Solid State

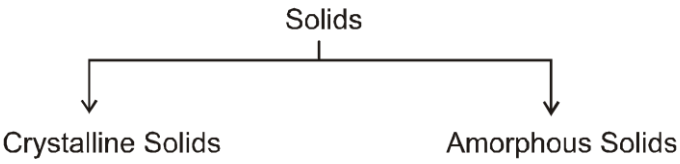
Section (A) : Basics of Solid State

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

❖ **Properties of Solids :**

(a) In solid state the particles are not able to move randomly.
(b) They have definite shape and volume.
(c) Solids have high density.
(d) Solids have high and sharp melting point which is depend on the strength or value of binding energy.
(e) They are very less compressible.
(f) They show very slow diffusion.

❖ **Types of Solids :**



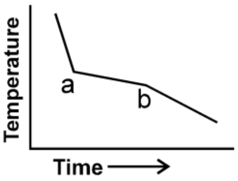
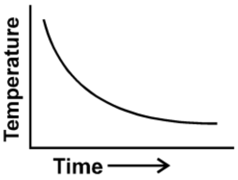
❖ **Crystalline solids :**

(a) In this type of solids the atoms or molecules are arranged in a regular pattern in the three dimensional network.
(b) They have well defined geometrical pattern, sharp melting point, definite heat of fusion and anisotropic nature.
(c) Anisotropic means they exhibit different physical properties in different directions.
e.g. The electrical and thermal conductivities are different directions.
(d) They are generally incompressible.
(e) The general examples of crystalline solids are as Quartz, diamond etc.

❖ **Amorphous Solids :**

(a) In this type of solids, the arrangement of building constituents is not regular.
(b) They are regarded as super cooled liquids with high viscosity in which the force of attraction holding the molecules together are so great, that the material becomes rigid but there is no regularity in structure.
(c) They do not have sharp melting points.
(d) They are isotropic as they exhibit same physical properties in all the directions.
(e) The general examples of this solids are as glass, Rubber, plastics etc.

Difference between crystalline and amorphous solids :

	Property	Crystalline solids	Amorphous solids
1.	Shape	They have definite and regular geometrical form.	They do not have definite and regular geometrical form.
2.	Melting point	They have definite melting point	They do not have definite melting point.
3.	Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion.
4.	Compressibility	They are rigid and incompressible	These may be compressed to any appreciable extent.
5.	Cutting with a Sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces.  	They are given irregular cleavage i.e. they break into two pieces with irregular surface. 
6.	Isotropy and Anisotropy	They are anisotropic.	They are isotropic.

Solved Examples

Ex.1 A solid X melts slightly above 273K and is a poor conductor of heat and electricity. To which of the following categories does it belong :
(1) Ionic solid (2) Covalent solid (3) Metallic (4) Molecular

Ans. **(4)**

Ex.2 In a crystal, the atoms are located at the position of :
(1) Zero P.E. (2) Infinite P.E. (3) Minimum P.E. (4) Maximum P.E.

Ans. **(3)**

Ex.3 Graphite is an example of :
(1) Ionic solid (2) Covalent solid (3) Vander waal's crystal(4) Metallic crystal

Ans. **(2)**

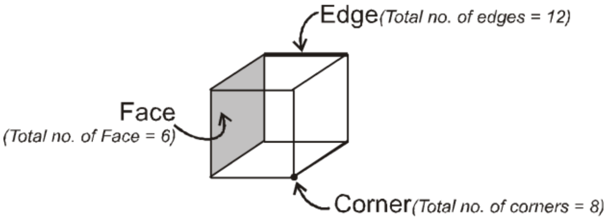
Ex.4 Amorphous solids :
(1) Possess sharp melting points
(2) Undergo clean cleavage when cut with knife
(3) Do not undergo clean cleavage when cut with knife
(4) Possess orderly arrangement over long distances

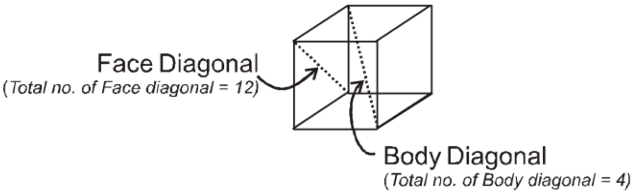
Ans. **(3)**

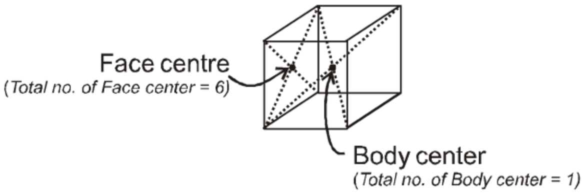
STUDY OF CRYSTALS :

- **Crystal :** A crystal is a homogeneous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.
- **Space lattice :** The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

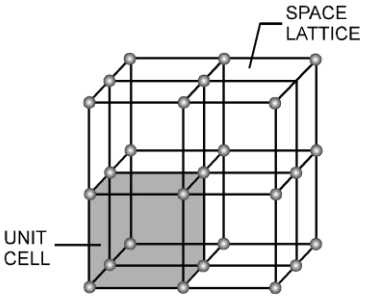
- **Unit cell :** The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.
- **Properties of a cube :**



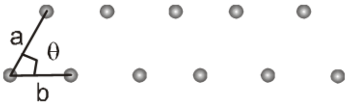




- **Face :** The plane surface of the crystal are called faces.
- **Edge :** An edge is formed by the intersection of two adjacent faces.
- **Interfacial angles :** The angle between the perpendiculars two intersecting faces called interfacial angles.

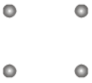


UNIT CELL IN TWO DIMENSIONS :



Now in order to uniquely explain a regular arrangement in two dimensions we need the help of three parameters, two distance parameters and one angular parameter. Based upon their different relationships we can define different cases

Case 'A' (a = b) angle = 90º



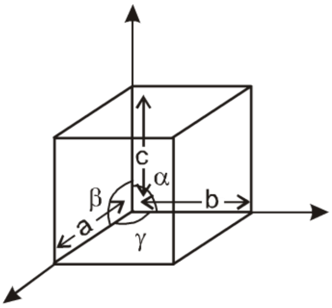
The unit cell in such a case is a **square**. Placing such square side by side we will obtain the entire two dimensional arrangement.

Case 'B'(a ≠ b) angle = 90º

The unit cell formed in this case is a rectangle.

❖ **UNIT CELL IN THREE DIMENSIONS :**

It has six parameters, 3-distance parameters and 3-angular parameter.



a, b, c are lengths of unit cell (also known as the crystallographic axes).

α, β, γ are known as the crystallographic angles.

❖ **DIFFERENT CLASSES OF CRYSTALS :**

Based on different permutations of a, b, c and α, β, γ we define different crystal classes.

Seven Crystal System

S. No.	Crystal System	Edge length	Angles	Unit cell found	Examples
1	**Cu**bic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	SC, BCC, FCC (3)	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, Na_2O, CaF_2, KCl, Pb, Alum.
2	**Te**tragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	SC, BC (2)	Sn (white tin), SnO_2, TiO_2, ZnO_2, $NiSO_4$, urea.
3	**Or**thorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	SC, BC, FC, EC (4)	Rhombic sulphur, $BaSO_4$, KNO_3, $PbCO_3$, $CaCO_3$ (aragonite)
4	**Mo**noclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o$ $\beta \neq 120^o$, $\neq 90^o$, $\neq 60^o$	SC, EC (2)	Monoclinic sulphur, $PbCrO_4$, Na_2SO_4, $10H_2O$, $Na_2B_4O_7.10H_2O$
5	**T**riclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	SC (1)	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3
6	**He**xagonal	$a = b \neq c$	$\alpha = \beta = 90^o$ $\gamma \neq 120^o$	SC (1)	Graphite, ZnO, CdS, Mg, PbI_2, SiC.
7	**R**hombohedral or **T**rigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	SC (1)	$CaCO_3$ (Calcite), HgS(Cinnabar), $NaNO_3$, ICl.

Hint for memorise : Ca**TOR**ac**HMT**

Note : In 3-D 14 different types of unit cell are found and these are also known as 14 **Bravais lattice**.

Section (B) : Body Centered Cubic (BCC), Simple Cubic, Face Centered Cubic (FCC)

❖ **TYPES OF UNIT CELL :**

In every crystal class, the positioning of the lattice points may be different. Based upon these different positions occupied by the lattice points, we have different types of unit cells.

1. **Simple / primitive type of unit cell :** If lattice points or the particles of the solid are present only at the corners of the unit cell.

