# CHAPTER / 01

# Solid State

# Topics Covered

General Characteristics and Classification of Solids

- Characteristic Properties of Solids
- Classification of Solids
- Classification of Crystalline Solids on the Basis of Bonding
- Crystal Lattice and Unit Cell
  - Close Packing in Crystalline Solids
  - Interstitial Voids
  - Types of Cubic Crystals
  - Packing Efficiency
  - Coordination Number (CN)

Imperfections in Crystalline Solids, Electrical and Magnetic Properties of Solid

- Point Defects
- Magnetic Properties of Solids

# **TOPIC ~01** General Characteristics and Classification of Solids

Solids differ from liquids and gases in the fact that gases and liquids possess fluidity, i.e. they can flow and hence called fluids, whereas solids do not possess fluidity, instead they possess rigidity. The fluidity in gases and liquids is due to the fact that their constituent particles are free to move around, while solids are rigid because molecules, atoms or ions that constitute a solid are closely packed and held by strong attractive (cohensive) forces. So the solids have well ordered molecular arrangement.

# **Characteristic Properties of Solids**

The solids possess following characteristic properties:

- (i) **Shape** Solid substances have definite shape which does not depend upon the shape of container in which it is kept.
- (ii) **Volume** The volume of a solid substance is always fixed regardless of the container in which it is kept.
- (iii) Rigidity Due to fixed position of constituent particles, solids are highly rigid.
- (iv) **Compressibility Solids** are usually incompressible as there is very small interparticle distance between two constituent particles of solids.
- (v) **Diffusion** Due to high interparticle force of attraction, the constituent particles are held very tightly. Thus, diffusion of two solid substance is very rare.
- (vi) **Melting Point** Transformation of solid into liquid is called melting. The constant temperature at which a solid is transformed into liquid is called melting point of the solid. All solids have characteristic melting point.

# **Classification of Solids**

Solids are classified into two categories :

#### **Crystalline Solids**

In these solids, the building constituents, i.e. atoms, ions, etc. are arranged in a three-dimensional regular geometric pattern. They have sharp melting point. They are **anisotropic in nature**, i.e. they possess different magnitudes of physical properties in different directions. They possess long range order, e.g. in NaCl crystal, the structural units are  $Na^+$  and  $Cl^-$ .

#### **Amorphous Solids**

In these solids, the building constituents are not arranged in a regular pattern. They do not have a sharp melting point. They are **isotropic** in nature, i.e. the magnitude of their physical properties is equal in all directions. Thus, these solids possess short range order, e.g. glass, wax, rubber, starch, plastic, etc.

Amorphous solids are generally regarded as supercooled liquids as the arrangement of structural units in them is almost similar to that in the liquids, e.g. glass can flow up to some extent as the liquids flow.

Property	Crystalline solids	Amorphous solids
Structure	These have definite geometry due to ordered arrangement of particles in three-dimensional space. They possess long range order.	These do not have any order or pattern of constituent particles. They possess short range order.
Melting point	They have sharp melting point.	They do not have sharp melting point.
Anisotropic or isotropic	The magnitude of physical properties like refractive index, thermal conductivity, etc. are different in different directions within the crystal. Hence, anisotropic in nature.	Magnitude of all physical properties is equal in all directions. Hence, isotropic in nature.
Nature	They are true solids.	They are supercooled liquids or pseudo solids.
Cleavage	When crystalline solid is cut with a sharp edged knife, it gives two pieces with plane surface.	When amorphous solid is cut with a sharp edged knife, it gives two pieces with irregular surface.
Symmetry	These have symmetry in crystal.	These do not have symmetry in crystal.

Difference between crystalline and amorphous solids

# Classification of Crystalline Solids on the Basis of Bonding

#### **Ionic Solids**

These are made up of cations and anions. Each ion is surrounded by a definite number of ions of opposite charge, e.g. in NaCl crystal, each  $Na^+$  is surrounded by six  $Cl^-$  and *vice-versa*. Coordination number of NaCl is 6.

Sodium chloride has a face centred cubic (fcc) structure. These ions are held by **electrostatic forces of attraction**. The other examples are KCl, LiF,  $BaSO_4$ , etc.



### **Metallic Solids**

In metallic crystals, particles forming the crystals are positive ions (known as *kernels*) surrounded by a sea of electrons. These ions are held together by **metallic bond**. The common closest packing is face centred cubic (fcc) type, e.g. Cu, Au, Ag, etc. In crystal, metal ions occupy the corners of the cube and the centres of its faces. The coordination number of copper is 12.

## **Covalent or Network Solids**

These crystals are formed by the neutral atoms of same elements (e.g. diamond) or different elements, (e.g. SiC) which are held together by covalent bonds. The bonds in covalent solids extend throughout the crystal and results in the formation of giant three dimensional structure. e.g. graphite, diamond.

**Diamond** In diamond, each carbon is  $sp^3$ -hybridised.



Network structure of diamond

It is bonded tetrahedrally to four carbon atoms by simple covalent bonds. It has a huge 3D lattice. So, no

free electrons are present, thus making it a bad conductor of electricity.

