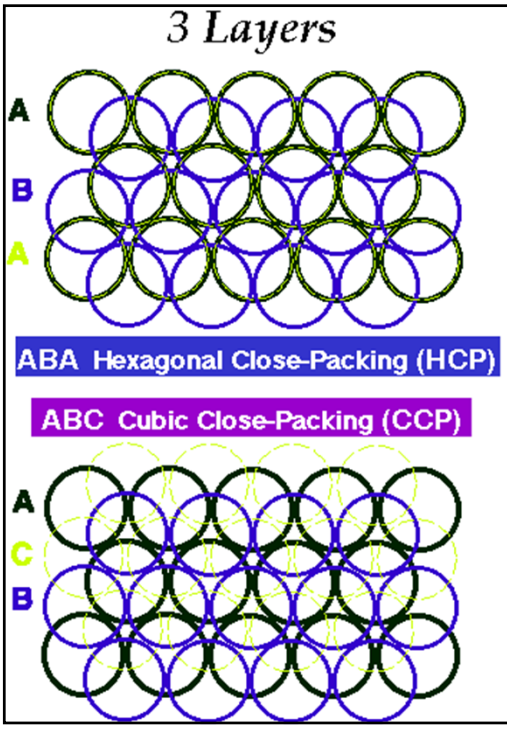
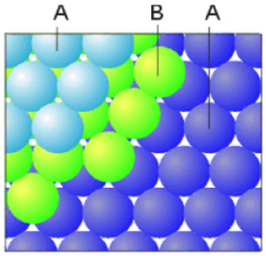
Descriptive Crystal Chemistry
West Chapter 7,8



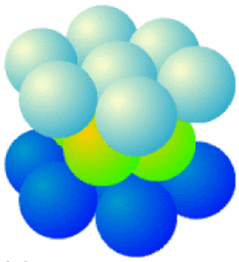


Close packing structures:
Cubic vs. Hexagonal

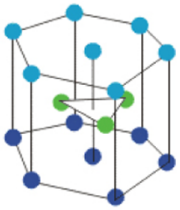
Close Packing of Spheres



(a)

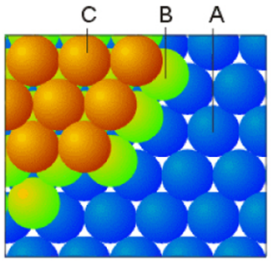


(a) **Hexagonal Close Packing**

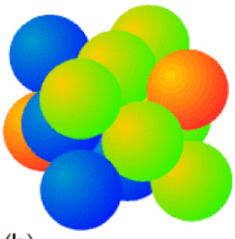


hcp

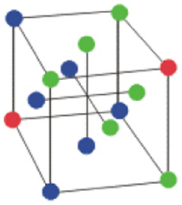
Mg, Be, Sc, Ti…



(b)



(b) **Cubic Close Packing**



ccp/fcc

Cu, Ca, Sr, Ag, Au, …

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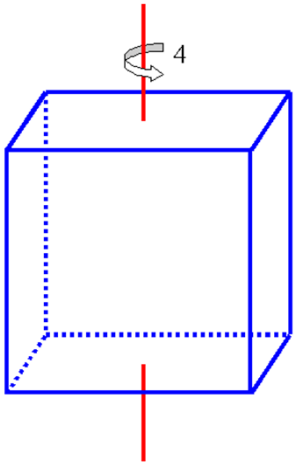
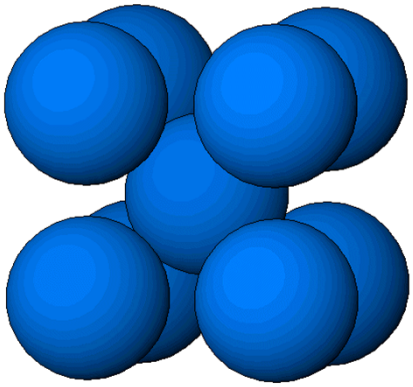
Unit cell symmetries - cubic



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

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%

Close Packing of Spheres

The most efficient way to fill space with spheres

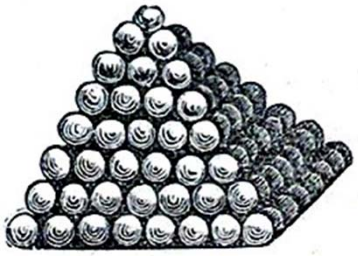
Is there another way of packing spheres that is more space-efficient?

In 1611 Kepler asserted that there was no way of packing equivalent spheres at a greater density than that of a face-centred cubic arrangement. This is now known as the **Kepler Conjecture**.

This assertion has long remained without rigorous proof. In 1998 Hales announced a computer-based solution. This proof is contained in over 250 manuscript pages and relies on over 3 gigabytes of computer files

http://www.math.pitt.edu/

The square pile is formed, as in the annexed figure.



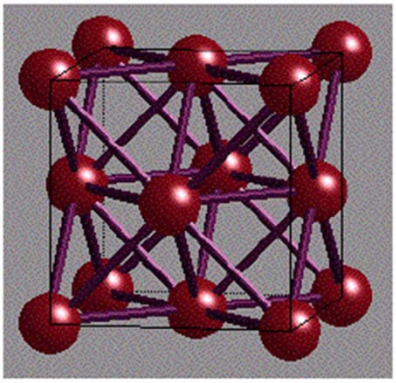
The number of balls in the top layer is 1^2, in the next layer 2^2, in the next, 3^2, and so on. To find the number of balls in a pile of n layers, we have the series,

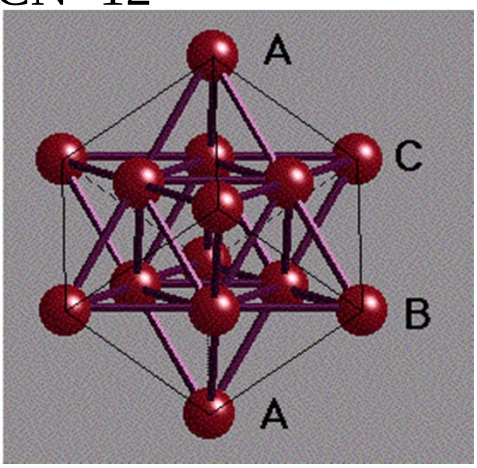
	1	4	9	16	25	36,	&c.
1st order of diff.,	3	5	7	9	11		&c.
2d " "		2	2	2	2		&c.
3d " "			0	0	0		&c.

Hence,

$a=1,\ d_1=3,\ d_2=2,\ d_3=0,\ d_4=0,$ &c.

CN=12

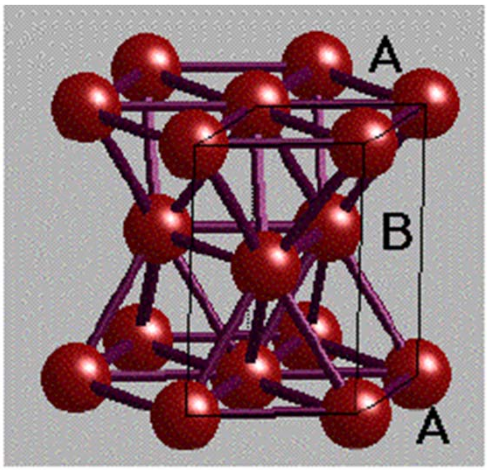




CCP Cubic Close-Packing

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

For BCC; 68.02%



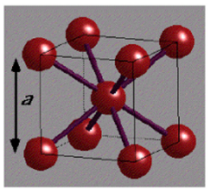
CN=12

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

HCP **Hexagonal Close-Packing**

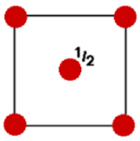
Close Packing of Spheres

Alternatives



Body-Centred Cubic

BCC



$4r = \sqrt{3}a$

$a = b = c$, $\alpha = \beta = \gamma = 90°$

2 atoms in the unit cell:

