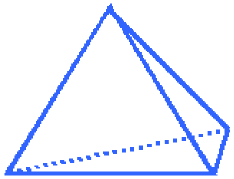
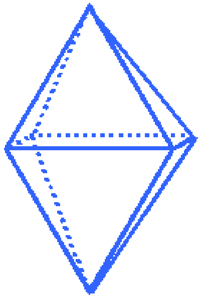
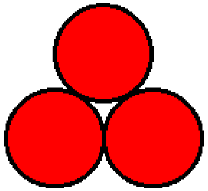
(Inorganic) Crystal Structures



- All crystal structures may be described in terms of symmetry, unit cell and atomic coordinates.
- Many inorganic structures may be described as arrays of polyhedra - tetrahedra, octahedra, etc..
- Many structures - ionic, metallic, covalent - may be described as close packed structures.

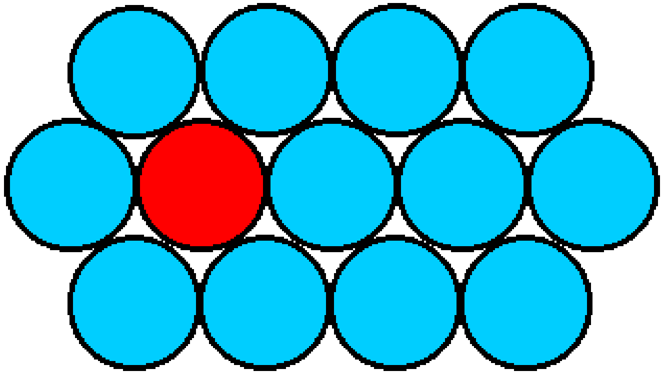




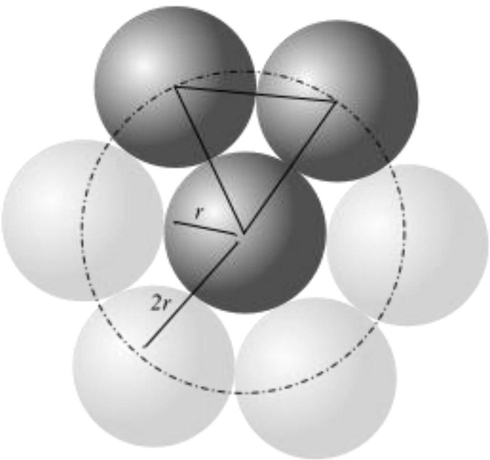
Packing

You can pack with irregular shapes…

Close Packed Structures – 2D

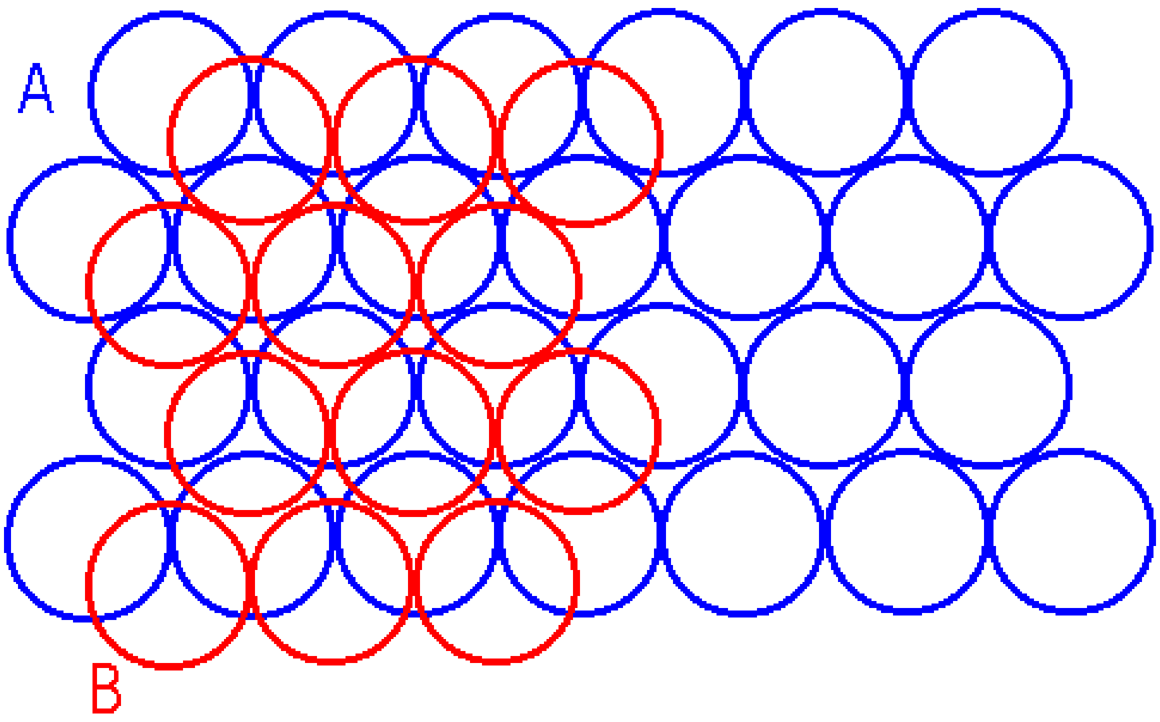


- A hexagonal close packed (cp) layer is the most efficient way to pack equal sized spheres.
- Coordination number (CN) = 6. This is the maximum possible for 2D packing.
- The density of this arrangement is: $\frac{\pi}{\sqrt{12}} \simeq 0.9069$
- In 1940, the Hungarian mathematician L. F. Tóth proved that the hexagonal lattice is the densest of all possible circle packings, both regular and irregular.



