

Bonding and Packing: building crystalline solids

The major forces of BONDING

Gravitational forces:

$$F = G \frac{m_1 m_2}{r^2}$$

F = attractive forces between 2 bodies

G = universal gravitational constant ($6.67 * 10^{-11} \text{ Nm}^2/\text{kg}^2$)

m^1 & m^2 = masses of two bodies

r = distance between the two bodies

Electrostatic attractions:

$$F = \frac{1}{4 \pi \epsilon_0} \frac{q_1 q_2}{r^2}$$

q^1 & q^2 = charges of two bodies

r = distance between the two bodies

$4\pi\epsilon_0$ = vacuum permittivity constant

Slide 3

I1

Introduce the curve relating the ionic character of a bond A-B

localuser, 8/9/2006

Expressions of electronegativity

Ionization energy: energy required to move one electron to infinity from an outer shell of an atom

$$I = E(X \rightarrow X^+ + e^-)$$

- Where the expression is set-up to calculate the energy required to move an electron and atom (X) to infinity
- Ionization energy increases from left to right across the periodic table

Electron affinity: energy required to make a neutrally charged atom an anion

$$E_a = E(X + e^- \rightarrow X^-)$$

- Where the expression is set-up to calculate the energy required to attract an electron to an atom from infinity

Expressions of electronegativity

By knowing the degree of electronegativity, it is possible to predict the types of bond between different atoms

When the electronegativity between two elements is very large – ionic bonding tends to dominate

When the electronegativity between two species are very similar – covalent bonding (sharing) is more likely to occur

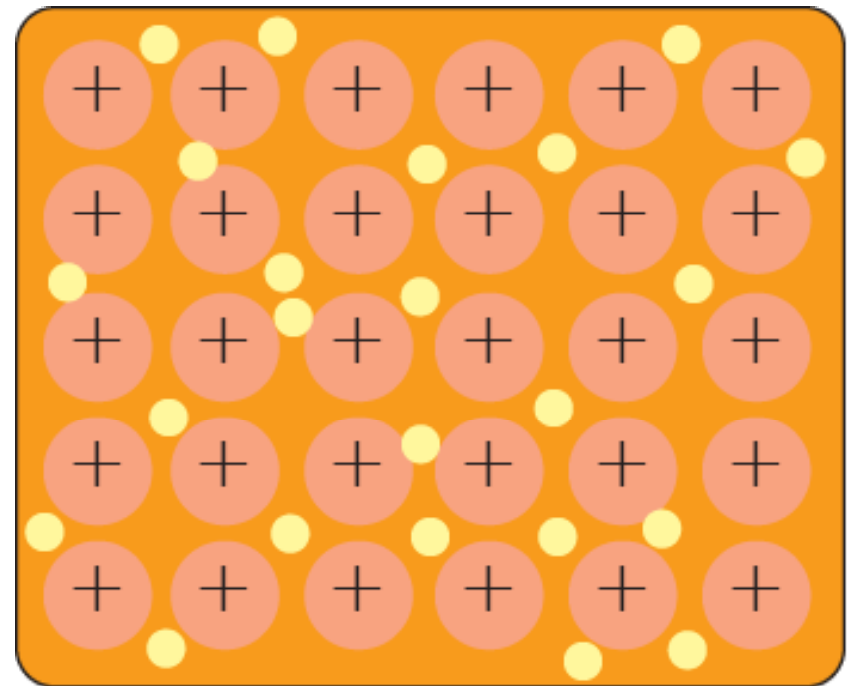
- Bonding with extreme differences: **ionic**
- Bonding with high but similar electronegativity: **covalent**
- Bonding with intermediate differences: **combination of ionic & covalent**
- Bonding with low but similar electronegativity: **metallic**

The metallic bond

All true metals are good conductors of heat and electricity, while X-ray diffraction analysis reveals that they have regular repetitive pattern of true crystalline solid.

Electrons are very poorly associated with a specific nuclei and are free to move through the structure.

The metal is held together by the combined attractive force between nuclei with their filled electron orbitals and the dense cloud of “free” valence electrons.