2. **Body centred unit cell :** lattice point are at the corners as well as at the body centre.
3. **Face centred unit cell :** lattice points are at corners as well as at each of the face centres.
4. **End centred unit cell :** lattice points are at the corners as well as at centre of any of two opposite faces.

Each of these arrangements corresponds to a unique and different type of arrangement. These 14 different arrangements are called the 14 Bravais lattices.

☞ In any lattice, the surrounding of each and every lattice point is exactly identical.

MATHEMATICAL ANALYSIS OF CUBIC SYSTEM (TYPES AND ANALYSIS) :

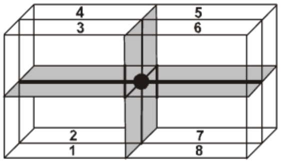
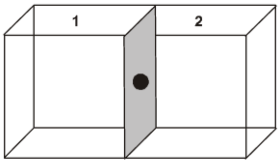
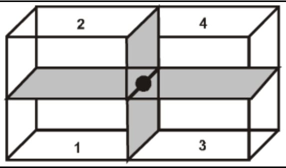
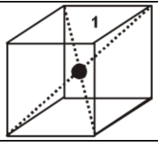
Simplest crystal is to be studied in cubic system. Three types of cubic systems are following.

(a) Simple Cubic (SC) : Atoms are arranged at the corners of the cube.

(b) Body Centered Cubic (BCC) : Atoms are arranged at the corners and at the centre of the cube.

(c) Face Centered Cubic (FCC) : Atoms are arranged at the corners and at centered of the each faces.

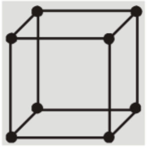
Contribution of different Lattice point in one Cubical unit cell :

(i)	Contribution from **one corner lattice point** = $\frac{1}{8}$ th. (shared in 8 identical cubes)	
(ii)	Contribution from **one face centered lattice point** = $\frac{1}{2}$. (shared in 2 identical cubes)	
(iii)	Contribution from **edge centered lattice point** = $\frac{1}{2}$ th. (shared in 4 identical cubes)	
(iv)	Contribution from **body centered lattice point** = $\frac{1}{4}$ 1. (it is present inside or at the centre of cube)	

Number of atoms per unit cell / unit cell contents :

The total number of atoms contained with in the unit cell for a simple cubic called the unit cell content.

(a) Simple cubic structure (sc) :

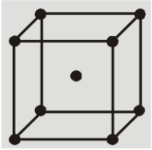


$\because$ Each corner atom is shared by eight surrounding cubes.

Therefore, it contributes for $\frac{1}{8}$ of an atom.

$\therefore$ z = 8 × $\frac{1}{8}$

(b) Body centered cubic structure (bcc) :



(i) Eight Corner atoms contribute one atom per unit cell.
(ii) Centre atom contribute one atom per unit cell.
(iii) So, total 1 + 1 = 2 atoms per unit cell.

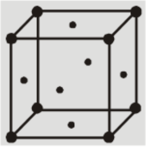
$$Z = 8 \times \frac{1}{8} + 1 = 2$$

(c) Face centered cubic structure (fcc) :

(i) The eight corners atoms contribute for of an atom and thus one atom per unit cell.

(ii) Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centered atom contribute half of its share. Means

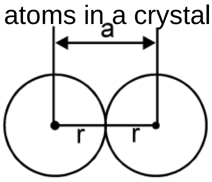
$$6 \times \frac{1}{2} = 3 \text{ atom per unit cell.}$$



(iii) So, total Z = 3 + 1 = 4 atoms per unit cell.

ATOMIC RADIUS :

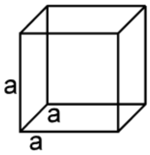
It is defined as the half of the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.



(a) **Simple cubic structure [S.C.]**

Radius of atom 'r' = $\frac{a}{2}$

(b) Face centered cubic structure (FCC) 'r' = $\frac{a}{2\sqrt{2}}$



(c) Body centered cubic structure (BCC) 'r' = $\frac{\sqrt{3}a}{4}$

$a = b = c$

$\alpha = \beta = \gamma = 90^{o}$

Solved Examples

Ex.5 A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Derive the formula of the compound.

Sol. As A atoms are present at the 8 corners of the cube, therefore numbers of atoms of A in the unit cell

$$= \frac{1}{8} \times 8 = 1$$

As B atoms are present at the face centres of the 6 faces of the cube, therefore, numbers of atoms of atoms of B in the unit cell = $\frac{1}{2} \times 6 = 3$

∴ Ratio of atoms A : B = 1 : 3

Hence, the formula of the compound is AB_3

Ex.6 A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at body centre. What is the formula of the compound ?

Sol. As atoms Y are present at the 8 corners of the cube, therefore, numbers of atoms of Y in the unit cell = 1/8 × 8 = 1

As atoms X are present at the body centre. therefore, numbers of atoms of X in the unit cell = 1

∴ ratio of atoms X : Y = 1 : 1

Hence, the formula of the compound is XY

Section (C) & (D) : Hexagonal Close Packing & Face Centered Cubic (FCC)

Arrangement of the atom / particles of the solids in three dimensions :

Now having gained a knowledge of some of the terms, let us study how the different arrangements in space are brought about.

Firstly we will focus our attention on the solids containing only one type of lattice points.

The solids which contain only one type of lattice points are:

☞ metallic solids (eg. Iron)

☞ molecular solids (eg. dry ice)

☞ covalent network solids (eg. diamond)

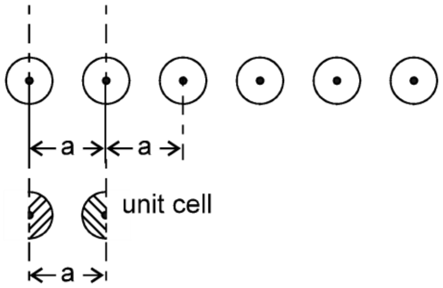
(Ionic solids do not fall into this category as they contain more than one type of particles,they will be studied in the later parts of the chapter)

All the atoms or particles of the solids will be represented by solid spheres, each of radius ‘r’.

We will be taking these spheres of radius ‘r’ and explore how we can arrange these in three dimensions. Firstly we will begin with arrangement in one dimension.

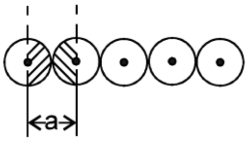
ARRANGEMENT IN 1-D : In one dimension it is possible to arrange the spheres in two possible ways.

1.



Not Stable [because the potential energy of the system is not minimum]

2.



$a = 2r$

Coordination number = 2

1-D close packing stable arrangement

This is the predominant way of packing in one dimension and as such most of the space lattices will show such an arrangement in one dimension along the planes of close packing.

ARRANGEMENT IN TWO DIMENSION :

In two dimensions also there are two ways of packing the spheres(in moving from one dimension to two dimensions it can be imagined that the two dimensional array will be made up of 1-D closed pack arrays / lines which are stacked one on top of other.

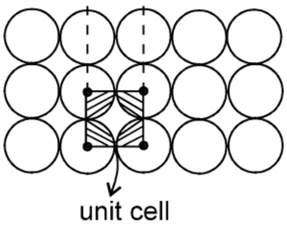
1. **Square packing :** If the one dimensional arrays are placed on top of one another, we get the square packing in two dimensions.

   One sphere will be in contact with 4 other spheres.

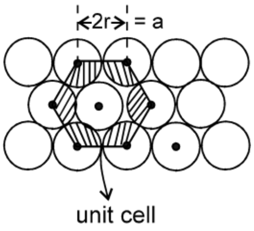
   area of square = $a^2 = 4r^2$

   area of atoms in the square = $\frac{1}{4}\times\pi\ r^2\times 4 = \pi r^2$

   fraction of area occupied by spheres = $\frac{\pi r^2}{4r^2} = \frac{\pi}{4}$ **= 78%**



2. **Hexagonal close packing :** (in 2-D) If in a two dimensional arrangement, every one dimensional array is placed in the cavity of the just preceding array, we get the hexagonal packing in two dimensions.



area of hexagon = $6 \times \frac{\sqrt{3}}{4} a^2 = 6 \times \frac{\sqrt{3}}{4} \times 4r^2 = \mathbf{6\sqrt{3}\ r^2}$

area of atoms = $\pi r^2 + \frac{1}{3} \times 6\pi r^2 = \mathbf{3\pi r^2}$

fraction of area occupied = $\frac{3\pi r^2}{6\sqrt{3} r^2} = \frac{\sqrt{3}\pi}{6} \simeq$ **91%**

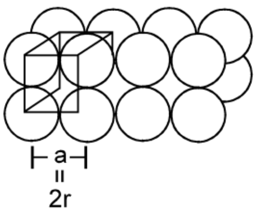
As is evident from the above calculations, the spheres are in closer contact in the hexagonal arrangement, hence the hexagonal arrangement is considered to be a better way of packing as compared to the square packing.