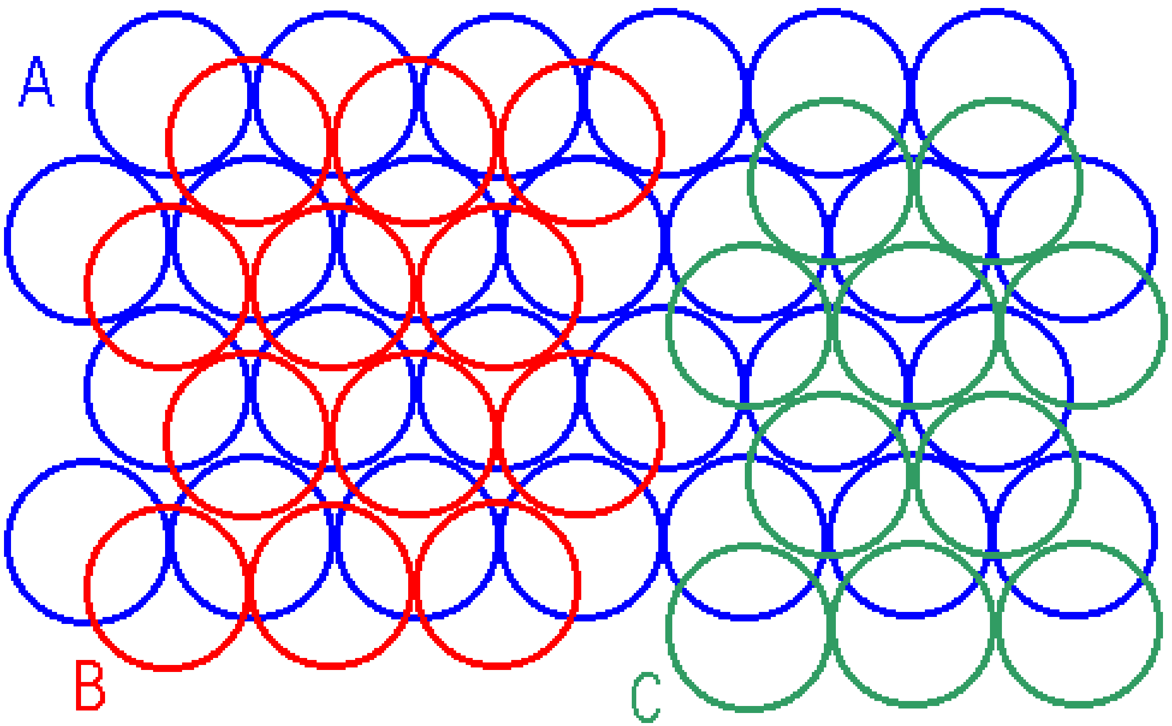
Close Packed Structures – from 2D to 3D

If we start with one cp layer, there are two possible ways of adding a second layer (can have one or other, but not a mixture) :