The ionic bond

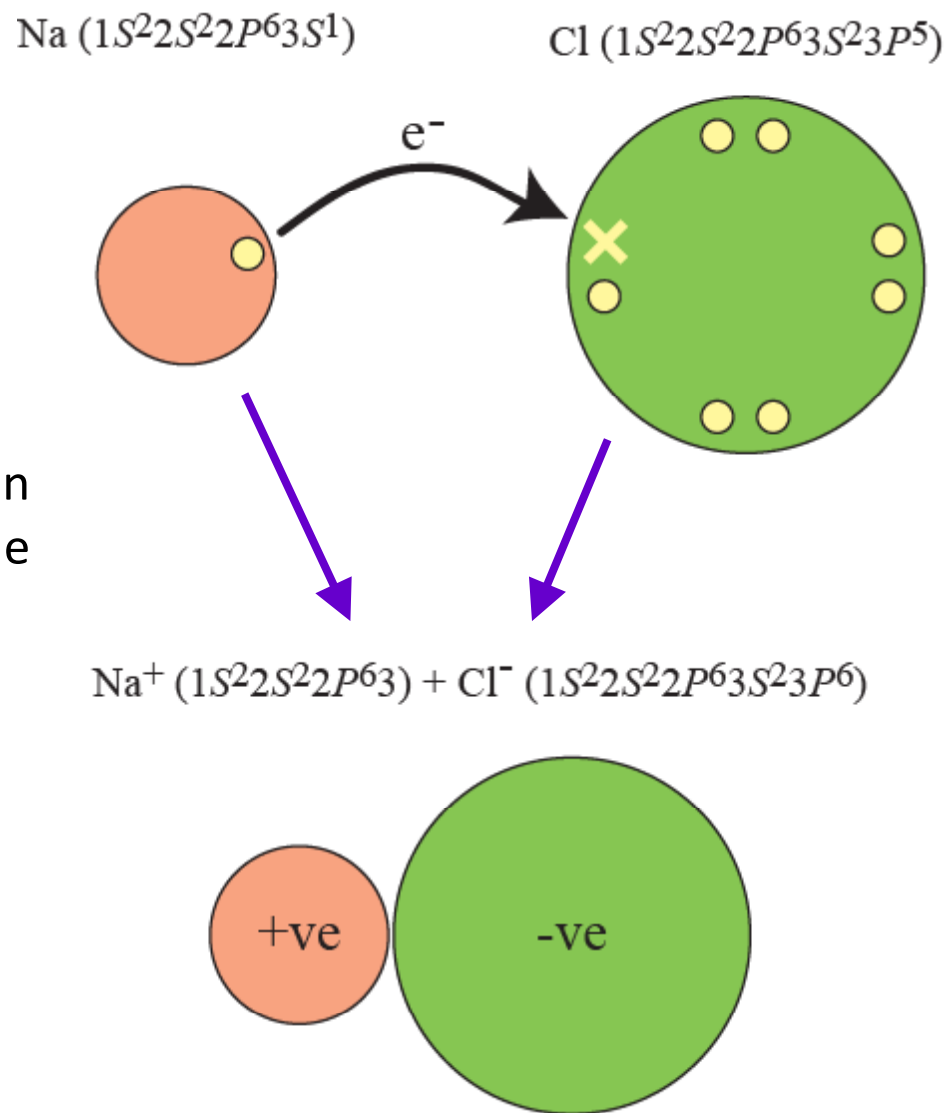
When electron(s) in the valence shell of a metallic atom are transferred to the valence shell of a non-metallic atom an ionic bond is formed.

In this example the single outer electron of Na is readily lost, and captured by the Cl atom, resulting in two ions

The new ions are attracted to one another because they are of opposite charge.

The electrostatic charge of the ionic bond is evenly spread.

Ionic bonds are *non-directional*.



The covalent bond

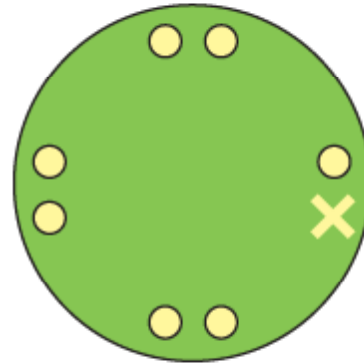
Non-metallic elements have a strong affinity for electrons, and elements such as Cl have high reactivity.

Cl will seize and combine with anything that can provide the electron required to fill the valence shell.

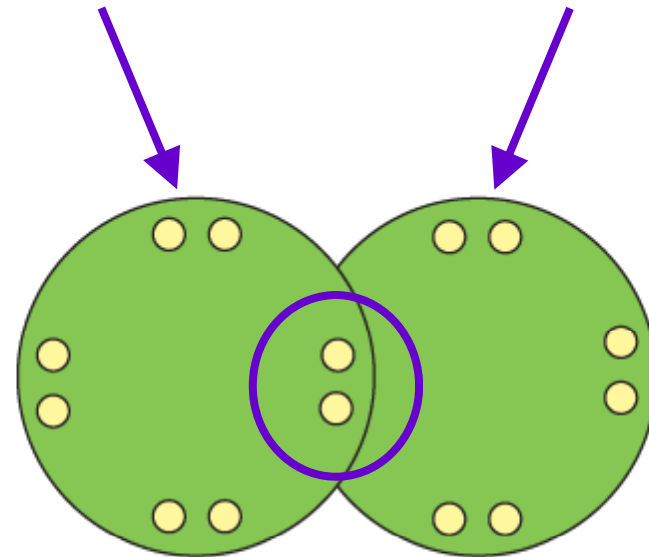
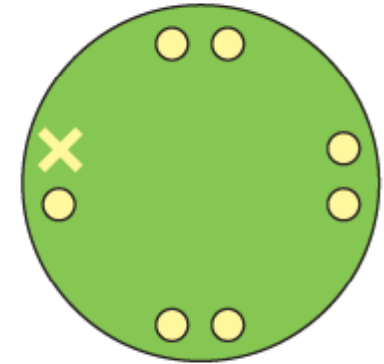
In a mixture of Cl gas it is a second Cl atom that provides the electron, but not by giving up the electron, but by sharing it.

Covalent bonds are very strong and are characteristic of minerals that are insoluble and generally quite stable.