**Graphite** It has a layer structure. In each layer,  $sp^2$ -hybridised carbon atoms are situated at the corners of a regular hexagonal ring. These rings are arranged parallelly. Each of the carbon atom is bonded to adjacent three carbon atoms of the same layer. Out of four valence electrons in each carbon atom, three are involved in three C—C  $\sigma$ -bonds



Structure of graphite

formation, while fourth valency of carbon is unsatisfied. Each layer is held together by weak van der Waals' forces.

Due to these weak forces, layers slide on one another, making graphite slippery. Due to free delocalised electrons, it is a good conductor of electricity.

# Molecular Solids (Crystals)

These are the solids in which molecules or atoms are polar or non-polar except in solidified noble gases. In these solidified noble gases, atoms are held either by dipole-dipole forces or van der Waals' forces. Examples of molecular solids are dry ice, iodine, ice, etc.

Property	Ionic solids	Metallic solids	Covalent solids	Molecular solids				
Constituent particles forming crystal	Positive and negative ions	Metallic positive ion surrounded by electrons	Neutral atoms	Polar or non-polar molecules				
Forces holding constituents	Electrostatic forces	Electrostatic forces	Covalent bonds	Weak van der Waals' forces				
Hardness	Hard and brittle	Malleable and ductile	Hard	Soft				
Solubility	Soluble in polar solvents	Dissolve in solvents by chemical action	Insoluble in most solvents	Polar molecule in polar solvent and non-polar molecule in non-polar solvent				
Melting and boiling points	High	High	Very high	Low				
Conductivity	Bad conductors in solid state but good conductor in ionic state	Good conductors	Bad conductors	Bad conductors				

#### Comparison of properties of different types of crystalline solids

# **PRACTICE** QUESTIONS

# Exams', Textbook's Other Imp. Questions

# **1 MARK** Questions

#### Important Questions

- Choose the correct option (Q.Nos 1 to 3)
  - Q.1 Which among the following will show anisotropy? [Textbook] (a) Glass (b) Barium chloride
    - (c) Wood (d) Paper
  - **Sol** (b) Barium chloride is a crystalline solid and will show anisotropy.
  - **Q.2** Which of the following statements about amorphous solids is incorrect?
    - (a) They melt over a range of temperature
    - (b) They are isotropic
    - (c) There is orderly arrangement of particles
    - (d) They are rigid and incompressible
- **Sol.** (c) There is no orderly arrangement of particles in amorphous solids. Therefore, option (c) is incorrect.
- **Q.3** Which one of the following exists as crystals in the solid state?

(a) Iodine	(b) Silicon
(c) Sulphur	(d) Phosphorus
Sol. (b) Silicon	

- Fill in the blanks (Q.Nos 4-6)
  - Q.4 Diamond and graphite are .......... (allotropes, isomorphous). [Textbook]
  - Sol allotropes
  - Q.5 Diamond is ..... solid. (covalent, ionic, molecular) [Textbook]
  - Sol covalent
  - **Q.6** The type of solids which have sharp melting points is .......
- Sol. crystalline solids
- Q.7 Why are crystalline solids anisotropic?
- Sol Refer to text on page 2.
- **Q.8** Some of the glass objects recovered from ancient monuments look milky instead of being transparent. Why?
- **Sol** Some of the glass objects from ancient monuments looks milky instead of being transparent because, it undergoes heating during the day and cooling at night over a number of years. As a result, it becomes crystalline in nature and a bit opaque also.

- **Q.9** What type of interactions hold the molecules together in a polar molecular solid?
- **Sol** In polar molecular solids, the molecules are held together by relatively stronger dipole-dipole interactions.

Q.10 Explain isotropy. [Textbook]

Sol Refer to text on page 2.

**Q.11** Define anisotropy.

[Textbook]

Sol Refer to text on page 2.

# **2 MARK** Questions

Q.12 Why are solids incompressible?

- **Sol.** Compressibility is the ability of the substance to change its shape by applying external pressure. Solids form closed packed structure with negligible intermolecular space and possesses very strong intermolecular forces of attraction. Thus, they do not change their shape in the presence of external pressure. (2)
- **Q.13** Inspite of long range order in the arrangement of particles, why are the crystals usually not perfect?
- Sol. Crystals have long range repeated pattern of arrangement of constituent particles but in the process of crystallisation, some deviations from the ideal arrangement, (i.e. defects) may be introduced because the constituent particles may not get sufficient time to arrange themselves in a perfect order. Therefore, crystals are usually not perfect. (2)
- **Q.14** Metallic solids are conductors of heat and electricity. Why?
- Sol. Metallic solids are collections of positive ions embedded in a sea of electrons around it. These free electrons are responsible for electric conduction in metallic solids. (2)
- Q.15 Classify the following as amorphous or crystalline solids.