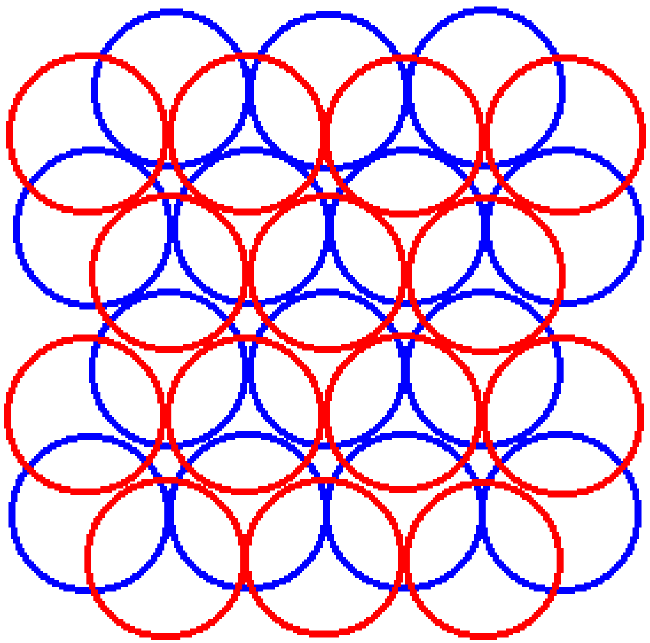


Close Packed Structures – from 2D to 3D

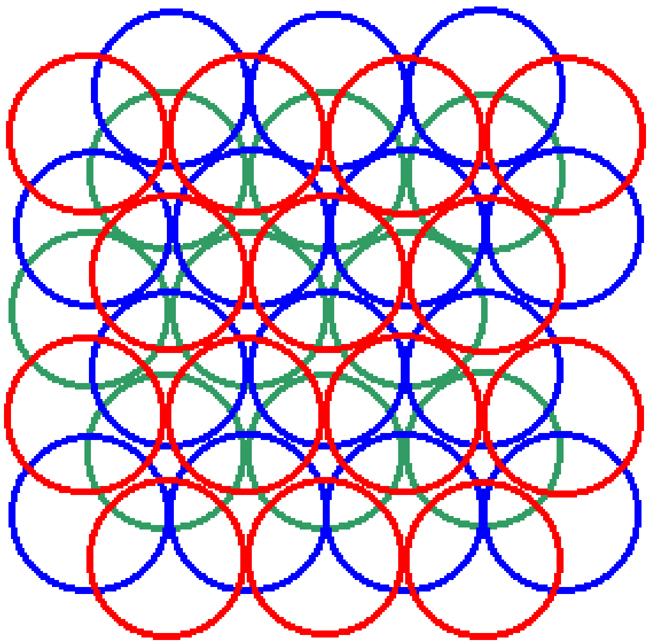
If we start with one cp layer, there are two possible ways of adding a second layer (can have one or other, but not a mixture) :



Close Packed Structures

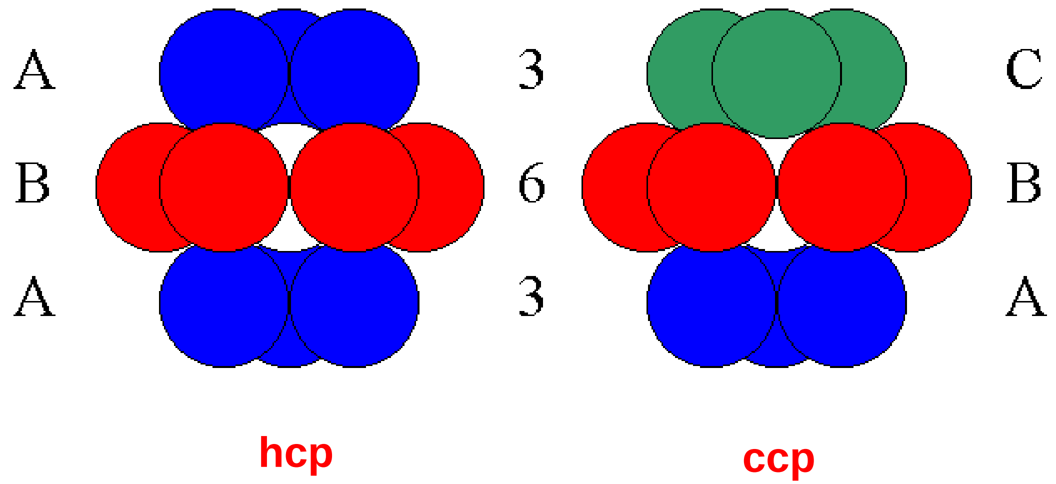


Hexagonal close packed (hcp)



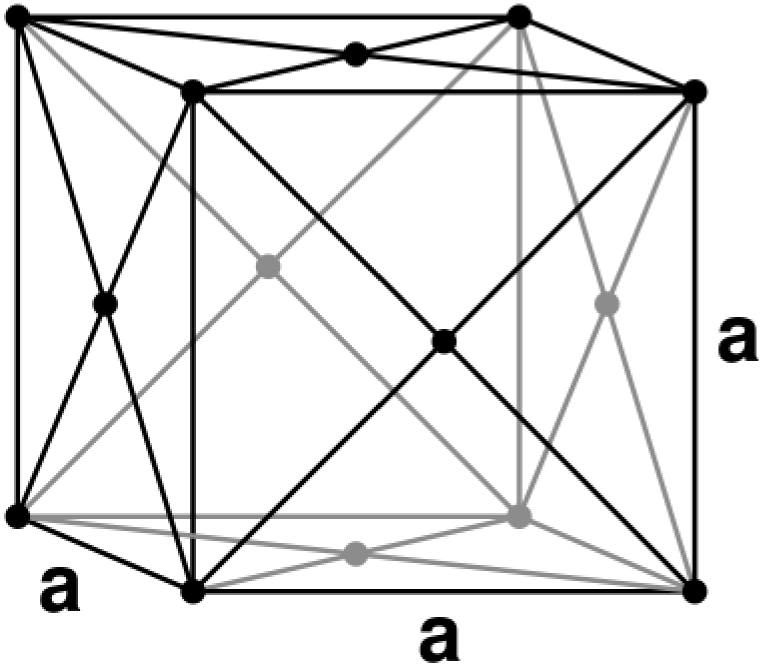
Cubic close packed (ccp)

Close Packed Structures



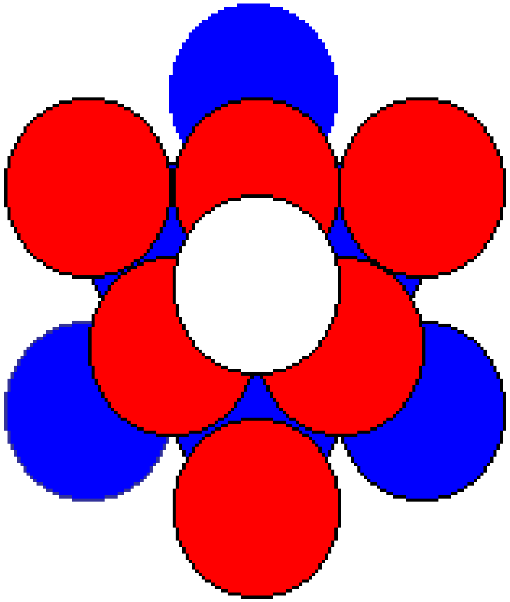
- No matter what type of packing, the coordination number of each equal size sphere is always 12. Other coordination numbers are possible for non-equal size spheres.
- Both arrangements have an average density of: $\frac{\pi}{\sqrt{18}} \simeq 0.74048$
- The Kepler conjecture states that this is the highest density that can be achieved by any arrangement of spheres, either regular or irregular.