Cl ($1S^22S^22P^63S^23P^5$)



Cl ($1S^22S^22P^63S^23P^5$)



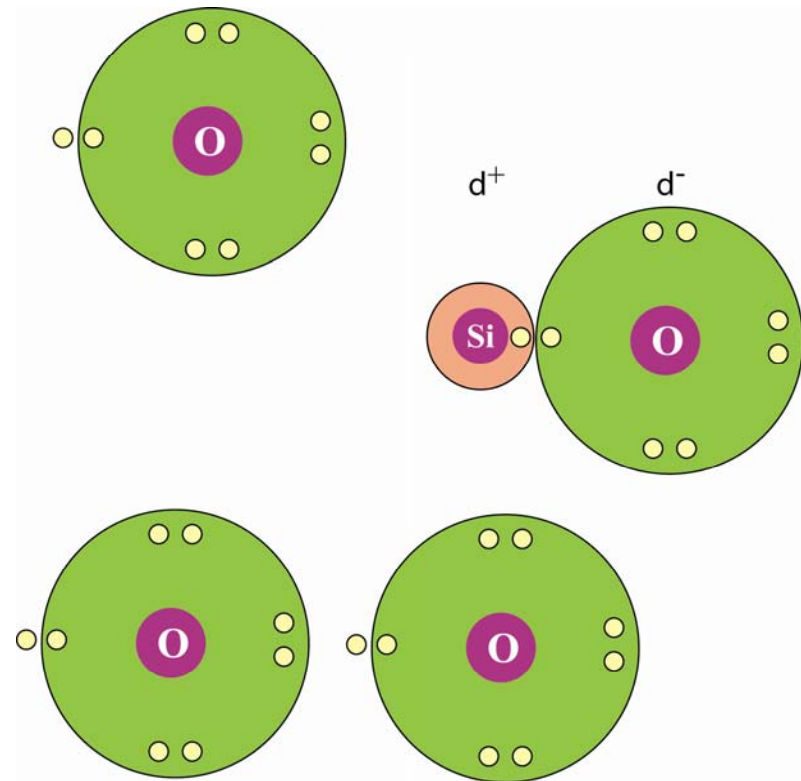
The stable form of chlorine gas is Cl_2 .

Ionic + covalent bonding

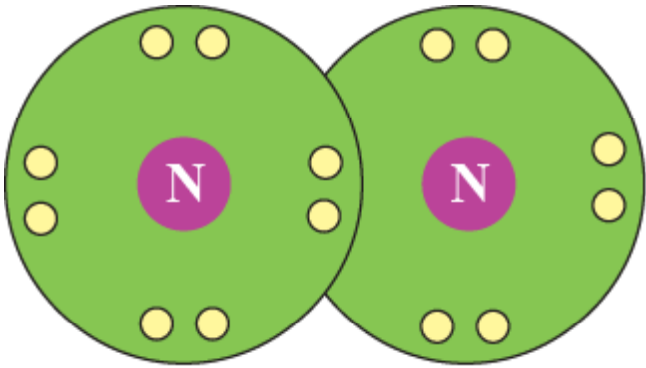
Commonly, multiple bond types coexist to create mineral structures. A good example of this is Si^{4+} and O^- to create the silica tetrahedra, one of the fundamental building blocks of many minerals.

In such cases, the association of electrons with one nuclei or another changes depending on the P/T conditions of the situation.

Given a particular set of conditions, it will be more likely to find a majority of either covalent or ionic bonds.

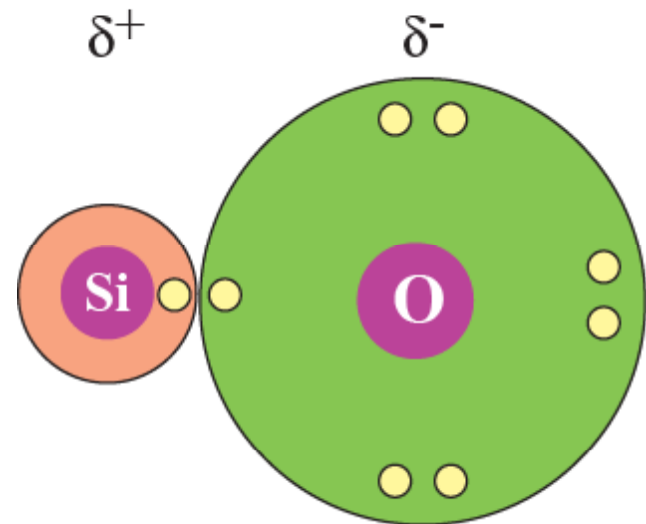


Bond Polarisation



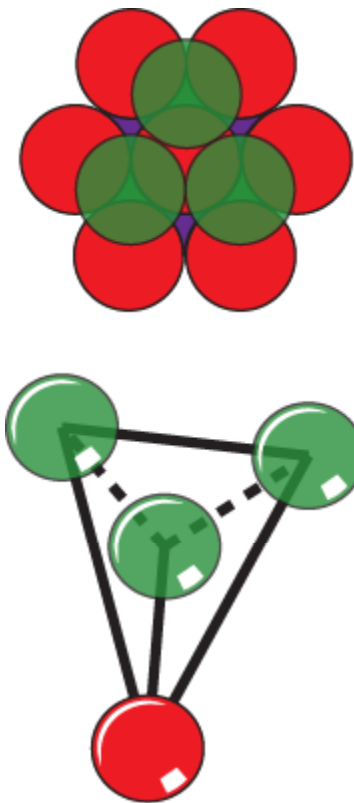
The partial-positive charge of each N nuclei in a N_2 molecule has an equal attraction to the electrons. The bond is effectively neutral with no polarisation.

