

# THE SOLID STATE

## SECTION I

### STRUCTURE AND CLOSE PACKING

A solid is a state of matter which possesses

- i) definite shape and volume.
- ii) incompressibility, rigidity and mechanical strength.
- iii) the particles in solids are very closely packed in some geometric pattern with small voids and interparticle forces are very strong.
- iv) particle motion is restricted to vibratory motion only.

#### CLASSIFICATION OF SOLIDS

The solids are of two types:

##### (i) Amorphous solids

Solids in which constituents do not possess the orderly arrangement over the long range are called **amorphous** solids. Region in an amorphous solid having an orderly arrangement are known as **crystallite**. They may have only short range order and do not possess sharp melting points. They undergo irregular cleavage (cut). Structures of amorphous solids are similar to that of liquid. Amorphous solids soften over range of temperature and can be molded and blown in to various shapes. On heating they become crystalline at some temperature. Therefore some time they are called as **pseudo solids** or **super cooled liquids**. Glass become milky some times on heating is due to this property. Due to lack of long range arrangement of particles or irregular arrangement of particles, amorphous solids are isotropic in nature. It is physical properties like resistivity. Refractive index is independent of direction

Examples: Glass rubber and plastics are typical examples of amorphous solids. Structure of quartz is crystal while quartz glass is amorphous. Amorphous silicon is one of the best photovoltaic materials available for conversion of sunlight to electricity

##### (ii) CRYSTALLINE SOLIDS

Solids in which various constituents unit like atoms, ions or molecules are arranged in an orderly manner which repeats itself over long distance are called **crystalline** solids. They exhibit very sharp melting points and undergo clean cleavage (cut). Crystalline solids are **anisotropic** in nature, that is, some physical property like electrical resistance, refractive index shows different values when measured along different direction in the same crystal. Reason for such behavior is particles are arranged differently along different direction. Examples: all metallic elements, non-metallic elements like sulphur, phosphorous and ionic compound like sodium chloride, zinc sulphide and naphthalene

## CLASSIFICATION OF CRYSTALLINE SOLIDS

Crystalline solids can be classified on the basis of nature of intermolecular forces operating between them in to following four categories

i) Molecular ii) Ionic iii) metallic iv) covalent

### (i) Molecular solids:

Further divided in into three categories

a) *Non-polar molecular solids :*

i	Constituent particles	Non-polar molecules
ii	Bonding force	Dispersion forces or London forces
iii	Binding energy in (kJ/mol)	0.05-40
iv	Melting point	Very low about 84
v	Physical nature	Soft
vi	Electrical conductivity	Insulator
	Examples	H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> , He, NA Ar, Kr

b) *Polar molecular solids:*

i	Constituent particles	Polar molecules
ii	Bonding force	Dipole -dipole interaction
iii	Binding energy in (kJ/mol)	5-25
iv	Melting point	low about 158
v	Physical nature	Soft
vi	Electrical conductivity	Insulator
	Examples	HCl, HBr, SO <sub>2</sub> , SO <sub>3</sub> etc

c) *H-bonded molecular solids :*

i	Constituent particles	Polar molecules containing O, N F and H
ii	Bonding force	Hydrogen bonding and Dipole -dipole interaction
iii	Binding energy in (kJ/mol)	10-40
iv	Melting point	low about 273
v	Physical nature	Hard
vi	Electrical conductivity	Insulator
	Examples	H <sub>2</sub> O ( ice)

### (ii) Ionic solids:

i	Constituent particles	Ions
ii	Bonding force	Electrostatic force of attraction
iii	Binding energy in (kJ/mol)	400-4000
iv	Melting point	High 1500
v	Physical nature	Hard but brittle
vi	Electrical conductivity	Insulator in solid state but conductor in molten and in aqueous state
	Examples	NaCl, KCl, CuSO <sub>4</sub> CaF <sub>2</sub> CsCl etc

**iii) Metallic solids:**

i	Constituent particles	Positively charged ions (kernels) in a sea of mobile electrons
ii	Bonding force	Metallic bonding
iii	Binding energy in (kJ/mol)	70-1000
iv	Melting point	800-1000
v	Physical nature	Hard but malleable and ductile except Na, K, Li etc
vi	Electrical conductivity	conductor
	Examples	Fr, Cu, Zn, Ni, Co, Al, Au, Pt etc

**iv) Covalent or Network solids:**

i	Constituent particles	Atoms
ii	Bonding force	Covalent bonds
iii	Binding energy in (kJ/mol)	150-500
iv	Melting point	High 4000
v	Physical nature	Hard
vi	Electrical conductivity	Insulator except graphite
	Examples	SiO <sub>2</sub> , diamond, graphite, SiC ( carborundum)

**CRYSTAL LATTICE AND UNIT CELL****Crystal lattice:**

The regular arrangement of an infinite set of points which describes the three dimensional arrangement of constituent particles ( atom, ions, molecules) in space is called a **crystal lattice or space lattice**. The space lattice may be one, two or three dimensional depending upon the number of parameters required to define it.

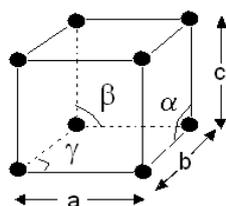
There are only 14 possible three dimensional lattices. They are called **Bravais Lattice**

Following are the characteristics of a crystal lattice

- (i) Each point in a lattice is called lattice point or lattice site
- (ii) Each point in a crystal lattice represents one constituent particle which may be atom, ion or molecule
- (ii) Lattice points are joined by straight line to bring out the geometry of the lattice

The smallest repeating units of space lattice which when repeated over and over again in three dimensions, result into whole of the space lattice of crystal is called **unit cell**. The crystal may, therefore be considered to consists of infinite number of unit cells.

A unit cell is characterized by :



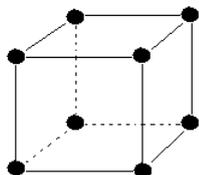
- (i) its dimensions along the three edges a, b, c. These edges may or may not be perpendicular to each other
- (ii) angle between edges  $\alpha$  ( between b and c ) ;  $\beta$  ( between a and c ) and  $\gamma$  ( between a and b).

Thus unit cell is characterized by six parameters

## Types of unit cells:

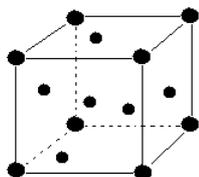
### (i) Simple or primitive

The unit cells in which, particles (i.e. atoms ions, or molecules) are present only at the corners of the unit cell are called simple or primitive cells



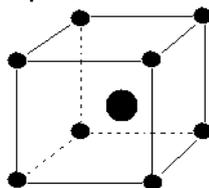
### (ii) Face-centered

In this type of unit cells, points are represented at the corners as well as centers of each six faces



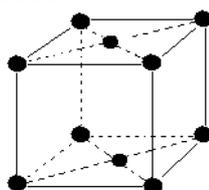
### (ii) Body-centered

These are the unit cells in which points are present at the corners and an additional point is present at the centre of the unit cell



### (iv) End centered

The unit cell in which points are present at the corners and at the centre of the two ends faces



## Number of atoms in unit cell

It should be noted that

(i) An atom present at the corner is equally shared by eight unit cells. Therefore contribution of an atom present at the corner to each unit cell is  $\frac{1}{8}$

(ii) An atom present at the face centre is equally shared between two unit cells. Therefore, contribution of an atom present at the face centre towards each unit cell is  $\frac{1}{2}$

(iii) An atom present within the body of the unit cell (body centre) is shared by no other unit cell. Hence, contribution of an atom present within body of unit cell is 1.