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

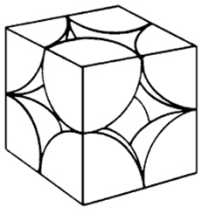
Packing efficiency $R_{fill} = V_{atoms}/V_{cell}$

With Z = 2, $V_{cell} = a^3$, $3a^2 = (4r)^2$

$R_{fill} = 0.68$

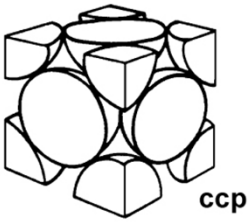
Close Packing of Spheres

Comparison of Packing Efficiencies



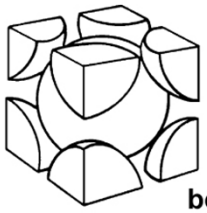
Primitive Cubic [α-Po]
Coordination Number 6
52% Packing Efficiency

V_{atoms}/V_{cell} = 0.52, since
$V_{cell} = a^3$ and
$V_{atoms} = Z\ 4/3\ \pi\ r^3$
with $a = 2r$ and $Z = 1$



ccp

Close-Packed (ccp or hcp)
Coordination Number 12
74% Packing Efficiency



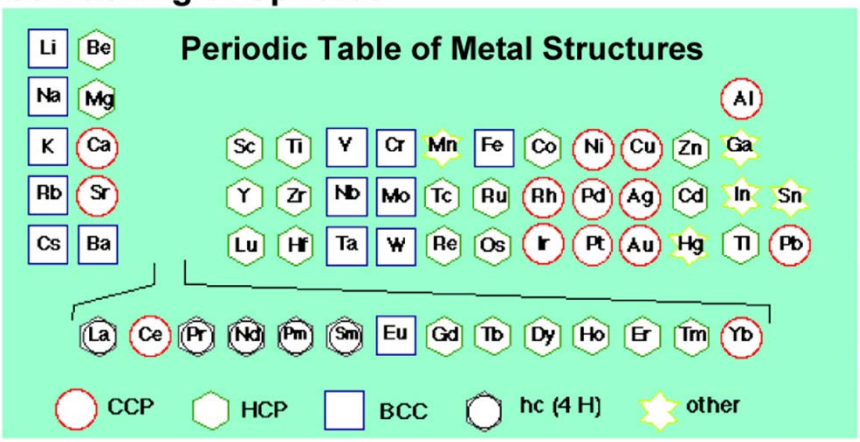
bcc

Body-Centered Cubic [W]
Coordination Number 8
68% Packing Efficiency

hcp

(increased pressure favors higher packing efficiency)

Close Packing of Spheres



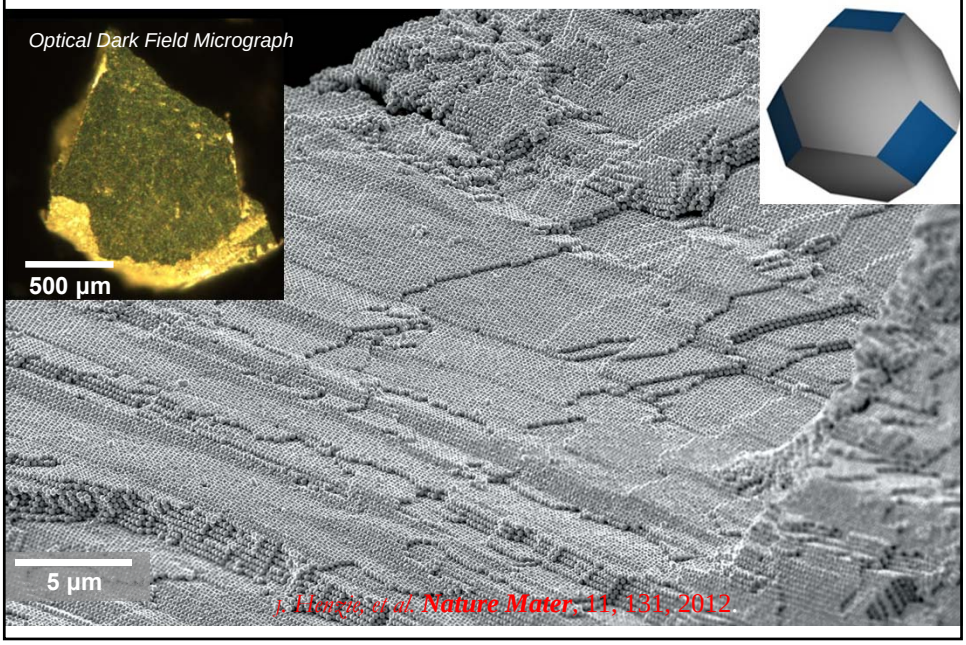
Rare Gas: Ne, He, Ar, Kr, Xe (**ccp; fcc**)

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

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

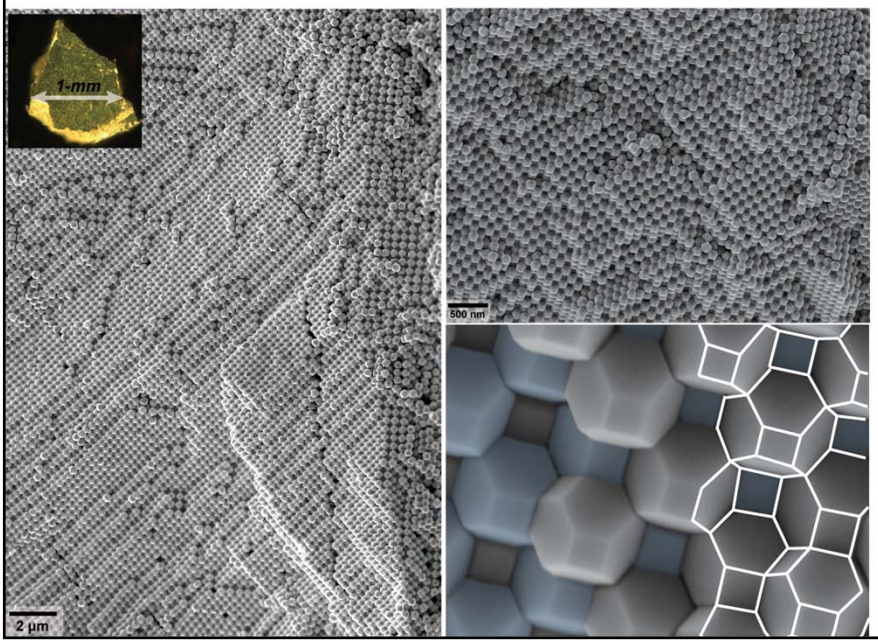
Fe, Cr, Mo (**bcc**)

