THE SOLID STATE

1.   INTRODUCTION :

Matter can exist in three physical states namely ; solid, liquid and gas. Matter consists of tiny particles (atoms, ions or molecules). If the particles are very far off from one another, they behave like gases; nearer, they behave like liquids, and nearest, like solids. The three states of matter are thus known as the three states of aggregation from Latin word meaning **"Flacking together"**.

The fundamental difference between the three states of aggregation lies essentially in the difference of the relative amounts of energy possessed by the particles in the three states. The relative energies in the different states of matter are governed by two universal opposing tendencies associated with the particles :

(i)   They have tendency of mutual attraction.

(ii)   They have tendency of escape from one another which is known as escaping tendency.

Whether a given system would exist as a solid, liquid or gas depends upon the relative strengths of these opposing tendencies. If the escaping tendency is greater than the attraction between them, the molecules will be carried far from each other to distances which are large as compared with their diameters, the system will exists in gaseous state. But in the liquid state the molecular attraction exceeds the escaping tendency and in the solid state the forces of attraction are so much greater than those of escaping tendency that each particle is bound into a definite place in a rigid position by the mutual attraction of molecules. In other words, in the solid state, the system possesses the amount of energy of motion i.e. kinetic energy.

2.   THE SOLID STATE :

The solid are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possesses the unique property of being rigid. Such solids are known as true solids e.g. NaCl, KCl, Sugar, Ag, Cu etc. On the other hand the solid which loses shapes on long standing, flows under its own weight and easily distorted by even mild distortion forces are called pseudo solids e.g. glass, pitch etc.

Some solids such as NaCl, Sugar, Sulphur etc. have properties not only of rigidity and incompressibility but also of having typical geometrical forms. These solids are called as crystalline solids. In such solids there is definite arrangements of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal. This is named as long-range order. This three dimensional arrangement is called **crystal lattice or space lattice**. Other solids such as glass, rubber, plastics etc. have rigidity and incompressibility to a certain extent but they do not have definite geometrical forms or do not have long range order are known as amorphous solids.

3.   DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS :

(i)   **Characteristic Geometry :** In the crystalline solids the particles (atoms, ions, or molecules) are definitely and orderly arranged thus these have characteristic geometry while amorphous solids do not have characteristic geometry.

(ii)   **Melting Points :** A crystalling solids has a sharp melting point i.e. it changes into liquid state at a definite temperature. On the contrary an amorphous solid does not has a sharp melting point. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt or sharp change from solid to liquid state. Therefore, amorphous solids are regarded as "liquids at all temperatures".

(iii)   **Cooling curve :** Amorphous solids show smooth cooling curve while crystalline solids show two breaks in cooling curve. In the case of crystalline solids two breaks points 'a' and 'b' are appear. These points indicate the beginning and the end of the process of crystallization. In this time interval temperature remains constant. This is due to the fact that during crystallisation process energy is liberated which compensates for the loss of heat thus the temperature remains constant.

Cooling curve of an amorphous solid

Cooling curve of crystalline solid
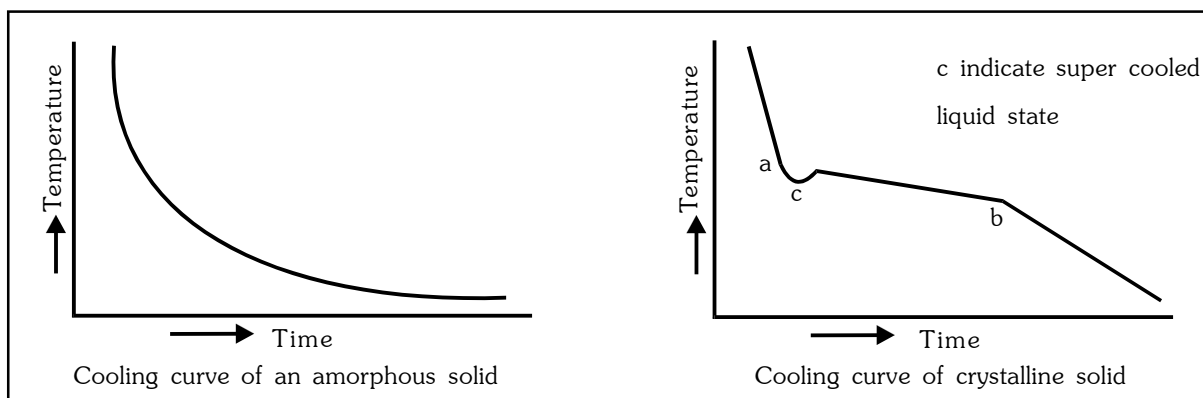
(iv) Isotropy and Anisotropy : Amorphous solids differ from crystalline solids and resemble liquids in many respects. The properties of amorphous solids, such as electrical conductivity, thermal conductivity, mechanical strength, refractive index, coefficient of thermal expansion etc. are same in all directions. Such solids are known as isotropic. **Gases and liquids are also isotropic.**

On the other hand crystalline solids show these physical properties different in diferent directions. Therefore crystalline solids are called anisotropic. The anisotropy itself is a strong evidence for the existence of orderly molecular arrangement in crystals. For example, the velocity of light passing through a crystal is different in different directions. A ray of light entering in a crystal may split up into two components each following a different path and travelling with a different velocity.

This phenomenon is called double refraction. In the figure two different kinds of atoms are shown in two dimensional arrangement. If the properties are measured along the direction CD, they will be different from those measured along the direction AB. This is due to the fact that in the direction AB each row is made up of one type of atoms while in the direction CD each row is made up of two types of atoms. It is important of note that in the case of amorphous solids, liquids and gases atoms or molecules are indentical and all properties are same in all directions.

Anisotropic behaviour of crystals
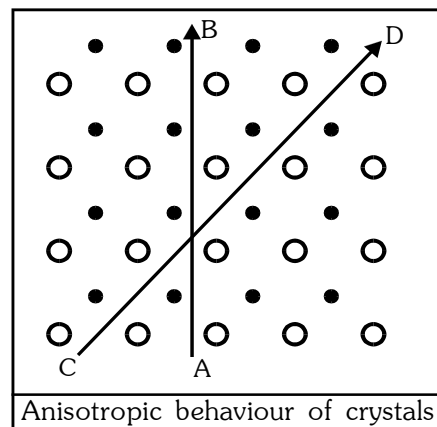
(v) Cutting :

Crystalline solids give clean cleavage while amorphous solids give irregular cut, due to conchoidal fracture on cutting with a sharp edged tool.

4. CRYSTALLINE STATE :

"A crystal is a solid composed of atoms (ions or molecules) arranged in an orderly repetitive array".

Most of the naturally occuring solids are found to have definite crystalline shapes which can be recognised easily. These are in large size because these are formed very slowly thus particles get sufficient time to get proper position in the crystal structure. Some crystalline solids are so small that appear to be amorphous. But on examination under a powerful microscope it is also seen to have a definite crystalline shape. Such solids are known as micro crystalline solide. Thus the crystallinity of a crystal may be defined as "a condition of matter resulting from an or orderly, cohesive, three dimensional arrangement of its component particles (atoms, ions or molecules) in space". This three dimensional arrangement is called crystal lattice or space lattice. The position occupied by the particles in the crystal lattice are called lattice sites or lattice points. The lattices are bound by surface that usually planar and known as faces of the crystal.

"The smallest geometrical position of the crystal which can be used as repetitive unit to build up the whole crystal is called a unit cell."

The angle between the two perpendiculars to the two intersecting faces is termed as the interfacial angle which may be same as the angle between the unit cell edges. Goniometer is used to measure the interfacial angle. It is important to note that interfacial angle of a substance remains the same although its shape may be different due to conditions of formation.


Interfacial angles of crystal
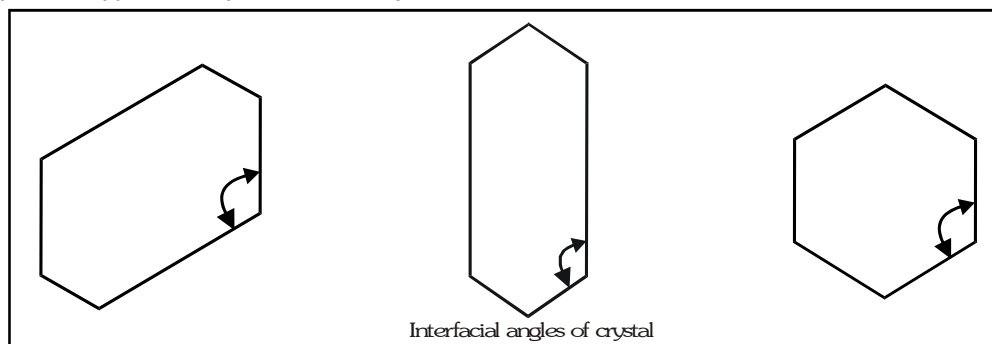
This is known as law of constancy of interfacial angle or law of crystallography.

5.   **TYPES OF THE CRYSTALS :**

Crystal are divided into four important types on the basis of chemical bonding of the constituent atoms.

   (i)   Ionic Crystals :

These are formed by a combination of highly electro-positive ions (cations) and highly electronegative ions (anions). Thus strong electrostatic force of attraction acts with in the ionic crystals. Therefore, a large amount of energy is required to separate ions from one another. The type of the crystal lattice depends upon (i) The size of the ion (ii) The necessity for the preservation of electrical neutrality. Therefore alternate cations and anions in equivalent amounts are arranged in the ionic crystal e.g. NaCl, KF, CsCl etc.

