

## Chapter-01

## The Solid State

## LECTURE-1

**Properties of Solid :**

01. They have definite mass, volume, and shape.
02. Intermolecular distances are short.
03. Intermolecular forces are strong.
04. Their constituent particles (atoms, molecules, or ions) have fixed positions and can only oscillate about their mean positions.
05. They are incompressible and rigid.

**Classifications :**➤ **Crystalline solids :**

These are the substances in which the constituent particles are having a regular orderly arrangement.

Example: Diamond, Graphite, Sic, etc.

Some substances adopt different arrangements of particles, in solid-state giving rise to different crystal structures. These are called polymorph or polymorphic forms.

➤ **Amorphous Solids**

These are the substances where the constituent particles do not possess a regular arrangement.

Example: Glass, plastic, rubber.

In amorphous solids, the crystalline part is called crystallites.

**Crystalline****Amosphous**

- |  |   |
|--|---|
| 1. Possess long-range order                  | 1. Posses short-range order.                      |
| 2. Possess a sharp melting point.            | 2. Don't possess a sharp melting point.           |
| 3. <b>They have</b> definite heat of fusion. | 3. They do not have a definite heat of fusion.    |
| 4. They have definite cleavage points.       | 4. They do not have any definite cleavage points. |

5. They are anisotropic (physical Properties like melting point, refractive index is different in different directions)
5. They are isotropic.

### Classification based on Binding Forces.

#### 1. Molecular Solids :

- ❖ In this case, the constituent particles are molecules.
- ❖ The molecules may be polar like,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{HCl}$  etc. Non-polar like  $\text{I}_2$ ,  $\text{CCl}_4$ ,  $\text{CO}_2$  etc.
- ❖ In the case of polar molecules, the intermolecular force of attraction is either dipole-dipole forces or hydrogen bonds.
- ❖ Nowadays hydrogen-bonded solids are classified under different categories. Ex:  $\text{H}_2\text{O}$ ,  $\text{HF}$ .
- ❖ In the case of non-polar molecules, the intermolecular force of attraction is weak vanderwaal forces.

#### Properties:

- i. They generally range from soft to very hard.
- ii. Their melting point is low to moderate.
- iii. They are bad conductors of heat and electricity.
- iv. They have a lower density.

#### 2. Ionic Solids :

In this case, the constituent particles are ions and the binding forces are an electrostatic force of attraction or ionic bond eg:  $\text{NaCl}$ ,  $\text{MgO}$ , etc.

#### Properties :

- i. They are hard, brittle, and less volatile.
- ii. They have high melting and boiling point.
- iii. They are bad conductors of heat and electricity in the solid-state but they can conduct electricity in their molten state and their aqueous solution.
- iv. They are soluble in polar solvents like water.

#### 3. Covalent Solids : (Network Solids)

- ❖ In this case, the constituent particles are the atoms of the same or different substances connected by a covalent bond. Eg: Diamond, Graphite, carborundum(SiC), etc.

**Diamond:**

- ❖ In diamond, each carbon is linked to 4 other carbon atoms in a tetrahedral manner, but the giant structure looks like an octahedron.
- ❖ In diamond, each carbon is  $sp^3$  hybridized.
- ❖ Due to the absence of free electrons diamond is a bad conductor of heat and electricity.

**Graphite: (Layer Lattice)**

- ❖ In this case, one carbon atom is linked to three other carbon atoms in a hexagonal manner and thereby forming hexagonal layers. The force of attraction between different layers is very weak, therefore each layer can slip over other - & graphite is soft and slippery.
- ❖ The carbon atom in graphite is  $sp^2$  hybridized.
- ❖ Due to the presence of free electrons, it is a good conductor of heat and electricity.

**Properties:**

- They are hard and brittle except graphite.
- They possess a high melting point.
- They are bad conductors of electricity except for graphite.

**4. Metallic Solids :**

In this case, the constituent particles are metallic atoms and the force of attraction is metallic bonding.

**Properties:**

- They range from soft to very hard.
- They are malleable, ductile, sonorous.
- They have high melting and boiling point.
- They are good conductors of heat and electricity.

**LECTURE-2****Crystal Lattice/ Space Lattice:**

It may be defined as a regular 3D arrangement of identical points in space which represents a crystal.