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

SolCrystalline solidsNaphthalene, benzoic acid,<br/>potassium nitrate, copper.(1)Amorphous solidsPolyurethane, teflon,<br/>polyvinyl chloride, fibre glass, cellophane.(1)

# **3 MARK** Questions

#### Exams' Questions

Q.16	Explain, what are ionic and covalent solids. Give one
	example of each? [2019]
Sol	Refer to text on page 2. (3)
Q.17	Write four important characteristic of solids.
<b>. .</b>	[Textbook]
Sol	Refer to text on page 1. (3)
Q.18	Give two points to distinguish between crystalline and amorphous solids. [Textbook]
Sol	Refer to text on page 2. (3)
Q.19	What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?
Sol.	Glass is an example of amorphous solid in which the constituent particles $(SiO_4, tetrahedral)$ have only a short range order and there is no long range order, whereas in quartz, the constituent particles $(SiO_4, tetrahedral)$ have short as well as long range order. (2)
	On melting quartz and then cooling it rapidly, it is converted into glass. (1)
Q.20	Classify the following solids in different categories based on the nature of intermolecular forces operating in them: Potassium sulphate tin benzene urea ammonia
Sal	water, zinc sulphide, graphite, rubidium, argon, silicon carbide.
501.	Molecular solids Benzene, ammonia, argon, urea, water. Ionic solids Potassium sulphate, zinc sulphide.
Q.21	Explain metallic crystal and their properties.
Sol	Refer to text on pages 2 and 3. (3)
Q.22	Explain, why diamond is hard, while graphite is soft?
Sol	Refer to text on pages 2 and 3. (3)
<u>7  </u>	MARK Questions

Q.23 Discuss the characteristic of solids. Give the	ie
classification of solids into ionic, covalent,	molecular
and metallic solids.	[Textbook]
<i>Sol</i> Refer to text on pages 1 and 2.	(7)

**Q.24** (i) Explain,

- (a) the basis of similarities and differences between metallic and ionic crystals.
- (b) ionic solids are hard and brittle.
- (ii) Stability of a crystal is reflected in the magnitude of its melting point, comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from data book. What can you say about the intermolecular forces between these molecules?

*Sol.* (i) (a) Similarities between ionic and metallic crystals

- Both ionic and metallic crystals have electrostatic forces of attraction. In ionic crystals, these are between the oppositely charged ions. In metals, these are between kernels and valence electrons. That is why, both have high melting points.
- In both cases, the bond is non-directional. Refer to text on page 2.
- (b) Strong electrostatic forces of attraction among oppositely charged ions make ionic crystals hard and brittle.
   (2)

# **TOPIC TEST 1**

- 1. Which one of the following forms a molecular solid when solidified?
  - (a) Silicon carbide (b) Calcium fluorite
  - (c) Rock salt (d) Methane
- 2. Which one of the following forms a covalent crystal?

(a) Rock salt	(b) Ice
(c) Quartz	(d) Dry ice
	[Ans. 1. (d), 2. (c)]

[Ans. Amorphous]

4. ..... solids are called pseudo solids or supercooled liquids.

(Fill in the blank).

5. Ionic solids conduct electricity in molten state but not in solid state. Explain.

(ii)

Compounds	Melting point (°C)
Solid water, i.e. ice (H <sub>2</sub> O)	0
Ethyl alcohol (C <sub>2</sub> H <sub>5</sub> OH)	-114
Diethyl ether $[(C_2H_5)_2O]$	-116.3
Methane (CH <sub>4</sub> )	-182

Higher the melting point, greater are the forces holding the constituent particles together and hence greater is its stability. (1)

(2)

The intermolecular forces in water and ethyl alcohol are mainly the hydrogen bonding but the intermolecular H-bonding in water is stronger than that in ethyl alcohol.

Therefore, water has a higher melting point than ethyl alcohol. Diethyl ether is a polar molecule. The intermolecular forces present in them are dipole-dipole interaction.

Methane is a non-polar molecule. Therefore, the intermolecular forces operating in them are the weak

van der Waals' forces (London dispersion forces). (2)

- Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.
  - (i) Tetraphosphorus decaoxide  $(P_4O_{10})$
  - (ii) Ammonium phosphate (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>
  - (iii) SiC

(iv)	I <sub>2</sub>	(v)	$P_4$
(vi)	Graphite	(vii)	Brass
(viii)	Rb	(ix)	LiBr
(x)	Si	(xi)	Plastics

- 7. Explain, why graphite is soft and can be used as lubricant?
- 8. Diamond is hard and a bad conductor of electricity, while graphite is soft and a good conductor of electricity. Explain.

# TOPIC~02 Crystal Lattice and Unit Cell

- The regular arrangement of the constituent particle of a crystal in the three dimensional space is known as **crystal lattice** or **space lattice**.
- Lattice points are the positions which are occupied by the atoms, ions or molecules in the crystal lattice.
- **Unit cell** It is the smallest portion (both in 2D and 3D) of a complete space lattice which when repeated over and again in different direction produces the complete space lattice.

# **Close Packing in Crystalline Solids**

The constituent particles are closely packed together in the formation of crystals. The closely packed arrangement is that in which the maximum available space is occupied.

The packing also vary according to the shape and size of the constituent particle.

# 1. Close Packing in One Dimension

In one dimension close packed structure, spheres or particles are arranged in a row and touching each other. In this arrangement, each sphere is in contact with two of its neighbouring spheres.

Thus, in one direction close packed arrangement, the coordination number is 2.

# 2. Close Packing in Two Dimensions

When the rows of close packed spheres are stacked over each other, a two dimensional close packed structure (known as **crystal plane**) is produced.