Face Centered Cubic (fcc)

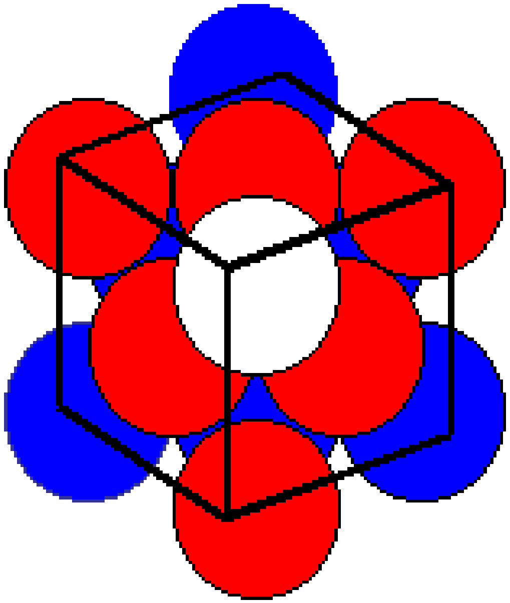


The face centered cubic has atoms on the faces of the cube of which each unit cube gets exactly one half contribution, giving a total of 4 atoms per unit cell ((1/8 for each corner) * 8 corners + (1/2 for each face) * 6 faces).

ccp = fcc

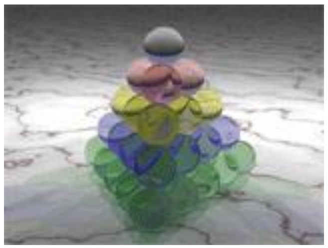


Build up ccp layers (ABC… packing)

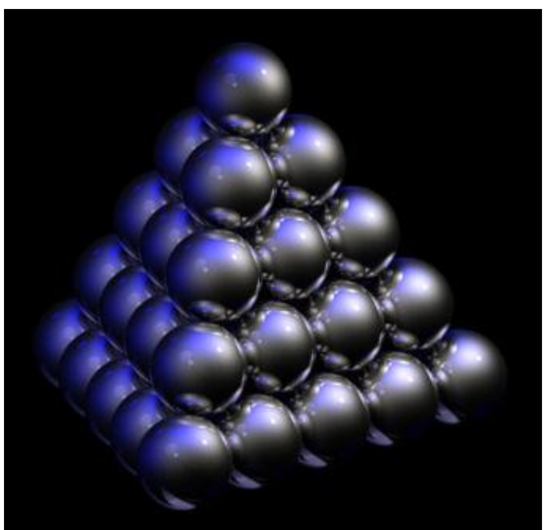


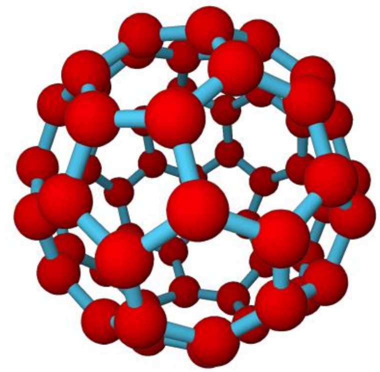
Add construction lines → fcc unit cell
cp layers are oriented perpendicular to the diagonal of the cube

Examples

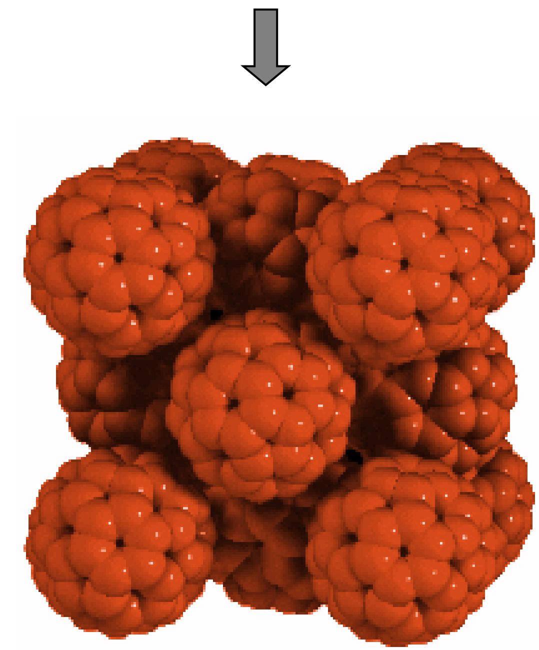


Stacking spheres in a pyramid is an example of cubic close packing.