❑ **ARRANGEMENT IN THREE DIMENSIONS :**

1. **Simple cubical arrangement in three dimensions :**

(will be made up of 2-D sheets arranged one over other)

The simple cubical packing is obtained by arranging the square pack sheets of two dimension one over the other such that spheres of the second sheet are exactly (vertically) above the spheres of first sheet.



Simple cubic

a = b = c

(Note that $\alpha = \beta = \gamma = 90^\circ$, hence crystal thus formed will belong to the cubic crystal class, and as the lattice points are only at the corners, hence the unit cell will be simple, therefore what we get is the **simple cubic**)

(i) Relation between 'a' and 'r'

a = 2r (because atoms along the edge are touching each other)

(ii) Effective no. of atoms per unit cell :

$$\mathbf{(Z) = \frac{1}{8} \times 8 = 1}$$

(iii) Packing fraction :

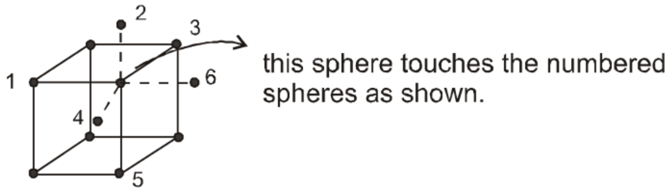
$$\text{Packing efficiency} = \frac{\text{Volume of atoms in a unit cell}}{\text{Total volume of a unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4}{3(2r)^3}\pi r^3 = \frac{4\pi r^3}{3 \times 8\, r^3} = 0.52 \text{ (or 52\%)}$$

(Note : This is not a very efficient way of packing as the packing fraction is very low**)**

(iv) Coordination Number :

It is defined as the number of atoms touching any one particular atom. For simple cubic, coordination number = 6.



this sphere touches the numbered spheres as shown.

(v) Density of unit cell : It is the ratio of mass of the spheres present in unit cell and total volume of unit cell.

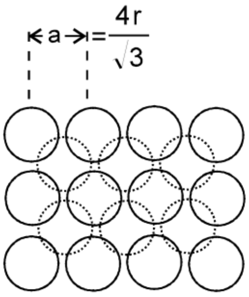
Density of the unit cell = $\frac{\text{Mass of total atoms present in a unit cell}}{\text{Volume of that unit Cell}}$

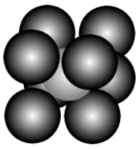
$$d = \frac{Z(M/N_A)}{a^3 \times 10^{-30}}\,\text{gcm}^{-3} \Rightarrow \boxed{d = \frac{ZM}{N_A\,(a^3 \times 10^{-30})}\,\text{gcm}^{-3}}$$

Where Z = no. of atoms in a unit cell
M/N_A = mass of a single atom
M = molar mass
N_A = Avogadro number (6.023×10^{23})

2. Body centred cubic :

The body centred cubic is a unique way of packing, as the 2D-arrays that can be imagined to constitute the space lattice are themselves formed in a unique way. The lattice points in the 2D array do not touch each other. The spheres start touching each other only upon moving from 2D to 3D, i.e. when the 2D arrays are placed on top of each other in such a fashion that the spheres of the next plane are into the cavities of the first plane of spheres. The third plane of spheres is then exactly identical to the first plane of spheres.





(i) a ≠ 2r (as atoms along the edge are not touching each other)

they touch along the body diagonal, hence $\sqrt{3}$ **a = 4r.**

(ii) **Effective number of atoms (Z) = 1 + $\frac{1}{8}$ × 8 = 2.**

(iii) **Packing fraction =** $\frac{2\times\frac{4}{3}\pi r^3}{4\times4\times4r^3}\ \sqrt{3}\times\sqrt{3}\times\sqrt{3}$ **=** $\frac{\pi\sqrt{3}}{8}$ ≃ **0.68 = 68%**

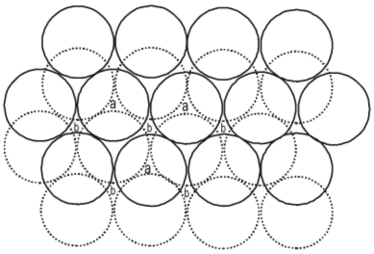
(iv) **Coordination No.= 8**

(the sphere at the body centre will be touching the spheres at the eight corners)

(v) **Density =** $\frac{ZM}{N_A\,a^3} = \frac{2M}{N_A\,a^3}$ ($\because$ Z = 2)

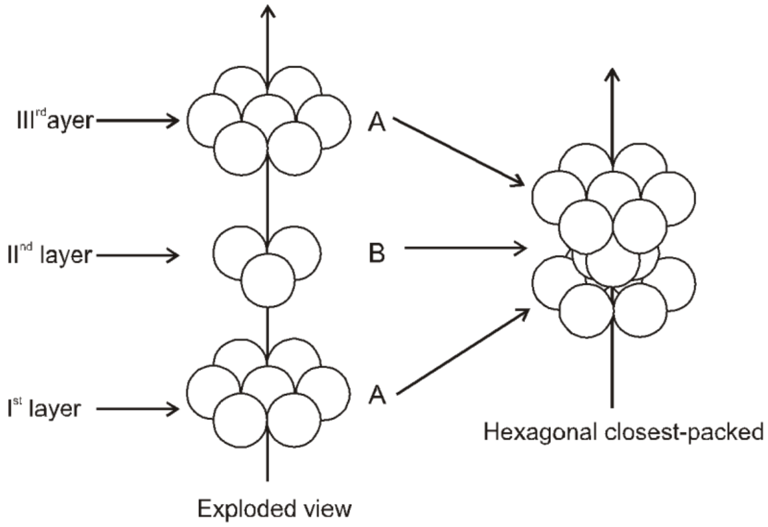
3. Close packing in three dimensions :

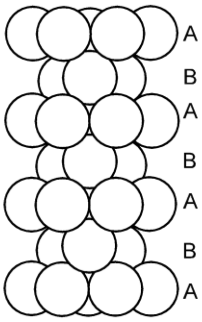
(These are made up of two dimensional hexagonally packed sheets)
In second layer we have two kinds of voids.
(i) Voids of second layer below which there are spheres of first layer (all voids of type ‘a’).
(ii) Voids of second layer below which there are voids of first layer (all voids of type ‘b’).
For third layer, we have two possibilities.



(A) AB_AB Type :

If spheres of IIIrd layer are placed in voids of IInd layer below which there are spheres of Ist layer (voids of type 'a') then Ist layer and IIIrd layer are identical so this is called AB–AB pattern repeat or hexagonal close packing)

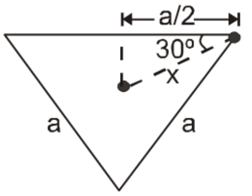


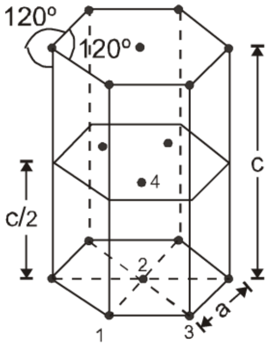


Hcp unit cell : a = 2r = b

(i) Calculation of 'c' :

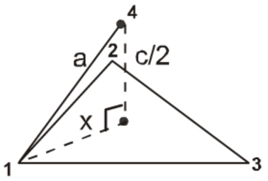
For the estimation of 'c', consider the spheres marked 1,2,3,4 in the unit cell as shown.These four spheres form a regular tetrahedron. The length of the perpendicular from '4' to the equilateral triangle 1-2-3 will be equal to c/2.





$$\cos 30^\circ = \frac{a}{2x}$$

$$x = \frac{a}{2\cos 30} = \frac{2a}{2\sqrt{3}} = \frac{a}{\sqrt{3}}$$



Apply pythagoras theorem.

$$x^2 + (c/2)^2 = a^2 \quad \Rightarrow \quad C = \sqrt{\frac{2}{3}}\,4r$$

Volume of the hexagon = Area of base x Height.