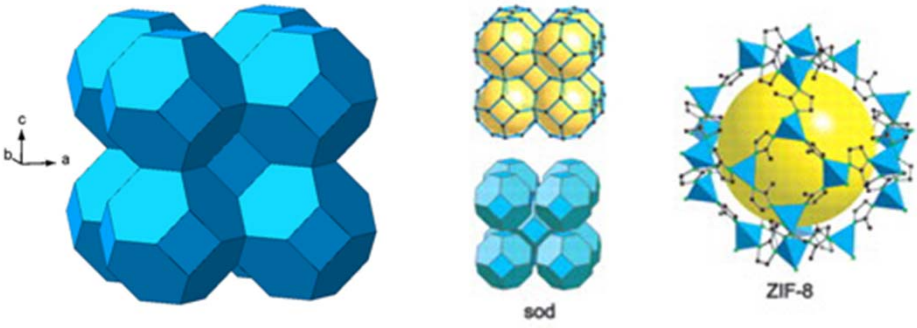
Packing of Truncated octahedron



J. Huang, et al. *Nature Mater.* 11, 131, 2012.

Truncated octahedron





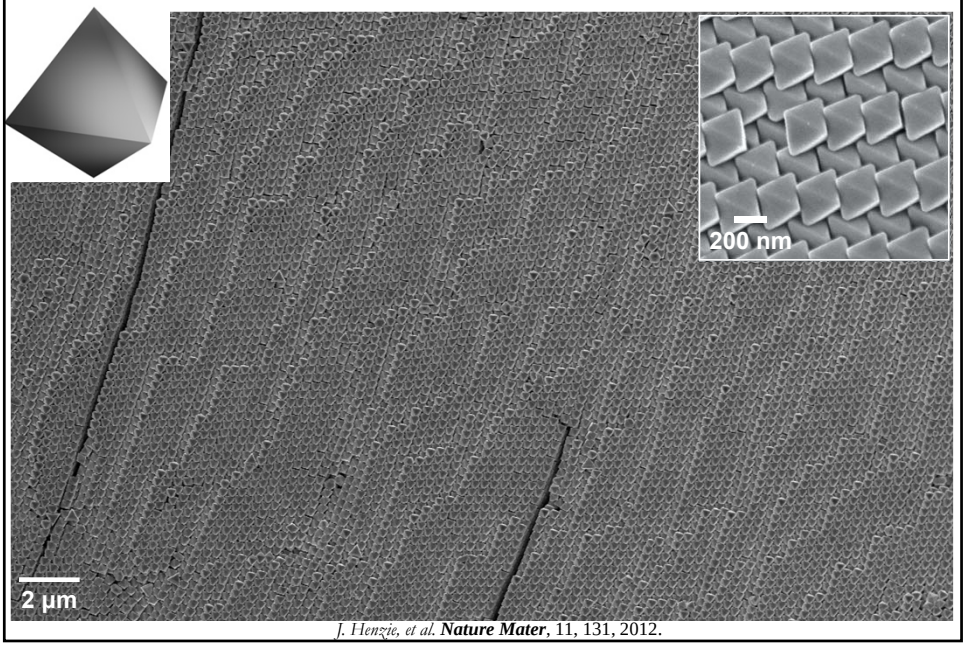
Yaghi, Science 2008

Densest lattice packing of an octahedron

The density of a densest lattice packing of an octahedron was already calculated by Minkowski in 1904. In 1948 Whitworth generalized Minkowski's result to a family of truncated cubes. The density of a densest lattice packing is equal to 18/19 = 0.9473...,

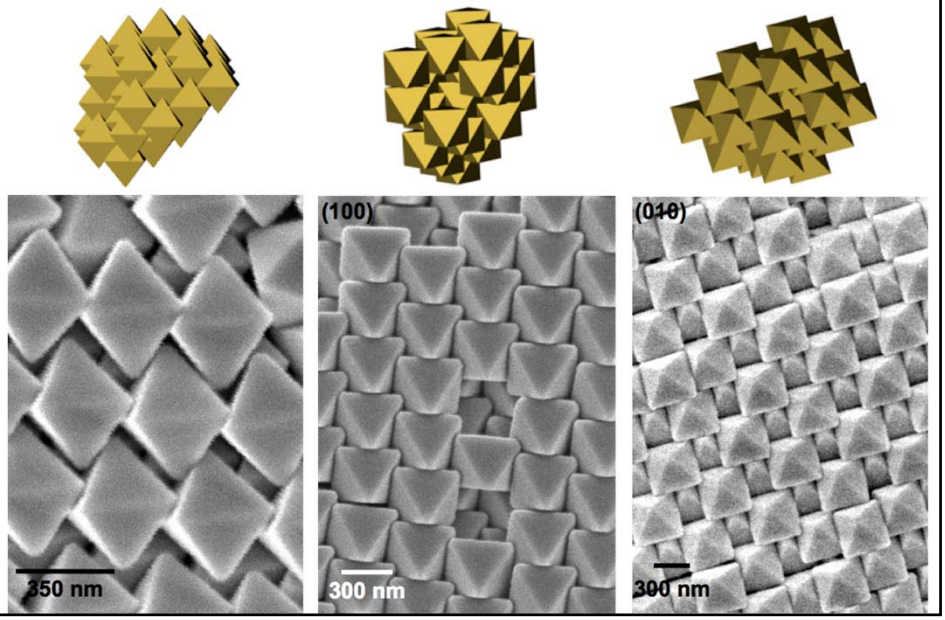
Hermann Minkowski: *Dichteste gitterförmige Lagerung kongruenter Körper*, Nachr. K. Ges. Wiss. Göttingen, Math.-Phys. KL (1904) (1904), 311 - 355

Octahedra



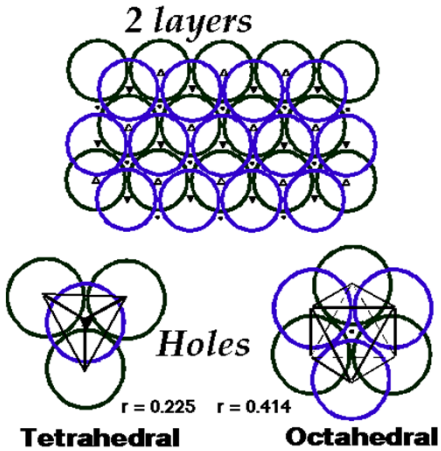
J. Henzie, et al. **Nature Mater**, 11, 131, 2012.

Close Packing Octahedra: Minkowski Lattice



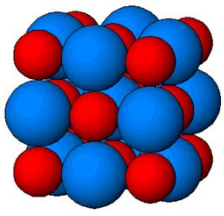
Ionic structures

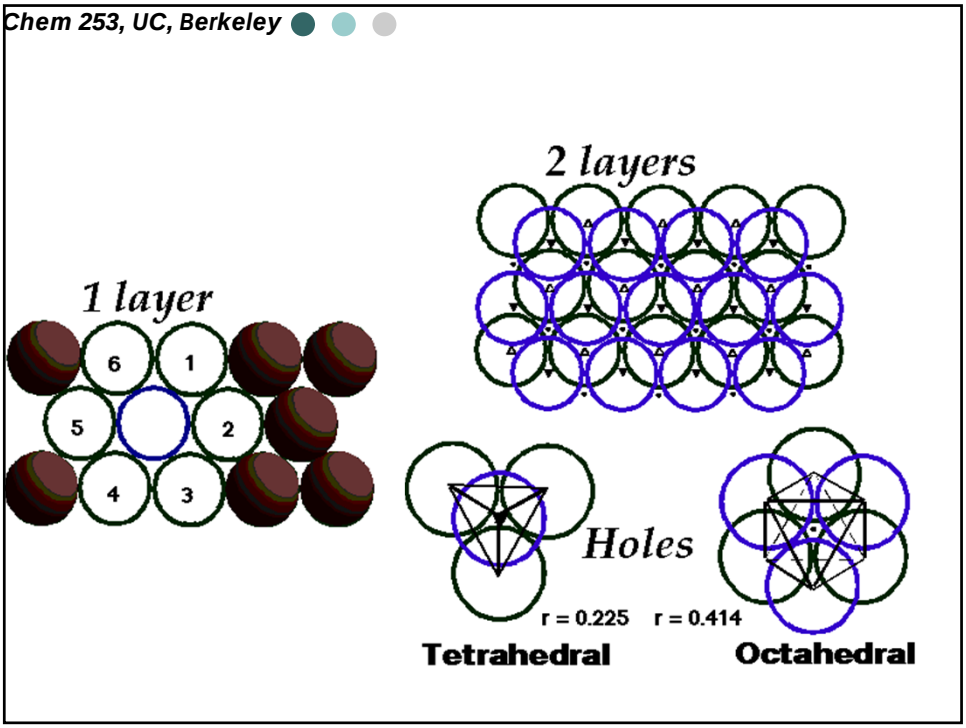
Can be considered as close packing of large anions with Cation filling in the interstitial sites.