**Characteristics:**

- ❖ Each point in a crystal lattice is called a lattice point, which represents the constituent particles like atoms, ions & molecules.
- ❖ Lattice points are joined by straight lines to bring out the geometry of the lattice.

**Unit Cell:**

A unit cell may be defined as a group of lattice points that generate the whole lattice by stacking or the smallest repeating pattern of a crystal lattice is called a unit cell.

**2D Lattices:**

A 2D lattice is a regular arrangement of identical points in a plane. There are five main types of **2D lattices**. These are square, rectangular, parallelogram, hexagonal & rhombic.

Unit cells having only points at corners are called a simple or primitive unit cell.

The unit cells in which lattice points are present other than the corners as well as the corners are called a centered unit cell.

**Body Centred Unit Cell:**

In this type, particles are present at the corners of the unit cell and one particle is at the body center.

**Face centered unit cell:**

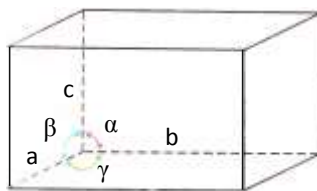
In this type, particles are present at the centers of each face along with the corners.

**End Centred Unit cell:**

In this type, particles are present at the face centers of any one set of faces along with the corners.

**3D Lattices:**

3D lattices are characterized by these edge length and edge angles.



There are 7 main types of unit cells. These are

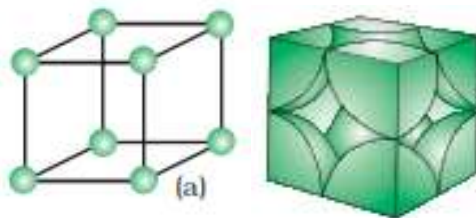
- (i) Cubic
- (ii) Tetragonal
- (iii) Orthorhombic
- (iv) Hexagonal
- (v) Rhombohedra/Trigonal
- (vi) Monoclinic
- (vii) Triclinic

| Crystal system           | Possible variations                                | Axial distances or edge lengths | Axial angles  | Examples  |
|--------------------------|--|---------------------------------|---|---|
| Cubic                    | Primitive, Body-centred, Face-centred              | $a = b = c$                     | $\alpha = \beta = \gamma = 90^\circ$                  | NaCl, Zinc blende, Cu   |
| Tetragonal               | Primitive, Body-centred                            | $a = b \neq c$                  | $\alpha = \beta = \gamma = 90^\circ$                  | White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$  |
| Orthorhombic             | Primitive, Body-centred, Face-centred, End-centred | $a \neq b \neq c$               | $\alpha = \beta = \gamma = 90^\circ$                  | Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$   |
| Hexagonal                | Primitive  | $a = b \neq c$                  | $\alpha = \beta = 90^\circ$<br>$\gamma = 120^\circ$   | Graphite, ZnO, CdS,   |
| Rhombohedral or Trigonal | Primitive  | $a = b = c$                     | $\alpha = \beta = \gamma \neq 90^\circ$               | Calcite ( $\text{CaCO}_3$ ), HgS (cinnabar)   |
| Monoclinic               | Primitive, End-centred                             | $a \neq b \neq c$               | $\alpha = \gamma = 90^\circ$<br>$\beta \neq 90^\circ$ | Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                                 |
| Triclinic                | Primitive  | $a \neq b \neq c$               | $\alpha \neq \beta \neq \gamma \neq 90^\circ$         | $\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$ |

These are 14 3D lattices these are called Bravais lattices.

**No of Atoms In-Unit Cell:**

**1. Simple cubic Type :**

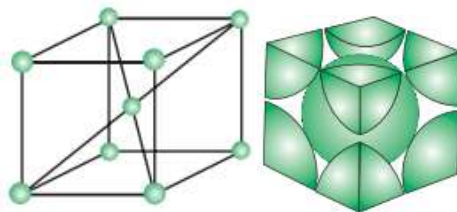


In this case, atoms are present only at the corners of the cube.