In an Si-O bond, the greater concentration of electrons towards oxygen, *which has a higher electronegativity*, leads towards a partial polarisation of the bond.



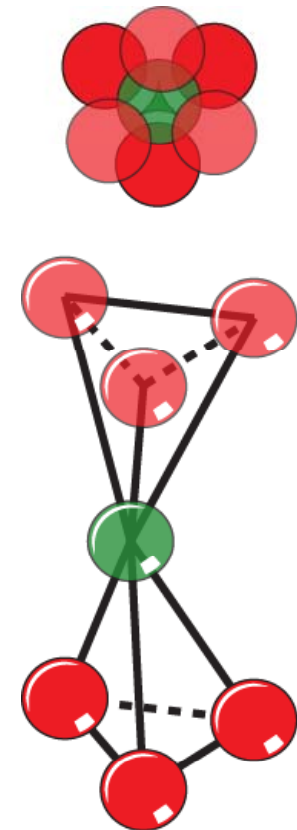
Common structure types and packing

When the radius ratio equalled 1 and the C.N. equalled 12, two close-packing arrangements were identified.



Careful examination of the of packing arrangements shows that there are two types of interstitial site – tetrahedral and octahedral.

However, as we will see when we examine basic structures, not all sites need necessarily be fully occupied by cations.



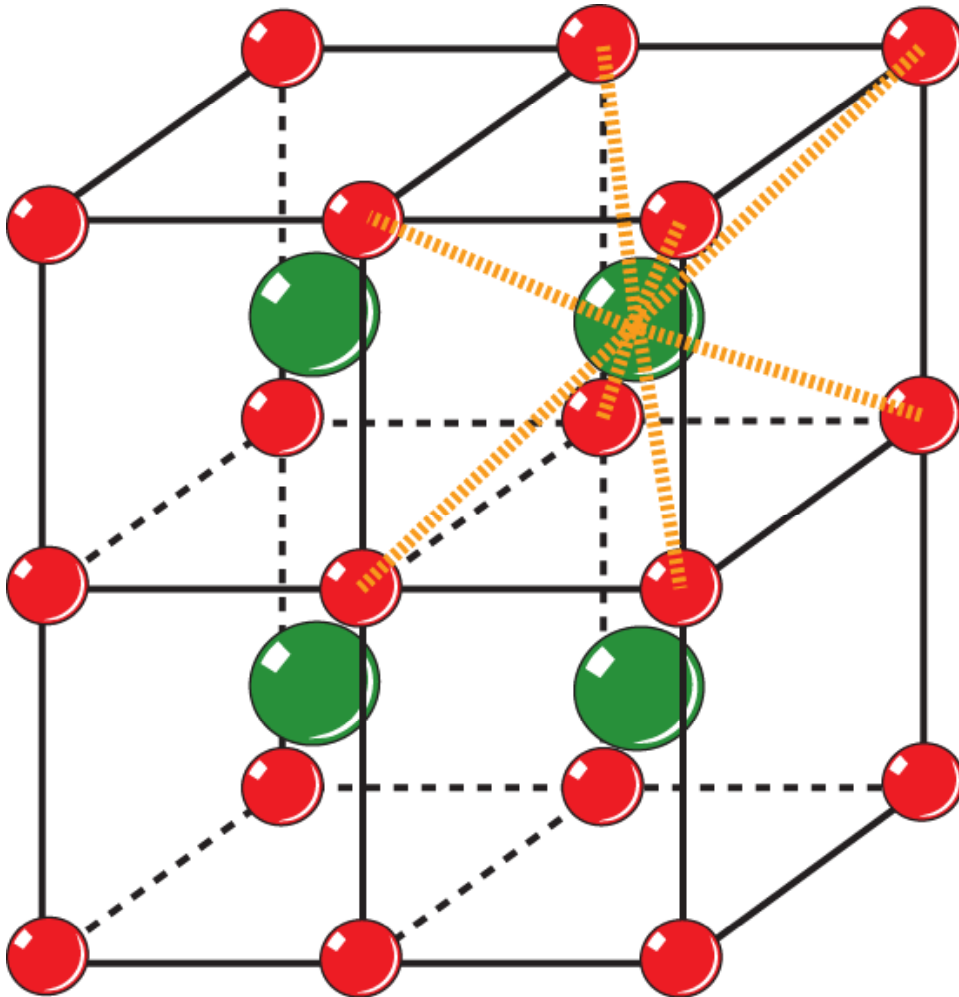
PACKING

Body-centered cubic packing: lattice has motifs at the corners of the cube with an additional motif in the center i.e. [Kamacite](#)

Hexagonal closest packing: 12-coordination, repeated stacking of two identical closely packed layers. [Common in Be, Mg, Zn, Ti, Zr, Ru.](#)

Cubic closest packing: 12-coordination, repeated stacking of three identical closely packed layers each with a slight off-set. [Common in Ag, Au, Al, Ni, Pb.](#)