(iv) An atom present at the edge centre of unit cell is equally shared by four unit cells.

Therefore, contribution of an atom present at the edge centre towards each unit cell is  $\frac{1}{4}$

The point representing the atoms, molecules or ions in a unit cells are known as **lattice point** and is denoted by Z. also called as **Rank of a crystal**

The number of lattice point ( or number of atoms) per unit cell in the above four types of unit cells may be calculated as follows -

a	Simple or Primitive	$8 \times \frac{1}{8} (\text{from corners}) = 1$
b	Face-centered	$8 \times \frac{1}{8} (\text{from corners}) + 6 \times \frac{1}{2} (\text{from face centre}) = 4$
c	Body-centered	$8 \times \frac{1}{8} (\text{from corners}) = 1 + 1 (\text{from body centre}) = 2$
d	End-centered	$8 \times \frac{1}{8} (\text{from corners}) + 2 \times \frac{1}{2} (\text{from end faces}) = 2$

### Unit cells of 14 types of Bravais Lattices

	System	Axial Ratio	Axial angles	Unit cells	Examples
1	Cubic regular	$a = b = c$	$\alpha = \beta = \gamma$ all $90^\circ$	1) simple 2) face centered 3) body centered	NaCl, KCl, ZnS, $\text{Cu}_2\text{O}$ , Pb, Ag, Au, Hg, diamond, Alums
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma$ all $90^\circ$	4) simple 5) Body centered	$\text{SnO}_2$ , $\text{ZnO}_2$ , $\text{TiO}_2$ , $\text{NiSO}_4$ , $\text{ZrSiO}_4$ , $\text{PbWO}_4$ , White Sn
3	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	6) simple	$\text{ZnO}$ , $\text{PbI}_2$ , CdS, HgS, Graphite, Ice, Beryl, Mg, Zn, Cd
4	Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma$ $\neq 90^\circ$	7) simple	$\text{NaNO}_3$ , $\text{CaSO}_4$ Calcite, , Quarts, As, Sb, Bi
5	Orthorhombic ( Rhombic)	$a \neq b \neq c$	$\alpha = \beta = \gamma$ all $90^\circ$	8) Simple 9) face centered 10) Body centered 11) end centered	$\text{KNO}_3$ , $\text{K}_2\text{SO}_4$ , Calcite, $\text{BaSO}_4$ Rhombic sulphure, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
6	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	12) Simple 13) End centered	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Monoclinic sulphur
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$ $\neq 90^\circ$	14) Simple	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{H}_3\text{BO}_3$

#### Solved example :

Q) A compound formed by the element X and Y crystallizes in cubic structure in which X atoms are at the corners of the cube with Y atoms are at the centre of the face. What is the formula of the compound.

Solution :

The number of X-atoms per unit cell  $8 \times \frac{1}{8}$  (from corners) = 1

Number of Y atoms per unit cell =  $6 \times \frac{1}{2}$  (from face centre) = 3

Thus chemical formula =  $XY_3$

## CLOSE PACKING OF CRYSTALLINE SOLIDS

**Close packing** refers to tight arrangement of spheres in a given space in such a way that they occupy the maximum available space and hence the crystal has maximum density.

The number of nearest neighbors of a particle is called **coordination number**

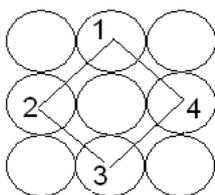
### a) Close packing in one dimension:

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange in row and touching each other. Coordination number is 2

### b) Two dimensional close packing

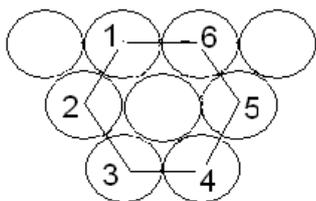
#### (1) Square close packing

Here spheres are arranged in such a way that every sphere is in contact with four other spheres coordination number 4 since second row exactly below first such arrangement is called AAA type arrangement



#### (2) Hexagonal close packing :

In this kind of packing, spheres are arranged in such a way that every sphere is in contact with six other spheres. Coordination number 6



The second row may be placed above the first in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of first row is called A type, the one in second row is different type and may be called B type. When third row is placed are line with first row then this row is also A. And arrangement is known as ABAB type

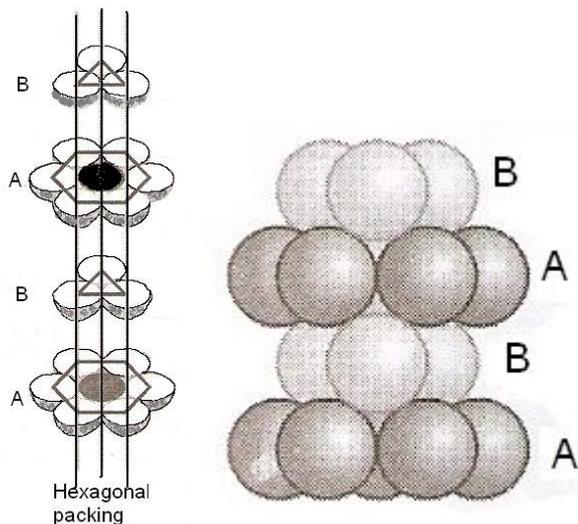
### c) Three dimensional close packing

Two types of three dimensional close packing are obtained from hexagonal close packing layers a) Hexagonal close packing (hcp) b) Cubic close packing (ccp)

While other two types of three dimensional close packing are obtained from square close packed layers. c) Body Centered cubic arrangement (bcc) and d) simple cubic arrangement

### a) Hexagonal Close –packing (hcp)

In this arrangement, atoms are located at the corners and centre of two hexagonal placed parallel to each other, three more atoms are placed in a parallel to midway between these two planes:



#### Characteristic features of hcp

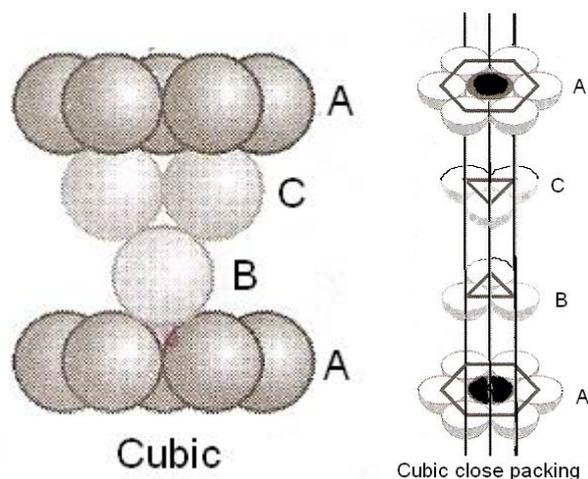
- (i) This type of packing is ABAB... type of arrangement of the layers which indicates that every alternate layers are alike
- (ii) It has a 6-fold axis of symmetry
- (iii) Each atom is surrounded by 12 another atoms, 6 in own layer and 3 above and 3 below layers. Coordination number 12
- (iv) In hcp arrangement, the atom occupy 74% of the available space and thus 26% of space is empty
- (v) It has only one set of parallel close –packed layers. Hence, the chances for slipping of one layer over the other is less..

