

N.B.

Question:- Find the Co-ordination number of Na^+ and Cl^- ion in NaCl. It is given $r_{\text{Na}^+} = 0.90 \text{ \AA}$ and $r_{\text{Cl}^-} = 1.50 \text{ \AA}$ & What is its structure.

Now radius ratio,

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{0.90 \text{ \AA}}{1.50 \text{ \AA}} = 0.6$$

Since the radius ratio is 0.6, hence the Co-ordination number of both Na^+ and Cl^- ion is Six and its structure is Octahedral.

Crystal structure of NaCl:- The Sodium chloride, NaCl crystallises as face Centred Cubic lattice (f.c.c.). It has alternate and equal Na^+ and Cl^- ions. The limiting radius ratio is 0.526 which indicates Six Co-ordination number of Na^+ & Cl^- ions and also suggest its Octahedral shape.

The number of atoms at the corner is Eight (8) and each corner atoms contributes $\frac{1}{8}$ to the Unit Cell. and each face atom is shared by two.

$$\text{Hence effective number of atoms per unit cell} = \left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 1 + 3 = 4$$

So, each Na^+ ion surrounded by six Cl^- ions situated at the Six corners of a regular Octahedron, similarly each Cl^- ion is surrounded by Six Na^+ ion.

In the Octahedral structure of NaCl, Cl^- ion may be regarded as having a Cubic close packing in which all octahedral holes are filled by Na^+ ions.

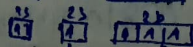
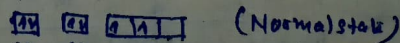
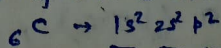
Crystal Structure of CsCl:- The Cesium chloride crystallises as body Centred Cubic (b.c.c.) lattice.

The Co-ordination number of CsCl ions i.e. Cs^+ and Cl^- ion is Eight. The radius ratio 0.92 is also justify it. The number of atoms at corners is Eight and the Co-ordination number is also eight. The Central atom is not shared by any atom.

$$\text{Hence the effective number of atoms per unit cell} = \frac{1}{8} \times 8 + 1 = 2$$

The Cs^+ ion is sufficiently large enough to allow eight Cl^- ions to surround it without touching each other and vice-versa. It is neither close packed nor strictly b.c.c. arrangement.

Crystal Structure of Diamond:- In Diamond each Carbon atom is in sp^3 hybrid state and it is attached to four other similarly hybridised C-atoms by σ bond. These bonds are formed by the overlapping of sp^3 hybrid orbitals of one C-atom with another sp^3 hybrid orbital of another carbon atom.



4 sp^3 hybrid orbitals

C.N of each C-atom is 4 (tetrahedral)

Hence Diamond has three dimensional network and having giant structure. The C bond is strong and extended by three dimension so it is exceptionally hard having high M.P.

Crystal structure of CaF_2 :- The radius ratio is 0.7, it suggests that it has b.c.c. structure. The Number of F^- (Fluoride) ion is double than that of Ca^{2+} ion. The Co-ordination number of Ca^{2+} and F^- ions are 8 and 4 respectively.

The structure is not close packed structure. Each Ca^{2+} ion is surrounded by 8 F^- ions at the corners of the cube and each F^- (Fluoride) ions is surrounded by 4 (four) Ca^{2+} ions in tetrahedral arrangement manner.

It is CsCl structure with the diagonal pairs missing. The Ca^{2+} ions are present in position of C.C.P. with the F^- ions in tetrahedral holes.

Crystal structure of Li_2O . In Li_2O , every O^{2-} ion is surrounded by eight Li^+ ion just reverse to CaF_2 structure. So it has antifluoride structure.

The O^{2-} ions are in the position of C.C.P. with the Li^+ ions in tetrahedral holes.

The number of Li^+ ions is double than that of O^{2-} ions. The Co-ordination Number (C.N.) of Li^+ ion is 4 and that of O^{2-} ion is 8 (eight).

Close Packing Cubical Close Packing. (C.C.P.)
& Hexagonal Close Packing. (H.C.P.)

The Close packing refers to the arrangement of a given number of equal spheres leaving the minimum amount of space.

There are two types of Close packing arrangements i.e. h.c.p and C.C.P.

In other words we can say That the arrangement of atom molecules or ions in a crystal in which a given Number of equal spheres resist the minimum vacant space, is called Close packed Structure.

In a Plane, Spheres pack together in such a way that each sphere touches six other spheres.
i.e. Centres of the spheres lie at the corners of an Equilateral triangle.

A 2nd layer of spheres can be superimposed on the 1st layer so that each sphere is in the contact with three spheres of the 1st layer.

A 3rd similar layer of spheres may be added in one of the two ways.

The first way is that sphere in the 3rd layer are centered immediately above the sphere in the first layer. This gives rise to h.c.p (Hexagonal Closed Packed) in which the structure is repeated after two layers.

The 2nd way is that the spheres in the 3rd layer are over holes in the 1st layer which are not occupied by 2nd layer. This gives rise to c.c.p (Cubical Closed Packed).

This is in fact an assemblage of spheres at the corners and face centres of a cubic unit cell.

In c.c.p. the structure is repeated after three layers.

The c.c.p is shown by Al, Cu, Ag, Au & Sr etc.
& h.c.p is shown by Mg, Zn, Cd, Ti, Hf etc.

In c.c.p (Cubical Closed Packed) there are two types of holes (a) Tetrahedral holes (b) Octahedral holes.

Tetrahedral holes: - In which each hole is (surrounded) bounded by four spheres.

Octahedral holes: - In Octahedral holes, each hole is bounded by six spheres with their centres at the corners of a regular Octahedron.

There are as many Octahedral holes as there are spheres. and there are twice as many tetrahedral holes

If all tetrahedral holes are filled, the structure is XY_2
for examples - CaF_2 , Na_2O etc.

If all Octahedral holes are filled, the structure is XY
for example: - $NaCl$, MgO etc.