CsCl Structure – Body Centered Cubic

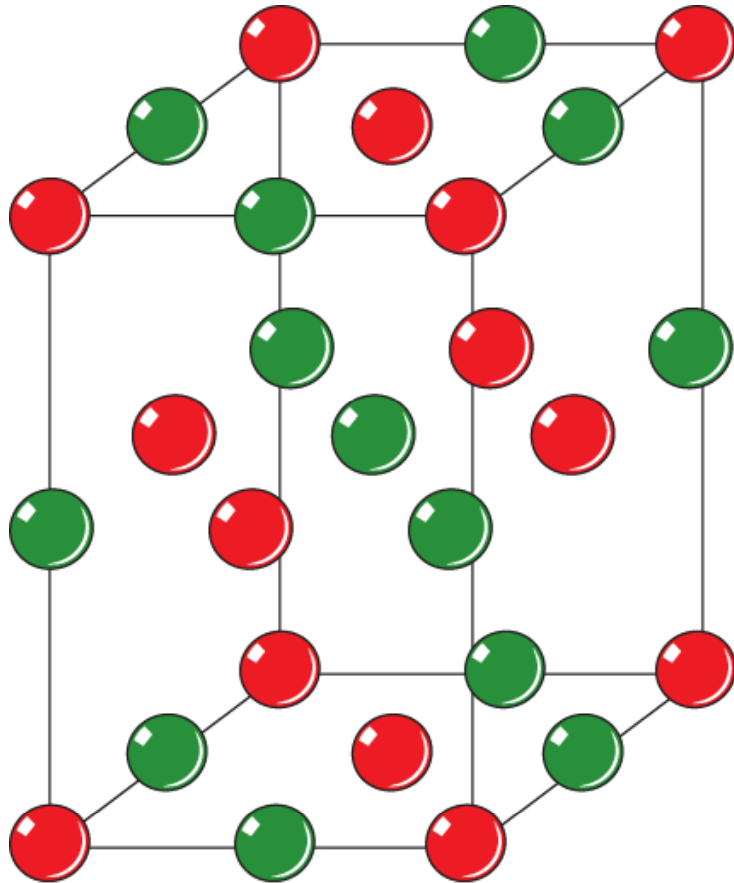


The larger ionic radius of Cs decreases the r.r. and C.N.

The anions have a SCP arrangement with cations filling the large interstitial sites.

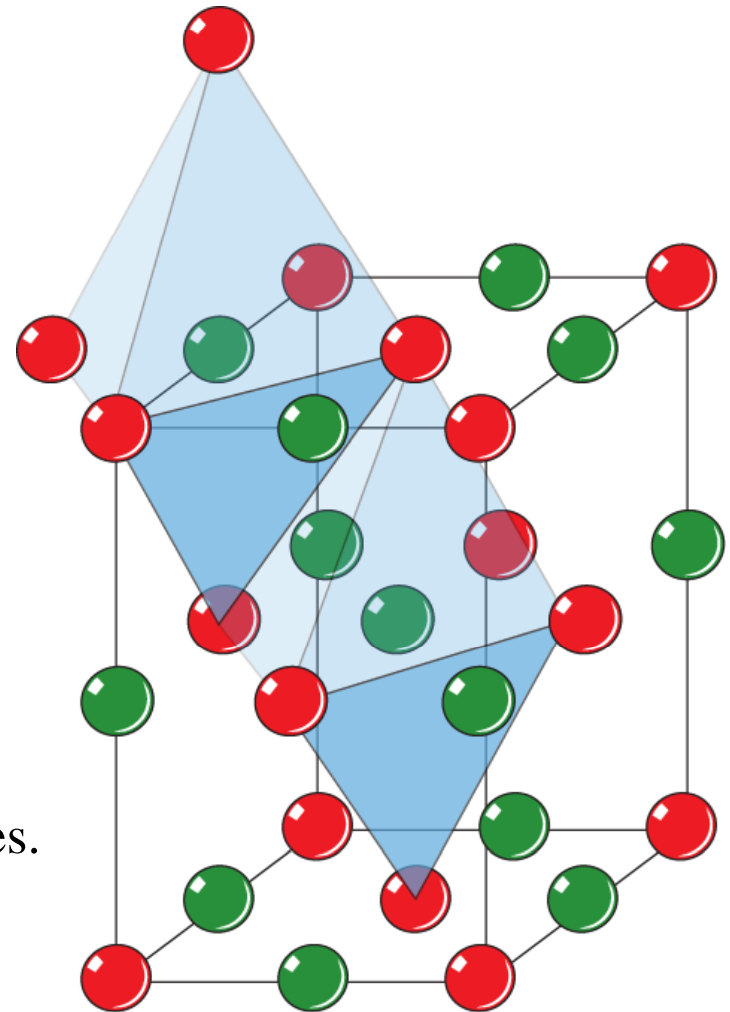
Overall structure is centred cubes that share faces.
(Unattractive for highly charged cations)

Simple Cubic Packing (SCP) – NaCl Structure



CCP structure with cations filling octahedral sites.
All tetrahedral sites are empty.

Structure contains edge sharing octahedra.