Example : BE, Cd, Li, Ca, Cr, Mo, V, Mg, Zn, Ce, Zr, OS, Ru, He

### b) Cubic closed packing (ccp) or face centered cubic (fcc)

In this type of close packing, atoms are arranged at the corners and at the centers of all six faces of a cube.

If we start with hexagonal layers of spheres as shown in figure and second layer of spheres is arranged placing the spheres over the holes in first layer, one half of the holes can be filled by these spheres. Suppose that spheres in third layers are so arranged that they cover holes in second layer. , the third layer neither resembles first layer or second layer. The fourth layer resembles first , fifth resembles second and sixth resembles third layer, then this type of arrangement is known as cubic closed-packed (ccp) arrangement or face centered cubic (fcc) arrangement. The percentage of free space is 26% and coordination number is 12.



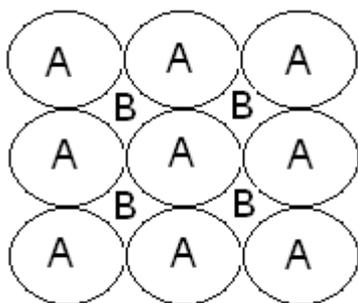
Characteristic features of ccp:

- (i) This type of packing has ABCABC.... type of arrangement of the layer i.e. the first three layers are quite different from each other but this set of layer is repeated over and again the addition of more layers
- (ii) It has cubic symmetry, the whole structure has four 3-fold axis of symmetry
- (iii) As in hcp, each atom in ccp arrangement has 12 nearest has 12 nearest neighbors i.e. the coordinate number of each atom is 12
- (iv) The ccp arrangement of atoms occupies 74% of the available space and thus 26% of the space remains empty.
- (v) It has four sets of parallel close packed layers. Hence, the chances for slipping of one layer over the other are more in the ccp arrangement than in the hcp arrangement. Hence, metals having ccp structure
- (vi) Example : Cu, Ag, Au, Pt, Al, Cr, Co, Ni, Ca, Sr, Pt all noble gases except He are found to possess cubic close packed structure. Nearly 60% of the metals have been found to possess either hcp or ccp structure.

c) Body – Centered cubic structure ( bcc)

Characteristic feature of body centered cubic arrangement:

- i) In a body centered cubic arrangement, the atoms occupy corners of a cube with an atom at its centre.
- (ii) Each atom is in contact with eight other atoms ( four atoms in the layer just above and four atoms in the layer just below) and hence the coordination number in this type of arrangement is only eight
- (iii) This arrangement of atoms occupies only 68% of the total volume, so this arrangement is found in Na, K, Cs, Rb, W, V, Mo, and Ba. Only 20% of the metallic elements found to possess bcc arrangement.



#### d) Simple cubic arrangement

The particles in the adjacent rows may show a horizontal as well as a vertical alignment forming cubic. A central sphere is surrounded by four other spheres in two dimension and in three dimension surrounded by 6 spheres

### VOIDES OR HOLES

A crystal is formed as result of close packing of its constituting particles which are supposed to have spherical shape. Since they are touching each other only at one point, there must remain some empty spaces are called **voids or holes or interstitial site**

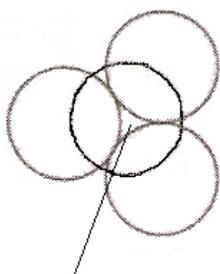
#### a) Tetrahedral voids

The voids, which are surrounded by four spheres which lie at the vertices of a regular tetrahedron are called **tetrahedral void**. There are 8 tetrahedral voids around each sphere. If N are the number of close packed sphere than tetrahedra voids are 2N. coordination number of tetrahedral void is 4

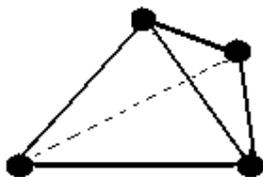
If  $r$  = radius of the spherical tetrahedral site

$R$  = radius of closely packed sphere

Size of the tetrahedral void =  $0.225R$



Tetra hedral void



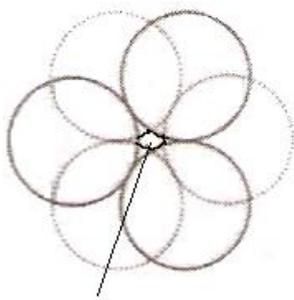
#### b) Octahedral voids

The void, which are surrounded by six sphere which lie at the vertices of a regular octahedron, is known as **octahedral void**. There are six octahedron void around each sphere . There is one void per atom in a crystal. If N are the number of close packed sphere than octahedral voids are N . coordination number of octahedral void = 6

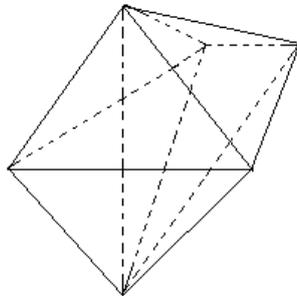
If  $r$  = radius of the spherical octahedral site

$R$  = radius of closely packed sphere

Size of the tetrahedral void =  $0.414R$



Octahedral void



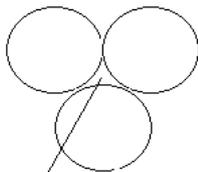
### c) Trigonal void

The void, enclosed by three sphere in contact is called a **Trigonal void**. This void and the spheres surrounding it are in same plane. There are 24 void around each sphere. There are 8 Trigonal voids per atom in a crystal.

If  $r$  = radius of the spherical Trigonal site

$R$  = radius of closely packed sphere

Size of the tetrahedral void =  $0.155R$



Trigonal void

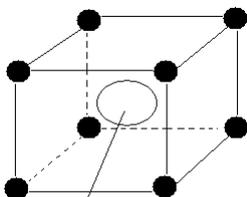
### d) Cubic void

This type of void is formed between 8 closely packed spheres which occupy all eight corners of cube. This site is surrounded by eight spheres which touches each other. Size of the cubical void is given as

If  $r$  = radius of the spherical cubical site

$R$  = radius of closely packed sphere

$R = 0.732R$



Cubic void

Decreasing order of the size of the various voids :

Cubic > Octahedral > Tetrahedral > Trigonal

Number of tetrahedral void = 2 ( Number of atoms or octahedral voids)