It can be done in two ways :

(i) Two Dimensional Square Close Packing (scp)

In this packing, spheres of second row are placed exactly above the spheres of first row. Similarly, spheres of third are just above second row and so on. If the first row is called as 'A' type row, the second row being exactly the same as the first one, is also known as 'A' type row.

As on joining the centres of four immediate neighbouring spheres form a square. Hence, the packing is called **square close packing** (scp) **in two dimensions**.



Square close packing of sphere in two dimensions

#### (ii) Two Dimensional Hexagonal Close Packing (hcp)

In this type of close packing, the second row may be placed above the first one in a staggered manner, such that spheres of second row fit in the depressions of the first row. Similarly, the spheres in the third row are placed in the depressions between the spheres of second row and so on. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer.

Hence, this layer is also of 'A' type.

The centres of these six spheres when joined forms a regular hexagon, hence this packing is called **two dimensional hexagonal close-packing** (hcp).



Hexagonal close packing of spheres in two dimensions

### 3. Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. Three dimensional close packing can be obtained by the following ways:

#### (i) Three Dimensional Close Packing from Two Dimensional Square Close-Packed Layers

Each layer of lattice has two dimensional square close packing arrangement. When two dimensional square close-packed layers are stacked exactly one over the other, three dimensional lattice is obtained.



Simple cubic lattice formed by A A A... arrangement

#### (ii) Three Dimensional Close Packing from Two Dimensional Hexagonal Close-Packed Layers

When second and third layers are placed over first layer in the depressions, it leads to the formation of three dimension closed-packed structure.

The placing of second and third layer can be explained in the following cases:

(a) In this case, the spheres of third layer are exactly aligned with those of the first and fourth layer with the second and so on. Thus, the pattern of spheres is repeated in alternate layers. This pattern is called *ABAB*...... pattern. This structure is called **hexagonal close packed** (hcp) **structure**. Metals like zinc, magnesium crystallises in hcp structure.



(b) In this case, the spheres of the third layer are not aligned with those of either the first or the second layer. This layer is different from layers A and B. Let us call it as layer C.

Continuing further, a packing is obtained, where spheres in every fourth layer will vertically aligned with those of the first layer. This pattern is called *ABCABC*..... pattern.

This structure is called **cubic closed packed** (ccp) or **face-centred cubic** (fcc) **structure**. Metals like copper, silver, etc. crystallise in ccp structure.



# **Interstitial Voids**

In close packing sphere, certain hollows are left vacant. These hollows in crystal are known as interstitial voids or interstitial sites. These are of two types:

(i) **Tetrahedral Voids** A void surrounded by four spheres occupying the corners of a tetrahedron is called tetrahedral void. A tetrahedral void is formed when a sphere of second layer is placed above the void of first layer.





close-packed spheres per unit cell) Coordination number of tetrahedral voids = 4 Radius of tetrahedral void (r) = 0.225R(where, *R* is the radius of sphere).

 (ii) Octahedral Voids A void surrounded by six spheres along the corners of an octahedron is called octahedral void. All the voids of first row which remain unoccupied form octahedral void. It is formed when two triangular voids of two adjacent layers combine in opposition.



Octahedral voids : (a) top view (b) exploded side view (c) geometrical shape

**The number of octahedral voids** = N (where, N is the number of lattice points or close-packed spheres per unit cell). **Coordination number of octahedral void** = **6**. **Radius of octahedral void** (r) = 0.414 R (where, R is the radius of sphere).

# **Types of Cubic Crystals**

Cubic crystals are of three types which are as follows:

### Simple or Primitive Cubic Unit Cell

Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells, four unit cells in the same layer and four unit cells of the upper (or lower) layer.

Therefore, only  $\frac{1}{8}$ th of an atom actually belongs to a

particular unit cell.



In a simple cubic unit cell, each corner atom is shared between 8 unit cells

Contribution of each atom present at the corner =  $\frac{1}{8}$ 

:. Number of atoms present in the unit cell =  $\frac{1}{8} \times 8 = 1$ 

# Body Centred Cubic (bcc) Unit Cell

A body centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre.

This lattice possesses 8 atoms on the corners and one atom within the body.

:. Contribution by  $\frac{1}{8}$  per corner atom present on the each

corner (8 corners) =  $\frac{1}{8} \times 8 = 1$ 

Contribution by 1 body centre atom = 1

:. Total number of atoms present per unit cell = 1 + 1 = 2



(a) open structure, (b) space filling structure (c) actual portions of atoms belonging to one unit cell

### Face-Centred Cubic (fcc) Unit Cell

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. Each atom located at the face-centre is shared between  $\frac{1}{2}$ 

two adjacent unit cells and only  $\frac{1}{2}$  of each atom belongs

to a unit cell.



An atom at face centre of unit cell is shared between 2 unit cells

Thus, contribution of each atom on the face =  $\frac{1}{2}$ 

As this lattice has 8 atoms on the corners and 6 atoms on the faces.