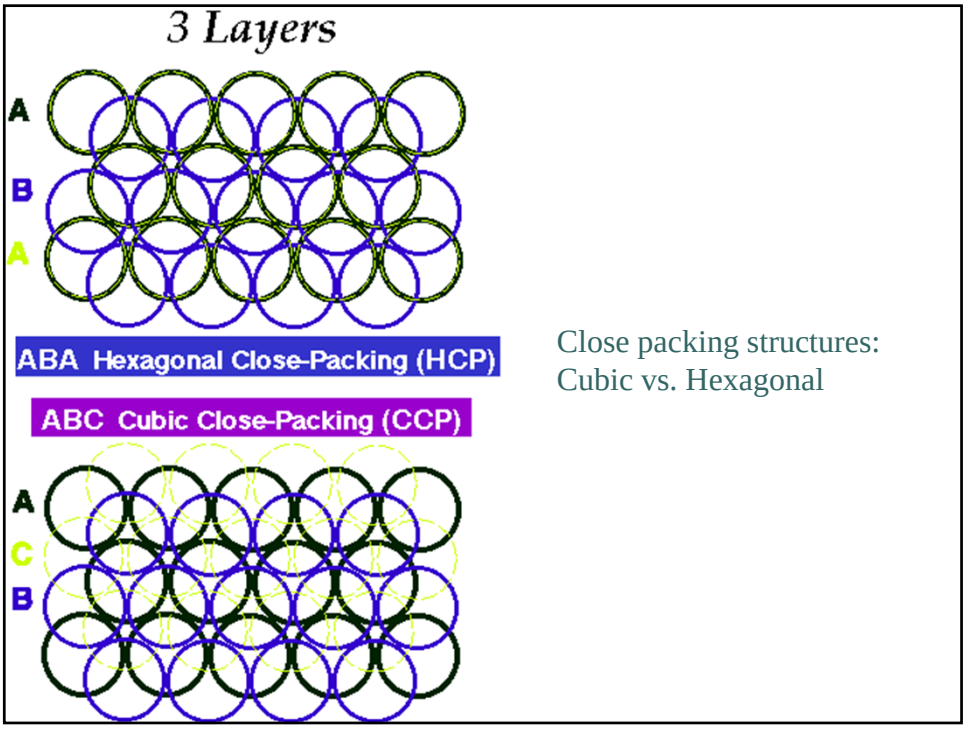


For every anion, there are

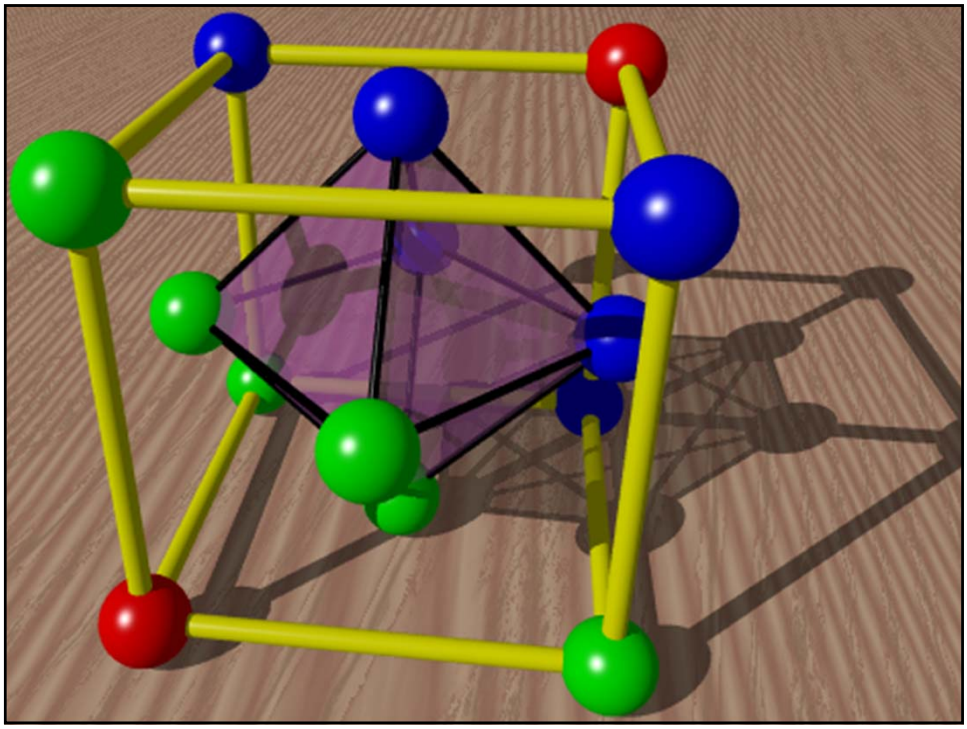
1 Octahedral site
2 tetrahedral sites.