Therefore, no of atoms in one unit cell

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

### 2. Body-centered cubic type (bcc)



$$\text{No. of atoms at corners} = 8 \times \frac{1}{8} = 1$$

$$\text{No. of atoms at body center} = 1$$

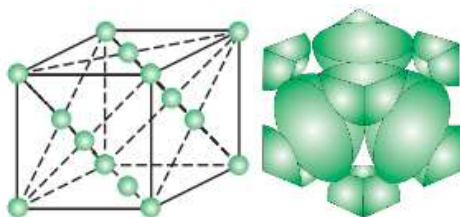
$$\text{Total no. of atoms} = 1 + 1 = 2$$

### 3. Face centered cubic type (fcc)

$$\text{No. of atoms at corners} = 8 \times \frac{1}{8} = 1$$

$$\text{No. of atoms at face centers} = 6 \times \frac{1}{2} = 3$$

Therefore total no. of atoms in a face-centered cubic unit cell is 4.



### 4. End centered cubic Unit Cell

$$\text{No. of atoms at corners} = 8 \times \frac{1}{8} = 1$$

$$\text{No. of atoms at end centered} = 2 \times \frac{1}{2} = 1$$

Total no. of atoms in an end centered.

Cubic unit cell = 2

**Co-ordination Numbers:**

The no. of nearest neighboring particles around one particle is called coordination no. of that particle.

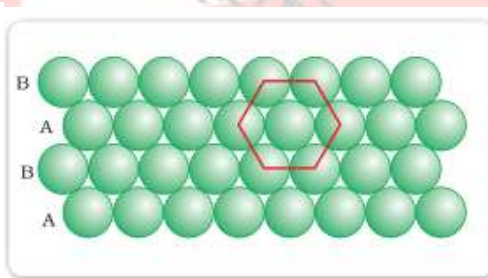
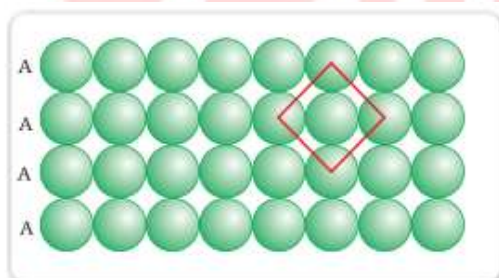
**Packing In One Dimensional System:**



Here, the coordination No. is 2.

**Packing In Two Dimensional Systems:**

1. In a square closed packed structure, the arrangement is AAAA.... and the coordination No. is 4.
2. In the hexagonal closed packed structure, the arrangement is ABAB....& the CN = 6.



## LECTURE-3

**Packing In Three Dimensional Systems:**

- (i) In simple cubic lattice, the arrangement is AAA...
- (ii) In hcp type, the arrangement is ABABAB..... that means the third layer duplicates the first layer and the fourth layer duplicate the 2<sup>nd</sup> layer, and so on.
- (iii) In ccp type, the arrangement is ABC ABC....that means the fourth layer duplicates 1<sup>st</sup> layer fifth layer duplicate 2<sup>nd</sup> layer and the sixth layer duplicates the 3<sup>rd</sup> layer, and so on.

Ex: Mg, Zn, etc.

Ex : Cu, Ag, Au

In ccp, hcp&fcc, the C.N = 12

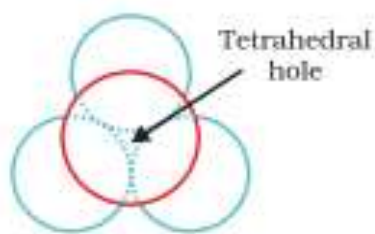
But in bcc the CN = 8

**Interstitial voids or Interstitialsites :**

In a closed pack structure the free spaces or holes present are called interstitial voids or sites.

**(i) Tetrahedral Voids :**

It is formed b/w four spheres. The centers of these four spheres are at the corners of a regular tetrahedron. The vacant space between these four spheres is called tetrahedral voids. In a closed pack structures, the no. of tetrahedral voids are double the no. of atoms present.

**(ii) Octahedral Voids :**

It is formed between six spheres - If the centers of these six spheres are connected an octahedron is formed, therefore the void is called an octahedral void.





### Tetrahedral Void

1. Coordination No = 4

$$2. \frac{S_{\text{void}}}{S_{\text{sphere}}} = 0.225$$

### Octahedral Void

Coordination No = 6

$$\frac{S_{\text{void}}}{S_{\text{sphere}}} = 0.414$$

- 01.** Atoms of element B form hcp lattice. And these of element A occupy  $\frac{2}{3}$  of the tetrahedral void. What is the formula of the compound?