:. Contribution by atoms on the corners =  $\frac{1}{8} \times \frac{8}{1} = 1$ 

Contribution by atoms on the face-centred =  $\frac{1}{2} \times 6 = 3$ 

:. Total number of atoms present per unit cell = 1 + 3 = 4

## **Packing Efficiency**

It is the percentage of total space filled by the particles. It is given by the formula packing efficiency = volume occupied by total no. of spheres in unit cell.

#### Packing Efficiency in hcp and ccp (fcc) Structures

Both hcp and ccp are equally efficient. Hence, we will calculate packing efficiency by taking example of a ccp structure.



Cubic close packing, other sides are not provided with spheres for sake of clarity

In 
$$\triangle ABC$$
,  $a = BC =$  unit cell edge length

b = AC =face diagonal

AC<sup>2</sup> = 
$$b^2 = BC^2 + AB^2 = a^2 + a^2 = 2a^2$$
 or  $\Rightarrow \sqrt{2}a = b$   
Suppose 'r' is the radius of sphere

 $\therefore$  Total volume of four spheres =  $4 \times \frac{4}{3} \pi r^3$ 

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

Packing efficiency in fcc

 $= \frac{\text{Volume occupied by 4 spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$ 

$$=\frac{4\times(4/3)\pi r^3}{(2\sqrt{2}r)^3}\times100\%=\frac{(16/3)\pi r^3}{16\sqrt{2}r^3}\times100\%=74\%$$

#### Packing Efficiency in Body Centred Cubic Lattice

In bcc structure, atom at the centre touches the other two atoms diagonally arranged.



Body-centred cubic unit cell (spheres along the body diagonal are shown with solid boundaries)

In  $\triangle EFD$ ,  $b^2 = a^2 + a^2 = 2a^2$ ,  $b = \sqrt{2}a$ 

Now, in  $\triangle AFD$   $c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2 \Rightarrow c = \sqrt{3}a$ 

where,  $c = \text{length of the body diagonal} \Rightarrow c = 4r$ As all the three spheres along the diagonal touch each other.

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

In bcc, total number of atoms is 2 and their volume

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

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

Therefore, packing efficiency

$$= \frac{\begin{bmatrix} \text{Volume occupied by two spheres in} \\ & \text{the unit cell} \end{bmatrix}}{\text{Total volume of the unit cell}} \times 100\%$$
$$= \frac{2 \times (4/3)\pi r^3}{[(4/\sqrt{3})r]^3} \times 100\% = \frac{(8/3)\pi r^3}{64/(3\sqrt{3})r^3} \times 100\% = 68\%$$

#### Packing Efficiency in Simple Cubic Lattice

Here, atoms are located only on the corners of the cube. The atoms touch each other along the edge.



Simple cubic unit cell (the spheres are in contact with each other along the edges of the cube)

If side edge length of the cube = a

Radius of each atom = r

Volume of the cubic unit cell = 
$$a^3 = (2r)^3 = 8r^3$$

- : A simple cubic unit cell contains only 1 atom.
- $\therefore$  Volume of the occupied space =  $\frac{4}{3}\pi r^3$

a = 2r

:. Packing efficiency =  $\frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$ 

$$=\frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\% = \frac{\pi}{6} \times 100\% = 52.36\% = 52.4\%$$

#### Calculation of Density of Unit Cell

If edge length of a unit cell of a cubic crystal

(determined by X-ray diffraction) = a

Density of the solid substance =  $\rho$  and Molar mass = M

For a cubic crystal, volume of the unit cell =  $a^3$ 

Mass of the unit cell = Number of atoms per unit cell (Z)  $\times$  Mass of each atom (m)

Mass of an atom present in the unit cell,

$$m = \frac{M}{N_A}$$

(: M = molar mass)

: Density of the unit cell,

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{Z \cdot m}{a^3} = \frac{Z \cdot M}{a^3 \cdot N_A}$$

Density of the unit cell,

$$\rho = \frac{ZM}{a^3 N_A} \text{ g/cm}^3$$
 (where,  $N_A$  = Avogadro's

constant)

# **Coordination Number** (CN)

For solids, coordination number of a particular atom or ion pertains to the number of nearest neighbours with which it is in contact, is called coordination number.

#### **Radius Ratio**

For ionic solids, the ratio of radius of cation to that of anion is called radius ratio. For a given coordination number radius ratio has fixed value in limiting case irrespective of the nature of particle.

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

# Structure of Substances Related to Close Packed Lattices

#### 1. NaCl "Rock Salt"



The main features of the structure are as follows :

- (i) It has a face-centred cubic (fcc) arrangement (also called cubic close packing, ccp) in which Cl<sup>-</sup> ions occupy the corners and face centers of the cube.
- (ii) The Na<sup>+</sup> ions occupy all the octahedral sites.
- (iii) Each Na<sup>+</sup> ion is surrounded by six Cl<sup>-</sup> ions and each Cl<sup>-</sup> ions is surrounded by six Na<sup>+</sup> ions. In other words, the Na<sup>+</sup> ions as well as Cl<sup>-</sup> ion have coordination number of 6, i.e. this structure has 6 : 6 coordination.
- (iv) There are four sodium ions and four chloride ions per unit cell.