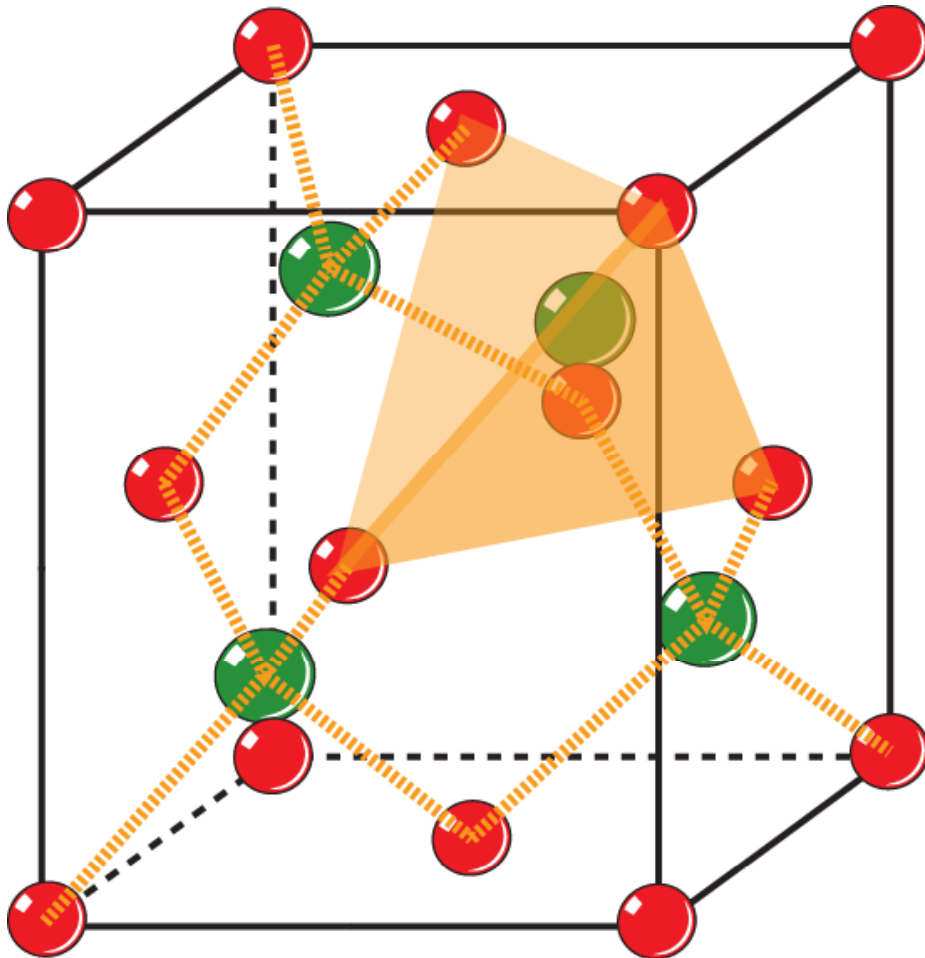
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ZnS (sphalerite) Structure – Tetrahedral coordination analogous with diamond.