**Solution:** Let the no. of atoms of B = x

No. of tetrahedral void = 2x

$$\begin{aligned} \text{No. of atoms of A} &= \frac{2}{3} \times 2x \\ &= \frac{4x}{3} \end{aligned}$$

$$\begin{aligned} \text{Formula} &= A_{\frac{4x}{3}}B_x \\ &= A_4B_3 \end{aligned}$$

- 02.** Atoms of element B forms ccp lattice if one half of the octahedral is filled by element A. Then find the formula of the compound.

**Solution:** Let the no. of atoms of B = x.

No. of Octahedral void = x

$$\text{No. of atoms of A} = \frac{x}{2}$$

$$\begin{aligned} \text{Formula} &= A_{x/2}B_x \\ &= AB_2 \end{aligned}$$

- 03.** A compound is formed b/w two elements A & B, the B atoms in ccp, and A atoms are equally distributed b/w all the tetrahedral voids and octahedral voids. If all the octahedral voids are filled with A. Then find the formula of the compound?

**Solution:** Let the no. of atoms of B = x

$$\begin{aligned} \text{No. of T.V.} &= 2x \\ \text{No. of O.V.} &= x \\ \text{No. of atoms of A} &= 2x. \\ \text{Formula} &= A_{2x}B_x \\ &= A_2B \end{aligned}$$

04. In a compound y atoms are present at the corners of a simple cubic arrangement x atoms are present at the face centers. If two lattice points are missing from the corners. Find the formula of the compound.

**Solution:**

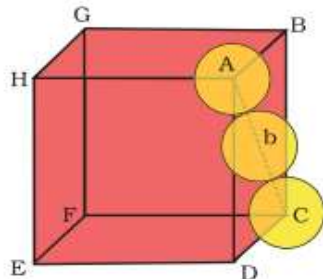
$$\begin{aligned} \text{The formula of the compound} &= X_B Y_{3/4} \\ &= X_4 Y \end{aligned}$$

### LECTURE-4

**Packing Efficiency:**

The percentage of total space filled by the particles is called packing efficiency.

**In fcc type:**



Let the edge length of the cube = a

And the radius of the sphere = r.

No. of atoms present in one unit cell of fcc = 4.

$$\text{The volume of 4 sphere} = 4 \times \frac{4}{3} \pi r^3$$

$$= \frac{16}{3} \pi r^3$$

In right angle  $\triangle ABC$ ,  $AC = \sqrt{AB^2 + BC^2}$

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

$$= \sqrt{2a^2}$$

$$= \sqrt{2}a$$

Again  $AC = 4r$

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

$$\text{Or } a = \frac{4r}{\sqrt{2}}$$

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

$$\text{Packing efficiency} = \frac{\text{Volume of the sphere}}{\text{Volume of the unit cell}} \times 100$$

$$= \frac{16}{3} \frac{\pi r^3}{a^3} \times 100$$

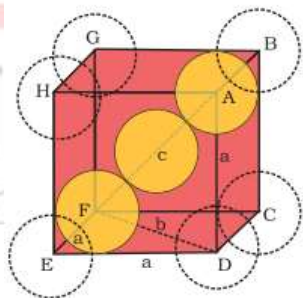
$$= \frac{16\pi r^3}{3 \times (2\sqrt{2}r)^3} \times 100$$

$$= \frac{16\pi r^3}{3 \times 16\sqrt{2}r^3} \times 100$$

$$= \frac{\pi}{3\sqrt{2}} \times 100$$

$$= 74\%$$

**In bcc type:**



No. of atoms in bcc = 2.

If the edge length is 'a' and radius of the sphere is 'r' then

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

$$= \frac{8}{3} \pi r^3$$

In  $\Delta EFD$ ,

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

$$b = \sqrt{2}a$$

Now in  $\Delta AFD$

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

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

Again  $c = 4r$

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

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

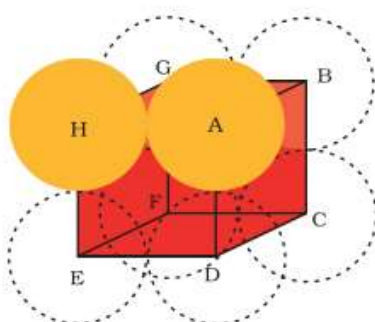
Packing efficiency =  $\frac{\text{Volume of the sphere}}{\text{Volume of tube}} \times 100$

$$= \frac{\frac{8}{3}\pi r^3}{a^3} \times 100$$

$$= \frac{8\pi r^3}{3\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100$$

$$= 68\%$$

**In a simple cubic Arrangement:**



Let the edge length is 'a' and radius of the sphere is 'r'.