Crystal structure of NaCl
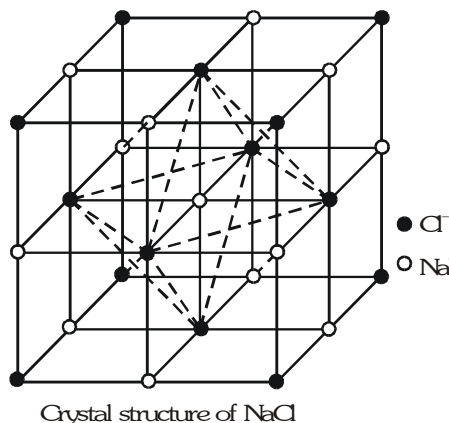
   (ii)   Covalent Crystals :

These are formed by sharing of valence electrons between two atoms resulting in the formation of a covalent bond. The covalent bonds extend in two or three dimensions forming a giant interlocking structure called network. Diamond and graphite are the good examples of this type.

   (iii) Molecular Crystals :

In these crystals, molecules occupy the lattice points of the unit cells, except in solidified noble gases in which the units are atoms, where the binding is due to vander Waal's' forces and dipole-dipole forces. Since vander Waal's forces are non-directional hence structure of the crystal is determined by geometric consideration only. Solid H_2, N_2, O_2, CO_2, I_2, sugar etc. are well known examples of such crystal in which vander Waal's forces are acting . Ice is the common example in which dipole-dipole forces of attraction (hydrogen bonding) are active. Many organic and inorganic crystals involve hydrogen bonds. Although these are comparatively weaker but play a very important role in determining the structures of substances e.g. polynucleoides, proteins etc.

   (iv)   Metallic Crystals :

These are formed by a combination of atoms of electropositive elements. These atoms are binded by metallic bonds. It may be defined as :

The force that binds a metal ion to a number of electrons within its sphere of influences is known as metallic bond OR

A bond which is formed between electropositive elements OR

The attractive force which holds the atoms of two or more metals together in a metal crystal or in an alloy.

We know that the force of attraction between metal ions and valency electrons is very strong. This force of attraction is responsible for a compact solid structure of metal.

The important characteristics of the various types of crystals are given in the following table:

Some Important Characteristics of Various types of Crystals

|	Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1.	Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2.	Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole-dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3.	Hardness	Hard	Very hard Graphite is soft	Soft	Hard or soft
4.	Brittleness	Brittle	Interme-diate	Low	Low
5.	Melting point	High	Very high	Low	Varying from moderate to high
6.	Electrical Conduction	Semi cond-uctor due to crystal impe-rfections,con-ductor in fused state	Non-con-ductor Graphite is good conductor	Bad condu-ctor	Good conductors
7.	Solubility in Polar solvents	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
8.	Heat of Vaporisation (kj mol^{-1})	NaCl(s) 170-75	Graphite 718-43	NH_3(s) 23.55	Cu(s) 304.59
9.	Heat of fusion (kj mol^{-1})	NaCl 28.45	– –	NH_3 (s) 5.65	Cu(s) 13.016
10.	Example	NaCl, KNO_3 CsCl, Na_2SO_4 ZnS	Diamond, graphite, Quartz (SiO_2), SiC	H_2O(s), CO_2(s), Sulphur, Sugar, Iodine,noble gases	Na, Cu, Ag, Fe, Pt, alloys

6. **ISOMORPHISM** : The occurence of a given substance in more than one solid crystalline forms have different physical properties is known as polymorphism. This property when occurs in elements is known as allotropy.

Sometimes we come across examples of chemically different solids which crystallise in the same crystalline shape. Such substances are said to be Isomorphous (same shape). Their chemical constitutions are very similar and in some cases crystals of one substance may continue to grow when placed in a saturated solution of the other e.g. potash alum and chrome alum crystals have the same shape and can be grown in each other's solutions. Mitscherlich deduced that isomorphous substances have similar chemical formula e.g. phosphates and arsenates are said to be isomorphous with one another viz.

1. $Na_2HPO_4.12H_2O$ and $Na_3AsO_4.12H_2O$
2. K_2SO_4 , K_2CrO_4
3. $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$
4. $KMnO_4$, $KClO_4$
5. $K_2SO_4.Al_2(SO_4)_3.24H_2O$, $K_2SO_4. Cr_2(SO_4)_3.24H_2O$. However, the law is not without exceptions.

7. **SPACE LATTICE/CRYSTALLINE LATTICE/3–D LATTICE :**
Space lattice is a regular arrangement of lattice points showing how the particles are arranged at different sites in 3D–view.
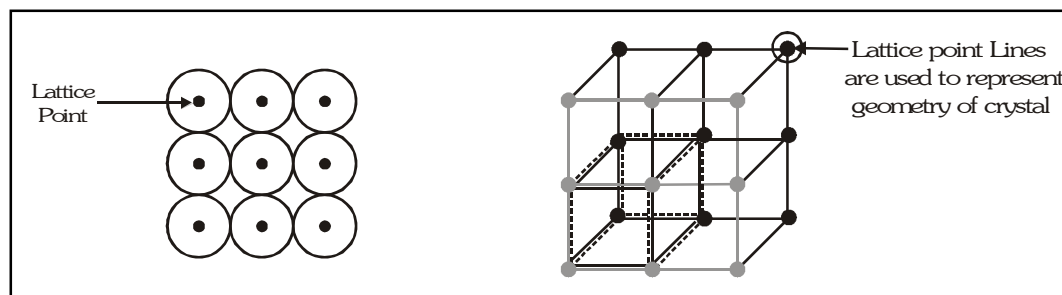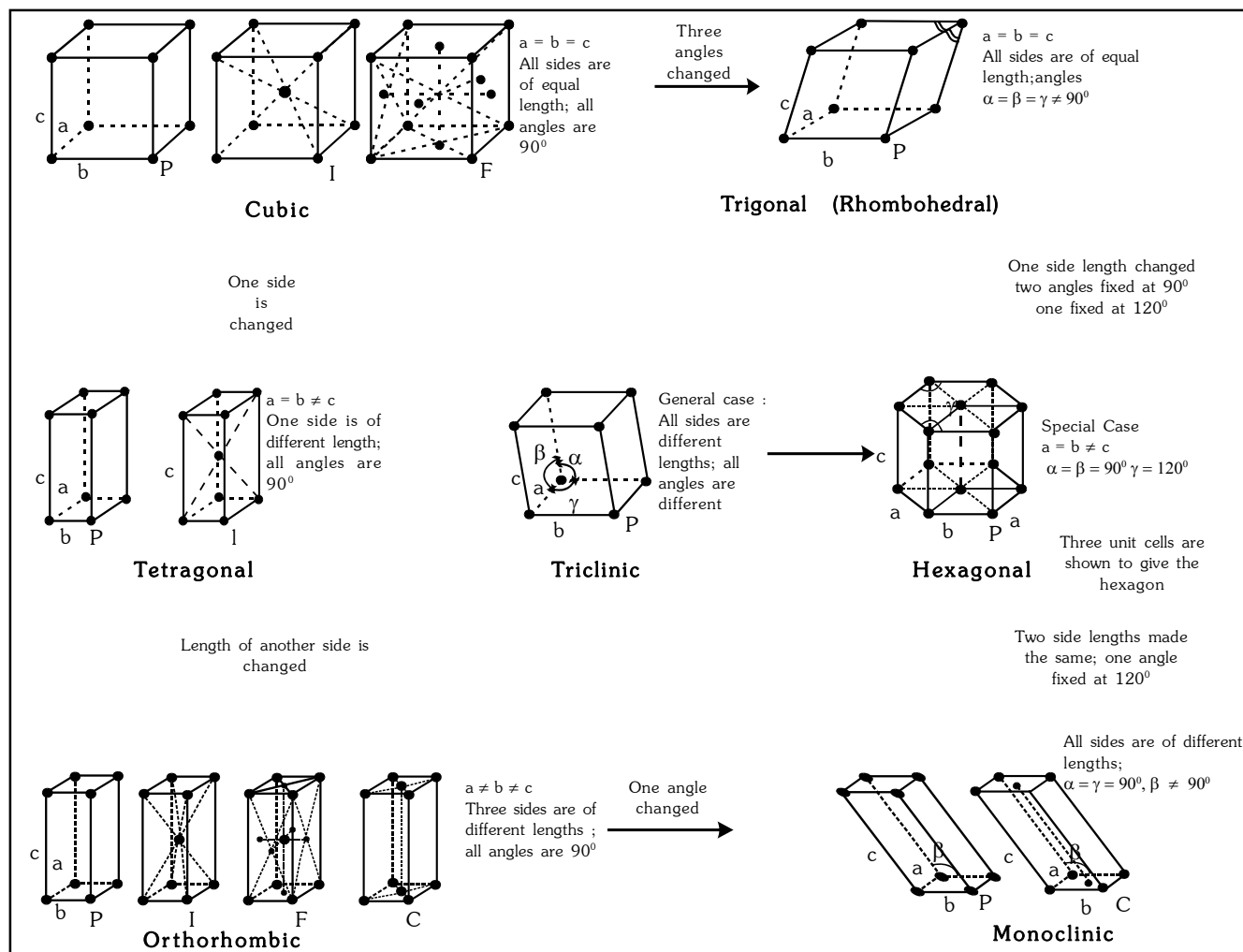

" The three dimensional distribution of component particles in a crystal can be found by X-ray diffraction of different faces of the crystal.

On the basis of the classification of symmetry, the crystals have been divided into seven systems. These can be grouped into 32 classes which in turn can be regrouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table.