C_{60}

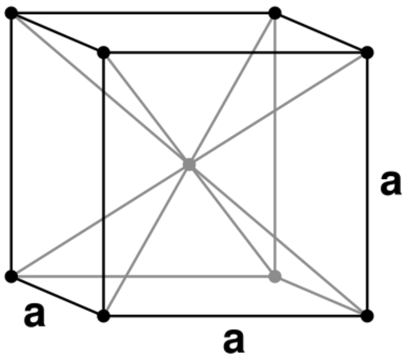


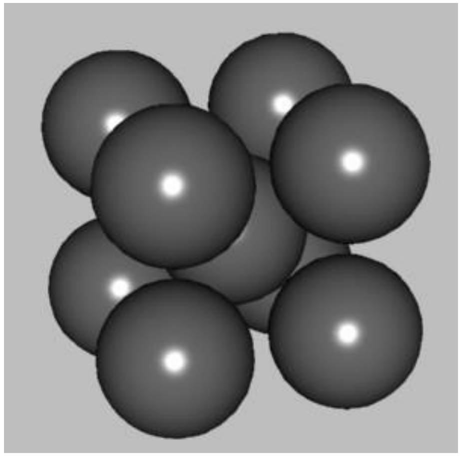
Body Centered Cubic (bcc)

- The body centered cubic (bcc) system has one atom in the center of the unit cell in addition to the eight corner points. It has a contribution from 2 atoms per cell ((1/8)*8 + 1).

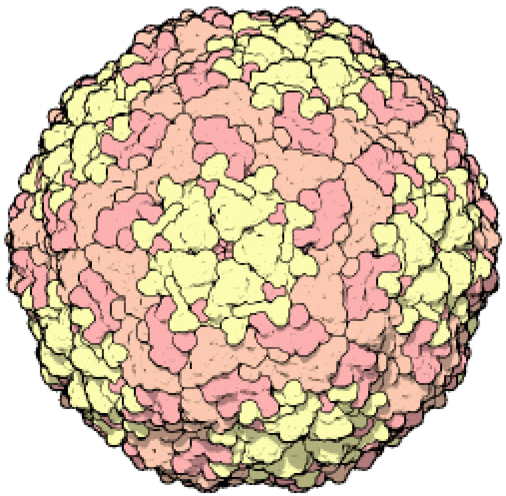
- Each corner atom touches the central atom along the body diagonal of the cube, and it is easy to show by that the unit cell edge, an irrational number, is about 2.3r. Thus, the corner atoms do not touch one another.

- The packing efficiency of a bcc lattice is 68 %.

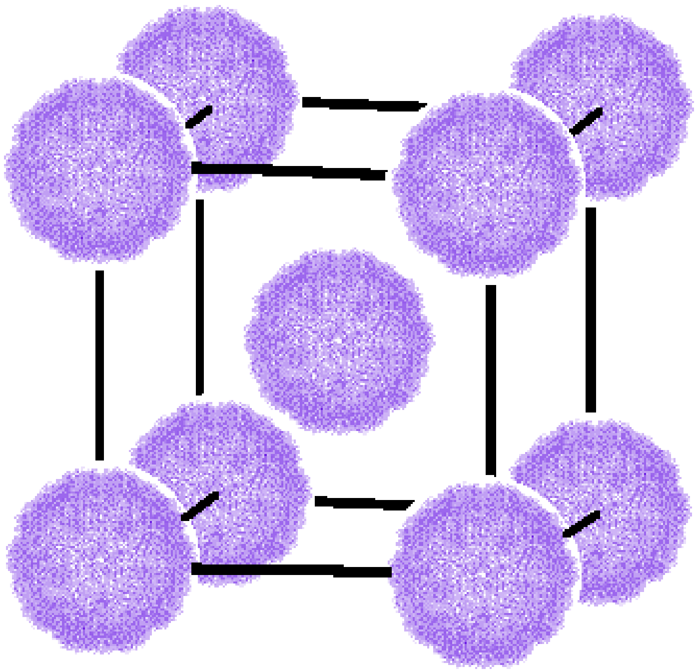




Body Centered Cubic (bcc)



Foot-and-mouth disease
virus coating protein

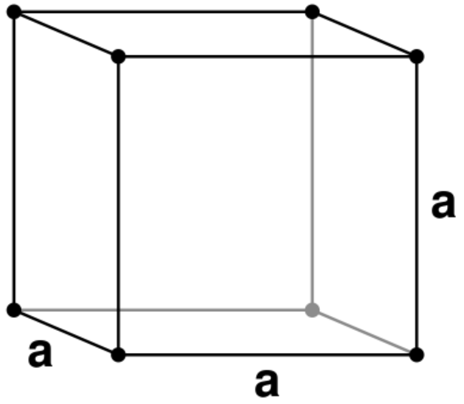


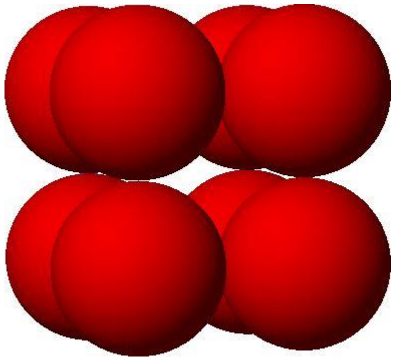
Simple Cubic

- The simple cubic system consists of one lattice point on each corner of the cube. Each atom at the lattice points is then shared equally between eight adjacent cubes, and the unit cell therefore contains in total one atom (1/8 * 8).