The volume of sphere =  $\frac{4}{3}\pi r^3$

Here,  $a = 2r$

Packing Efficiency =  $\frac{\text{Volume of sphere}}{\text{Volume of cube}} \times 100$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} \times 100$$

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

$$= 52.4\%$$

## LECTURE-5

**Calculation of density of unitcell:**

$$\text{The density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\begin{aligned} \text{Mass of unit cell} &= \text{Mass of one atom} \times \text{total no. of atoms in one unit cell.} \\ &= m \times z \end{aligned}$$

$$\therefore d = \frac{m \times z}{a^3}$$

$$\text{or } d = \frac{z \times M}{a^3 \times N_A}$$

- 05.** Lithium metal crystal has a bcc structure, its density is  $0.53 \text{ g/cm}^3$  and its molar mass is  $6.94 \text{ g/mol}$ . Calculate the volume of the unit cell.

**Solution :** Density =  $0.53 \text{ g/cm}^3$   
Molar mass =  $6.94 \text{ g/mol}$ .

$$\text{The density of unit cell} = \frac{M \times z}{a^3 d \times N_A}$$

$$a^3 = \frac{z \times M}{d \times N_A}$$

$$a^3 = \frac{2 \times 6.94}{0.53 \times 6.022 \times 10^{23}}$$

$$a^3 = 4.348 \times 10^{-23} \text{ cm}^3$$

$\therefore$  The volume of the unit cell is  $4.348 \times 10^{-23} \text{ cm}^3$

- 06.** Silver crystallizes in fcc each side of the unit cell has a length of  $409 \text{ pm}$ . What is the radius of an atom of silver?

**Solution:** In fcc,  $a = 2\sqrt{2}r$ .

$$r = \frac{a}{2\sqrt{2}}$$

$$r = \frac{409}{2\sqrt{2}} \times 10^{-10}$$

$$= \frac{409}{2\sqrt{2}} \times 10^{-10}$$

$$= \frac{409 \times 10^{-10}}{2 \times 1.414}$$

$$= \frac{409 \times 10^{-10}}{2.828}$$

$$=144.62 \times 10^{-10} \text{ cm}$$

07. An element has the bcc structure with a cell edge of 288 pm density of the element is  $7.2 \text{ g/cm}^3$ . How many atoms are present in 208 g of the element?

$$d = 7.2 \text{ g/cm}^3$$

$$a = 288 \text{ pm}$$

$$m = 200 \text{ g}$$

$$z = 2$$

$$d = \frac{z \times M}{a^3 \times N_A}$$

$$M = \frac{d \times a^3 \times N_A}{z}$$

$$= \frac{7.2 \times (288 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{2}$$

$$= 51.79 \text{ g}$$

51.72 g has  $6.022 \times 10^{23}$  an atom.

$$1 \text{ g} = \frac{6.022 \times 10^{23}}{51.79}$$

$$208 \text{ g} = \frac{6.022 \times 10^{23}}{51.79} \times 208$$

$$= 24.22 \times 10^{23} \text{ atoms}$$

08. Aluminum forms the fcc crystal structure and its atomic radius are  $125 \times 10^{-12} \text{ m}$ .

(i) Calculate the length of the side of the unit cell.

(ii) How many unit cells are there in  $1 \text{ m}^3$  aluminium?

**Solution:** (i)  $a = 2\sqrt{2}r$

$$a = 125 \times 10^{-12} \times 2\sqrt{2}$$

$$= 250 \times 1.414 \times 10^{-12}$$

$$= 353.5 \times 10^{-12} \text{ m}$$

$$= 3.53 \times 10^{-10} \text{ m}$$

(ii) The volume of one unit cell =  $a^3$

$$= (3.53 \times 10^{-10})^3$$

$$= 43.98 \times 10^{-30} \text{ m}^3$$

$$\therefore \text{No. of unit cells in } 1 \text{ m}^3 \text{ of aluminium} = \frac{1}{(3.53 \times 10^{-10})^3}$$

**Imperfections or Defects in Solids:**

The irregularities of the arrangement of particles in a solid are called defects in solids.