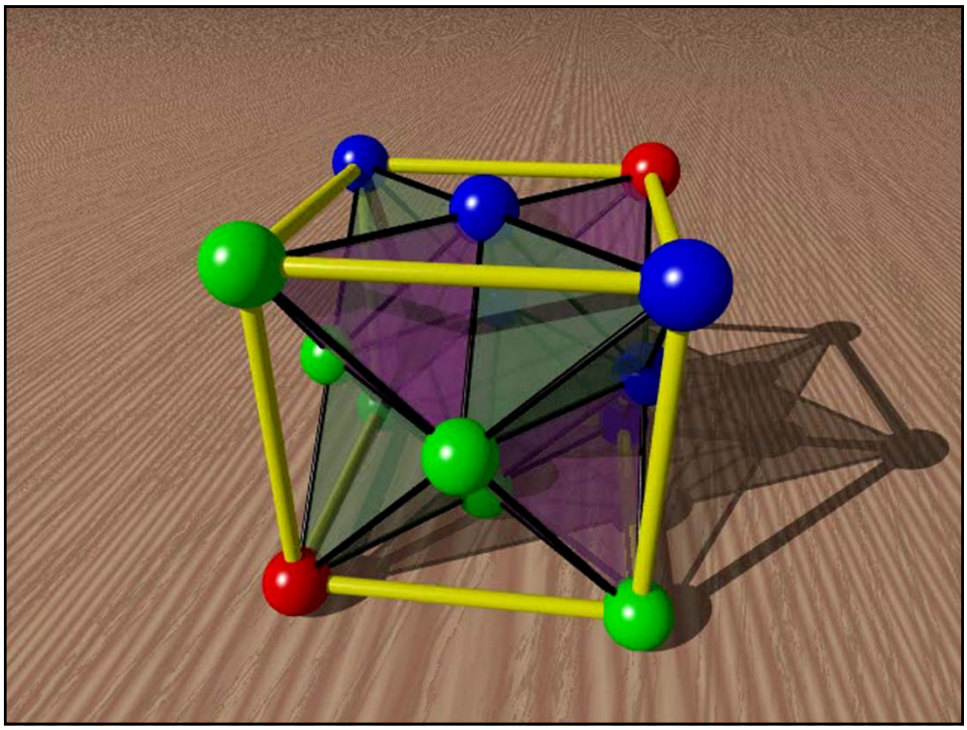


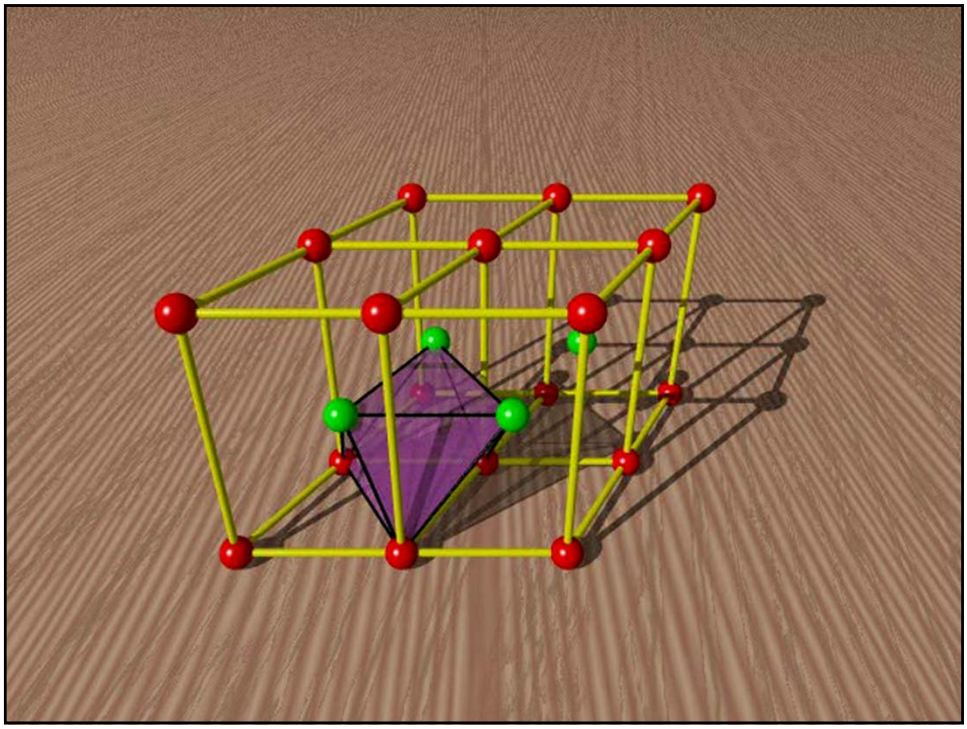




Close packing structures:
Cubic vs. Hexagonal

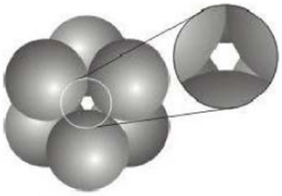


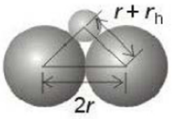




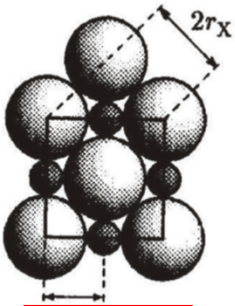
Close Packing of Spheres

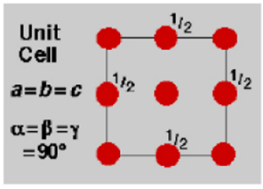
Different cavity sizes: the octahedral hole





face of unit cell



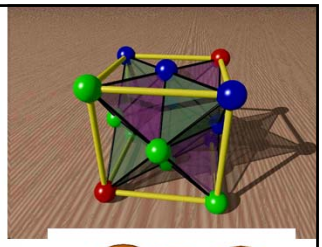


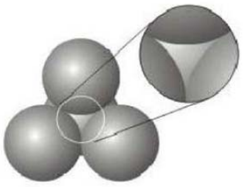
$$\frac{1}{2}a = r_X\sqrt{2}$$

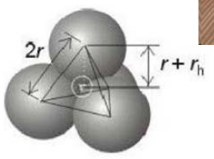
$$r_M + r_X = r_X\sqrt{2}$$
$$r_M/r_X = \sqrt{2} - 1$$
$$= 0,414$$

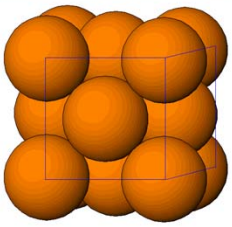
Close Packing of Spheres

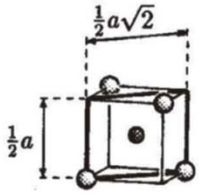
Different cavity sizes: the tetrahedral hole

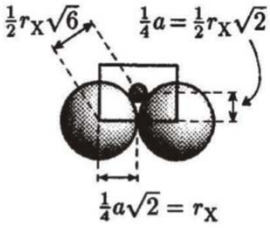












$$r_M + r_X = r_X \cdot \tfrac{1}{2}\sqrt{6}$$
$$r_M/r_X = \tfrac{1}{2}\sqrt{6} - 1$$
$$= 0,225$$

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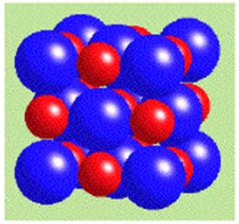
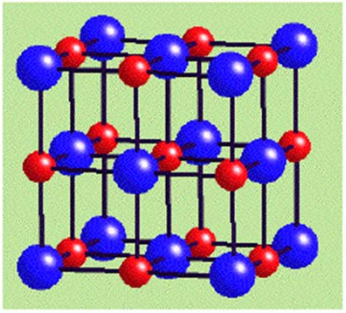
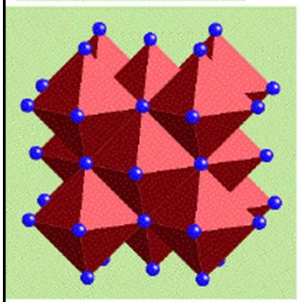
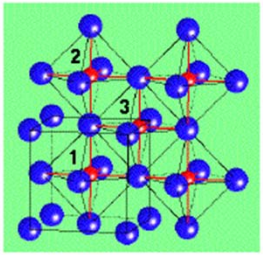
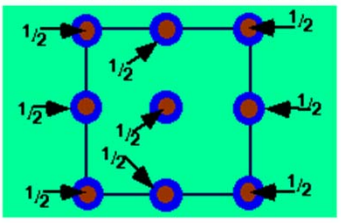


NaCl
Rock Salt
(*Halite*)