The Seven Crystal Systems

	Name of System	Axes	Angles	Bravais Lattices
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4.	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred = 4
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°;$ $\beta \neq 90°$	Primitive, End - centred = 2
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Primitive = 1 Total = 14

a = b = c
All sides are
of equal
length; all
angles are
90^0

Cubic

Three
angles
changed →

a = b = c
All sides are of equal
length;angles
$\alpha = \beta = \gamma \neq 90^0$

Trigonal (Rhombohedral)

One side
is
changed

One side length changed
two angles fixed at 90^0
one fixed at 120^0

a = b ≠ c
One side is of
different length;
all angles are
90^0

Tetragonal

General case :
All sides are
different
lengths; all
angles are
different

Triclinic

Special Case
a = b ≠ c
$\alpha = \beta = 90^0\ \gamma = 120^0$

Hexagonal

Three unit cells are
shown to give the
hexagon

Length of another side is
changed

Two side lengths made
the same; one angle
fixed at 120^0

a ≠ b ≠ c
Three sides are of
different lengths ;
all angles are 90^0

One angle
changed →

All sides are of different
lengths;
$\alpha = \gamma = 90^0, \beta \neq 90^0$

Orthorhombic

Monoclinic

These crystal systems differ in length of unit cell edges (a, b and c) and the angles between the unit cell edges 4. In cubic and trigonal (rhombohedral) systems, the three unit edges are of equal lengths but for the rest five systems it is not so. The interfacial angles are all 90^0 in the cubic, tetragonal and orthorhombic systems but it is not so for the rest four systems.

8. **UNIT CELL (U.C.) :** Unit cell of the crystalline substance is defined as the smallest repeating unit which shows the complete geometry of the crystalline substance. For eg. brick in wall. A unit cell is the smallest picture of the whole crystal. A unit cell is characterized by the edge lengths a, b and c along the three edges of the unit cell and the angles α, β and γ between the pair of edges bc; ca and ab respectively.
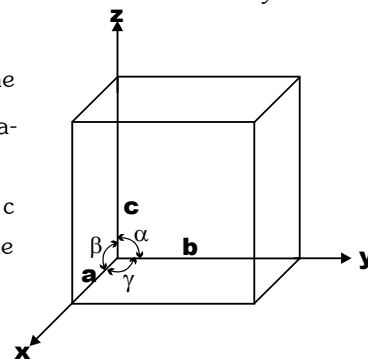
9. **CO-ORDINATION NUMBER :**

The number of nearest particles around a specific particle in a given crystalline substance is called as co-ordination number of that crystalline substance.

10. **PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :** Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance ie packing efficiency is equal to-

$$P.E. = \frac{\text{Volume occupied by atoms present in a crystal}}{\text{Volume of crystal}}$$

$$P.E. = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of Unit Cell}}$$

$$P.E. = \frac{n \times (4/3)\pi r^3}{V}$$

Where n = number of atoms present in unit cell

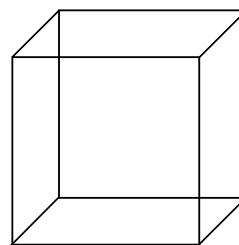## 11. GEOMETRY OF A CUBE

Number of corners = 8

Number of faces = 6
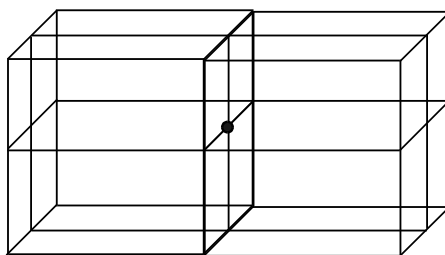
Number of edges = 12

Number of cube centre = 1

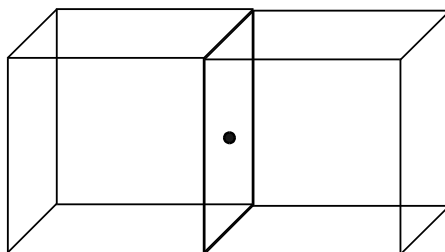Number of cube diagonals = 4

Number of face diagonals = 12

◆ **Contribution of an atom at different sites of cube :**
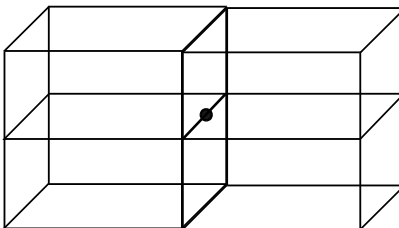
A corner of a cube is common in 8 cubes. So $\frac{1}{8}$ th part of an atom is present at this corner of cube.

A face of a cube is common is 2 cubes. So $\frac{1}{2}$ th part of of an atom is present at the face of a cube.

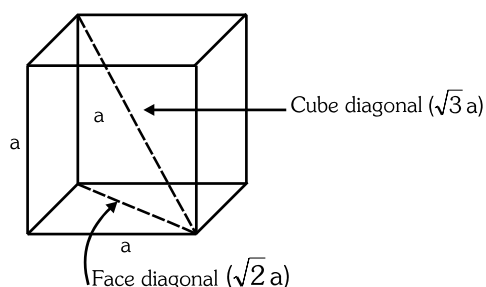An edge of a cube is common in four cubes, so $\frac{1}{4}$ th part of the atom is present at the edge of a cube

A cube centre is not common in any another cube, so one complete atom is present at the cube centre.
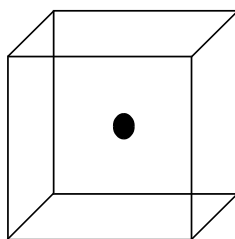
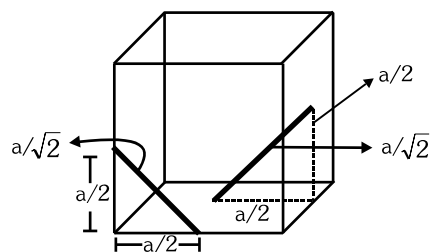❑   LANGTH OF FACE DIAGONAL AND CUBE DIAGONAL :

Distance between   Distance between

2 adjacent face centres $= \dfrac{a}{\sqrt{2}}$ 2 adjacent edge centre $= \dfrac{a}{\sqrt{2}}$

Consider the triangle ABC, with the help of pyathogorous theorem

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a \qquad \text{(length of face diagonal.)}$$

Consider the triangle DAC, with the help of phathogorous theorem

$$DC = \sqrt{DA^2 + AC^2}$$

$$= \sqrt{a^2 + (\sqrt{2}a)^2}$$

$$= \sqrt{3}a \quad \text{(length of cube diagonal)}$$

**12.**   **TYPE OF UNIT CELL (BRAVAIS LATTICE) :**

The distance between sucessive lattice planes of the same type is called the spacing of planes or interplanar distance between the planes. On the basis of this aspect, the lattices may be divided in following classes :

(1)   **Simple/Primitive/Basic Unit cell :**

A unit cell having lattice point only at corners called as primitive or simple unit cell. i.e. in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (atoms) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.
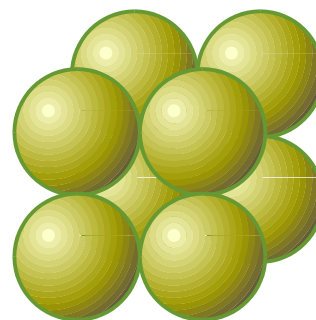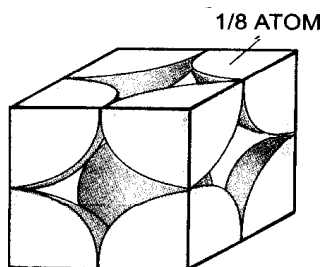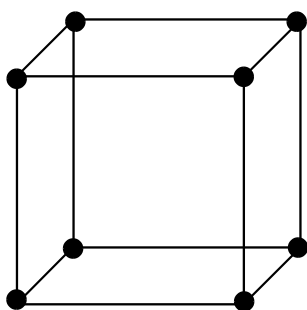
(a)   Relationship between edge length 'a' and atomic radius 'r' :
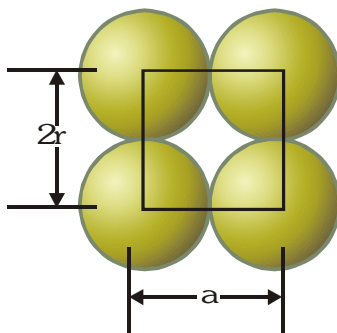
        a = 2r

i.e.   r = $\dfrac{a}{2}$ (One face of SCC)

(b)   **Number of atoms present in unit cell :** In this case one atom or ion lies at the each corner. Hence
simple cubic unit cell contains a total of $\dfrac{1}{8} \times 8$ = 1 atom or ion/unit cell.

(c)   **Packing efficiency (P. E.) :**

P.E. = $\dfrac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} = \dfrac{n \times \dfrac{4}{3} \pi r^3}{V}$ $\left[\because \text{Volume of atom} = \dfrac{4}{3} \pi r^3 \right]$

For SCC :   P.E. = $\dfrac{1 \times \dfrac{4}{3} \times \pi \times \left(\dfrac{a}{2} \right)^3}{a^3}$ $\left[\because r = \dfrac{a}{2} \text{ and } V = a^3, n = 1 \right]$

        = $\dfrac{\pi}{6} = 0.524$ or   52.4 %

2.   **Body centred cubic (b.c.c.) cell :** A unit cell having lattice point at the body centre in addition to the
lattice point at every corner is called as body centered unit cell.

Here the central atom is surrounded by eight equidistant atoms and hence the co-ordination number is eight.