#### 2. CsCl "Caesium Chloride"



The main features of the structure are as follows :

- (i) It has body centred cubic (bcc) arrangement.
- (ii) Here, Cs<sup>+</sup> ion is present at the body centre and chloride ions at eight corners.
- (iii) Each Cs<sup>+</sup> ion is surrounded by eight Cl<sup>-</sup> ions and each Cl<sup>-</sup> ion is surrounded by eight Cs <sup>+</sup> ions, i.e. this structure has 8 : 8 coordination.
- (iv) A unit cells of CsCl consists of only one unit of CsCl, i.e. one Cs<sup>+</sup> ion and one Cl<sup>-</sup> ion.

#### 3. ZnS "Zinc Sulphide"



The main features of the structure are as follows :

- (i) The arrangement as possessed by ZnS is called cubic close packing (ccp) in which S<sup>2-</sup> ions are present at the corners as well as at the center of each face.
- (ii) The zinc ions  $(Zn^{2+})$  occupy half of the tetrahedral holes.
- (iii) Each  $Zn^{2+}$  ion is surrounded tetrahedrally by four  $S^{2-} {\rm ions}$  and each  $S^{2-}$  ion is surrounded

tetrahedrally by four  $Zn^{2+}$  ions. Thus, this structure has 4:4 coordination.

#### 4. CaF<sub>2</sub> "Calcium Fluorite"



The main features of the structure are as follows :

- (i) The calcium ions, Ca<sup>2+</sup> are located at the face centered cubic lattice points and therefore, have cubic close packed arrangement.
- (ii) The fluoride ions ( $F^-$  ions) occupy all the eight tetrahedral voids.
- (iii) There are four  $Ca^{2+}$  ions and eight  $F^-$  ions in the unit cell of calcium fluoride. Thus, the coordination number of  $Ca^{2+}$  is eight and  $F^-$  is a four.

# **PRACTICE** QUESTIONS

# Exams', Textbook's Other Imp. Questions

# **1 MARK** Questions

#### **Exams' Questions**

- Q.1 The total number of atoms per unit cell of a face centred cubic crystal is [2018] (a) 1 (b) 2 (c) 3 (d) 4
- (a) 1
  (b) 2
  (c) 3
  (d) 4
  Sol (d) A face centred cubic unit cell contains atoms at all the corners and at the centre of all the faces of the cube.
  - :. Contributions by atoms on the corners  $=\frac{1}{8} \times 8 = 1$

Contributions by atoms on the face centred =  $\frac{1}{2} \times 6 = 3$ 

 $\therefore$  Total number of atoms present per unit cell of a face centred cubic crystal is 1 + 3 = 4

Q.2 In ZnS crystal, Zn<sup>2+</sup> ions occupy ...... void.[2018] Sol tetrahedral

#### Important Questions

**Q.3** The number of atoms in bcc arrangement is

(a) 1 (b) 4 (c) 2 (d) 6 Sol (c) In bcc, contribution by  $\frac{1}{8}$  per corner atom present

on the each corner  $=\frac{1}{8} \times 8 = 1$ 

Contribution by 1 body centre atom = 1

:. Total number of atoms per unit cell = 1 + 1 = 2

- Q.4 How many atoms are present per unit cell of a body centred cubic crystal? [2019]
- Sol Two atoms per unit cell are present in body centred cubic crystal, i.e.
  - (i) Contribution due to 8 corner atoms =  $8 \times \frac{1}{9} = 1$
  - (ii) Contribution due to atom present at the center of cube = 1
    - $\therefore \quad \text{Total} = 1 + 1 = 2$

Q.5	In hcp mode of stacking	, a sphere has	
	coordination number.		[Textbook]
	(a) 4	(b) 6	

(a) 4	(b) 6
(c) 8	(d) 12

- **Sol** (b) In hcp mode of staking, a sphere has coordination number = 6
- **Q.6** The arrangement *ABC*, *ABC* ... is referred to as
  - (a) octahedral close packing
  - (b) hexagonal close packing
  - (c) tetrahedral close packing
  - (d) cubic close packing
- Sol (d) The arrangement ABC, ABC is referred as cubic close packing.
- **Q.7** If edge of a bcc crystal of an element is '*a*' cm, M is the atomic mass and 'N' is the Avogadro number, then density of the crystal is [Textbook]

(a) 
$$\frac{4M}{a^3 N}$$
 (b)  $\frac{2N}{Ma^3}$   
(c)  $\frac{2M}{Na^3}$  (d)  $\frac{Ma^3}{2N}$ 

**Sol** (c) Density =  $\frac{2M}{a^3N}$ 

In bcc, Z = 2

:. Density of crystal = 
$$\frac{2M}{a^3 N}$$

Q.8 For an octahedral arrangement the lowest radius ratio limit is

(a) 0.155 (b) 0.732 (d) 0.225 (c) 0.414

- Sol (c) For an octahedral arrangement the radius ratio limit is 0.414-0.732.
- Q.9 Define coordination number of a crystal.

Sol Refer to text on page 9.