**These are of 2 types:**

- (i) Line defects                      (ii) Point Defects

**Line Defects:**

These defects are found along a line or in a row.

**Point Defects :**

These defects are found around a point.

**Types of Point Defects.**

- (i) Stoichiometric Defects                      (ii) Impurity Defects                      (iii) Non-stoichiometric Defects

**(i) Stoichiometric Defects :**

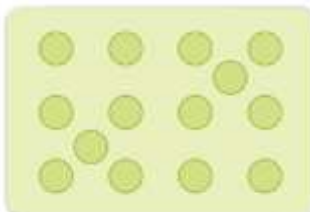
- These are the defects where the stoichiometry of the compound does not get disturbed.
- These defects are also called intrinsic defects, or thermodynamic defects.

- (a) Vacancy Defects:** In these defects, some of the lattice points are missing and creates vacant space in a crystal. In such defects density decreases.

Normally when crystals are heated vacancy defects are formed.



- (b) Interstitial defects:** In these defects, some of the particles occupy the interstitial site. In this defect density increases.

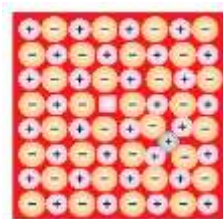


These two defects are found in non-ionic solids.

**For Ionic Solids:**

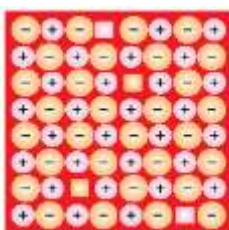
- (c) Frenkel Defects:** In ionic solids, if the cations are very much smaller than anions then some cations dislocate from their original position and occupy the interstitial sites. Therefore they create vacancy defects at their original position and interstitial defects at their new position. In these defects, density remains the same.

Ex: AgBr, AgCl, AgI, ZnS.



- (d) **Schottky Defect:** It is a type of vacancy defect in which the no. of missing cations and anions are equal due to their similar sizes. In this case density decreases.

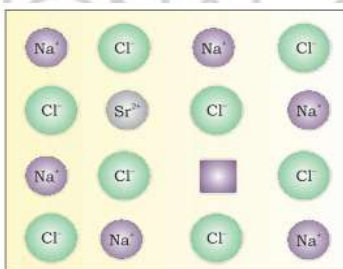
Eg. NaCl, KCl, CsCl, AgBr etc.



## 2. **Impurity Defect:**

The defect in the ionic solid may be introduced by adding impurity ions. If the impurity ions are having a different valence state than the host ions, then vacancies are created.

E.g. Addition of  $\text{SrCl}_2$  to NaCl or addition of  $\text{CaCl}_2$  to AgCl etc.



Ex: If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallized some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$  ions. 1  $\text{Sr}^{2+}$  ion replaces 2  $\text{Na}^+$  ions it occupies 1 vacant site and the other site remains vacant.



## LECTURE-6

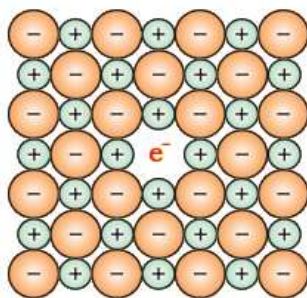
**3. Non-Stoichiometry Defect :**

The defect in which the stoichiometry of the compound gets disturbed.

**Metal Excess Defect:****(a) Metal excess Defect due to anionic vacancies:**

A negative ion may be missing from the lattice point that can be occupied by an electron. The electron thus trapped in the ionic vacancies is called the F-centre, which is responsible for the color of the crystal.

Ex: When NaCl crystal is heated in presence of Na vapor than some of the Na atom will be deposited over the surface of the crystal. Equal no.  $\text{Cl}^-$  ions will move to the surface and will interact with the Na atoms at the same time Na atoms will donate  $e^-$  and these  $e^-$  will occupy the anionic vacancies which are called F-centres.

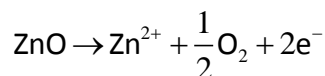


Due to the presence of F-Centre NaCl is yellow, KCl is violet in color, & LiCl is pink in color.

**(b) Metal excess defect due to the presence of extra cations at interstitial sites :**

In this case, an extra cation occupies the interstitial sites and  $e^-$  occupies the neighboring interstitial site to maintain electrical neutrality.