## PACKING EFFICIENCY OF ccp AND hcp STRUCTURE

**Packing efficiency** is the percentage of total space filled by the particles.

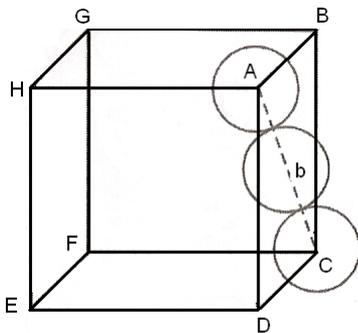
### a) Packing efficiency of ccp and hcp structure

In figure, let cell edge length be 'a' and face diagonal AC = b

In  $\triangle ABC$

$$AC^2 = BC^2 + AB^2$$

$$b^2 = a^2 + a^2 \text{ Thus } b = \sqrt{2} a \text{ --(i)}$$



other sides spheres are not shown for clarity

If radius of sphere is r, we find  $b = 4r$

$$\text{From eq(i) } \sqrt{2} a = 4r \text{ Thus } r = \frac{a}{2\sqrt{2}}$$

There are four spheres per unit cell in ccp structure.

$$\text{Volume of four spheres} = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the cube} = a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$$

Percentage of packing efficiency =

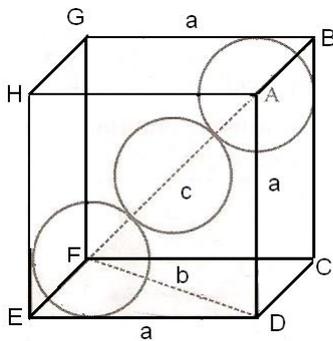
$$\begin{aligned} & \frac{\text{Volume occupied by four spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\% \\ &= \frac{4 \times \frac{4}{3} \pi r^3 \times 100}{16\sqrt{2}r^3} \times 100\% \\ &= \frac{\pi}{3\sqrt{2}} \times 100\% \end{aligned}$$

Thus efficiency = 72%

$$\text{OR Packing factor} = \frac{\pi\sqrt{2}}{6} = 0.72$$

### b) Packing efficiency of Body Centered Cubic Structure

In figure, let cell edge length be 'a' and face diagonal FD = b, diagonal FD = c



From  $\triangle EFD$   $b^2 = a^2 + a^2$  Thus  $b = \sqrt{2} a$  –(i)

From  $\triangle AFD$   $c^2 = a^2 + b^2$

From eq(i)

$$c^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3} a \text{ –(ii)}$$

The length of the body diagonal c is equal to 4r. Here r is the radius of the sphere (atom)

From eq(ii) we get  $\sqrt{3} a = 4r$

$$r = \frac{\sqrt{3}}{4} a$$

There are two spheres per unit cell in bcc

$$\text{Volume of two sphere} = 2 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of cube} = a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3$$

Percentage of packing efficiency =

$$\frac{\text{Volume occupied by two spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\%$$

$$= \frac{2 \times \frac{4}{3} \pi r^3 \times 100}{\left(\frac{4}{\sqrt{3}} r\right)^3} \times 100\%$$

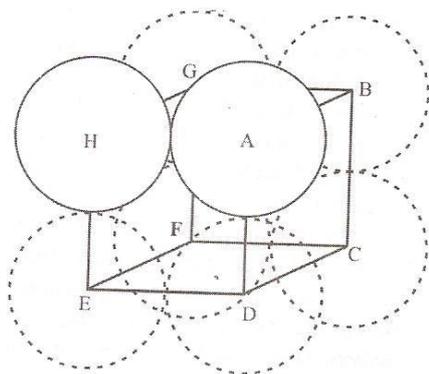
$$= \frac{\sqrt{3}\pi}{8} \times 100\% = 68\%$$

Thus efficiency = 68%

$$\text{OR Packing factor} = \frac{\pi\sqrt{3}}{6} = 0.68$$

### c) Packing efficiency in simple cubic lattice

In simple cubic lattice, 8 lattice points are on the corners of the cube. Since a simple cubic has only one atom. Let edge length be a then  $a = 2r$ , here r is the radius of sphere



Percentage of packing efficiency =

$$\frac{\text{Volume occupied by one spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3 \times 100}{(2r)^3} \times 100\%$$

$$= \frac{\pi}{6} \times 100\% = 52.4\%$$

### Density of cubic crystal

Density of unit cell ( $\rho$ )

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

Mass of unit cell = number atoms in a unit cell X mass of one atom

$\text{mass of unit cell} = Z \times \frac{M}{N_0}$  here  $N_0$  = Avogadro's number and  $M$  = Molar mass

If length of edge =  $a$  then volume =  $a^3$

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

### SUMMARY OF STRUCTURE OF METALS

Sr.No	Property	Hexagonal close packed (hcp)	Cubic close packed (ccp or fcc)	Body centered cubic (bcc)
1	Arrangement of packing	Closed pack	Closed pack	<b>Not</b> closed pack
2	Type of packing	AB AB AB A...	ABC ABC AB...	AB AB AB A...
3	Packing efficiency	74%	74%	68%
4	Coordination number	12	12	8
5	Malleability and ductility	Less malleable, hard and brittle	malleable and ductile	-----
6	Examples	BE, Mg, Ca, Cr, MO, V, Zn	Cu, Ag, Au, Pt	Alkali metals, Fe

## Radius ratio

In ionic compounds, the geometrical shape of ionic crystals as well as the coordinate number depends on the relative size of the ions. Positive ions are small in size thus occupy positions in voids. And negative ions are larger in size occupy positions in corners.

The ratio of the radii of the cation to the anion in crystal lattice is called **radius ratio**

$$\text{Radius ratio} = \frac{r_+}{r_-} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}}$$

Relation ship between Radius ratio, Coordinate Number and Geometrical Shape

Radius ratio	Coordination number	Structural arrangement	Structure type	Example
0.155 – 0.225	3	Planer triangular	--	B <sub>2</sub> O <sub>3</sub>
0.225-0.414	4	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
0.414 – 0.732	6	Octahedral	Sodium chloride	NaBR, KBr, MgO, MnO, CaO, CaS
0.732 -1	8	Body- centred cubic	Cesium chloride	CsI, CsBR, NH <sub>4</sub> Br

## Solved examples

**Example 1:** Potassium metal crystallises in face-centred cubic arrangement with rdge length 574pm. What is the shortest separation of any two potassium nuclei

Solution: For fcc arrangement dittance of neighbour =  $2r = 2 \times \frac{a}{2\sqrt{2}} = \frac{a}{\sqrt{2}} = 0.707a$   
 $= 0.707 \times 574 = 46\text{pm}$

**Example 2:** The cubic unit cell of aluminium ( molar mass 27.0 g/mole) has an edge length of 405 pm and density 2.70 g/cm<sup>3</sup>. What tpe of unit cell is?