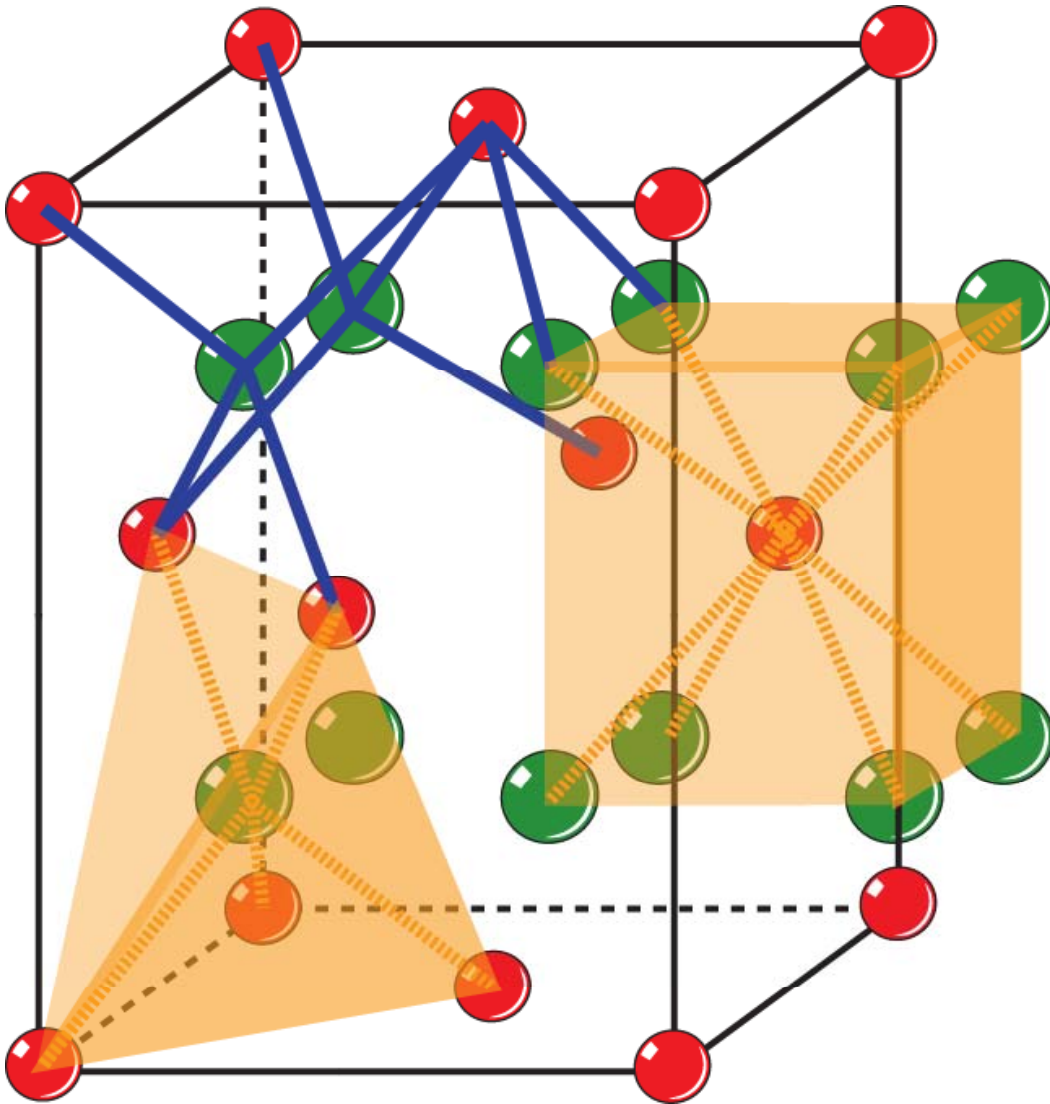


The S²⁻ anions create a face centred cube structure.

The interstitial tetrahedrally coordinated sites are filled by Zn²⁺.

It is a derivative of the diamond structure – 50% of the carbon atoms replaced by S, the rest by Zn.

CaF₂ Structure



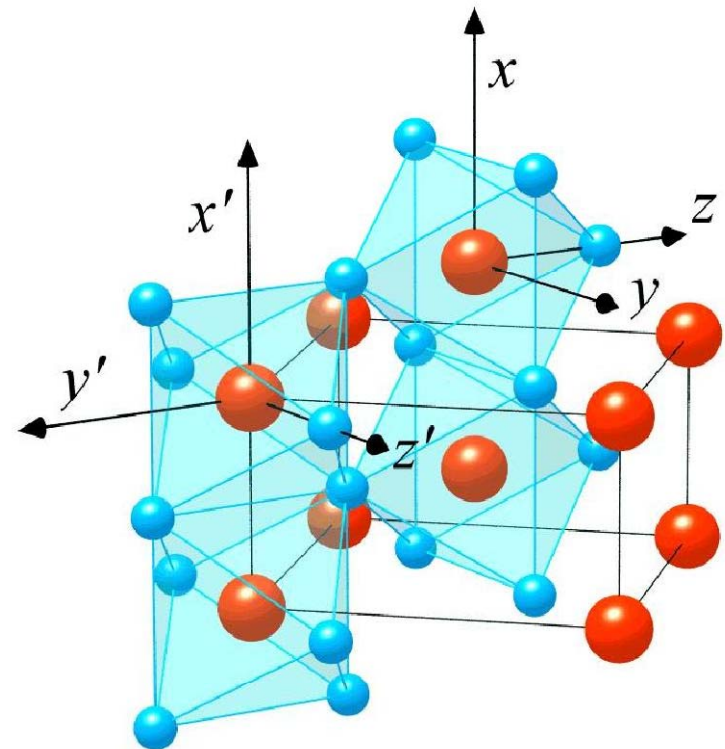
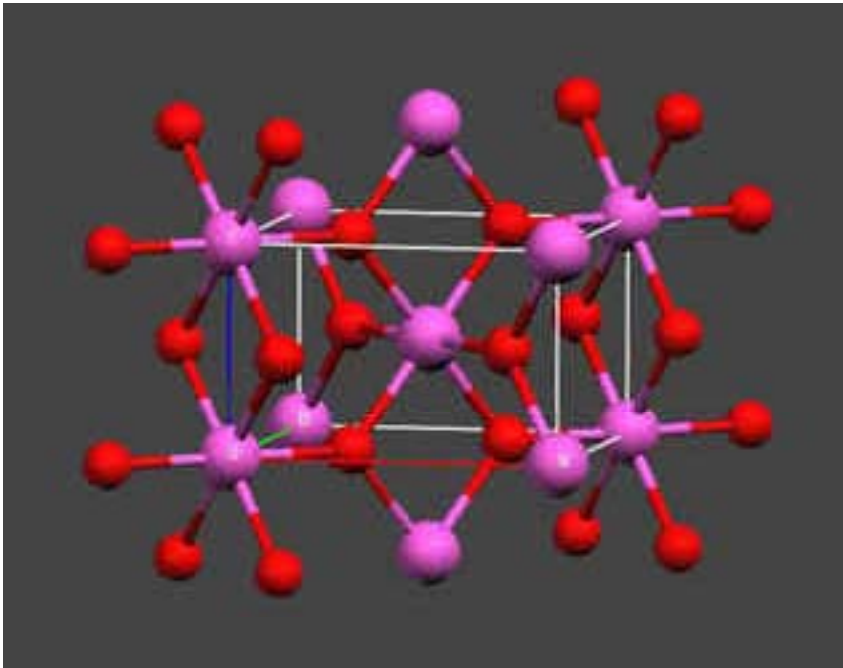
Ca²⁺ cations are arranged at the corners and face centres of a cubic unit cell (FCC).