Ex: ZnO is white at room temperature, when heated it liberates oxygen and changes to yellow color. In this case, the cases  $\text{Zn}^{2+}$  ion & the  $e^-$  occupy the neighboring interstitial sites.

**(ii) Metal Deficiency Defect :**

There are certain solids which are very difficult to prepare in their stoichiometric composition and contain less amount of the metal.

Ex:  $\text{Fe}_{0.92-0.96}\text{O}$

These defects arise due to the presence of higher valence cations.

## LECTURE-7

### Conduction of Electricity in metals:

**Conductors:** The metal in which conductivity ranging between  $10^4$  to  $10^7 \Omega^{-1}\text{m}^{-1}$  is called a conductor.

**Insulators:** The metal in which the conductivity ranging between  $10^{-20}$  to  $10^{-10} \Omega^{-1}\text{m}^{-1}$  is called an insulator.

**Semiconductor:** The metal in which the conductivity ranging between  $10^{-6}$  to  $10^4 \Omega^{-1}\text{m}^{-1}$  is called a semiconductor.

### Band Theory:

- Metal conducts electricity due to the presence of free electrons.
- The atomic orbitals of metals having the same energy intermix with each other to form molecular orbitals and thereby forming bands.
- The bands having lower energy one called valence bands and the bands forming higher energies are called conduction bands.

### For Metals:

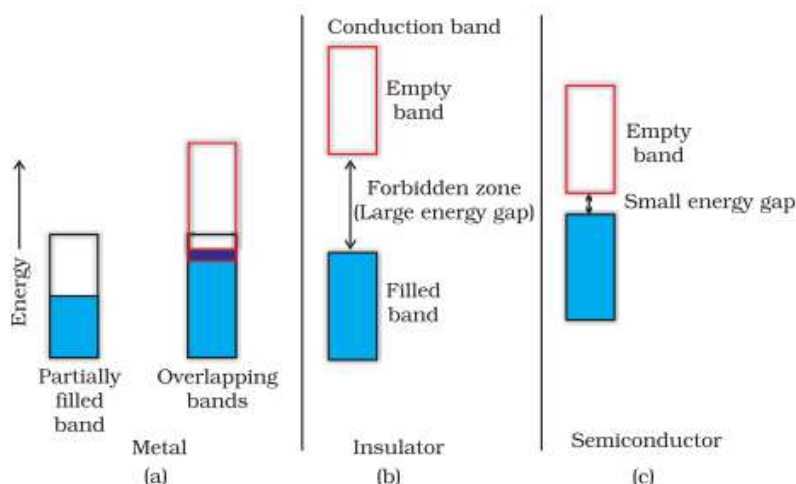
In the case of metals, the valence band is either half-filled or overlaps with the conduction band. Therefore  $e^-$  can easily be excited and which is the cause of conduction in metals.

### For semiconductors:

In this case, the gap between the valence band and the conduction band is small, due to which by using temperature  $e^-$  can easily be excited to the conduction band, which is the cause of an increase in conductivity of a semiconductor by increasing temperature.

### ➤ For Insulators :

An insulator, there is a large gap b/w valence band and conduction band, which is called the forbidden zone.



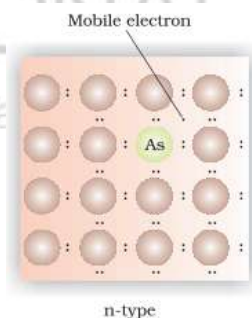
Electrons cannot be excited from the valence band to the conduction band even by increasing temperature. Therefore, insulators cannot conduct electricity.

In actual practice the conductivity of a semiconductor is too low to be measured so, the conductivity of a semiconductor can be increased by adding foreign elements to it, which is called doping.

Pure semiconductors like pure Si, Ge are called intrinsic semiconductors.

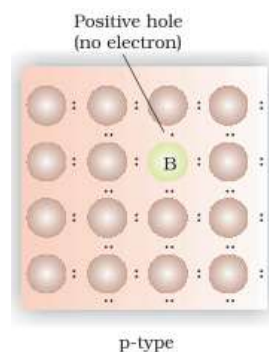
Doping can be done by adding  $e^-$  rich species or electron-deficient species.

**01. Doping with electrons rich species [ n-type semiconductor]**



Si&Ge(Grp-14 elements) share their 4 valence  $e^-$  to form 4 covalent bond. These elements when doped with (Grp-15 elements) like (P,As),etc, the extra electrons occupy the interstitial sites and are delocalized, which is the cause of improvement of conductivity of the semiconductor.