**Solution :** from formula for density  $\rho = \frac{M \times Z}{N_0 a^3}$

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

$$Z = \frac{2.7 \times 6.023 \times 10^{23} \times (405 \times 10^{-10})^3}{27.0} = 4$$

i.e number of atoms per unit cell is 4. Hence, unt cell is face centred type

**Example 3:** Crystalline CsCl has density 3.988 g/cc. Caluclate the volume occupied by single CsCl ion pair in the crystal ( CsCl = 168.4)

**Solution:** CsCl has simple cubic arrangement hence Z=1

Thus volume of unit cell = volume of single CsCl ion pair

From formula for density  $\rho = \frac{M \times Z}{N_0 a^3}$

$$a^3 = \frac{M \times Z}{N_0 \rho} = \frac{168.4 \times 1}{6.023 \times 10^{23} \times 3.998} = 7.014 \times 10^{-23} \text{ cc}$$

**Example 4:** A metal is found to have a specific gravity of 10.2 at 25°C. It crystallises in a body-centred cubic lattice with a unit cell edge length of 3.0 Å. Calculate the atomic weight

**Solution :** From formula for density  $\rho = \frac{M \times Z}{N_0 a^3}$ , for body centred  $Z=1$

$$M = \frac{\rho N_0 a^3}{Z} = \frac{10.2 \times 6.023 \times 10^{23} \times (3 \times 10^{-8})^3}{2} = 82.9 \text{ u}$$

**Example 5:** If the anions (B) form hexagonal close packing and cation (A) occupy only 2/3 octahedral sites in it, then what would be the general formula of the compound

**Solution:** Number of anions (B) per unit cell = 6 ( for hcp arrangement )

Total number of octahedral sites = 6

Number of cations per unit cell = 6 X (2/3) = 4

A:B = 4 : 6 or A:B = 2 : 3

Hence formula of compound is  $A_2B_3$

**Example 6:** A metallic element has cubic lattice. Each edge of unit cell is 3 Å . the density of the metal is 8.5 g/cc. How many unit cells will be present in 50g of metal?

**Solution :** Volume of unit cell =  $a^3 = (3 \times 10^{-8})^3 \text{ cm}^3$

Mass of unit cell = density X volume =  $8.5 \times (3 \times 10^{-8})^3$

Number of unit cell = Mass of sample / mass of unit cell

Number of unit cell =  $\frac{50}{8.5 \times 27 \times 10^{-24}} = 2.178 \times 10^{23}$

**Example 7 :** Tungsten is arranged in face-centred cube having unit cell volume of  $31.699 \text{ \AA}^3$  Calculate the radius and atomic volume of tungsten.

**Solution :** Volume ( $a^3$ ) =  $31.699 \text{ \AA}^3$

Edge length  $a = 3.165 \text{ \AA}$ .

For fcc arrangement

$$\text{Radius } r = \frac{\sqrt{2}a}{4} = \frac{1.414 \times 3.165}{4} = 1.1188 \text{ \AA}$$

**Example 8:** A substance has a face centred cubic crystal with density of  $1.984 \text{ g/cm}^3$  and edgelength 630 pm. Calculate the molar mass of the substance.

**Solution :**

From the formula of density  $\rho = \frac{M \times Z}{N_0 a^3}$  for fcc  $Z = 4$

$$M = \frac{\rho N_0 a^3}{Z} = \frac{1.984 \times 6.023 \times 10^{23} \times (630 \times 10^{-10})^3}{4} = 74.70$$

**Example 9 :** Analysis shows that nickel oxide has formula  $\text{Ni}_{0.98} \text{O}_{1.0}$ . What fraction of the nickel exists as  $\text{Ni}^{+2}$  and  $\text{Ni}^{+3}$  ions?

**Solution:** If there are 100 oxygen then  $\text{Ni} = 98$ .

Let  $\text{Ni}^{+2}$  ions = x

then  $\text{Ni}^{+3}$  ions =  $98-x$

Since electric neutrality is maintained

Charge on Ni ions = Change on oxygen

$$2(x) + 3(98-x) = 2(100)$$

$$-x + 294 = 200$$

$$x = 94$$

Thus  $\text{Ni}^{+2} = 94\%$  and  $\text{Ni}^{+3} = 6\%$

**Example 10:** A mineral having the formula  $\text{AB}_2$  crystallises in the cubic closed lattice, with the A atoms occupying the lattice points. What are the co-ordination number of the A and B

**Solution :** In ccp of  $\text{AB}_2$ , A- atom occupy the lattice points, and number of B are twice the A thus must be occupying tetrahedral void. Thus A must have Coordination number 8 and B coordination number 4.

**Example 11:** An element ( atomic mass = 60) having face-centred cubic unit cell has a density of  $6.23 \text{ g/cm}^3$ . What is the edge length of the unit cell

**Solution**

From the formula for density  $\rho = \frac{ZM}{a^3 N_A}$

$$a = \left( \frac{ZM}{\rho N_A} \right)^{\frac{1}{3}} \text{ For fcc } Z = 4,$$

$$a = \left( \frac{4 \times 60}{6.23 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}}$$

[First adjust power of 10 such that we can find cube root we will make power from 23 to 24 ]

$$a = \left( \frac{4 \times 60}{0.623 \times 6.023 \times 10^{24}} \right)^{\frac{1}{3}} = \left( \frac{240}{0.623 \times 6.023 \times 10^{24}} \right)^{\frac{1}{3}}$$

[Take log of all the terms]

$$\log(240) = 2.3802$$

$$\log(0.623) = \bar{1}.7945$$

$$\log(6.023) = 0.7771$$

[ Apply log rules]

Denominator terms are in multiplication thus log should be added

$$\log(0.623) = \bar{1}.7945$$

+

$$\log(6.023) = 0.7771$$

$$= 0.5716 \text{ ---(1)}$$

Subtract (1) from  $\log(240)$

$$\log(240) = 2.3802$$

$$- \quad = 0.5716$$

$$1.8086 \text{ -- (2)}$$

[ Totake cube root divide (2) by three]

$$1.8086 / 3 = 0.6029 \text{ --(3)}$$

Now take antilog of (3) = 4.007

$$\text{And cube root of } 10^{24} = 10^8$$

thus answer is  $4 \times 10^8$  cm or 400 pm

## Important formulae

1) Density of the unit cell  $\rho = \frac{ZM}{a^3 N_A}$

Z : rank of unit cell ( number of atoms per unit cell)

M : Molecular mass

A : length of edge

$N_A$  : Avogadro's number

2 ) Relation ship between nearest neighbour distance(d) edge length of unit cell(a) and radius of atom(r)

Simple	Face-centered	Body-centered
$d = a$	$d = \frac{\sqrt{2}}{2} a = 0.707a$	$d = \frac{\sqrt{3}}{2} a = 0.866a$
$r = a/2$	$r = \frac{\sqrt{2}}{4} a = 0.3535a$	$r = \frac{\sqrt{3}}{4} a = 0.433a$

## STRUCTURE OF SIMPLE IONIC COMPOUNDS

Ionic compounds consisting of cations and anions are of the type AB, AB<sub>2</sub> and A<sub>2</sub>B

### A) Ionic compounds of AB type

AB type compounds may have one of the following types of structure.

- (1) Rock Salt ( NaCl) type structure
- (2) Cesium Chloride (CsCl) type structure
- (3) Zinc blend (ZnS) type structure

#### (1) Rock Salt ( NaCl) type structure

(i) NaCl has fcc ( also called ccp) arrangement of Cl<sup>-</sup> ions in which Cl<sup>-</sup> is present at the corners and face centres of the cube

(ii) Na<sup>+</sup> ions occupy all the tetrahedral site. i.e body centre and edge centres.