- Assuming one atom per lattice point, the density of the simple cubic system is only 52 %. Consequently, this is a high energy structure and is rare in Nature, but is found in **polonium**.

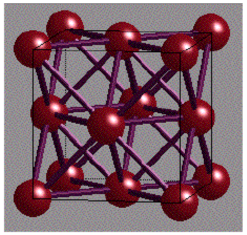
- Coordination number = 6.



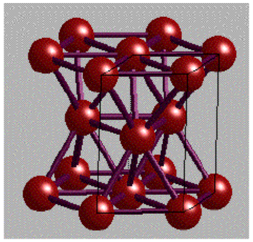


The Structures of Metals - Overview

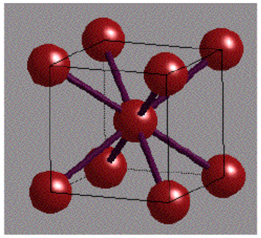
	'Density'	CN
ccp	0.74	12
hcp	0.74	12
bcc	0.68	8+6
simple cubic	0.52	6
diamond	0.34	4



CCP Cubic Close-Packing



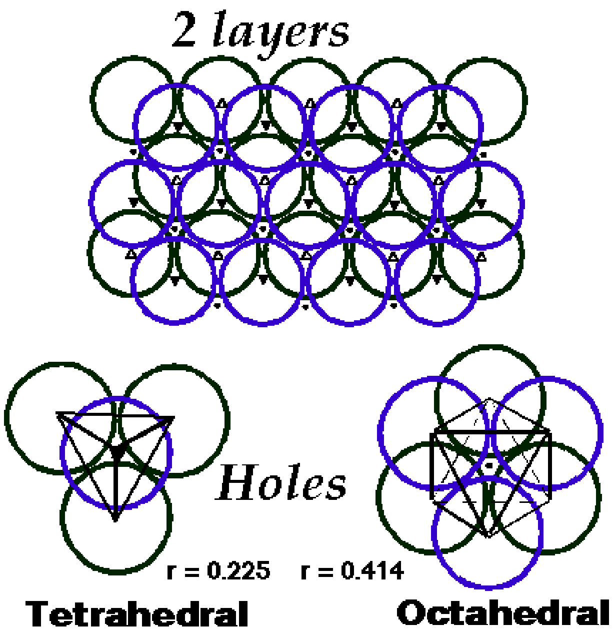
HCP Hexagonal Close-Packing



BCC Body-Centred Cubic

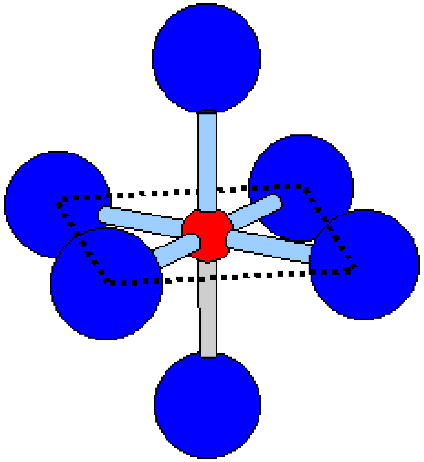
Close Packed Ionic Structures

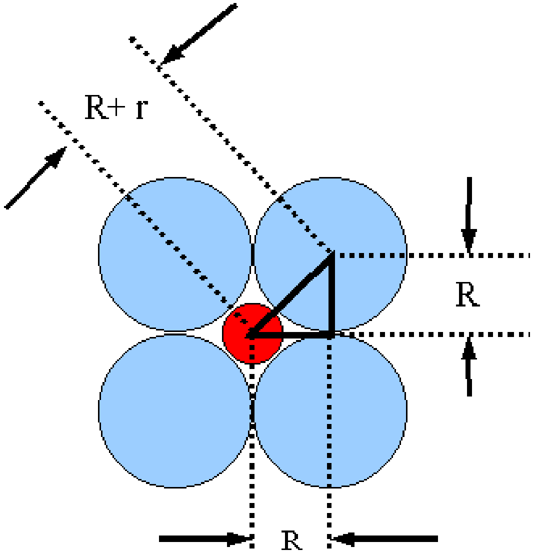
- In many ionic structures, the anions, which are larger than the cations, form a c.p. array and the cations occupy interstitial holes within this anion array.
- Two main types of interstitial sites: Tetrahedral (CN = 4) and octahedral (CN = 6).
- For N atoms of a close packed structure, there are N octahedral sites and 2N tetrahedral sites.



Radius Rules

Rationalization for octahedral coordination:
R = radius of large ion, r = radius of small ion





$$\frac{R}{R+r} = \cos 45^\circ = \frac{1}{\sqrt{2}}$$

$$\Rightarrow \sqrt{2}R = R+r$$

$$\Rightarrow (\sqrt{2}-1)R = r$$

$$\Rightarrow \frac{r}{R} = 0.414$$

Radius Rules

Coordination	r/R
Tetrahedral, 4	0.225
Octahedral, 6	0.414
Cubic, 8	0.732
Close packed, 12	1.000

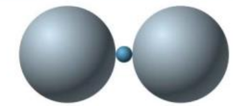
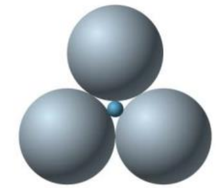
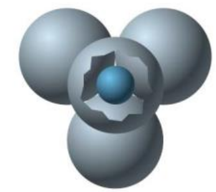
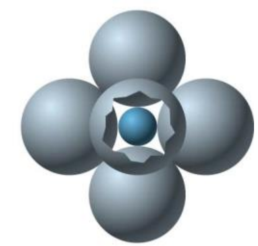
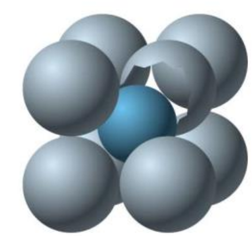
A simple prediction tool, but beware - it doesn't always work!