The nearest distance between two atoms will be $\dfrac{a\sqrt{3}}{2}$

1/8 ATOM

1 ATOM
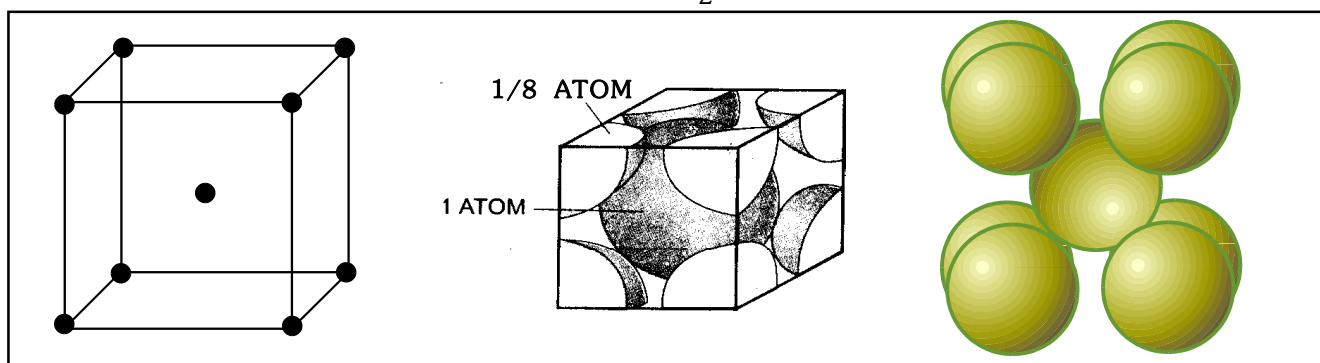
(a)   Relationship between edge length 'a' and atomic radius 'r' :-
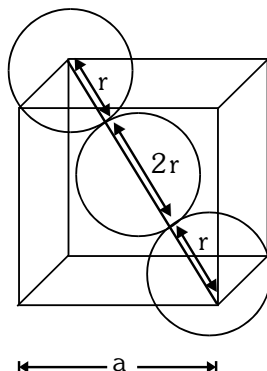
In BCC, along cube diagonal all atoms touches each other and the length of cube diagonal is $\sqrt{3}a$.

So, $\sqrt{3}a = 4r$

i.e. $r = \dfrac{\sqrt{3}a}{4}$

(b) **Number of atom present in unit cell :**

$$\left(\frac{1}{8} \times 8\right) + \left(1 \times 1\right) = 1 + 1 = 2 \text{ atoms/unit cell}$$

(Corner)   (Body centre)

In this case one atom or ion lies at the each corner of the cube. Thus contribution of the 8 corners is

$\left(\dfrac{1}{8} \times 8\right) = 1$, while that of the body centred is 1 in the unit cell. Hence total number of atoms per unit cell is 1 + 1 = 2 atoms (or ions)

(c) **Packing efficiency :**

$$P.E. = \frac{n \times \dfrac{4}{3}\pi r^3}{V} = \frac{2 \times \dfrac{4}{3} \times \pi \left(\dfrac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \quad \left[\because \ n = 2, \ r = \frac{\sqrt{3}a}{4}, \ V = a^3\right]$$

In B.C.C.   68% of total volume is occupied by atom or ions.

3. **Face centred cubic (f.c.c.) cell :** A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. Considering an atom at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number

will be twelve and the distance between the two nearest atoms will be $\dfrac{a}{\sqrt{2}}$.
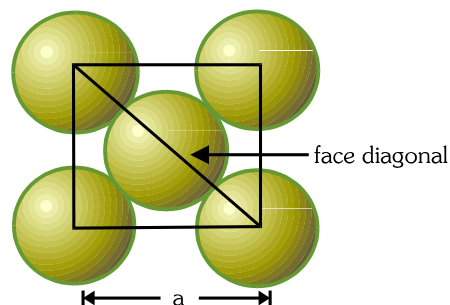

1/8 ATOM

1/2 ATOM
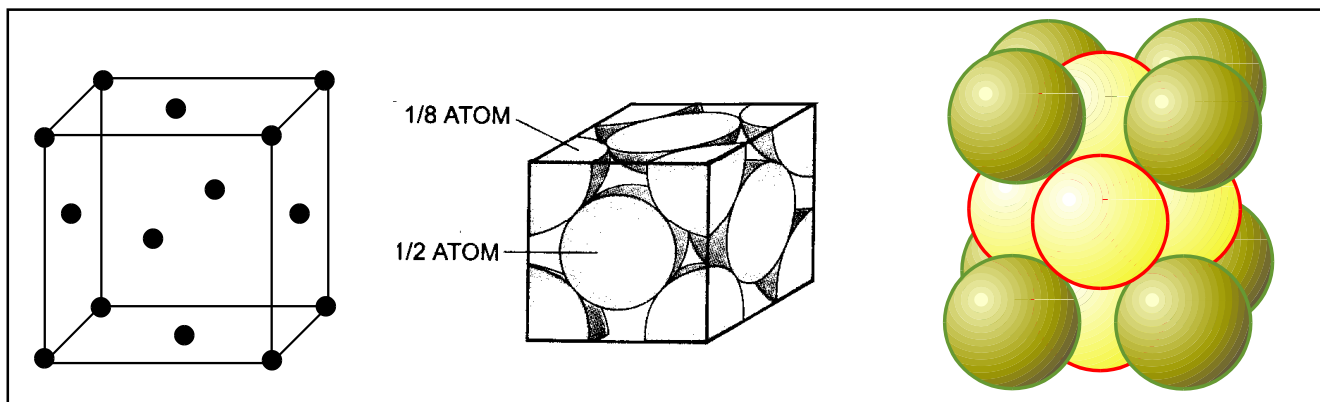
(a) **Relationship between edge length 'a' and atomic radius 'r' :**

In FCC, along the face diagonal all atoms touches each other and

the length of face diagonal is $\sqrt{2}a$.

So $4r = \sqrt{2}a$

i.e. $r = \dfrac{\sqrt{2}a}{4} = \dfrac{a}{2\sqrt{2}}$ $\boxed{r = \dfrac{a}{2\sqrt{2}}}$

face diagonal

a

(b) **Number of atoms per unit cell :**

$$\left(\frac{1}{8} \times 8\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4 \text{ atoms/unit cell}$$

$\underset{\text{Corner}}{} \quad \underset{\text{faces}}{}$

In this case one atom or ion lies at the each corner of the cube and one atom or ion lies at the centre of each face of the cube. It may noted that only $\frac{1}{2}$ of each face sphere lie with in the unit cell and there are six such faces. The total contribution of 8 corners is $\left(\frac{1}{8} \times 8\right) = 1$, while that of 6 face centred atoms is $\left(\frac{1}{2} \times 6\right) = 3$ in the unit cell.

Hence total number of atoms per unit cell is $1 + 3 = 4$ atoms (or ions).

(c) **Packing efficiency :**

$$\text{P.E.} = \frac{n \times \frac{4}{3}\pi r^3}{V} \qquad\qquad [\because \text{ for FCC } n = 4, \ r = \frac{a}{2\sqrt{2}}, \ V = a^3]$$

$$= \frac{4 \times \frac{4}{3}\pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \qquad \text{or} \qquad 74\ \%$$

i.e. In FCC, 74% of total volume is occupied by atoms.

4. **End Centered Unit Cell :**

A unit cell having lattice point at the centres of only one set of opposite faces in addition to the lattice point at every corner called as end centered unit cell.

Note : This type of Bravais lattice is obtained only in orthorhombic and monoclinic type unit cell.

Number of atoms per unit cell in cubic close packed structure of atoms ·

Unit cell	Number of atoms at			No. of atoms per unit cell	Volume occupied by particles (%)
	Corners	Centres	Faces		
Simple cube	$8 \times \frac{1}{8} = 1$	0	0	1	52.4
Body centred cube (BCC)	$8 \times \frac{1}{8} = 1$	1	0	2	68
Face centred cube (FCC)	$8 \times \frac{1}{8} = 1$	0	$6 \times \frac{1}{2} = 3$	4	74

13. **CRYSTAL DENSITY OF THE CRYSTAL :**

If the length of edge of the unit cell is known we can calculate the density of the crystal as follow :

Let length of edge of the unit cell be ℓ.

$\therefore$ Volume of the unit cell $= \ell^3 = V \text{ cm}^3$

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

Mass of the unit cell = Number of atoms present in a unit cell $\quad$ Mass of one atom

$$= n \quad m \quad g$$

But mass of one atom (m) $= \dfrac{\text{Atomic mass}}{\text{Avogadro Number}} = \dfrac{M}{N_A}$

$$\text{Mass of the unit cell} = n \times \frac{M}{N_A} g \text{ , Density of the unit cell} = \frac{n \times \dfrac{M}{N_A}}{V} \text{ gm cm}^{-3}$$

$$\therefore \quad \text{Density of the unit cell} = \frac{n \times M}{V \times N_A} g \text{ cm}^{-3}$$

$$\rho(C.D.) = \frac{n \times M}{V \times N_A} g \text{ cm}^{-3}$$

Ex. An element (atomic mass = 60) having face centred cubic crystal has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell (Avogadro constant, N_A = 6.02 $\times$ 10^{23} mol^{-1}) :-

Sol. Since element has fcc structure hence there are 4 atoms in a unit cell (or n = 4), Atomic mass is 60 (or M = 60), N_A = 6.02 $\times$ 10^{23} and ρ = 6.23 g cm^{-3}.

$$\because \quad \rho = \frac{n \times M}{V \times N_A}$$

or $\quad V = \dfrac{n \times M}{\rho \times N_A}$

$$= \frac{(4)\left(60 \text{ g mol}^{-1}\right)}{\left(6.23 \text{ g cm}^{-3}\right)\left(6.02 \times 10^{23} \text{mol}^{-1}\right)}$$

$$= \frac{240 \times 10^{-23} \text{ cm}^{-3}}{37.5046} = 6.4 \times 10^{-23} \text{ cm}^3 = 64 \times 10^{-24} \text{ cm}^3$$

Let ℓ be the length of the edge of the unit cell.

$\therefore \quad \ell^3 = V = 64 \times 10^{-24}$ cm^3 $\qquad$ or $\qquad \ell = 4.0 \times 10^{-8}$ cm

Ex. The density of KBr is 2.75 g cm^{-3}. The length of the edge of the unit cell is 654 pm.

Show that KBr has face centred cubic structure.