(iii) Each Na<sup>+</sup> ion is surrounded octahedrally by six Cl<sup>-</sup> ions and each Cl<sup>-</sup> ion is surrounded octahedrally by six Na<sup>+</sup> ions. Hence, coordination number of both Na<sup>+</sup> ion and Cl<sup>-</sup> ion is six

(iv) On applying pressure NaCl structure ( 6:6 coordination) changes to CsCl structure ( 8:8 coordination)

(v) edge length = 2( nearest neighbour distance)

Other examples : Halides of Li, Na, K, AgCl, AgBr, CaO etc

### 2) Caesium Chloride (CsCl) type structure

(i) In this type of ionic crystal, the size of  $\text{Cs}^+$  ion is quite big as compared to  $\text{Cl}^-$  ion. Therefore, it acquires the body centred cubic lattice structure

(ii) It has bcc arrangement

(iii) The  $\text{Cl}^-$  ions arranged in a simple cubic arrangement i.e. are present at the corners of the cubic unit cell

(iv)  $\text{Cs}^+$  ion is surrounded by 8 chloride ions and each  $\text{Cl}^-$  ion is surrounded by 8 $\text{Cs}^+$  ions. Therefore, the structure has 8:8 coordination

(v)  $\text{Cs}^+$  ion occupy cubic interstitial site i.e. body centre

(vi) At high temperature CsCl (8:8 coordination) changes to NaCl structure ( 6:6 coordination)

Other examples : CsBr, CsI, CsCn, TlCl, TlBr, TlI, TlCN, CaS

### 3) Zinc Blend ( zinc sulphide) type structure

(i) The sulphide ions ( $\text{S}^{2-}$ ) form fcc by occupying corners and face centres of cubic unit cell.

(ii) Zinc ions( $\text{Zn}^{2+}$ ) occupy half of the total available tetrahedral voids in alternate manner

(iii) Each sulphide ion is surrounded tetrahedrally by 4  $\text{Zn}^{2+}$  ions and each  $\text{Zn}^{2+}$  ion is surrounded tetrahedrally by 4 $\text{S}^{2-}$  ions. therefore, ZnS has 4:4 coordination

Other examples having structure : ZnCl, CuCl, CuBr, CuI, CgS, AgI, BES etc.

Note : Zinc sulphide ZnS exists in two forms: Zinc blend and Wurtzite which differs only in terms of arrangement of  $\text{S}^{2-}$  ions. In case of zinc blends,  $\text{S}^{2-}$  ions have cubic close packing (ccp) arrangement thus, 4 formula units per unit cell. Whereas in Wurtzite,  $\text{S}^{2-}$  ions have hexagonal close packing (hcp)

**B) Ionic compounds of  $\text{AB}_2$  type**  
Fluorite ( $\text{CaF}_2$ ) type structure (i) It has ccp arrangement of  $\text{Ca}^{2+}$  in which  $\text{Ca}^{2+}$  ions are present at the corners and face centres of unit cell (ii) Fluoride ions( $\text{F}^-$ ) occupy all available tetrahedral voids

(iii) Each calcium atom is surrounded by eight fluoride ions i.e coordination number of calcium ion is eight. Each fluoride ion is in contact with four calcium ion its coordination number is 4. Thus  $\text{CaF}_2$  has 8:4 coordination

Other examples :  $\text{SrF}_2$ ,  $\text{BaF}_2$ ,  $\text{CdF}_2$ ,  $\text{HgF}_2$ ,  $\text{PbF}_2$ ,  $\text{CuF}_2$ ,  $\text{SrCl}_2$  etc

### **C) Ionic compounds of $\text{A}_2\text{B}$ type**

Antifluorite ( $\text{Na}_2\text{O}$ ) type structure

(i) In the crystal structure of  $\text{Na}_2\text{O}$ , the  $\text{O}^{2-}$  ions constitute a cubic close packed lattice ( fcc structure) and the  $\text{Na}^+$  ions occupy all available tetrahedral voids

(ii) Each oxide ion,  $O^{2-}$  ion, is in contact with 8  $Na^+$  ions and each  $Na^+$  ion is surrounded by 4 oxide ions. Therefore  $Na_2O$  has 4:8 coordination  
 Other example :  $Li_2O$ ,  $K_2O$ ,  $K_2O$  and  $Na_2S$  etc

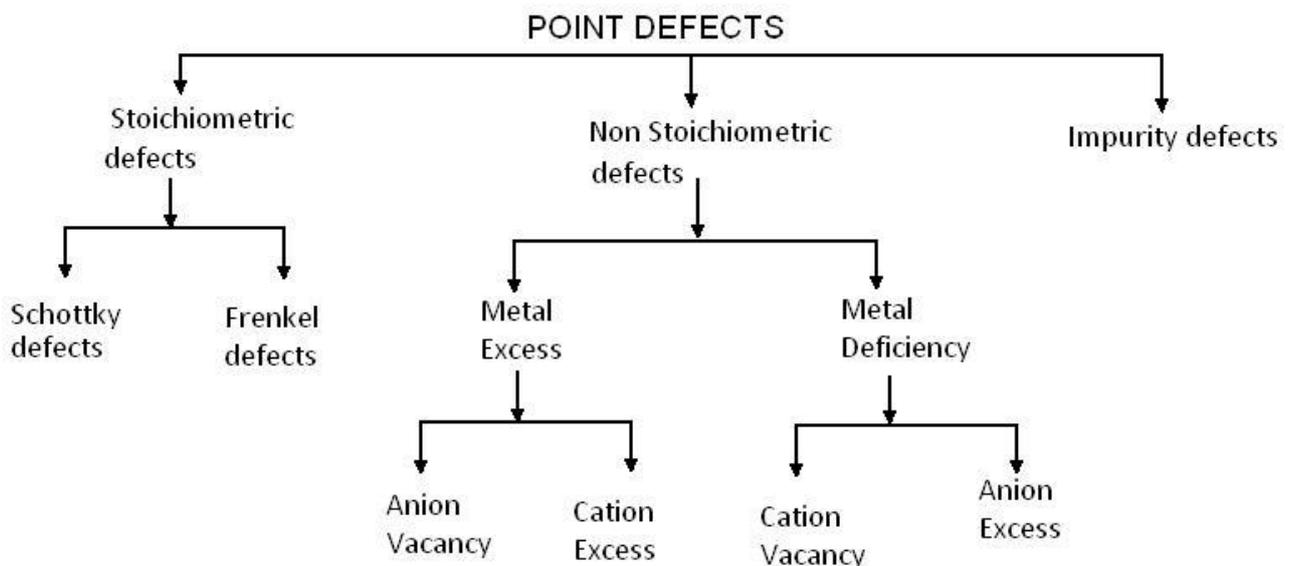
## SECTION II

# DEFECTS AND PROPERTIES OF SOLIDS

Any deviation from regular arrangement in crystalline solids are called as **crystal defect**  
 Broadly defects are of two types i) Line defect ii) Point defect  
 The **line defects** are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

**Point defects** are the irregularities or deviations from ideal arrangement around point or an atom in crystalline substance.