The NaCl Structure

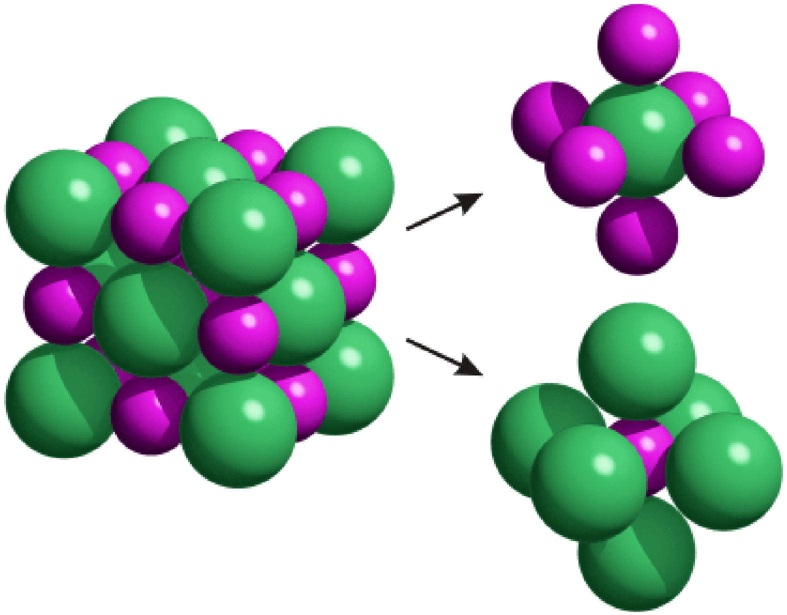
Na^+: $r = 0.102$ nm
Cl^-: $R = 0.181$ nm
Ratio: $r/R = 0.564$

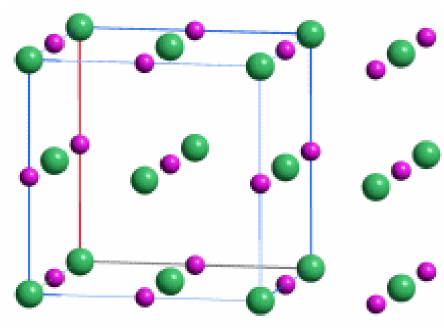
Charge neutrality (Na^+:Cl^- = 1:1)

What structure to expect ?

Coordination Number	*Cation-Anion Radius Ratio*	*Coordination Geometry*
2	< 0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

The NaCl Structure





- Each Na^+ is coordinated to 6 Cl^- and each Cl^- is coordinated to 6 Na^+. Similar: all other alkali metal halides except CsCl, CsBr and CsI.

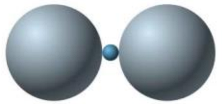
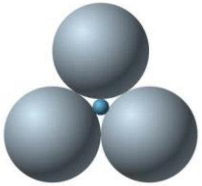
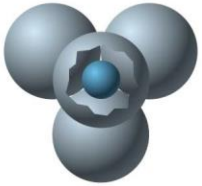
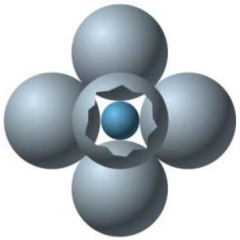
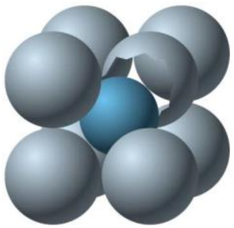
- Can be considered as ccp of Cl^- with Na^+ in all octahedral sites

The CsCl Structure

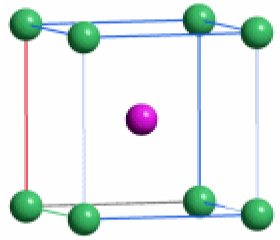
Cs^+: r = 0.170 nm
Cl^-: R = 0.181 nm
Ratio: r/R = 0.939

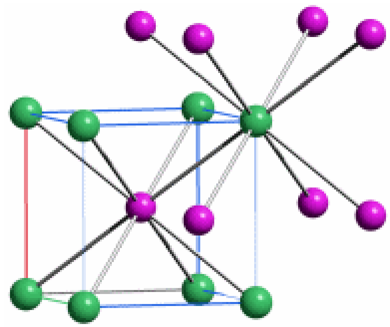
Charge neutrality (Cs^+:Cl^- = 1:1)

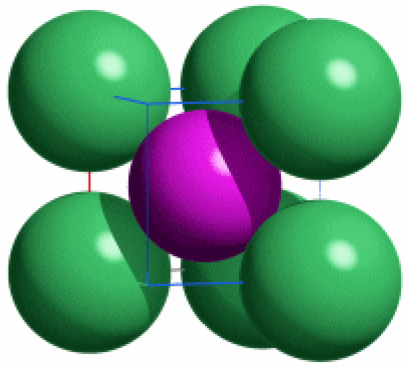
What structure to expect ?