**Q.10** Explain interstitial voids. [Textbook]

[Textbook]

- Sol Refer to text on page 7.
- Q.11 The coordination number of each type of ions in a rock salt type crystal structure are ..... and ..... respectively.
- Sol. Rock salt, i.e. NaCl type structure has 6:6 coordination number. Thus, in NaCl crystal, each Na<sup>+</sup> ion is surrounded by 6 Cl<sup>-</sup> ions and each Cl<sup>-</sup> is surrounded by 6 Na<sup>+</sup> ions.
- Q.12 What is meant by radius ratio? [Textbook]
- Sol Refer to text on page 9.
- **Q.13** What are the coordination numbers of  $Cs^+$  and  $Cl^{-}$  in CsCl lattice? [Textbook]
- Sol Refer to text on pages 9 and 10.

# 2 MARK Questions

- Q.14 How will you distinguish between the following pairs of terms?
  - (i) Tetrahedral and octahedral voids
  - (ii) Crystal lattice and unit cell
- Sol. (i) Refer to text on page 7. (ii) Refer to text on page 6.
- **Q.15** An element with density 2.8 g cm<sup>-3</sup> forms fcc unit cell with edge length  $4 \times 10^{-8}$  cm. Calculate the molar mass of the element. (Given,  $N_4 = 6.022 \times 10^{23} \text{ mol}^{-1}$ )
- **Sol.** Given that, density  $d = 2.8 \text{ g cm}^{-3}$

Edge length,  $a = 4 \times 10^{-8}$  cm For fcc, Z = 4

Applying the formula,

$$d = \frac{ZM}{a^{3}N_{A}}$$
(1)  

$$\therefore M = \frac{da^{3}N_{A}}{Z}$$
$$= \frac{2.8 \text{g cm}^{-3} \times (4 \times 10^{-8} \text{ cm})^{3} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{4}$$
$$M = 26.98 \approx 27 \text{ g mol}^{-1}$$
(1)

# **3 MARK** Questions

- Q.16 Define coordination number in crystals. Is the coordination number of a sphere in ccp and hcp arrangement same or different? [Textbook] Sol Refer to text on pages 9 and 10. (3) **Q.17** Discuss the following types of cubic structures. (i) Simple cubic (ii) Body centred cubid[Textbook] (iii) Face centred cubic (3)
- Sol Refer to text on pages 7 and 8.
- **Q.18** An element with molar mass  $27 \text{ g mol}^{-1}$  forms a cubic unit cell with edge length  $4.05 \times 10^{-8}$  cm. If its density is  $2.7 \text{ g cm}^{-3}$ , what is the nature of the cubic unit cell?
- Sol. Given, molar mass of the given element

$$M = 27 \text{ g mol}^{-1}$$

Edge length (a) =  $4.05 \times 10^{-8}$  cm

Density,  $d = 2.7 \text{ g cm}^{-3}$ 

Apply the relation,  

$$d = \frac{Z \times M}{a^3 \times N_A}$$
(1)

where, Z is the number of atoms in the unit cell and  $N_A$  is the Avogadro's number.

Thus, 
$$Z = \frac{d \times a^3 \times N_A}{M}$$

$$=\frac{2.7 \,\mathrm{g} \,\mathrm{cm}^{-3} \times (4.05 \times 10^{-8} \,\mathrm{cm})^3 \times 6.022 \times 10^{23} \,\mathrm{mol}^{-1}}{27 \mathrm{g} \,\mathrm{mol}^{-1}} = 4$$
(1)

Since, the number of atoms in the unit cell is four, the given cubic unit cell has a face-centred cubic (fcc) or cubic-closed packed (ccp) structure. (1)

- Q.19 Aluminium crystallises in a cubic closed packed structure. Its metallic radius is 125 pm.
  - (i) What is the length of the side of the unit cell?
  - (ii) How many unit cells are there in  $1.00 \text{ cm}^3$  of aluminium?
- Sol. (i) Cubic closed packing is same as fcc.

For fcc, 
$$a = (2\sqrt{2}) \times r = 353.5 \approx 354 \text{ pm}$$
 (1)  
(ii) Volume of unit cell ,  $a^3 = (353.5 \times 10^{-10} \text{ cm})^3$ 

 $= 442 \times 10^{-23} \text{ cm}^3$  (1)

Number of unit cells =  $\frac{1 \text{ cm}^3}{4.42 \times 10^{-23} \text{ cm}^3}$ 

 $= 2.26 \times 10^{22}$  unit cells (1)

(7)

# 7 MARK Questions

Q.20 Discuss

- (i) close packing in two dimension.
- (ii) close packing in three dimensions.
- Sol. (i) Refer to text on page 6. (ii) Refer to text on pages 6 and 7.
- Q.21 What do you understand by close packing of spheres? Discuss briefly hexagonal close packing and cubic close packing of spheres. [Textbook]
- Sol Refer to text on pages 6 and 7. (7)
- Q.22 Describe fcc, bcc and hcp crystals of simple ionic compounds. [Textbook]
- Sol Refer to text on pages 9 and 10. (7)

# **TOPIC TEST 2**

- When the centres of the four immediate neighbouring spheres are joined a square is formed. Thus, this packing is called
  - (a) square close packing
  - (b) hexagonal close packing
  - (c) rectangular close packing
  - (d) None of the above [Ans. (a)]
- 2. The molar volume of KCl and NaCl are 37.46 mL and 27.94 mL respectively. The ratio of the unit cube edges of the crystals is
  - (a) 1.296 (b) 1.102
  - (c) 1.341 (d) 0.950 [*Ans.* (b)]
- ZnS has ..... arrangement in which S<sup>2-</sup> ions occupy the corners and face centres of the cube. [Ans. FCC]
- An example of a compound, which forms a crystal system in which all the edges and angles are different from each other is ............. [Ans. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]
- 5. How many sodium ions and chloride ions are present in a unit cell of sodium chloride?