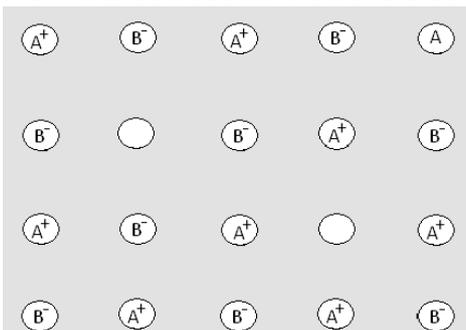
Various types of defects in ionic compounds are as follows



### (A) Defects in stoichiometric compounds

#### (i) Schottky defect

This type of defect is characterised by missing equal number of cations and anions from their lattice sites so that the electrical neutrality of the system is maintained



This type of defect is shown by the compound with

(a) High coordination number

(b) Small difference in size of the positive and negative

ions i.e.  $\frac{r^+}{r^-} \approx 1$

Or cations and anions do not differ in size appreciably

Consequences of Schottky defect

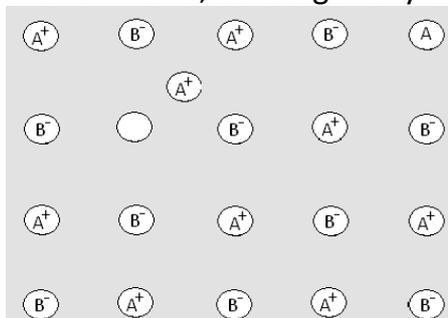
- (a) Since crystal lattice have lesser number of ions, density of the crystal decreases
- (b) The persence of a number of ionic vacancies lowers lattice energy or the stability of the crystal
- (c) The crystal shows electrical conductivity to small extent by ionic mechanism

Exampals: NaCl, CsCl, KBr, KCl

In NaCl there are approximately  $10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In  $1\text{cm}^3$  there are about  $10^{22}$ . Thus, there is one defect per  $10^{16}$  ions.

(ii) Frenkel defect

In this defect, an ion shifts from its original lattice site to interstitial site, so that electric neutrality as ell as stoichiometry of the compound is meaintained. Since carions are smaller in size, so it is generly cations that dshifts from lattice to interstetial site.



This type of defect is shown by

- (a) Compounds having low coordination number because in such compounds the attractive forces, being less, are very easy to overcome and hence the cation can easily move into the interstitial site

- (b) Compound having large difference in size of cations and anions. i.e  $\frac{r^+}{r^-}$  is low

- (c) Compounds having highly polarising cations and an easily polarizable anions.

Consequences of Frankel defect

- (a) Since nothing is lost from crystal as a whole, therefore density of the crystal is not effected
  - (b) The crystal shows electrical conductivity to a small extent by ionic mechanism
  - (c) The closeness of like charges tends to increase the dielectric constant of the crystal
- Note : The number of these two defects in a crystal generally increases with the rise of temperature, hence they are sometimes called as **thermodynamic defects**

AgBr shows both Frenkel and Skhottky defect.

**(B) Defects in non-stoichiometric compounds**

Non-stoichiometric defects are the defects by virtue of which stoichiometry of the compound gets distrubed. Ratio of positive and negative ions becomes different from the ratio indicated by their ideal chemical formulae.

For example in FeO ratio of positive and negative ions ia 0.94:1. The balnce of positive or negative charge is maintained either by having extra electrons or extra positive charge which makes the structure irregular. These defects arises due to the presence of either the metal or non-metal in excess.

- a) Metal excess defect

In this type of defect cations are in excess. This situation may arise either due to 1) Anion vacancies 2) Extra Cation in interstitial site

### 1) Anion excess

- i) In this case, anions are missing from their lattice site leaving a hole behind and causing excess in the cation (metal) concentration
- ii) The hole formed are occupied by electrons, thus system is electrically neutral
- iii) The nonmetal atom may leave the surface in the form of gas.
- iv) The electrons trapped in anion vacancies are called **F-centres** because they impart colour to the crystal

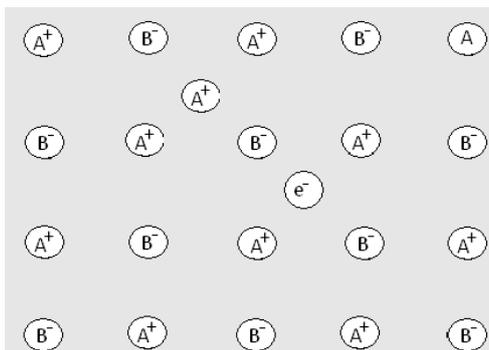
When alkali halide like NaCl is heated in an atmosphere of vapours of the sodium metal, Sodium atoms deposit on surface of crystal, the chloride ions (anion) diffused to the crystal surface to combine with newly generated sodium cation, leaving behind anionic vacancy behind. The electron lost by the sodium atom diffuses through the crystal to occupy the anion vacancies. These centres are known as F-centres



Note this defect is shown by the compounds which have Schottky defects.

### 2) Extra Cation in interstitial site

- i) In this type of metal excess, extra positive ions are present in interstitial site
- ii) Electrical neutrality is maintained by presence of an electron, in another interstitial position.



The common example is ZnO

When ZnO is heated, it loses oxygen atom and turns yellow. The excess  $\text{Zn}^{+2}$  are trapped in interstitial sites and the electrons in the nearest neighbouring interstitials. Yellow colour of ZnO, when it is hot is due to these trapped electrons.

Note this type of defect is found in crystals having Frenkel defect.

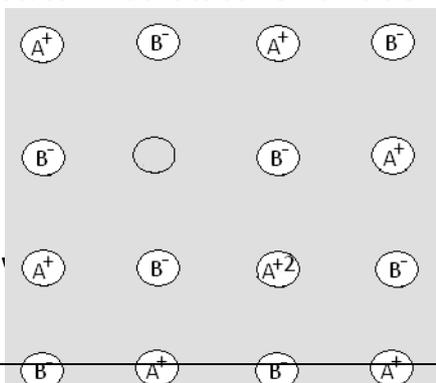
Consequences of metal excess defects

- (i) Compounds have increased conductivity due to the presence of free electrons
- (ii) Compounds are usually coloured. Excess Na makes NaCl yellow in colour. Excess Li makes LiCl pink, Excess K makes KCl violet (lilac)

### 2) Metal deficiency defect

Metal deficiency defect may also arise due to 1) Cation vacancies 2) Extra anion occupying the interstitial sites

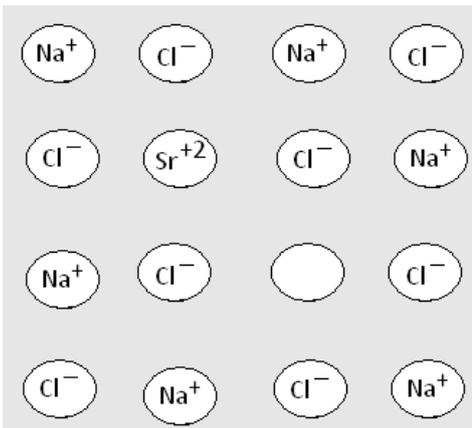
1) Cation vacancies: This type of defect occurs when a positive ion is missing from its lattice site and the charge is balanced by the oxidation of some of the cations to a higher valency state. Thus the lattice remains deficient of metal atoms