Sol. Length of the edge of the unit cell = 654 pm = 6.54 $\times$ 10^{-8} cm

$\therefore \quad$ volume (V) of the unit cell = (6.54 $\times$ 10^{-8} cm)^3

Molecular mass of KBr = 39 + 80

$$= 119 \text{ g mol}^{-1}$$

Density of KBr = 2.75 g cm^{-3}

$$\because \quad \rho = \frac{n \times M}{V \times N_A}$$

or $\quad n = \dfrac{\rho \times V \times N_A}{M}$

$$= \frac{\left(2.75 \text{ g cm}^{-3}\right)\left(6.54 \times 10^{-8} \text{cm}\right)^3 \left(6.023 \times 10^{23} \text{ mol}^{-1}\right)}{119 \text{ g mol}^{-1}}$$

$$= \frac{2.75 \times (6.54)^3 \times (6.023)(10^{-1})}{119}$$

= 3.9 = 4

Since number of atoms (or ions) in a unit cell is four hence the crystal must be face centred cubic.

Ex. An element crystallizes in a structure having f.c.c. unit cell of an edge 200 pm. Calculate its density, if 200 g of this element contains 24×10^{23} atoms.

Sol. Length of the edge of the unit cell $(\ell) = 200$ pm $= 2 \times 10^{-8}$ cm

∴ Volume (V) of the unit cell

$$= (2 \times 10^{-8} \text{ cm})^3 = 8 \times 10^{-24} \text{ cm}^3$$

Mass of the element (M) = 200 g

Number of the atoms $(N_0) = 24 \times 10^{23}$

the number of atoms per unit cell (fcc) = 4

∵ $$\rho = \frac{n \times M}{V \times N_0}$$

$$= \frac{(4)(200 \text{ g})}{(8 \times 10^{-24} \text{ cm}^3)(24 \times 10^{23})} = 41.7 \text{ g cm}^{-3}$$

Ex. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If volume of this unit cell is 24×10^{-24} cm^3 and density of the element is 7.2 g cm^{-3}. Calculate the number of atoms present in 200 g of the element.

Sol. Volume (V) of the unit cell

$$= 24 \times 10^{-24} \text{ cm}^3$$

Density of (ρ) of the element = 7.2 g cm^{-3}

Mass of the element = 200 g

Number of atoms (n) per unit cell = [The contribution of the 8 corner is

$(1/8) \times 8 = 1$ and two atoms on one of the

diagonal is $2 \times 1 = 2$] i.e. $1 + 2 = 3$ atoms

∵ $$\rho = \frac{n \times M}{V \times N_0} \quad \text{or} \quad N_0 = \frac{n \times M}{V \times \rho}$$

$$N_0 = \frac{(3)(200 \text{ g})}{(24 \times 10^{-24} \text{ cm}^3)(7.2 \text{ g cm}^{-3})}$$

$$N_0 = 3.472 \times 10^{24} \text{ atoms}$$

14. CLOSE PACKING OF IDENTICAL SOLID SPHERES :

The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as closed packing.

Now we describe the different arrangements of spherical particals of equal size.

When the spheres are packed in a plane i.e. There are two types of close packing.

(a) Two dimentionally close packing :

(i) The centres of the spheres lie one below another. This type of arrangement is called square close packing. In such packing one sphere touches four other spheres. In this case 52.4% of the volume is occupied. The remaining 47.6% of the volume is empty and is called void volume.

In square close packing co-ordination number is 4

Square close packing
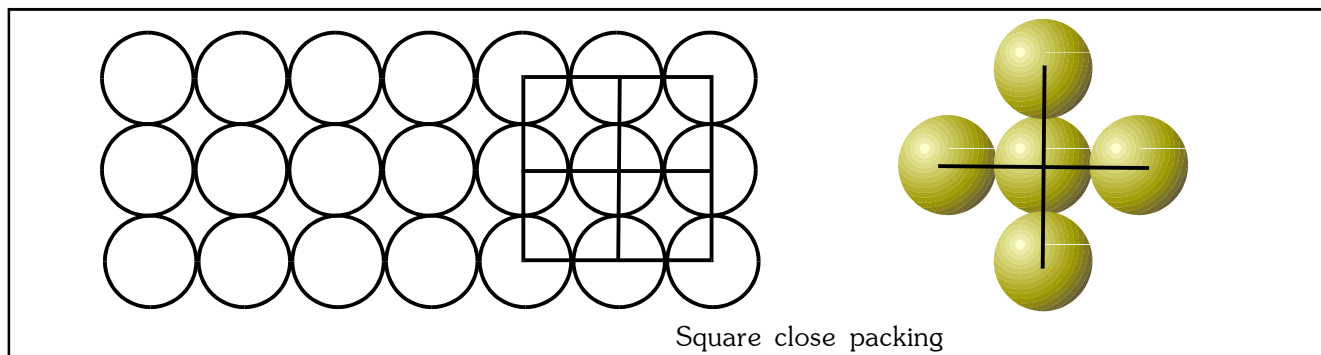
**(ii)** Another type of arrangement of atoms is shown below. This type of packing is called hexagonal close packing. In such packing one sphere touches six other spheres. In this case 60.4% of the volume is occupied. The remaining 39.6% of the volume is empty and is called void volume.Therefore this type of packing is more stable than the square close packing.

Hexagonal close packing
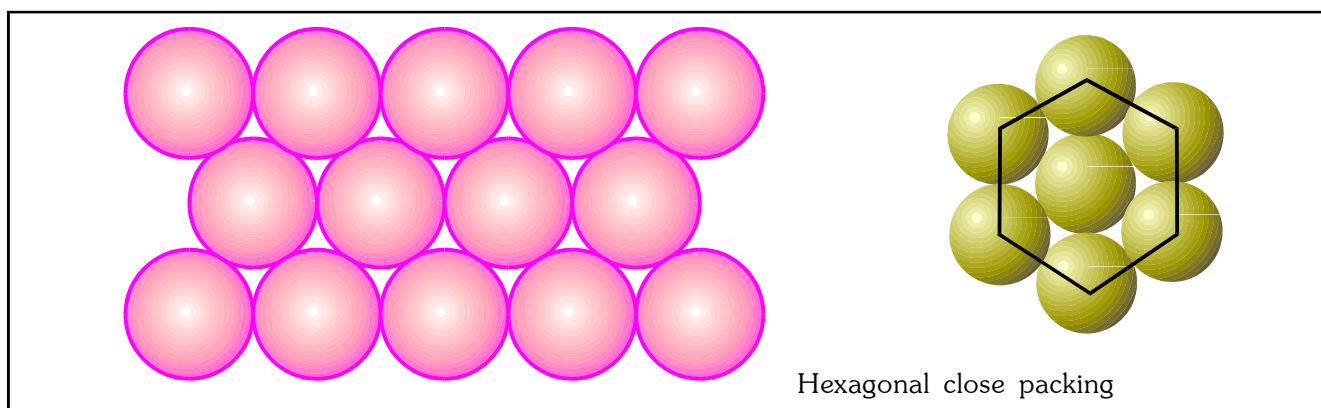
(b) **Three Dimentionally close packing :**