$$\frac{6\sqrt{3}}{4} = a^2 \times c = \frac{6\sqrt{3}}{4}(4r^2) \times \sqrt{\frac{2}{3}}(4r) = \mathbf{24\sqrt{2}\,r^3}$$

(ii) Effective no. of atoms per unit cell :

Z = $\frac{1}{6}$ × (no. of atoms at corner) + $\frac{1}{2}$ × (no. of atoms at face centres) + 1 × (no. of atoms inside the body)

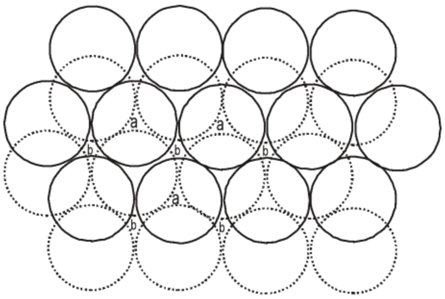
$$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 1 \times 3 = 2 + 1 + 3 = 6$$

(iii) Packing fraction : $= \frac{\text{volume of the atoms}}{\text{volume of unit cell}} = \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\,r^3} = \frac{\pi}{3\sqrt{2}}$ 0.74 = **74%**

(iv) Coordination No. : C.N. = 12

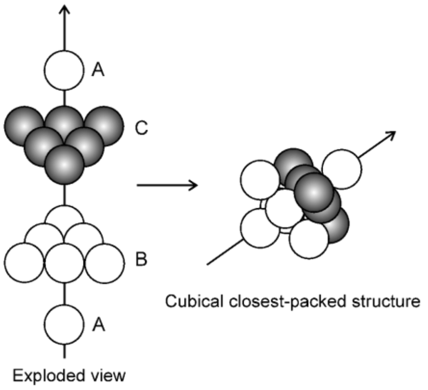
(v) Density $= \frac{\text{Mass}}{\text{Volume}} = \frac{ZM}{N_A\,(\text{volume})} = \frac{6M}{N_A\,(\text{volume})}$ ($\because$ Z = 6)

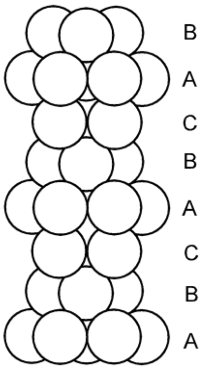
(B) ABC-ABC ARRANGEMENT :

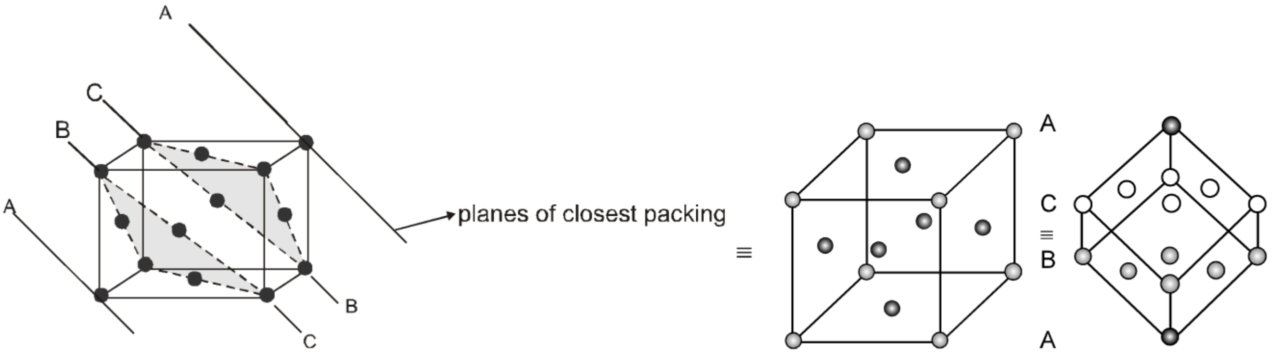


If the third layer spheres are placed in those voids of second layer under which there are voids of the first layer of spheres (voids of type 'b'), then the first and the third layer of spheres will not be identical. Such an arrangement will lead to an ABC-ABC type of arrangement.It is also known as the cubical close packing (ccp) or also as the Face Centred Cubic structure (FCC).

In the ABC – ABC pattern, the spheres of 4th layer are vertically above the spheres of Ist layer then these consecutive layers are different from each other, fourth layer will be idential to first layer so it will be called ABC – ABC repeat pattern.It is also called the ccp (cubical close packing) because a cubical type of unit cell is used for the study of this arrangement.







(i) Relation between 'a' and 'r' :

$a \neq 2r$

$\sqrt{2}a = 4r$ (as the spheres touch along the face diagonal)

(ii) Effective no. of atoms :

$Z = \frac{1}{2} \times 8 + \frac{1}{2} \times 6 = 4$

(iii) Packing fraction : $\frac{4 \times \frac{4}{3}\pi r^3}{4 \times 4 \times 4\, r^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

(iv) Coordination number : 12

(v) Density $= \frac{Z \times M}{N_A . a^3} = \frac{4 \times M}{N_A \times a^3}$

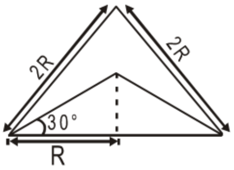
Note : In close packings, whenever two consecutive layers are of different kinds(FCC, HCP) then packing efficiency will always be 74%

Section (E) : Type of Voids

- **TYPES OF VOIDS FOUND IN CLOSE PACKINGS :**

Even though the close packed structures have the maximum packing efficiency, there are indeed empty spaces in between, let us analyse the types of such voids and the maximum radius of a particle that can be placed in such voids.

1. **Triangular void (2-Dimensional 3 co-ordinate void)** The triangular voids are found in the planes of the close packed structures, whenever three spheres are in contact in such a fashion.



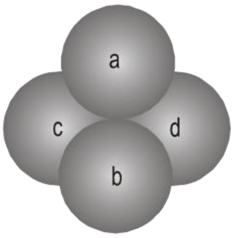
$\cos 30° = \frac{R}{R+r}$ R = Radius of the sphere,

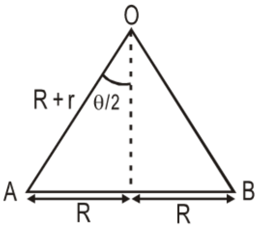
$\frac{\sqrt{3}}{2} = \frac{R}{R+r}$ r = maximum radius of a sphere that can be placed inside the void.

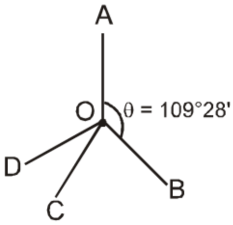
$\frac{2}{\sqrt{3}} = \frac{R+r}{R}$ ⇒ **$r = 0.155\,R$**

2. **Tetrahedral void (3-Dimensional 4 co-ordinate) :**

The tetrahedral void is formed whenever a sphere is placed on top of the triangular arrangement as in case of the triangular void.







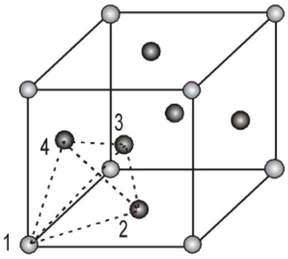
1° = 60’ (minute)

$$\sin\frac{\theta}{2} = \frac{R}{R+r}$$

$$\frac{R}{R+r} = \sin 54° 44' \quad \Rightarrow \quad r = R\left\{\frac{1}{\sin\frac{\theta}{2}} - 1\right\} \quad \Rightarrow \quad \mathbf{r = 0.225\ R}$$

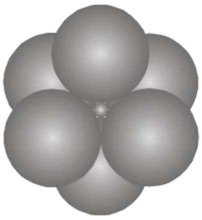
Location of tetrahedral voids in FCC unit cell :

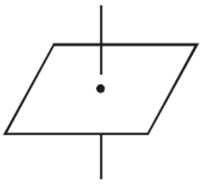
The FCC unit cell has eight tetrahedral voids per unit cell. Just below every corner of the unit cell, there is one. As there are eight corners, there are eight tetrahedral voids.

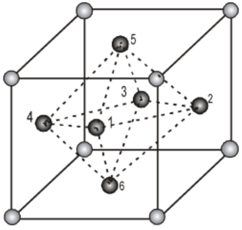


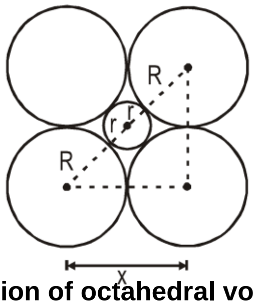
The spheres 1, 2, 3, 4 form a tetrahedral void.