As the improvement in conductivity is due to the presence of negatively charged  $e^-$  it is called an n-type semiconductor.

**02. Doping with Electron Deficient Species (P-type semiconductor)**

Si & Ge can be doped with group-13 elements like (B and Al) having three valence electrons. Due to the deficiency of  $1e^-$  a hole is formed and  $e^-$  from the neighboring atom will fill the vacancy and creates another hole at its original position. By applying the electric field it seems to be as if the holes are +vely charged and are moving towards the +vely charged field. As the increase in conductivity is due to the +vely charged hole it is called a p-type semiconductor.

**Applications of Semiconductors :**

01. The diode is a combination of n-type and p-type semiconductors which is used as a rectifier.
02. Transistors are n-p-n or p-n-p sandwich semiconductors.
03. Solar cells are made up of semiconductors.
04. Semiconductors are also made up of by the combination of group-13 and Group – 15 elements (Al-P, Ga-As, etc) or by mixing group – 12 & group – 16 elements (Zn-s, Cd-s, etc) to make the average valency 4.

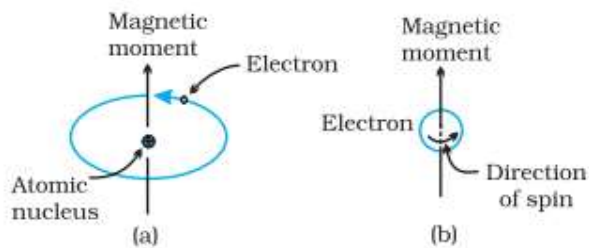
**Conduction of Transition Metal Oxide.**

01.  $TiO$ ,  $CrO_2$ ,  $ReO_3$  Behaves like a metallic conductor.
02.  $MnO$ ,  $CuO$ ,  $NeO$ ,  $CoO$ ,  $FeO$  , behaves like an insulator.
03.  $VO$ ,  $VO_2$ ,  $VO_3$  &  $TiO_3$  behaves are metallic or insulators depending upon the temperature.
04.  $ReO_3$  has the conductivity as well as the appearance like that of copper.

## LECTURE-8

Magnetic Properties of Solids

- The magnetic properties of a solid are associated with its electrons.
- The magnetic moment is due to the orbital motions of an electron as well as due to the spinning motion of the electron.
- In both cases, magnetic fields are formed.



- Thus each  $e^-$  may be considered as a small magnet having a permanent magnetic moment and is represented by an arrow. The magnetic moment can be expressed by the unit Bohr magneton ( $\mu_B$ ).
- Based on their magnetic properties substances are classified into 5 categories.
  - (i) Paramagnetic
  - (ii) Diamagnetic
  - (iii) Ferromagnetic
  - (iv) Ant ferromagnetic
  - (v) Ferromagnetic

1. **Paramagnetism:** The substances which are weakly attracted by the magnetic field are called paramagnetic substances and the phenomenon is called paramagnetism. This property is shown by those substances containing unpaired electrons.

Ex:  $O_2$ ,  $Cu^{2+}$ ,  $Fe^{3+}$  and  $Cr^{3+}$

These substances lose their magnetic properties in the absence of an external magnetic field.

2. **Diamagnetism:** The substances which are weakly repelled by the magnetic field are called diamagnetic substances and the phenomenon is called diamagnetism.

Ex:  $H_2O$ ,  $NaCl$ ,  $C_6H_6$  etc.

Diamagnetism is shown by those substances in which all the electrons are paired. The pairing of electrons cancels their magnetic moments.

- 3. Ferromagnetism:** A few substances like iron, cobalt, nickel, gadolinium, and  $\text{CrO}_2$  are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetized. In solid-state, the metal ions of ferromagnetic substances are grouped into small regions called domains. Thus. Each domain acts as a tiny magnet. In an unmagnified piece of a ferromagnetic substance, the domains are randomly oriented and their magnetic moments get canceled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.
- 4. Antiferromagnetism:** Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment.
- 5. Ferrimagnetism:** Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by the magnetic field as compared to ferromagnetic substances.  $\text{Fe}_3\text{O}_4$  (Magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



**Schematic alignment of magnetic moments in (a), ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.**