F⁻ anions have a SCP arrangement with Ca²⁺ occupying the void of alternating cubic interstices.

Each Ca is coordinated by 8 F.
Each F is coordinated by 4 Ca.

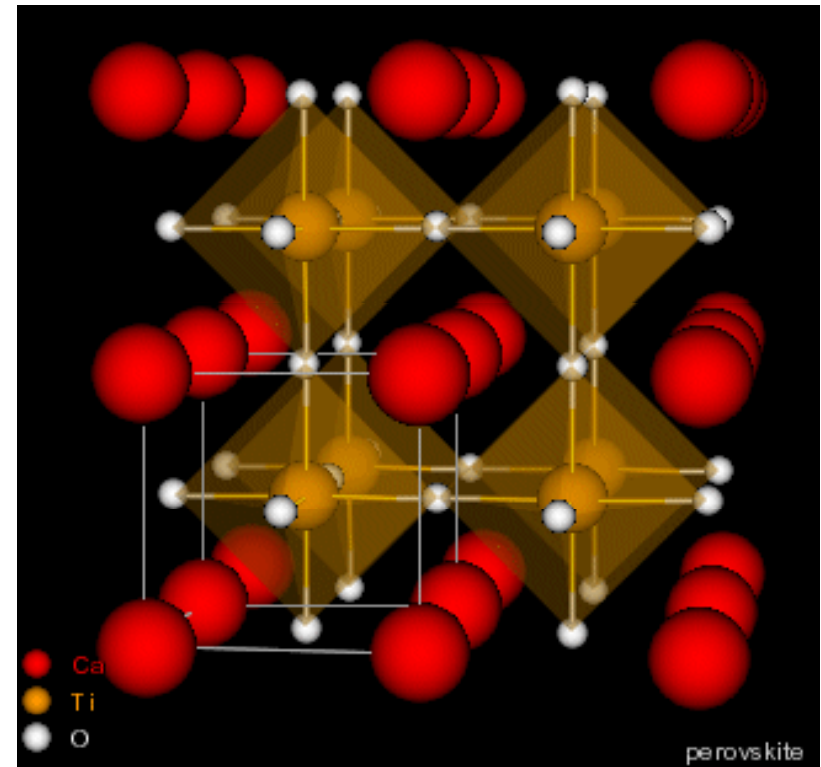
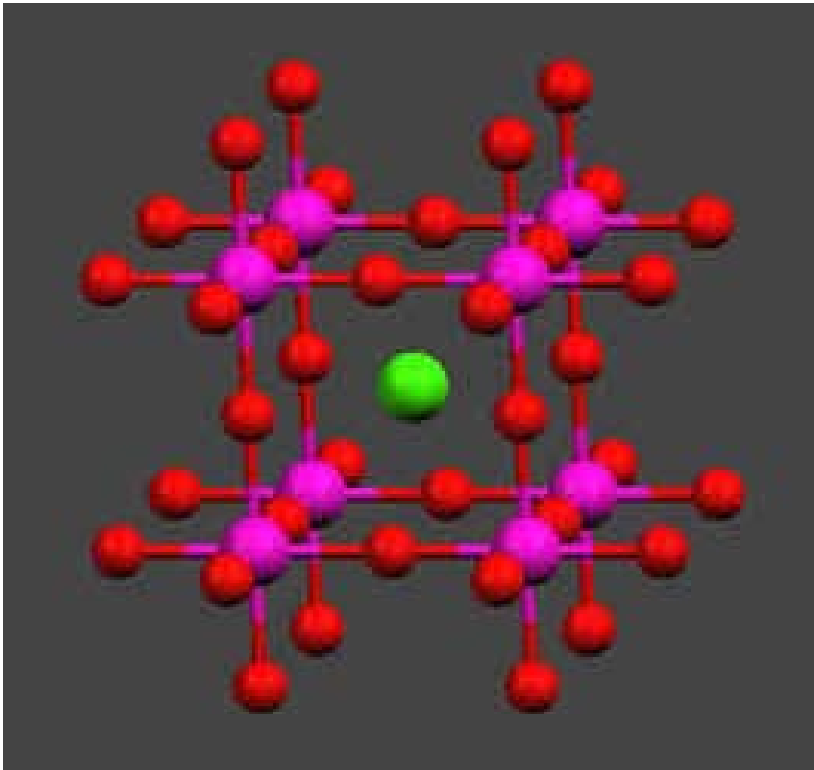
- Rutile (TiO_2)

- Based on HCP with Ti occupying half the octahedral interstitial sites.
- The anions are coordinated by 3 cations.



- Perovskite (ABO_3)

- Based on CCP of oxygen with 25% replaced by a large cation (A) with 10-fold coordination.
- B cation in apical sharing octahedron.



- Spinel (AB_2O_4)
 - Based on CCP of oxygen with $\frac{1}{8}$ of tetrahedral interstices (A) and $\frac{1}{2}$ of the octahedral interstices occupied.
 - The smaller T-site – smaller cations (Fe^{2+} , Mg^{2+} , Mn^{2+})
 - The larger O-site – larger cations (Al^{3+} , Cr^{3+} , Fe^{3+})