3. **Octahedral void (3-Dimensional 6 coordinate void)** The octahedral void is formed whenever two spheres are placed, one on top and the other below a square arrangement of spheres









$x = 2R$

⇒ $x\sqrt{2} = 2R + 2r$

⇒ $2R\sqrt{2} = 2R + 2r$

⇒ $R\sqrt{2} = R + r$

⇒ $r = (\sqrt{2} - 1)R$

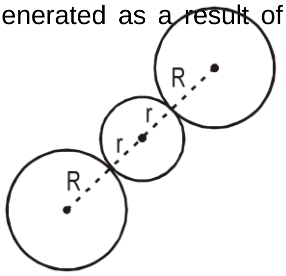
Location of octahedral voids in a FCC unit cell :

In a FCC unit cell, there are four octahedral voids. They are present at all the edge centres and at the body centre. The contribution of the edge centre void per unit cell is $\frac{1}{4}$.

Hence, total number of octahedral voids = $\underbrace{\left(12 \times \frac{1}{4}\right)}_{\text{edge centres}} + \underbrace{(1)}_{\text{body centre}} = 4$

4. **Cubical void (3-Dimensional 8-coordinate void)**

The cubical void is generally not found in closed packed structures, but is generated as a result of distortions arising from the occupancy of voids by larger particles.



Along body diagonal

$\sqrt{3}\,a = 2\,(R + r)$

$2\sqrt{3}\,a = 2\,(R + r)$

$r = (\sqrt{3} - 1)\,R$

$r = 0.732\,R$

Solved Examples

Ex.7 Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23)

Sol. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as d = $\frac{\sqrt{3}}{2}$ a

or $a = \frac{2}{\sqrt{3}}\,d = \frac{2}{1.732} \times 365.9 = 422.5$ pm

For bcc structure, Z = 2

For sodium, M = 23

$\therefore \quad D = \frac{Z \times M}{a^3 \times N_0} = \frac{2 \times 23 \mathrm{gmol^{-1}}}{(422.5 \times 10^{-10}\mathrm{cm})^3 \times (6.02 \times 10^{23}\mathrm{mol^{-1}})} = 1.51\ \mathrm{g/cm^3}$

Ex.8 X-ray diffraction studies shows that copper crystallizes in an fcc unit cell with cell edge of 3.608 × 10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3. Calculate the atomic mass of copper.

Sol. $D = \frac{Z \times M}{a^3 \times N_0}$; $M = \frac{D \times a^3 \times N_0}{Z}$

For fcc lattice, Z = 4 hence, $\frac{(8.92\ \mathrm{g\ cm^{-3}})(3.608 \times 10^{-8}\mathrm{cm})^3(6.022 \times 10^{23}\mathrm{atoms\ mol^{-1}})}{4\ \mathrm{atoms}} = 63.1\ \mathrm{g\ mol^{-1}}$

∴ Atomic mass of copper = 6.3.1

Ex.9 Density of Li atom is 0.53 g/cm^3. The edge length of Li is 3.5 Å. Find out the number of Li atoms in a unit cell (N = 6.023 × 10^{23}, M = 6.94)

Sol. The aim is to find Z in the formula

$D = \frac{Z \times M}{a^3 \times N_0}$

$Z = \frac{D \times a^3 \times N_0}{M} = \frac{0.53\ \mathrm{g\ cm^{-3}} \times (3.5 \times 10^{-8}\mathrm{cm})^3 \times (6.023 \times 10^3 \mathrm{mol^{-1}})}{6.94\,\mathrm{g\ mol^{-1}}} = 1.97 \cong 2$

Ex.10 Transition metals, when they form interstitial compounds, the non-metals (H, B, C, N) are accomodated in:

(1) Voids or holes in cubic-packed structure (2) Tetrahedral voids

(3) Octahedral voids (4) All of these

Ans. **(4)**

Ex.11 In a close pack array of N spheres, the number of tetrahedral holes are -

(1) 4N (2) N/2 (3) 2N (4) N

Ans. **(3)**

Ex.12 In antiflourite structure, the negative ions -

(1) Occupy tetrahedral voids (2) Occupy octahedral voids

(3) Are arranged in ccp (4) Are arrange in hcp

Ans. **(3)**

Section (F) : Radius Ratio & Ionic Structure

□ **IONIC SOLIDS :**

Ionic solids are characterised by the presence of atleast two types of particles,viz: the cation and the anion,even the simplest of ionic solids contains one cation and one anion.

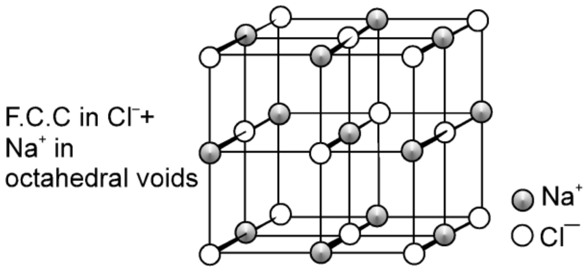
The Cations are generally found to be of smaller size, and the anions of larger sizes. The anions thus form the lattice by occupying the lattice positions and the cations are found inside the voids in such structures.

The types of void occupied by the cation would depend upon the the ratio of its radius to that of the anion, popularly termed as the radius ratio. Hence, radius ratio = r_+ / r_-

C.No.	Limiting radius ratio	Type of Void Occupied
3	0.155 – 0.225	Triangular
4	0.225 – 0.414	Tetrahedral
6	0.414 – 0.732	Octahedral
8	0.732 – 0.999	Cubical

Examples of ionic crystals :

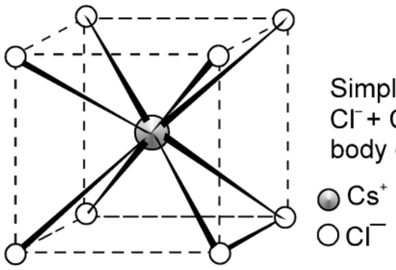
(a) Rock Salt (NaCl) Coordination number (6 : 6) NaCl crystallizes in the face centred cubic structure. The chloride ions are present at all the lattice position and the sodium ions occupy all the octahedral voids.



Rock salt (NaCl) structure

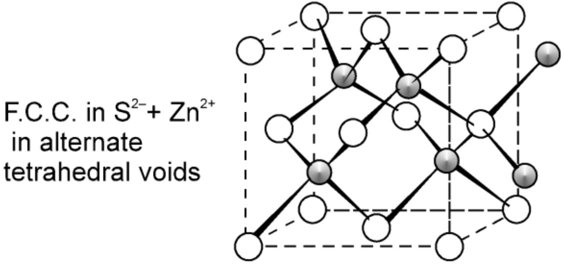
Every sodium is in contact with four chloride ions, and every chloride is in contact with four sodium ions

(b) CsCl C.No. (8 : 8)

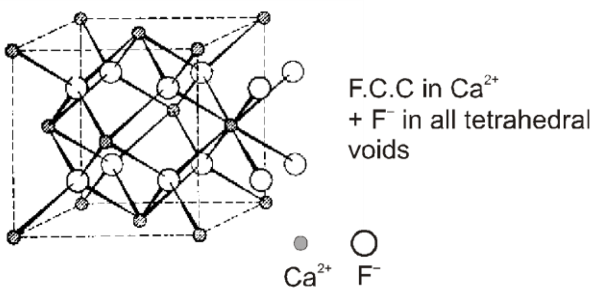


Caesium chloride (CsCl) structure

The cesium ion is at the body centre and the chloride ions are at the corners.
(c) Zinc Blend (ZnS) C.No. (4 : 4)



(d) Fluorite structure (CaF_2) C.No. (8 : 4)



STRUCTURES OF SOME CRYSTALS

S. No.	Crystal	C.N		Z	Structural arrangement	E.g.
		Cation	Anion	Total Formula unit		
1	NaCl	6	6	$Na^+ = 4$ $Cl^- = 4$	Na^+ = at all octahedral voids Cl^- □ FCC	LiCl
2.	ZnS (wurtizite)	4	4	$Zn^{2+} = 6$ $S^{2-} = 6$	Zn^{2+} = At 1/2 TV S^{2-} = HCP	Ag I
3.	ZnS (Blende)	4	4	$Zn^{2+} = 4$ $S^{2-} = 4$	Zn^{2+} = At 1/2 of TV S_2^{2-} FCC	CuCl CuBr CuI, Cds
4.	CaF_2 (Fluorite	8	4	Ca = 4 $F^- = 8$	Ca^{2+} = FCC F^- = All TV	BaF_2 SrF_2
5.	Na_2O	4	8	$Na^+ = 8$ $O^{2-} = 4$	Na^+ = All TV O^{2-} = FCC	
6.	CsCl	8	8	$Cs^+ = 1$ $Cl^- = 1$	Cr^+ = Body center Cl^- = At corners	CsCN CsI Cas

Rutile (TiO_2) CN

Cation	6
Anion	3

# Perovskite ($CaTiO_3$)		CN
At Body centre	Ca^{++}	12
At corner	Ti^{4+}	6
At Edge centre	O^{2-}	2

Section (G) : Crystal Defects and Properties of Solid & Thier Magnetic Behaviour

? **CRYSTAL DEFECT (POINT DEFECTS) :**

Imperfection can be because of :

– Conditions under which crystals have been developed.