Coordination Number	*Cation-Anion Radius Ratio*	*Coordination Geometry*
2	< 0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

The CsCl Structure







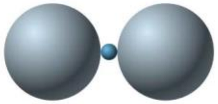
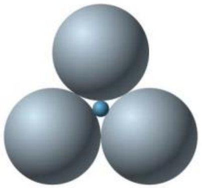
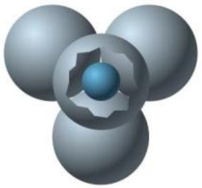
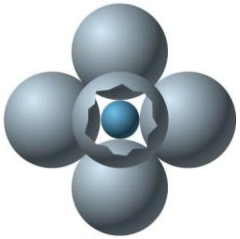
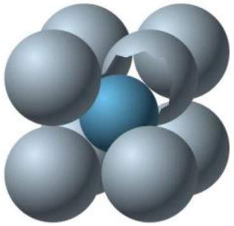
- Each Cs+ is coordinated to 8 Cl- and each Cl- is coordinated to 8 Cs+. Similar: CsBr and CsI.
- CsCl can be considered as simple cubic lattice of Cl^- with Cs^+ in all interstitial sites.

The ZnS (Zinc Blende) Structure

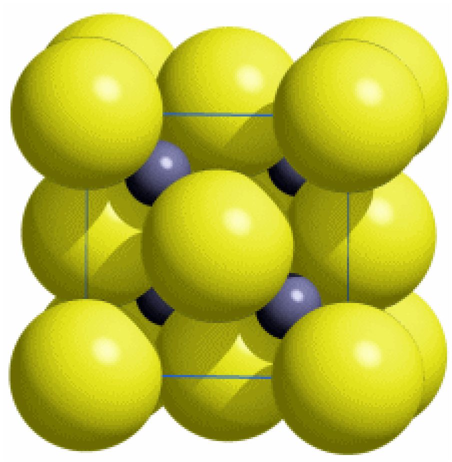
Zn^{2+}: $r = 0.074$ nm
S^{2-}: $R = 0.184$ nm
Ratio: $r/R = 0.402$

Charge neutrality (Zn^{2+}:S^{2-} = 1:1)

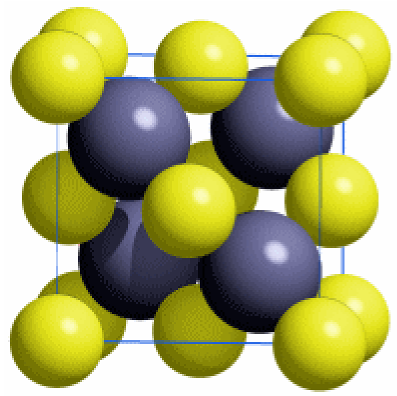
What structure to expect ?

Coordination Number	*Cation-Anion Radius Ratio*	*Coordination Geometry*
2	< 0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

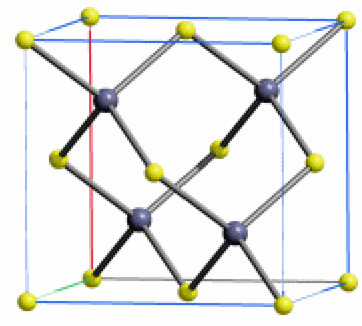
The ZnS (Zinc Blende) Structure



(with ionic radii)



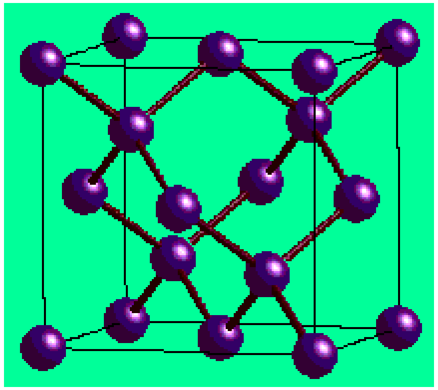
(with covalent radii)



(topology)

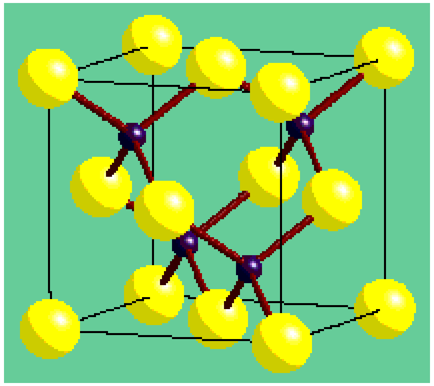
- Each Zn^{2+} is coordinated to 4 S^{2-} and each S^{2-} is coordinated to 4 Zn^{2+}. The structure is closely related to the structure of diamond.
- ZnS can be considered as a ccp lattice of S^{2-} with Zn^{2+} in half of the tetrahedral sites.
- Please note that the difference in electronegativity of Zn and S is not very large and that there is a strong covalent character of the bond.

Zinc Blende and Diamond



Diamond

The diamond network with a single atom type



Zinc Blende ZnS

The diamond network with alternate Zn & S atoms