Example: FeO which is mostly found with a composition of  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystal of FeO some  $\text{Fe}^{+2}$  ions are missing and the loss of positive charge is made up by the presence of the required number of  $\text{Fe}^{+3}$  ions

2) Extra anions occupying the interstitial sites : This type of defect involves the presence of an extra anion in an interstitial site, the electrical neutrality is maintained by an extra charge on cation. No example of crystal possessing this defect is known at present because anions are usually larger in size, so it is improper to expect them to fit into interstitial sites

( C ) Impurity defect : When some foreign atom is present in crystal, the defect is called impurity defect. If the foreign atom is present at lattice site, the solid is called **substitutional solid solution**, whereas if impurity is present at vacant interstitial site, the solid is called **interstitial solid solution**



Example: If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallized,

some of the sites of  $\text{Na}^+$  is occupied by  $\text{Sr}^{+2}$  ions.

Each  $\text{Sr}^{+2}$  replaces two  $\text{Na}^+$  ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies are produced equal in number to that of  $\text{Sr}^{+2}$

## PROPERTIES OF SOLIDS ( CRYSTALS)

The properties of solids depend on their composition, lattice structure and the nature of bond. Some properties of solids are as follows

- 1) Electrical properties
- 2) Magnetic properties
- 3) Dielectric properties

### 1) Electrical properties

Solids may be classified into three categories depending upon their values of electrical conductivity.

Conductors : electrical conductivity =  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ cm}^{-1}$

Insulators : electrical conductivity =  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$

Semiconductors: electrical conductivity =  $10^{-6}$  to  $10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$

Causes of conductance in solid

- (i) In most of the solids, conduction is through electron movement under an electric field
- (ii) In ionic solids conduction is by movement of ions
- (iii) The magnitude of electrical conductivity strongly depend upon the number of electrons available to take part in conduction process.
- (iv) In metals, conductivity strongly depends upon the number of electrons available per Atom
- (v) The atomic orbitals form molecular orbitals which forms band conduction band and valance band
- (vi) In a case of metals conduction band and valance bands are to close or overlap and electrons flow evry easily under electric file shoing conductivity
- (vii) gap between conduction band and valance band is kown as forbidden gap
- (viii) In case of insulators, the gap between valance band and conduction band is too large , so electrons cannot jump from valance band to conduction band and very small conductivity is observed.
- (ix) In case of semiconductors, the gap between valance band and conduction band is small and therefore some of the electons may jump from valance band and some condutivity is observed
- (x) electrical conductivity of semiconductors increases, with increase in temperature. This is due to the fact that with increase in temperature, large number of valence electrons from valance band can jump to conduction band. Pure substances like silicon and germanimum that exhibit this type conducting behavior are called ***intrinsic semiconductor***.

## Conduction in semiconductors

Conductivity of semiconductors can be increaed by by the introduction of impurity in semiconductors is called ***doping***

n-type semiconductors:

When a silicon crystal is doped with a group 15 elemnts such as P, As, Sb, Bi, structure of crystal lattice is left unchanged but an dopent atom with five valance electrons occupy the site normmaly occupied by silicon atom

The foreign atom ( dopent) uses four of its electrons for covalent bonding but fifth electron becomes delocalised and if thus free to contribute to electriccal conduction.

Silicon doped with group 15 element is called n-type semiconductor. 'n' stands for negative since electrons are responsible for conduction.

p-type semiconductors

When a silicon crystal is doped with a group 13 elemnts such as B, Al, Ga, In, structure of crystal lattice is left unchanged but an dopent atom with three valance electrons occupy the site normmaly occupied by silicon atom

The foreign atom ( dopent) uses three of its electrons for covalent bonding but fourth electron is missing is caled an electron vacancy or hole. Such holes can move through the crystal like positive charge giving rise to electrical conductivity. Direction of motion of

holes is opposite to that of electron. Silicon doped with group 13 element is called p-type semiconductor. 'p' stands for positive since electrons are responsible for conduction.

13-15 compounds: When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 13-15 compound.

Example InSb, AlP, GaAs

12-16 Compound. When the solid state compounds are obtained by combination of elements of group 12 and 16, the compounds are called 12-16 compounds.

Example ZnS, CdS, CdSe and HgTe

Transition metal oxides. Some transition metal oxide like TiO, CrO, ReO<sub>3</sub> behaves like metals. ReO<sub>3</sub> behaves like copper in appearance as well as conductance. VO, VO<sub>2</sub>, VO<sub>3</sub> and TiO<sub>3</sub> also show electrical conductance depending on temperature.

## 2) Magnetic properties

Magnetic property of an atom is due to i) electrons orbital motion around nucleus ii) its spin around its own axis

(i) Electron is being charge particles and undergoes above mentioned motion can be considered as a small loop of current which possesses a magnetic moment.

(ii) Each electron has a permanent spin and orbital magnetic moment associated with it

(iii) Magnitude of magnetic moment is small is measured in the unit called Bohr magneton

$\mu_B$ . Its value is  $9.27 \times 10^{-24} \text{ Am}^2$

On the basis of their magnetic properties substances are divided in five categories

(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic (v) ferromagnetic

### (i) Paramagnetic material:

Paramagnetism is due to presence of unpaired electrons. Paramagnetic materials are attracted by magnetic field. They are magnetized in a magnetic field in same direction. They lose their magnetism in absence of magnetic field.

Examples: O<sub>2</sub>, Cu<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+3</sup>

### (ii) Diamagnetic material:

Diamagnetism is shown by those substances in which all the electrons are paired and there is no unpaired electrons. Pairing cancels their magnetic moments and they lose their magnetic character.

Diamagnetic materials are repelled by magnetic field.

They are weakly magnetized in a magnetic field in opposite direction.

Examples: H<sub>2</sub>O, NaCl and C<sub>6</sub>H<sub>6</sub>

### (iii) Ferromagnetic material:

a) Ferromagnetic substances show permanent magnetism even when magnetic field is removed.

b) The metal ions of ferromagnetic substances are grouped together into small regions called as **domain**. Each domain acts like a tiny magnet.

c) In an unmagnetised piece of a ferromagnetic substance the domains are randomly arranged and their magnetic moment gets cancelled.

d) When a substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic field is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

e) On heating a ferromagnetic substance becomes paramagnetic.

Examples  $\text{CrO}_2$ , Co, Ni, Fe

(iv) Antiferromagnetic substance.

When magnetic moments of domains are aligned in such a way that the net magnetic moment is zero, then magnetism is called antiferromagnetism.

Example MnO

(v) Ferrimagnetism:

When magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in a net moment, then the magnetism is called ferrimagnetism.

Examples  $\text{Fe}_3\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$  etc