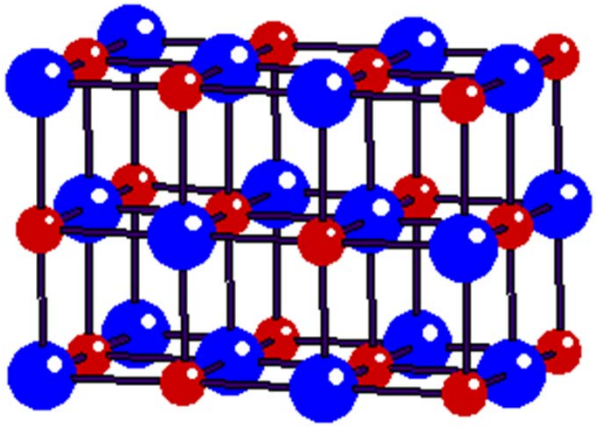




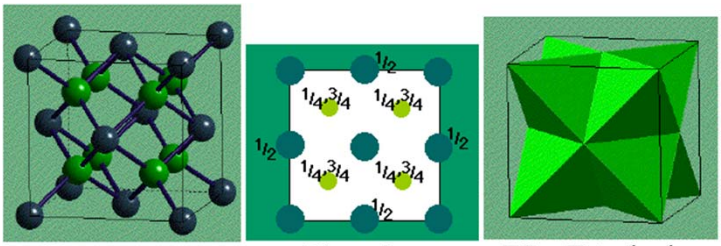




NaCl; ccp, O sites: 100%

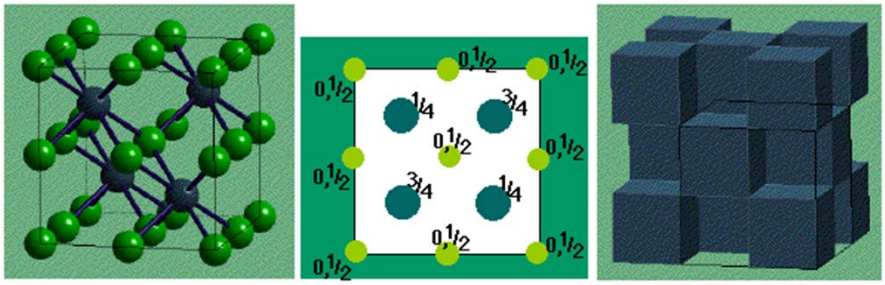


CaF_2



Fluorite A-cell | Plan view | FCa_4 Tetrahedra

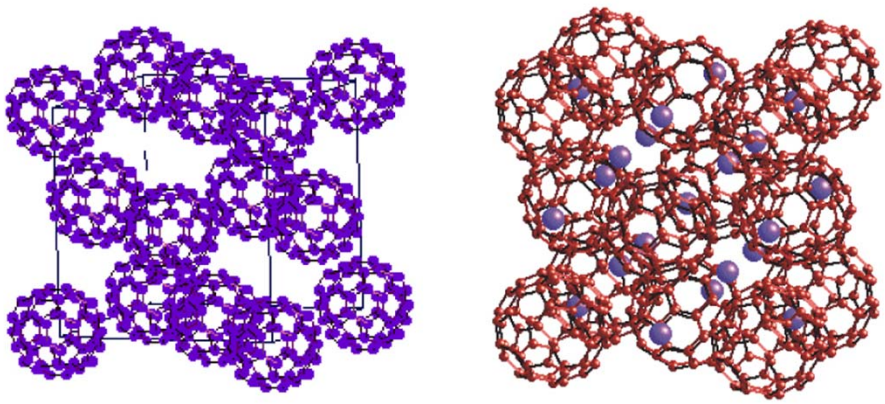
- **CCP Ca^{2+} with F^- in all Tetrahedral holes**
- ***Lattice*: fcc**
- ***Motif*: Ca^{2+} at (0,0,0); $2F^-$ at ($^1/_4$,$^1/_4$,$^1/_4$) & ($^3/_4$,$^3/_4$,$^3/_4$)**
- **4 CaF_2 in unit cell**
- ***Coordination*: Ca^{2+} 8 (cubic) : F^- 4 (tetrahedral)**
- **In the related Anti-Fluorite structure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



Fluorite B-cell | Plan view | CaF_8 Cubes

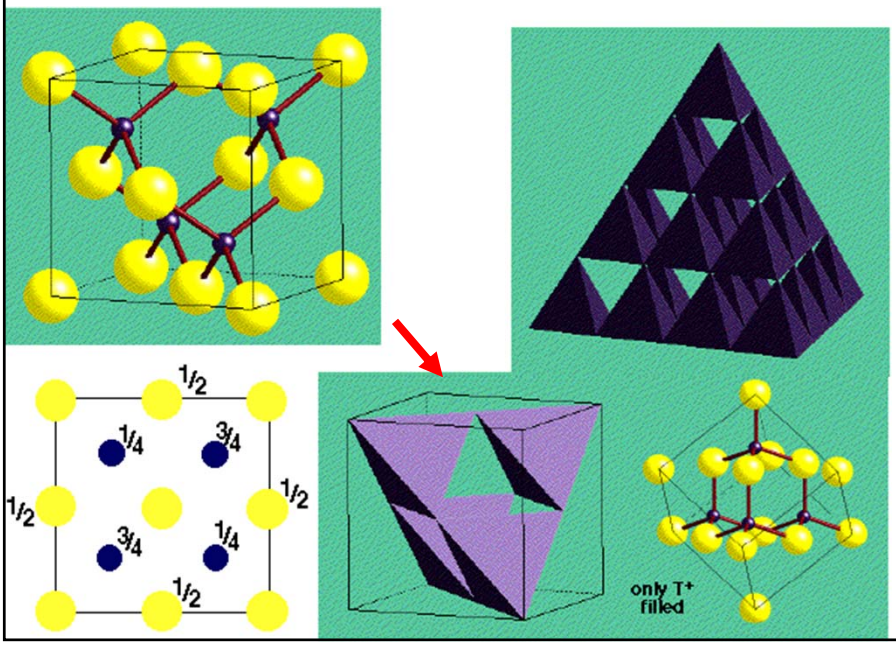
Close Packing of Spheres

ccp → filling of all O_h and T_d voids → Li_3Bi type



C_{60} | K_3C_{60}

Zinc Blende: ZnS



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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)
- Cation and anion sites are topologically identical

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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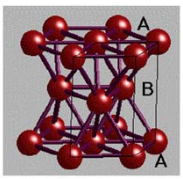
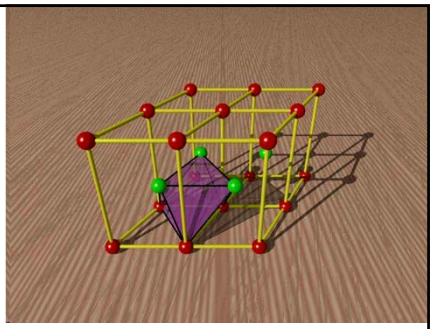
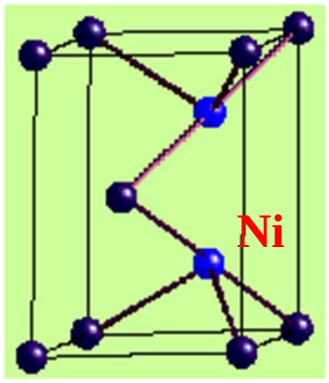