In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.
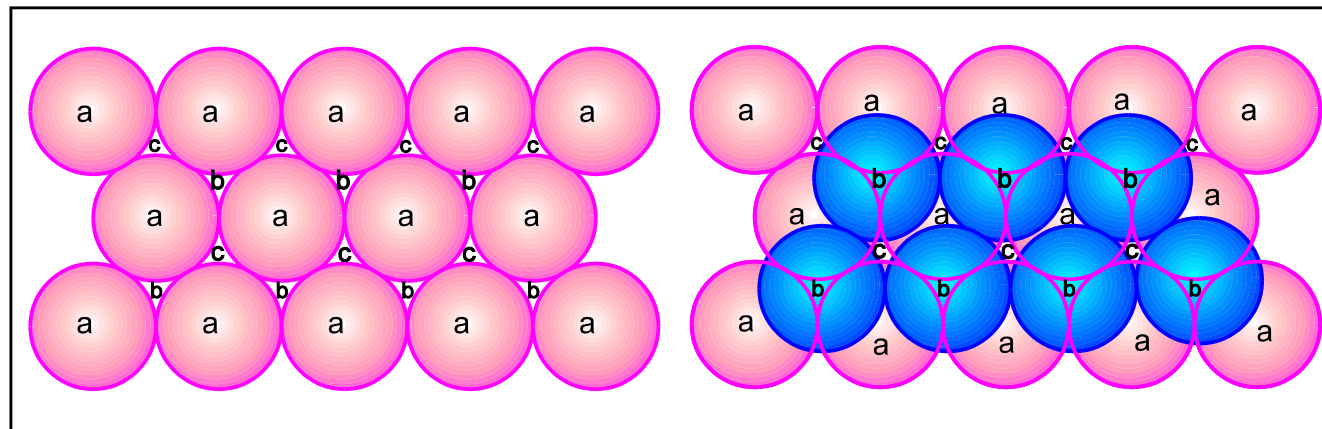
Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following two ways :
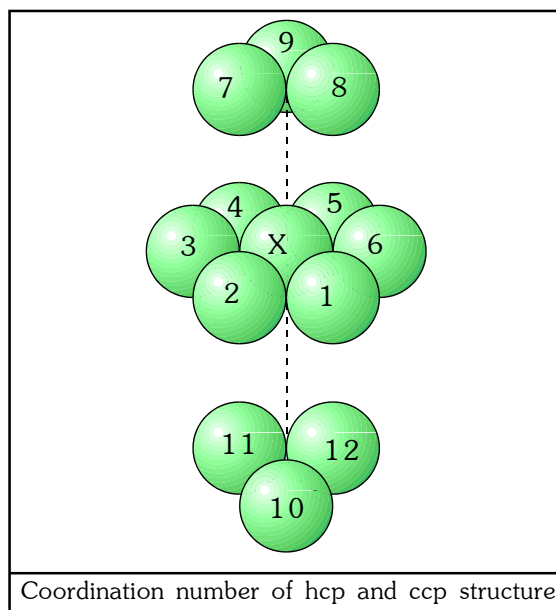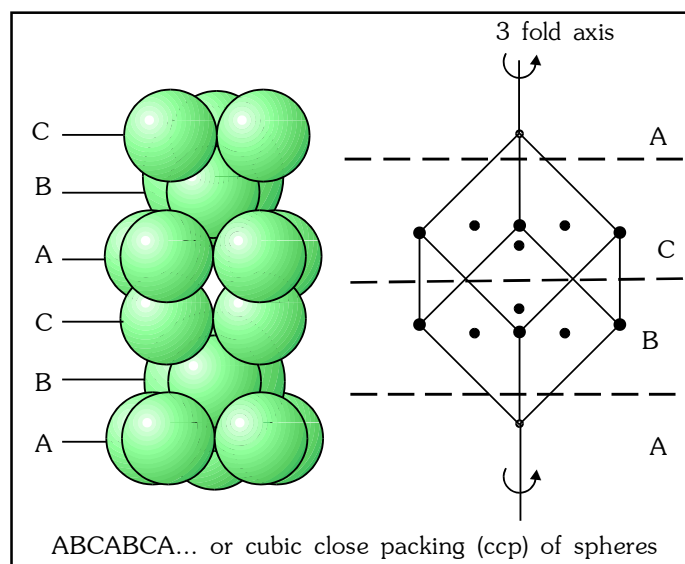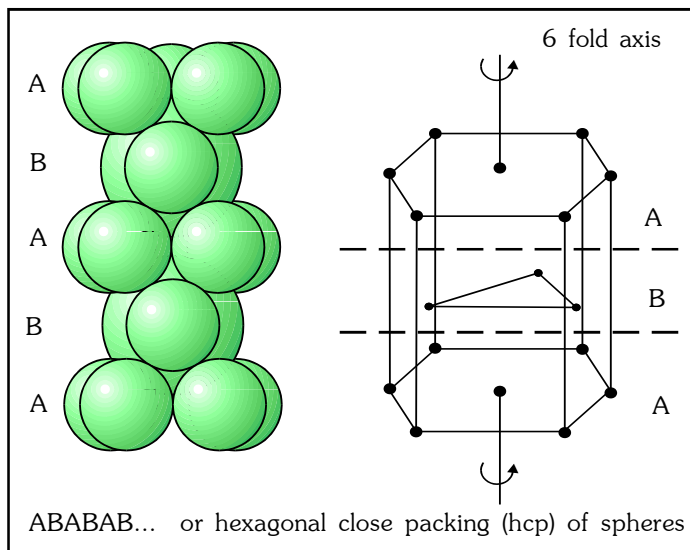
(i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lies directly above those in the first layer(A). In other words we can say that the third layer becomes indentical to the first layer. If this arrangement is continued idefinitely in the same order this represented as A BA BA B ....

This type of arrangement represent hexagonal close packing (hcp) symmetry (or structure), which means that the whole structure has only one 6-fold axis of symmetry i.e. the crystal has same appearance on rotation through an angle of 60^0.

(ii) In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer(A). If this arrangement is continuous in the same order this is represented as ABC ABC ABC.... This type of arrangement represent cubic close packed (ccp) structure.

ABABAB... or hexagonal close packing (hcp) of spheres

ABCABCA... or cubic close packing (ccp) of spheres

This structure has 3-fold axes of symmetry which pass through the diagonal of the cube. since in this system, there is a sphere at the centre of each face of the unit cell and hence this structure is also known as face-centred cubic (fcc) structure.

It may be noted that in ccp (or fcc) structures each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.

Coordination number of hcp and ccp structure

(iii) There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing (which is slightly opened that hexagonal close packing). In bcc arrangement the spheres of the second layer lie at the space (hollows or voids) in the first layer.

Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of IIIrd layer). Therefore coordination number of each sphere is 8 in bcc sturcture. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

Some examples of metals with their lattice types and coordination number are given in the following table.

Three dimensional close packing

Contents	BCC	CCP/FCC	HCP
Type of packing packing but not close packing	ABAB....... close packing	ABCABC ...... close packing	ABAB ......
No. of atoms	2	4	6
Co-ordination no.	8	12	12
Packing efficiency	68%	74%	74%
Examples V & Cr group Fe	IA, Ba Co group, Ni group, Copper group, all inert gases except helium	Ca, Sr, Al d-block elements Be & Mg	Remaining

Note :- Only Mn crystallizes in S.C.C.

15. INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

It has been shown that the particles are closely packed in the crystals even than there is some empty space left in between the spheres. This is known as interstices (or interstitial site or holest or empty space or voids). In three dimentional close packing (CCP & HCP) the interstices are of two types : (i) tetrahedral interstices and (ii) octahedral interstices.

(i) **Tetrahedral interstices :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp) each sphere of second layer touches with three spheres of first layer. Thus they, leave a small space in between which is known as **tetrahedral site or interstices.** or The vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may by noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.


Tetrahedral void

A tetrahedral interstices

Tetrahedron geometry
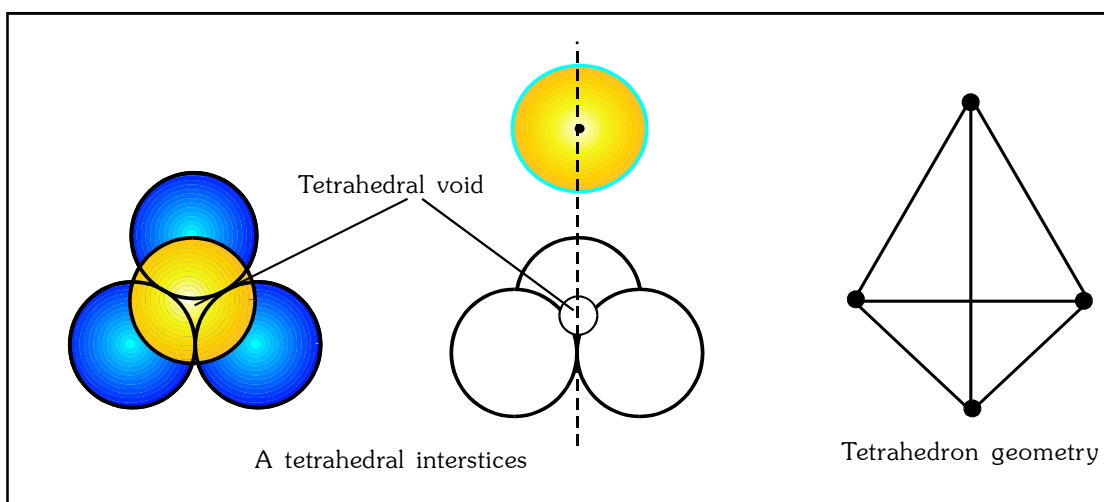
In FCC, one corner and its there face centres form a tetrahedral void

In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral void are present.

In FCC total number of atoms = 4

In FCC total number of tetrahedral voids = 8

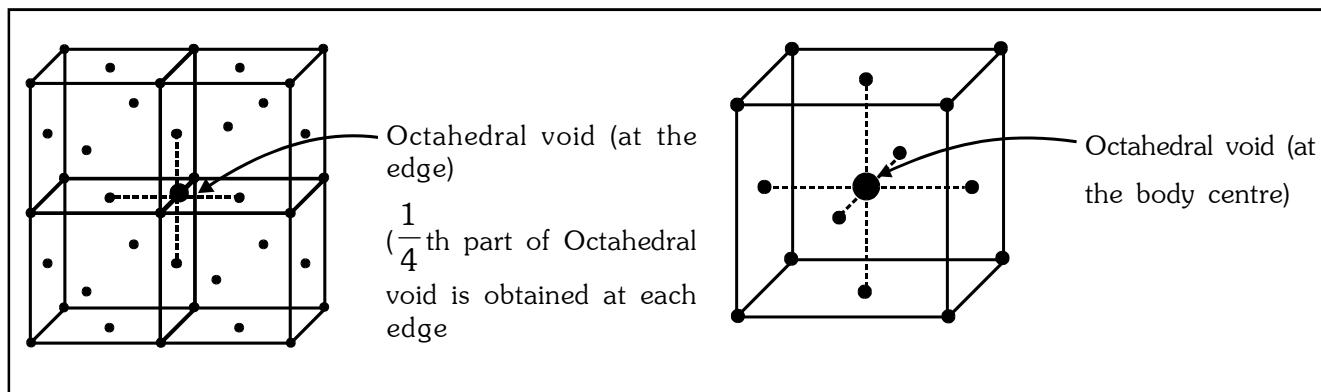So, we can say that, in 3D close packing 2 tetrahedral voids are attached with one atom.

Tetrahedral void
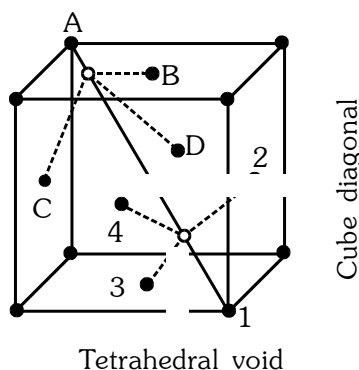
(ii) **Octahedral - interstices :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site)which is called octahedral site (or interstices). or The vacant space between 6 touching spheres is called as octahedral void.

In the figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers.