– Impurities

– Temp (because of thermal conductivity some atoms/ions can get displaced

These imperfections can be

(a) **Point defects** – defects will be only at certain lattice positions.

(b) **Line defects** – If atoms/ions are misplaced/missing/replaced by some other ions along a line

(c) **Plane (screw) defects** – If atoms/ions are misplaced/missing/replaced by some other ions along a line in a plane.

Types of point defects

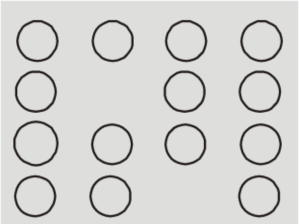
Point defect can be classified into three types :

(a) stoichiometric defects , (b) impurity defects and (c) non-stoichiometric defect

(a) Stoichiometric defect

These are the point defects that do not distrub the stoichiometry of the solid. They are also called intrinsic ot thermodynamic defects. basically these are two types. Vacancy defecs and interstitial defects.

(i) Vacancy defect : When some of the lattice site are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

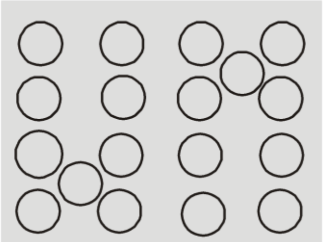


Vacancy defect

(ii) Interstitial defect : When some constituent particles (atoms or molecules)

occupy an interstitial site. the crystal is said to have interstitial defect. This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and schottky defects.

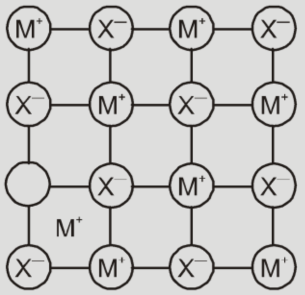


Interstitial defect

(iii) **Frenkel defect :** This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.

Frenkel defect is also called dislocation defect. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl,AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

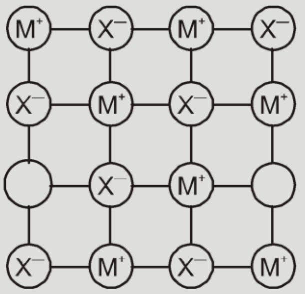
Eg. ZnS, AgCl, AgBr, AgI etc.



Frenkel Defect

(iv) **Schottky defect :** It is basically a vacancy defect in ionic solids. In order to maintain electrical netrality. The number of missing cations and anions are equal.

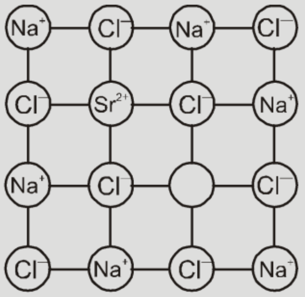
Like simple vacancy defect, schottky defect also decreases the density of the substance, Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one schottky defect per 10^{16} ions. Schottky defect is shown by ionic substance in which the cation and anion are of almost similar sizes. For example,NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as schottky defects.



Schottky Defect

(b) **Impurity defects**

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number is the solid solution of $CdCl_2$ and AgCl.



Impurity defect

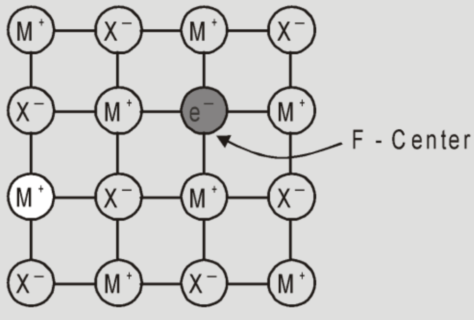
(c) **Non-stoichiometric defect**

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types :

(i) metal excess defect and (ii) metal deficiency defect.

(i) metal excess defect

(a) metal excess defect due to anionic vacancies : Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapours, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic site. As a result the crystal and now has an excess of sodium. The anionc sites occupied by unpaired electrons are called F-centres (from german word farbenzenter for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by



Metal excess defects due to anion vacancies excitation of these electrons when they absorb energy from the visible light falling on the crystals.

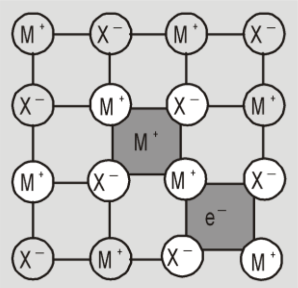
Eg. : * The excess sodium in NaCl makes the crystal appears yellow.
* Excess potassium in KCl makes it violet.
* Excess lithium in LiCl makes it pink.

Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky Defects.

(b) metal deficiency defect due to the presence of extra cations at interstitial sites : Zinc oxideis white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neghbouring interstitial sites.



Metal excess defects due to interstitial cation

(ii) metal deficiency defect : There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Solved Examples

Ex.13 CsCl has cubic structure. Its density is 3.99 g cm^{-3}. What is the distance between Cs^+ and Cl^- ions ? (At mass of Cs = 133)

Sol. CsCl has BCC structure. It has one formula unit in the unit cell So Z = 1

$$D = \frac{Z \times M}{a^3 \times N_0} \text{ or } \mathbf{a^3} = \frac{Z \times M}{D \times N_0} = \frac{1 \times (133 + 35.5)\text{g mol}^{-1}}{3.99 \text{ g cm}^{-3} \times 6.02 \times 10^{23}\text{mlo}^{-1}} = 70.15 \times 10^{-24} \text{ cm}^3$$

$a = (70.15)^{1/3} \times 10^{-8}$ cm $= (70.15)^{1/3} \times 10^2$ pm (1 pm $= 10^{-10}$ cm) $= 4.124 \times 10^2$ pm = 412.4 pm

$$\text{Interionic distance} = \frac{\sqrt{3}a}{2} = \frac{1.732}{2} \times 412.4 = 357 \text{ pm}$$

Ex.14 In a crystal both ions are missing from normal sites in equal number. This is an example of -
(1) F-centres (2) Interstitial defect (3) Frenkel defect (4) Schotty defect

Ans **(4)**

Sol. Schottky defects are arised when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.

Ex.15 Frenkel defect is noticed in :
(1) AgBr (2) ZnS (3) AgI (4) All

Ans **(4)**

Sol. Frenkel defect is arised when the cations are missing from their lattice sites and occupy interstitial sites. As a result of Frenkel defect, density remains unchanged but dielectric constant increases.

PROPERTIES OF SOLIDS :

1. **Electric Properties :**

On the basis of electrical conductivity the solids can be broadly classified into the three types:

(a) Metals (conductors) **(b) Insulators** **(c) Semi-conductors.**

Following are salient features of electrical conductance in solids.

(i) The electrical conductivity of metallic conductors is due to the motion of electrons or positive holes (electronic conductivity) or through the motion of ions (ionic conductivity)

(ii) The conductance through electrons is called n-type conduction and through positive holes is called p-type conduction.

(iii) The conductance in insulators and semiconductors is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections.

(iv) The conductivity of semiconductors and insulators increases with increase in temperature while that of metals decreases.

(v) Electrical conductivity of metal is in the order of 10^6–10^8 ohm^{-1} cm^{-1} while that of inculator is of the order of 10^{-12} ohm^{-1} cm^{-1}. Semiconductors have intermediate value in the range 10^{-9} ohm^{-1} cm^{-1}.

2. **MAGNETIC PROPERTIES :**

(a) Paramagnetic substances
(b) Ferromagnetic substances
(c) Diamagnetic substances

(a) Paramagnetic substances :

(i) Substances which are weakly attracted by the magnetic field are paramagnetic in nature.

(ii) These possess permanent magnetic dipoles due to the presence of unpaired electrons.