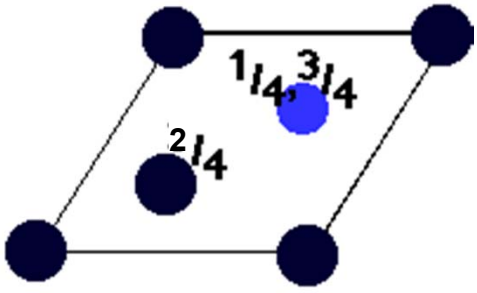
HCP Hexagonal Close-Packing

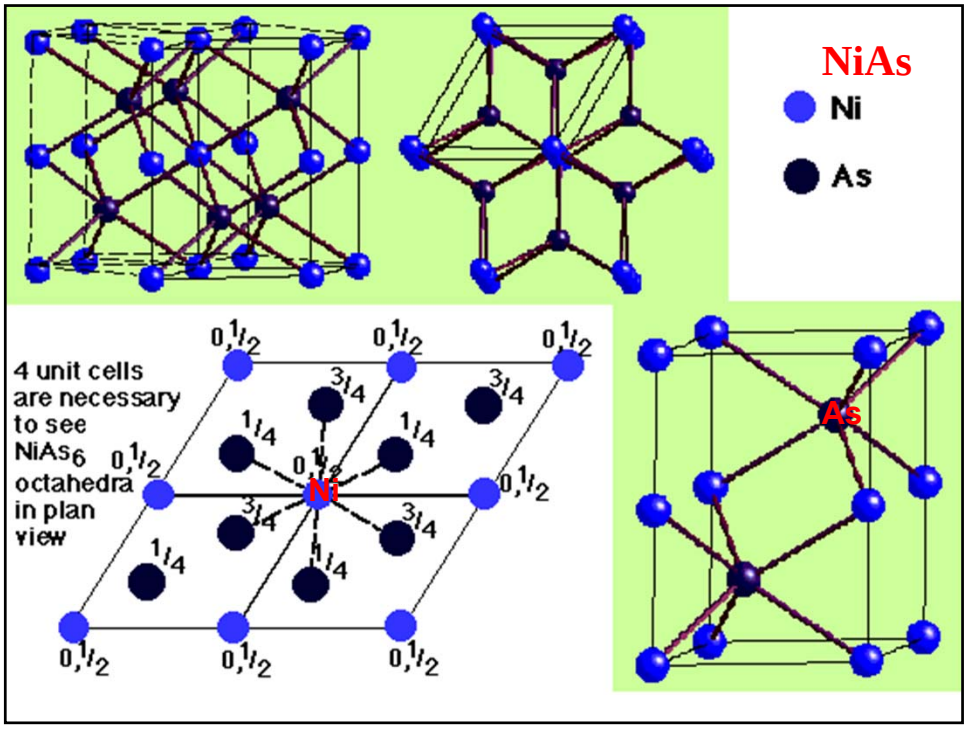
NiAs

As









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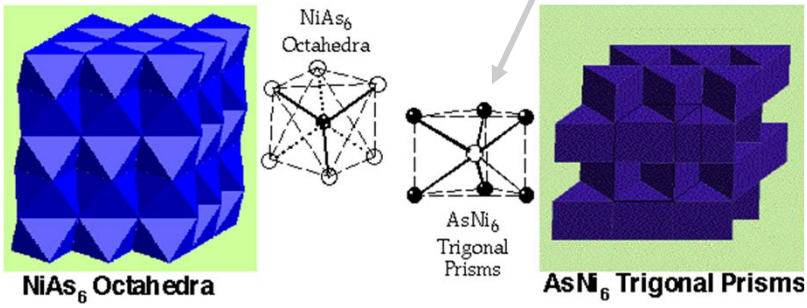
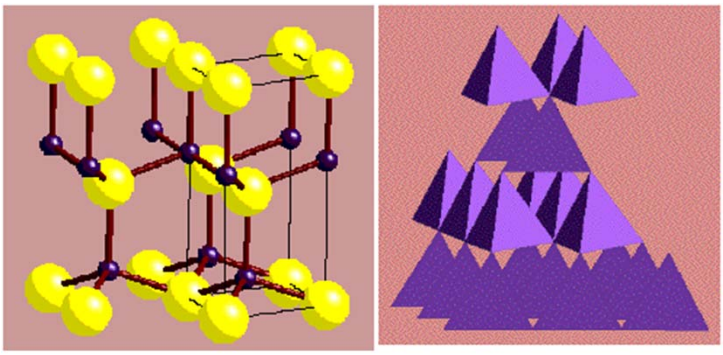
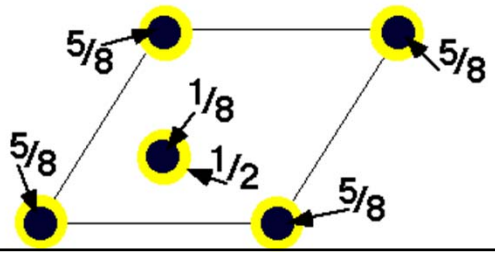
- **HCP As with Ni in all Octahedral holes**
- ***Lattice*: Hexagonal - P**
- ***a* = *b*, *c***
- ***Motif*: 2Ni at (0,0,0) (0,0,$^1/_2$) 2As at ($^2/_3$,$^1/_3$,$^1/_4$) & ($^1/_3$,$^2/_3$,$^3/_4$)**
- **2NiAs in unit cell**
- ***Coordination*: Ni 6 (octahedral) : As 6 (trigonal prismatic)**



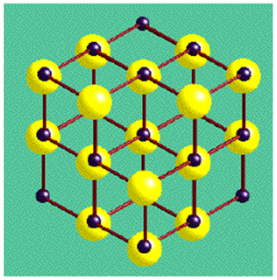
Wurtzite: ZnS



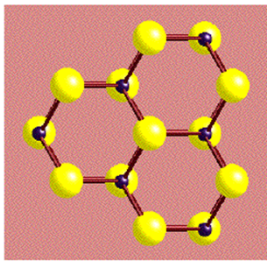


- **HCP S^{2-} with Zn^{2+} in half Tetrahedral holes (only T+ {or T-} filled)**
- ***Lattice*: Hexagonal - P**
- ***a* = *b*, *c***
- ***Motif*: 2S at (0,0,0) ($^2/_3$,$^1/_3$,$^1/_2$); 2Zn at ($^2/_3$,$^1/_3$,$^1/_8$) & (0,0,$^5/_8$)**
- **2ZnS in unit cell**
- ***Coordination*: 4:4 (tetrahedral)**

PLAN VIEWS

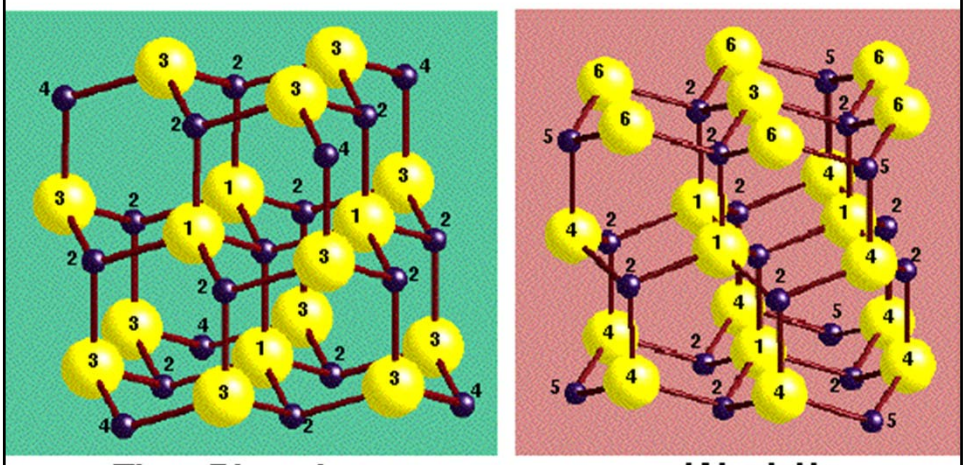


Zinc Blende
CCP ABC repeat



Wurtzite
HCP AB repeat

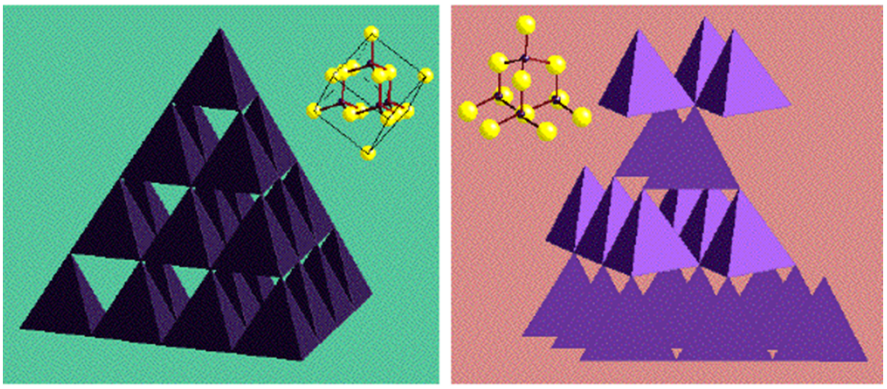
COORDINATION ENVIRONMENTS



Zinc Blende Wurtzite

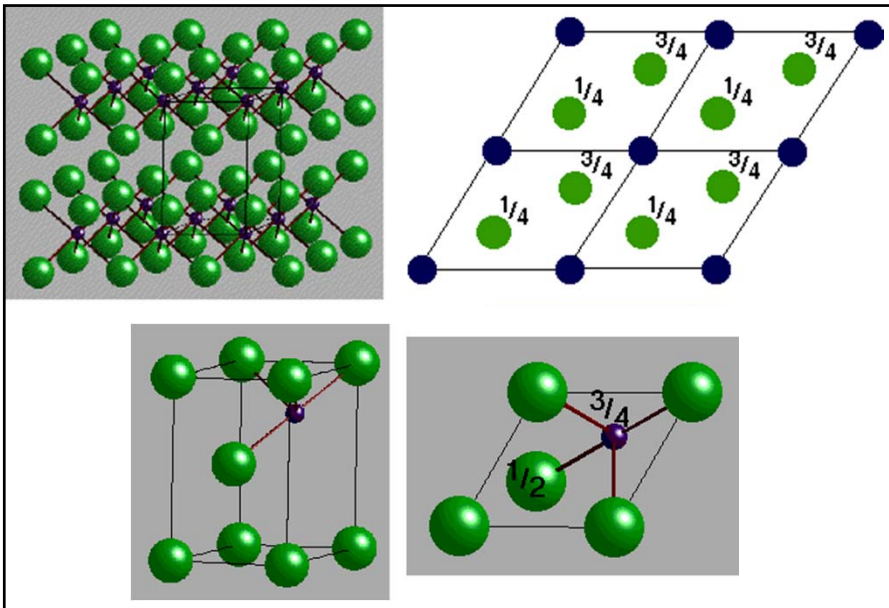
4 Nearest Neighbours (*Tetrahedral*)
12 Next-Nearest Neighbours
Cuboctahedral ← → *Anti-Cuboctahedral*
Very different Next, Next-Nearest Neighbour Coordinations & beyond