Octahedral void

Octahedral interstices

Octahedral geometry
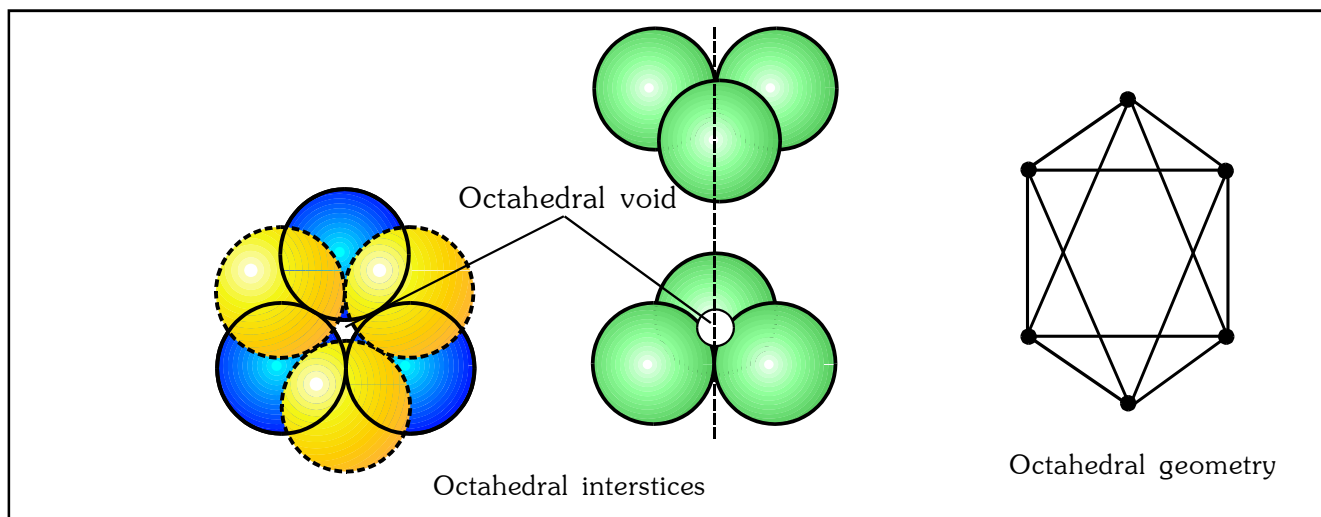
In FCC, 6 face centres form a octahedral void

The apices of these triangles point are in opposite directions. On super imposing these triangles on one another a octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.

Octahedral void (at the edge)

($\frac{1}{4}$th part of Octahedral void is obtained at each edge

Octahedral void (at the body centre)

In FCC, total number of octahedral voids are $(1 \times 1) + (12 \times \frac{1}{4}) = 1 + 3 = 4$

(Cube centre)   (edge)

In FCC, number of atoms = 4

In FCC, number of octahedral voids = 4

So, we can say that, in any type of close packing one octahedral void is attached with one atom.

Ex. Element A is every element of FCC, atom B is present at every Octahedral void, atom C is present at 25% of Tetrahedral void. Find out the possible molecular formula of the compound ?

Sol. Atom A is every element of FCC = 4 atoms of A

Atom B is present at every octahedral void = 4 atoms of B

Atom C is present at 25% of tetrahedral void = $8 \times \dfrac{25}{100}$ = 2 atom of C

So, the possible molecular formula is $A_4 B_4 C_2 = A_2 B_2 C$.

16. **LIMITING RADIUS RATIOS :**

An ionic crystal contains a large number of cations and anions. Generally cations are Smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability. The stability of the ionic crystal may be described in terms of radius ratio i.e. the ratio of the radius of cation (r) to that of anion (R) is (r/R). The range of (r/R) may be expressed as limiting radius ratio. This value is important to determine the arrangement of the ion in different types of crystals.

Evidently radius ratio (r/R) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.)

(i) **Triangular :** All anions touches each other and co-ordination number is 3

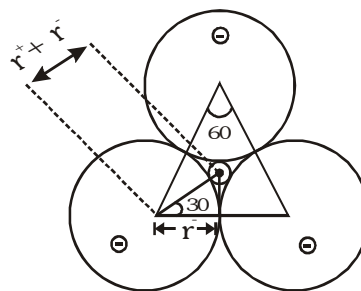$$Cos\theta = \dfrac{r^-}{r^- + r^+}$$

$$Cos\ 30 = \dfrac{\sqrt{3}}{2} = \dfrac{r^-}{r^- + r^+}$$

$$\sqrt{3}r^- + \sqrt{3}r^+ = 2r^-$$

$$\sqrt{3}r^+ = \left(2 - \sqrt{3}\right)r^-$$

$$\dfrac{r^+}{r^-} = \dfrac{2 - \sqrt{3}}{\sqrt{3}} = \dfrac{2 - 1.73}{1.73} = \dfrac{0.27}{1.73} = 0.155$$

L.R.R. = 0.155 = $\dfrac{r^+}{r^-} < 1$

(ii) **Tetrahedral void :** All anions touches each other and co ordination number of cation is 4.

Face diagonal AC = $\sqrt{2}a = 2r^-$

$$r^- = \dfrac{a}{\sqrt{2}} \text{ or } a = \sqrt{2}r^-$$

Triangle ACD -

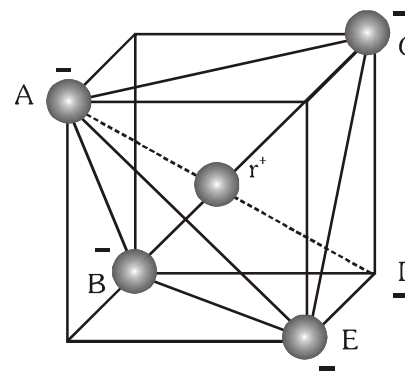$$AD^2 = AC^2 + CD^2$$

$$AD^2 = \left(\sqrt{2}a\right)^2 + \left(a\right)^2 = 2a^2 + a^2 = 3a^2$$

$$AD = \sqrt{3}\ a$$

According to cube diagonal AD

$$\therefore \quad \dfrac{\sqrt{3}a}{2} = r^+ + r^-$$

$$\therefore \quad \sqrt{3}a = 2r^+ + 2r^- = AD$$

Put the value of a = $\sqrt{2}\, r^-$

$$\sqrt{3} \times \sqrt{2}\ r^- = 2r^+ + 2r^-$$

$$\frac{\sqrt{3} \times \sqrt{2}\ r^-}{2r^-} = \frac{2r^+ + 2r^-}{2r^-}$$

$$\frac{\sqrt{3}}{\sqrt{2}} = \frac{r^+}{r^-} + 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}}{\sqrt{2}} - 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.73 - 1.414}{1.414} = 0.225$$

(iii) **Octahedral void :** All the anions are touch each other and co ordination number is 6.

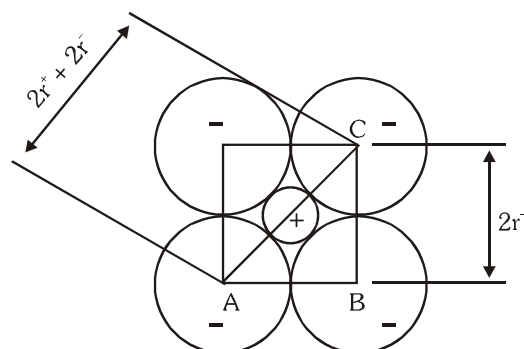In $\triangle ABC$ $\quad AC^2 \quad = AB^2 + BC^2$

$$= a^2 + a^2$$

$$AC \quad = \sqrt{2}\ a$$

$2r^+ + 2r^- = AC = \sqrt{2}\ a$

$BC = a = 2r^-$

$$\frac{2r^+ + 2r^-}{2r^-} = \frac{\sqrt{2} \times 2r^-}{2r^-}$$

$$\frac{r^+}{r^-} + 1 = \sqrt{2} \quad \Rightarrow \quad \frac{r^+}{r^-} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

(iv) **Cubic void :** All the anions are touch each other and co ordination number is 8.
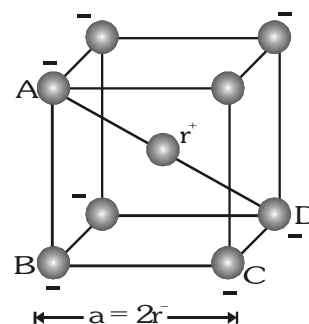
According to cube diagonal

$AD = \sqrt{3}\,a = 2r^+ + 2r^-$

$\quad\quad (a = 2r^- = BC)$

$\sqrt{3} \times 2r^- = 2r^+ + 2r^-$

Dividing by 2r$^-$ on both sides.

$$\sqrt{3} = \frac{r^+}{r^-} + 1 \Rightarrow \frac{r^+}{r^-} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$

The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular $\xrightarrow{\ 0.225\ }$ Tetrahedral $\xrightarrow{\ 0.414\ }$ octahedral $\xrightarrow{\ 0.732\ }$ Cubic

Limiting radius ratio for various types of sites

Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planaer	–
0.414 - 0.732	6	Octahedral	$NaCl$, MgO_2
0.732 - 1.000	8	Cubic	$CsCl$

Ex. A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

Sol. In Na^+Cl^- crystal each Na^+ ion is surrounded by 6 Cl^+ ions and vice versa. Thus Na^+ ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

or $\quad \dfrac{A^+}{B^-} = \dfrac{r}{R} = 0.414$

Given that radius of anion (B^-) R = 250 pm

i.e. radius of cation (A^+) $\quad$ r $\quad = \quad$ 0.414 R = 0.414 $\times$ 250 pm

or $\qquad\qquad\qquad\qquad$ r $\quad = \quad$ 103.5 pm

Thus ideal radius for cation (A^+) is r = 103.5 pm.

We know that (r/R) for tetrahedral hole is 0.225.

$\qquad \therefore \dfrac{r}{R} = 0.225$

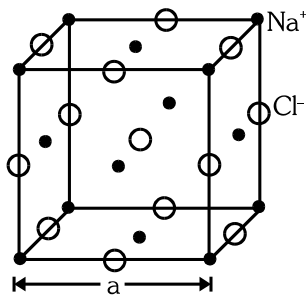**or** $\quad$ r = 0.225 $\times$ R = 0.225 $\times$ 250 = 56.25 pm

Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of C^+ is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slipped cation C^+ into the tetrahedral site.