(iii) e.g. TiO_2, VO_2, CuO, O_2 and $FeSO_4$.

(iv) These lose their magnetism in absence of magnetic field.

(b) Ferromagnetic substances

(i) The substances which are strongle attracted by magnetic field are ferromagnetic in nature.

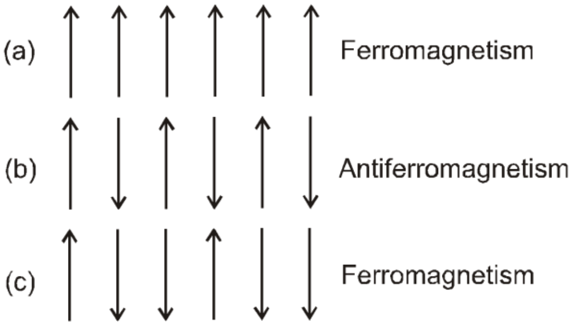
(ii) These also possess permanent magnetic dipoles due to presence of unpaired electrons relatively more in number than ordinary paramagnetic one.

(iii) e.g. Fe, Co, Ni, CrO_3

(iv) These retain magnetic properties even in absence of magnetic field.

(v) Ferromagnetic and ferrimagnetic substance change into paramagnetic substance at higher temperature due to randomisation of spins. Fe_3O_4, which is ferrimagnetic at room temperature, becomes paramagnetic at 850 K.

(vi) Ferromagnetism is due to a spontaneous alignment of the magnetic dipoles in the same direction. However, each ferromagnetic material has a characteristic temperature above which no ferromagnetism is noticed. This is known as curie temperature.



Alignment of magnetic dipoles in
(a) Ferromagnetic
(b) antiferromagnetic and
(c) ferrimagnetic substances

(vii) If the alignment of the dipoles is complimentary to give net moment equal to zero, the material is called antiferromagnetic and the phenomenon as antiferromagnetism, e.g. MnO, Mn_2O_3, MnO_2 are anti ferromagnetic.

(viii) When the magnetic dipoles are oriented in parallel and anti-parallel direction in unequal numbers to give some net magnetic moment, the material is called ferrimagnetic and the phenomenon as ferrimagnetism, e.g. Fe_3O_4, $ZnFe_2O_4$, $MgFe_2O_4$ etc. etc., are ferrimagnetism.

(c) Diamagnetic :

(i) The substances which are preebly repelled by the magnetic field are called diamafnetic

(ii) They have all their electrons paired.

(iii) Non-metallic elements (except O and S), inert gases and the smetals of II group, transition metals such as Zn, Cd, Hg and the substances TiO_2, V_2O_5, alkali metal salts and alkaline earth metal salts of +2 oxidation state, benzene, etc., are diamagnetic.

DIELECTRIC PROPERTIES :

A dielectric is a substance in which an electric field gives rise to no net flow of electric charge. This is due to the reason that electrons in a dielectric are tightly held by individual atoms. However, under the effect of applied field displacement of charges takes place, resulting in the creation of dipoles.

(i) Piezoelectricity : A dielectic crystal which has a resultant dipole moment can produce electricity or show electrical property when external pressure is applied. Such a crystal is known as **piezoelectric** crystal and this property is called **piezoelectricity.**

The mechanical stress caused by the applied pressure results in electric current because of the displacement of the ions in the crystals.

Such piezoelectric crystals find applications as pick-ups in record players since electric signals are produced on applying pressure.

(ii) Pyroelectricity : Some polar crystals upon heating produce small electric current. This phenomenon is known as **pyroelectricity**. Actually certain atoms or ions get displaced upon heating.

(iii) Ferroelectricity : In certain piezoelectric crystals, the dipoles are permanently polarised even in the absence of applied electric field. However, the direction of polarisation may change on applying current. This phenomenon is known as **ferroelectricity** and the effect involved is called ferroelectric effect. The examples of some ferroelectric solids are.

Potassium dihydrogen phosphate (KH_2PO_4) Potassium tartarate or Rochelle's salt (KOOCCH(OH)CH(OH)COOK) and barium titanate ($BaTiO_2$).

(iv) Anti-ferroelectricity : When the dipoles in alternate lattices point up and down, the two dipoles cancel on another so that there is no resultant dipole moment. Such crystals are known as antiferroelectric crystals and the phenomenon is called **antiferroelectricity.**

For example, lead zirconate ($PbZrO_3$) is an antiferroelectric solid.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Calculate the number of formula units in each of the following types of unit cells :

(a) MgO in a rock salt type unit cell

(b) ZnS in zinc blende structure

(c) platinum in a face-centred cubic unit cell.

Sol. (a) 4 (the same as in NaCl) (b) 4 (c) 4 (1 at the corner, 3 at the face-centres)

2. A mineral having the formula AB_2 crystallises in the cubic close-packed lattice, with the A atoms occupying the lattice points. What is the coordination number of the A atoms and B atoms ? What percentage fraction of the tetrahedral sites is occupied by B atoms ?

Sol. C.N. of A atom = 8 ; C.N. of B atom = 4

tetrahedral sites occupied by atoms B = 100% (all tetrahedral voids are occupied).

3. (a) What is the C.N. of Cr atom in bcc structure ?

(b) Cobalt metal crystallises in a hexagonal closest packed structure. What is the C.N. of cobalt atom ?

(c) Describe the crystal structure of Pt, which crystallises with four equivalent atoms in a cubic unit cell.

Sol. (a) 8, (b) 12, (c) fcc or cubic close packed.

4. Titanium metal has a density of 4.54 g/cm^3 and an edge length of 412.6 pm. In what cubic unit cell does titanium crystallise? (Ti = 48)

Sol. Density $d = \frac{zM}{a^3N_0}$

$d = 4.54\ g/cm^3$, $M = 48g\ mol^{-1}$, $Z = ?$ $N_0 = 6.023 \times 10^{23}\ mol^{-1}$

If value of z is known, structure can be decided

$$z = \frac{dN_0a^3}{M} = \frac{4.54 \times 6.023 \times 10^{23} \times (412.6 \times 10^{-10})^3}{48} = 4$$

Thus, titanium has **face-centred cubic** structure.

5. MgO has a structure of NaCl and TiCl has the structure of CsCl. What are the coordination numbers of ions in each (MgO and TiCl).

Sol. C.N. of Na^+ in NaCl = 6

C.N. of Cl^- in NaCl = 6

hence C.N. of Mg^{2+} is also = **6** and that of O^{--} or O^{2-} = **6 in MgO**

We know in CsCl

C.N. of Cs^+ = 8

C.N. of Cl^- = 8

Hence, **Ti^+ and Cl^- , in TiCl, have also C.N. 8 each.**

6. A solid AB has the NaCl structure, If radius of cation A^+ is 120 pm, calculate the maximum possible value of the radius of the anion B^-.

Sol. We know for the NaCl structure, for maximum of radius of B^-, the ratio r^+ / r^- should be minimum for octahedral void i.e. 0.414.

radius of cation/radius of anion = 0.414

$$\frac{r_{A^+}}{r_{B^-}} = 0.414$$

$$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = \mathbf{290\ pm.}$$

7. The C.N. of the barium ion Ba^{2+}, in BaF_2 is 8. What must be the C.N. of F^- ion ?

Sol. C.N.of barium ion tells us that it is surrounded by eight fluoride ions (charge 8 × (–1) = – 8). In order to balance out the eight negative charges, we need four barium ion (charge 4 × (+2) = +8). Hence, the C.N. of F^- ions must be **4.**

8. The radius of calcium ion is 94 pm and of oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Sol. The ratio $\frac{r_+}{r_-} = \frac{94}{146} = 0.644$

The prediction is an octahedral arrangement of the oxide ions around the calcium. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus CaO structure is similar to Rock Salt(NaCl) structure.

9. Sodium metal crystallises in body centred cubic lattice with cell edge = 4.29 Å. What is radius of sodium atom?

Sol. In 'BCC' structure.

body diagonal = $4 \times r_{Na} = \sqrt{3} \times a$

∴ $4 \times r_{Na} = \sqrt{3} \times 4.29$

$r_{Na} = \frac{\sqrt{3}}{4} \times 4.29$ = **1.86 Å**

10. CsCl crystallises in a cubic that has a Cl^- at each corner and Cs^+ at the centre of the unit cell. If (r_{Cs^+}) = 1.69 Å and r_{Cl^-} = 1.81 Å, what is value of edge length a of the cube?

Sol. We assume that the closest Cs^+ to Cl^- distance is the sum of the ionic radii of $Cs^{\oplus}$ and $Cl^{\ominus}$.