POLYHEDRAL REPRESENTATIONS



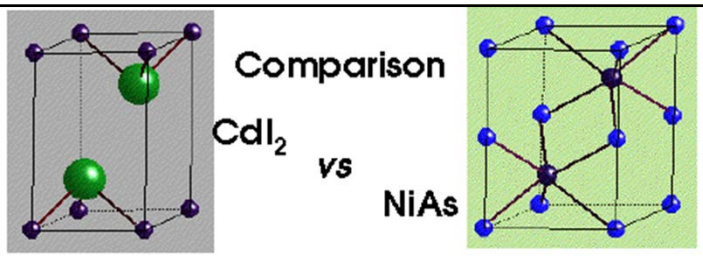
Zinc Blende Wurtzite

Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

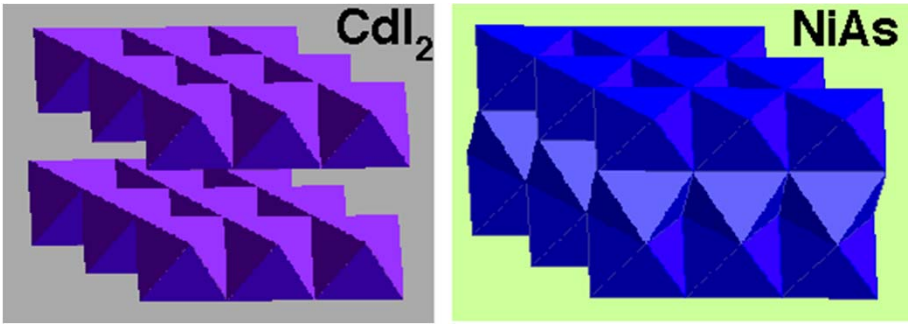


• **HCP I with Cd in Octahedral holes of alternate layers**

CdI_2



•***Lattice*: Hexagonal - P**
•***Motif*: Cd at (0,0,0); 2I at ($^2/_3$,$^1/_3$,$^1/_4$) & ($^1/_3$,$^2/_3$,$^3/_4$)**
•**1CdI_2 in unit cell**
•***Coordination*: Cd - 6 (Octahedral) : I - 3 (base pyramid)**



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NiAs

- **Transition metals with chalcogens, As, Sb, Bi**

***e.g.* Ti(S,Se,Te); Cr(S,Se,Te,Sb); Ni(S,Se,Te,As,Sb,Sn)**

CdI_2

- **Iodides of moderately polarising cations; bromides and chlorides of strongly polarising cations;**
  ***e.g.* PbI_2, $FeBr_2$, VCl_2**
- **Hydroxides of many divalent cations**
  ***e.g.* $(Mg,Ni)(OH)_2$**
- **Di-chalcogenides of many quadrivalent cations**
  ***e.g.* TiS_2, $ZrSe_2$, $CoTe_2$**

$CdCl_2$ (*CCP equivalent of* CdI_2)

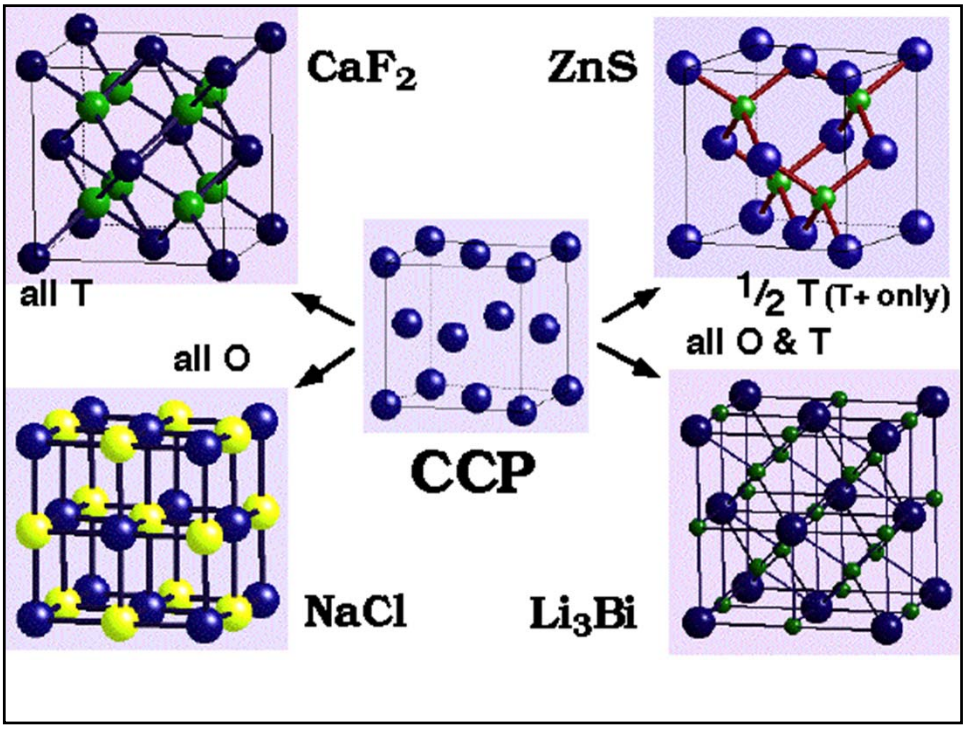
- Chlorides of moderately polarising cations
  e.g. $MgCl_2$, $MnCl_2$
- Di-sulfides of quadrivalent cations
  e.g. TaS_2, NbS_2 (CdI_2 form as well)

Cs_2O has the *anti*-cadmium chloride structure

HCP version of CaF_2 ?

No structures are known with all Tetrahedral sites (T+ and T-) filled in HCP

i.e. there is no HCP analogue of the *Fluorite/Anti-Fluorite* Structure



Formula	Type and fraction of sites occupied	CCP	HCP
AB	**All octahedral**	**NaCl** *Rock Salt*	**NiAs** *Nickel Arsenide*
	Half tetrahedral (T+ or T-)	**ZnS** *Zinc Blende*	**ZnS** *Wurtzite*
AB_2	**All tetrahedral**	**Na_2O** *Anti-Fluorite* **CaF_2** *Fluorite*	**Not known**
AB_3	**All octahedral & tetrahedral**	**Li_3Bi**	**Not known**
A_2B	**Half octahedral** *(Alternate layers full/empty)*	**$CdCl_2$** *(Cadmium Chloride)*	**CdI_2** *(Cadmium Iodide)*
	Half octahedral *(Ordered framework arrangement)*	**TiO_2** *(Anatase)*	**$CaCl_2$** **TiO_2** *(Rutile)*
A_3B	**Third octahedral Alternate layers $^2/_3$ full/empty**	**YCl_3**	**BiI_3**