NaCl type :

For NaCl : Distance between two nearest ions ($r^+ + r^-$) :-

$\qquad 2r^+ + 2r^- = a$
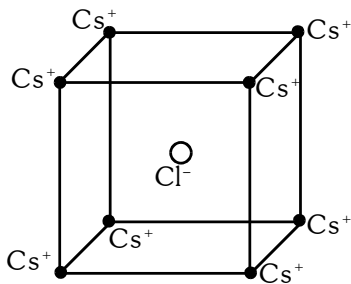
i.e. $\quad r^+ + r^- = \dfrac{a}{2}$

CsCl type :

For CsCl : Distance between nearest ions ($r^+ + r^-$) :-

$\qquad 2r^+ + 2r^- = \sqrt{3}a$

$\qquad r^+ + r^- = \dfrac{\sqrt{3}a}{2}$

JEEMAIN.GURU

TYPES OF IONIC CRYSTAL

Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples	
1. NaCl (1 : 1) (Rock Salt Type)		6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II–A (Some exception) $AgF, AgCl, AgBr, NH_4X$	● Na^+ O Cl^-
2. CsCl Type (1 : 1)		8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS	Cs^+ Cl^-
3. Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)		4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI	● Zn^{+2} O S^{-2}
4. CaF_2 Type (1 : 2) (Fluorite Type)			$4Ca^{+2} + 8F^-$ $4CaF_2$ (4)	$BaCl_2, BaF_2$ $SrCl_2, SrF_2$ $CaCl_2, CaF_2$	● Ca^{+2} O F^-
5. Na_2O Type (2 : 1) (Antiflourine)			$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S	● O^{-2} O Na^+
6. ZnS Type (1 : 1) (Wurtzite) another geometry of Zns		4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite	

17. **Defects or imperfections in solids :**

Ideal crystal :

The crystal in which all the lattice points are occupied by the component particles or groups of particles is called an ideal crystal.

Solid state is characterised by vibratory motion about the mean position of constituent particles. At absolute zero, all the types of motions cease, and therefore crystals tend to have a perfectly ordered arrangement. As the temperature increases, molecular motions (vibratory amplitudes) increase and therefore the ions may lose their usual sites and either get missed or occupy interstitial positions in the crystal, ie., deviations from ordered arrangement take place. Any deviation from the perfectly ordered arrangement gives rise to a defect or imperfection in the crystal. Defect in crystals are produced either due to thermal effects or by adding certain impurities in the pure crystals (doping). Defects in crystals may be discussed under two titles :

A. Stoichiometric defects

B. Non-stoichiometric defects

[A] **Defects in stoichiometric compounds :**

Stoichiometric compounds are those in which the number of positive and negative ions are exactly in the ratio as shown by their chemical formulae. Two types of defects are observed in these compounds.

(i) Schottky defect,

(ii) Frenkel defect

(i) **Schottky defect :**

This type of defect is produced when one cation and anion are missing from their respective positions leaving behind a pair of holes. The crystal as a whole remains neutral because the number of missing positive ions (cations) and negative ions (anions) is the same

◆ Schottky defect appears generally in ionic compounds in which radius ratio $[r^+/r^-]$ is not far below unity.

For this defect, the cations and anion should not differ much in size.

◆ For schottky defect, co-ordination numbers of the ions should be high, Examples of ionic solids showing this defect are NaCl, CsCl, KCl, KBr etc.

Consequences of schottky defect :

◆ Density of the crystal decreases

◆ The crystal begins to conduct electricity to small extenet by ionic mechanism.

◆ The presence of too many 'voids' lowers lattice energy or the stability of the crystal.
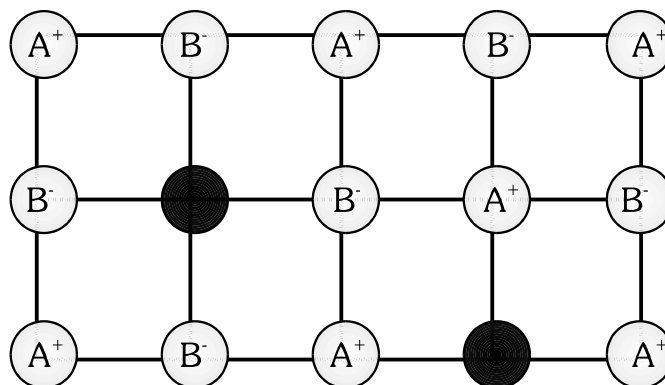
Schottky defect

(ii)   Frenkel defect :

This type of defect is created when an ion leaves its appropriate site in the lattice and occupies an interstitial site. A hole or vacancy is thus produced in the lattice.
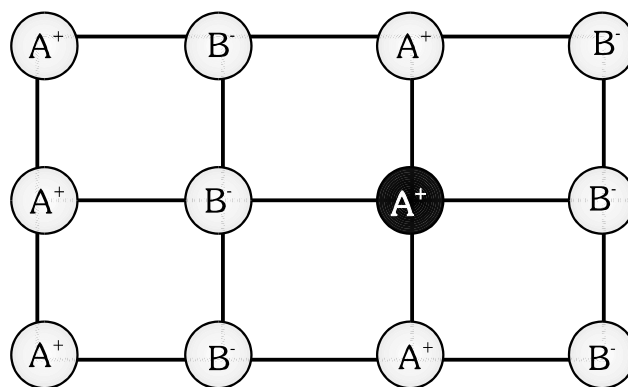
Frenkel defect

The electroneutrality of the crystal is maintained since the number of positive and negative ions is the same. Since positive ions are small, in size, they usually leave their positions in the lattice and occupy interstial positions.

Frenkel defect is exhibited in ionic compounds in which the radius ratio $[r^+/r^-]$ is low. The cations and anions differ much in their sizes and the ions have low co-ordination numbers. Examples are ZnS, AgBr, AgI, AgCl.

Consequences of Frenkel defect :

◆   The closeness of like charges tends to increase the dielectric constant of the crystal.

◆   The crystal showing a frenkel defect conducts electricity to a small extent by ionic mechanism.

◆   The density of the crystal remains the same.

[B]   Non-stoichiometric defect :

These types of defects are observed in the compounds of transitional elements. These defects arise either due to the presence of excess metal ions or excess non-metal ions.

(i)   Metal excess defect due to anion vacancies :

A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron.

Ionic crystal which are likely to posses schottky defect, may also develop this type of metal excess defect.

When alkali metal halides are heated in a atmosphere of vapours of the alkali metal, anion vacancies are created. The anions (halide ions) diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cations. The e^- lost by the metal atom diffuse through the crystal are known as F-centres. The main consequence of metal excess defect is the development of colour in the crystal. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow.

Similarly, KCI crystal when heated in an atmosphere of potassium vapours, it appear violet.

(ii)   Metal excess defect due to interstitial cations :

This type of defect is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial site. To maintain electrical neutrality, an electron is present in the intrestitial site. An example showing this type of defect is ZnO. When ZnO is heated, it loses oxygen reversibly. The excess Zn^{++} ions are accommodated in the interstitial sites, the, electrons are enclosed in the neightbouring interstitials. The yelllow colour of ZnO when hot is due to these trapped electrons. These electrons also explain electrical conductivity of the ZnO crystal.

◆ **Doping :** The addition of small amount of foreign impurity in the host crystal is called as doping. It results in an increase in the electrical conductivity of the crystal. Doping of group 14 elements (such as Si, Ge, etc.) with elements of group 15 (such as As) produces an excess of electrons in the crystals, thus giving n-types semiconductors. Doping of groups 14 elements with group 13 elements (such as Indium) produces holes (electron deficiency) in the crystals. Thus p-type semiconductors are produced. Then symbol 'p' indicates flow of positive charge.

18. ELECTRICAL PROPERTIES OF SOLIDS :

Solids have been classified as metals, insulators (bad conductors) and semi-conductors. Electrical conductivity of solids is due to motion of electrons and holes or ions. Conduction of ionic solids is due to absence of vacancies and other defects. Thus conductivity of semi conductors as well as insulators is mainly because of impurities and defects present in them. Electrons and holes produced by the ionization of defects contribute to conduction in these solids.

19. MAGENETIC PROPERTIES OF SOLIDS :

Solids can be divided into different classes. Depending on their response to magnetic fields.

(a) Paramagnetic (weakly magnetic) : Such materials contain permanent magnetic dipoles due to the presence of atoms, ion or molecules with unpaired electrons e.g. O_2, Cu^{+2}, Fe^{+3} and they are attracted by the magnetic field. They however lose their magnetism in the absence of a magnetic field.

(b) Diamagnetic : They are weakly repelled by magnetic fields. diamagnetism arises due to the absence of unpaired electrons e.g. H^-, Li^+, Be^{+2}, (2 electron type), O^{-2}, F^-, Na^+, Mg^{+2} (8 electron type), Ag^+, Zn^{+2}, Cd^{+2} (18 electron type).

(c) Ferromagnetic : It is caused by spontaneous alignment of magnetic moments in the same direction.

(d) Ferrimagnetism : It occurs when the moments are aligned in parallel and antiparalled direction in unequal number resulting in a net moment e.g. Fe_3O_4.

(e) Antiferromagnetism : It occurs if the alignment of moments is in a compensatory way so as to give zero net moment e.g. MnO.

All magnetically ordered solids (ferromagnetic and antiferromagnetic solids) transform to the paramagnetic state at some elevated temperatures. This is most probably due to the randomisation of spins.

↑↑	↑↑	↑↑

Ferromagnetic character

↑↓	↑↓	↑↓

Antiferromagnetic character

↑↑	↓↑	↑↓

Ferrimagnetic character

❏ ❏ ❏