= 1.69 + 1.81 = 3.50 Å

This distance is one-half of the cubic diagonal = $\frac{a\sqrt{3}}{2}$

∴ $\frac{a\sqrt{3}}{2}$ = 3.50 Å ∴ a = **4.04 Å**

11. Platinum (atomic radius = 1.38 Å) crystallises in a cubic closest packed structure. Calculate the edge length of the face-centred cubic unit cell and the density of the platinum (Pt = 195).

Sol. $r = \frac{a}{2\sqrt{2}}$ (for fcc), $a = 2\sqrt{2}\,r$ = 3.9 Å

density = $\frac{ZM}{a^3 N_0} = \frac{4 \times 195}{(3.9 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$ = 21.83 g/cm^3 .

12. Calculate the edge length of the unit cell of sodium chloride given density of NaCl is 2.17×10^3 kg m^{-3} and molecular weight 58.5×10^{-3} kg mol^{-1}.

Sol. NaCl is face-centred cubic lattice so that number of NaCl molecules in a unit cell (z) = 4.

We know density $d = \dfrac{zM}{a^3N_0}$

where a = length of the unit cell

Volume $= a^3 = \dfrac{Mz}{dN_0} = \dfrac{4 \times 58.8 \times 10^{-3}}{2.17 \times 10^3 \times 6.02 \times 10^{23}} = 1.79 \times 10^{-28}\ m^3$

$a = 5.64 \times 10^{-10}$ m

a = 5.64 Å = **564 pm**

13. The effective radius of an iron atom is 1.42 Å. It has a rock-salt structure. Calculate its density (Fe = 56).

Sol. Due to rock-salt (fcc) structure, number of atoms in a unit cell (z) = 4.

Thus, d (density) $= \dfrac{zM}{a^3N_0}$ $\quad a = 2\sqrt{2}\ r = 2\sqrt{2} \times 1.42 \times 10^{-8}$ cm

∴ $d = \dfrac{4 \times 56}{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3}$ = **5.743 g/cm^3**

14. In a CPS (close packed structure) of mixed oxides, it is found that lattice has O^{2-} (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A^{3+}) and one-eighth of tetrahedral voids are occupied by divalent cations (B^{2+}). Derive formula of the mixed oxide.

Sol. Number of octahedral voids per ion in lattice = 1

Hence, number of trivalent cations (A^{3+}) $= 1 \times \dfrac{1}{2} = \dfrac{1}{2}$

number of tetrahedral voids per ion in lattice = 2

Hence, number of divalent cations (B^{2+}) $= 2 \times \dfrac{1}{8} = \dfrac{1}{4}$

Thus, formula is $A_{1/2}\,B_{1/4}O$ or **A_2BO_4.**

15. An element crystallises as face-centred cubic lattice with density as 5.20 g/cm^3 and edge length of the side of unit cell as 300 pm. Calculate mass of the element which contains 3.01×10^{24} atoms.

Sol. z = 4 in fcc lattice M = ?, d = 5.20 g/cm^3

$a = 300\ pm = 3 \times 10^{-8}$ cm

∴ $a^3 = 27 \times 10^{-24}\ cm^3$

$N_0 = 6.02 \times 10^{23}$

∴ $M = \dfrac{dN_0\,a^3}{z} = \dfrac{5.20\,g/cm^3 \times 6.02 \times 10^{23}\,mol^{-1} \times 27 \times 10^{-24}\ cm^3}{4} = 21.13\ g\ mol^{-1}$

Thus, 6.02×10^{23} atoms have = 21.13 g

∴ 3.01×10^{24} atoms have $= \dfrac{21.13}{6.02 \times 10^{23}} \times 3.01 \times 10^{24}$ g = **105.65 g**

16. Calcium crystallises in a face-centred cubic unit cell with a = 0.556 nm. Calculate the density if

(i) it contained 0.1% Frenkel defects

(ii) it contained 0.1% Schottky defects

Sol. Thus, density can be determined using $d = \frac{zM}{a^3N_0}$

(i) $a = 0.556$ nm $= 0.556 \times 10^{-9}$ m $= 0.556 \times 10^{-7}$ cm

$$d \text{ (with Frenkel defects)} = \frac{4 \times 40}{(0.556 \times 10^{-7})^3 \times 6.02 \times 10^{23}} = 1.5463 \text{ g / cm}^3$$

$$\text{(ii) d(with Schottky defect)} = \frac{3.996 \times 40}{(0.556 \times 10^{-7})^3 \times 6.02 \times 10^{23}} = 1.5448 \text{ g/cm}^3$$

17. If the length of body diagonal for CsCl, which crystallise into a cubic structure with Cl^- ions at the corner and Cs^+ ions at the centre of unit cell, is 7 Å and the radius of Cs^+ ion is 1.69 Å, what is the radius of Cl^- ion ?

Sol. For CsCl structure, body diagonal $= 2r_+ + 2r_-$

$7 \text{ Å} = 2 \times 1.69 \text{ Å} + 2r_-$

$3.5 \text{ Å} = 1.69 \text{ Å} + r_-$

$r_- = 3.5 \text{ Å} - 1.69 \text{ Å} = 1.81 \text{ Å}$

18. An element of molar mass 98.5 g mol^{-1} occurs in fcc structure. If its unit cell edge length is 500 pm and its density is 5.22 g cm^{-3}, calculate the value of Avogadro's constant.

Sol. For fcc structure, the no. of atoms per unit cell z = 4

Molar mass , M = 98.5 g mol^{-1} ; Edge length, $a = 500 \times 10^{-10}$ cm,

Density of a cubic unit cell, $d = \frac{zM}{a^3N_A}$ $\therefore N_A = \frac{zM}{a^3d}$

19. A compound AB crystallises in bcc lattice with unit cell edge length of 380 pm. Calculate (i) the distance between oppositely charged ions in the lattice, (ii) radius of A^+ if radius of B^- is 175 pm. (assuming that cation fits exactly in the cubic void).

Sol. In bcc structure, body diagonal $= 2 (r_+ + r_-)$

If 'a' is the edge length of unit cell, then

Body diagonal $= a\sqrt{3} = 2(r_+ + r_-)$

(i) The distance between oppositely charged ions, $(r_+ + r_-) = \frac{a.\sqrt{3}}{2} = \frac{380 \times 1732}{2} = 329.1$ pm

(ii) For exact fitting the radius ratio for cubic void, $\frac{r_+}{r_-} = 0.732$

$\therefore$ $r_+ = 0.732 \times 175$ pm $= 128.1$ pm

20. The density of NaCl is 2.163 g cm^{-3}. The edge length of its cell is 564 pm. Calculate value of Avogadro's number. Molar mass of NaCl is 58.45 g.

Sol. Density, $d = \frac{zM}{a^3N_A}$

$$N_A = \frac{zM}{da^3} = \frac{4 \times 58.45 \text{ g mol}^{-1}}{(564)^3 \times 10^{-30}\text{cm}^3 \times 2.163 \text{ g cm}^{-3}} = 6.02 \times 10^{23}$$

21. Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3 ?

Sol. Mass of the unit cell = $\frac{52 \times 2}{6.02 \times 10^{23}}$ = 1.73×10^{-22} g

Volume of the unit cell = $(287 \times 10^{-10})^3$ cm^3 = 2.364×10^{-23} cm^3

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{1.73 \times 10^{-22}\text{g}}{2.364 \times 10^{-23}\text{cm}^3} = 7.32 \text{ g/cm}^3$$

In BCC structure body diagonal is 4 times the atomic radius.

$$\therefore \quad \text{Atomic radius} = \frac{\sqrt{3} \times 287}{4} = 124.3 \text{ pm}$$

22. If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å and 1.81 Å respectively then calculate the coordination number of cation in crystals MgO, MgS and CsCl.

Sol. For MgO, the radius ratio

$$r_+/r_- = \frac{0.65}{1.40} = 0.464$$

Since the radius ratio lies in the range 0.414 to 0.732, Mg^{2+} would occupy octahedral voids and hence its coordination number would be 6.

For MgS, the radius ratio, $r_+/r_- = \frac{0.65}{1.84} = 0.353$

Since the radius ratio lies in the range 0.225 – 0.414, Mg^{2+} ion would occupy tetrahedral void and hence its coordination number would be 4.

For CsCl, the radius ratio, $r_+/r_- = \frac{0.69}{1.81} = 0.934$

Since the radius ratio is in the range 0.732 – 1, Cs^+ would occupy cubic void and hence its coordination number would be 8.