- **6.** Which crystal has least and which one has higher volumes of empty spaces?
- 7. A compound AB has a cubic structure and molecular mass 99. Its density is  $3.4 \text{ g} / \text{cm}^3$ . What is the length of the edge of the unit cell?
- 8. In one type of crystal of an element there are more octahedral voids than tetrahedral ones, while in another type there are more tetrahedral voids than octahedral ones. Which of these two crystals has higher density and why?
- 9. An element occurs in bcc structure with cell edge 300 pm. The density of the element is  $5.2 \text{ g cm}^{-3}$ . How many atoms of the element does 200 g of the element contain?
- 10. (i) If the radius of the tetrahedral void is r and radius of the atoms in close packing is R, derive a relation between r and R.
  - (ii) Calculate the packing efficiency in hcp and ccp structures.

# **TOPIC ~03** Imperfections in Crystalline Solids, Electrical and Magnetic Properties of Solid

# **Point Defects**

Irregularities in the arrangement of constituent particles in a crystal is called **crystal defect**. Broadly crystal defects are classified as **point defects** and **line defects**. **Point defects** are the irregularities or deviations from ideal arrangement around a point (or an atom) in a crystalline solid, whereas the **line defects** are the irregularities or deviations from ideal arrangement in entire rows of lattice points. Point defects are of the following three types:

# 1. Stoichiometric Defects

Due to vacancy of ion, in which ratio of cation an anion is same. It is of following two types :

#### (i) Schottky Defect

It is a vacancy defect in ionic solids. This defect arises when equal number of cations and anions are missing from their lattice sites such that electrical neutrality is maintained. e.g. CsCl, NaCl, KCl, AgBr, etc.

Ξ	+	Ξ		Ξ	+	Ξ	+
+	=	+	-	+	-	+	-
Ξ	+	Ξ	+		+	Ξ	+
+	Ξ	+	=	+	-	+	•
Ξ	+	-		Ξ	+	Ξ	+
Ξ	+	Ξ	+	Ξ	+	Ξ	+
+	-	+	-	+	-	+	-
Ξ	+	Ξ	+		+	Ξ	+

Schottky defect

Due to this defect, density as well as covalent character of crystal decreases.

#### (ii) Frenkel Defect

This defect arises when 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. This defect is generally found in ionic crystals, where anion is much larger in size

than the cation. It is also known as

+	Ξ	+	Ξ	+	Ξ	+	-
-)	+	Ξ	+	Ξ	+	Ξ	+
+	Ξ	+	Ξ	+	Ξ	+	Ξ
-)	+	Ξ		Ξ	+	Ξ	+
+	Ξ	+	Ξ	+	-	+	-
-	+	Ξ	+	Ξ	+	Ξ	+
+	-	+	-	+	Ξ	+	-
-)	+	-	+	=	+	-	+

Frenkel defect

dislocation defect, e.g. AgBr, AgCl, AgI, ZnS, etc. due to small size of  $Ag^+$  and  $Zn^{2+}$  ions.

In non-ionic solid, stoichiometric defects is of two types:

(i) Vacancy Defects (ii) Interstitial Defects

### 2. Non-stoichiometric Defects

Those imperfections in the crystal, which lead to change in the composition of solids are called non-stoichiometric defects. They contain constituent elements in non-stoichiometric ratio due to defects in their crystal structures, e.g.  $Fe_{0.93}O$  and  $Ni_{0.94}O_{1.00}$ .

These defects are of two types :

#### (i) Metal Excess Defect

When the metal ions are in excess as compared to negatively charged ion, the solid is said to have metal excess defect. These defect are due to two phenomena.

(a) Metal Excess Defect due to Anionic Vacancies These types of defects are produced when metal halide is heated in metal vapours, e.g. alkali halides such as NaCl, KCl, shows this type of defect. When NaCl crystals are heated in an atmosphere of sodium vapours, the Na atoms are deposited on the surface of the crystal.



F-centre in a crystal

The Cl<sup>-</sup> ions diffuse to the surface of the crystal and combine with  $Na^+$  ( $Na \rightarrow Na^+ + e^-$ ) to form NaCl. The released electrons diffuse into the crystal and occupy anionic sites.

(b) Metal Excess Defect due to the Presence of Extra Cations at Interstitial Sites In this defect, an extra positive ion occupies interstitial position in the lattice and the free electron is trapped in the neighbouring interstitial site, the crystal remains neutral.

A <sup>+</sup>	B-	A <sup>+</sup>	B-
B-	A <sup>+</sup>	B-	A+
A+	<i>B</i> <sup>-</sup>	A+ e-	B-
B <sup>-</sup>	A+	B <sup>-</sup>	A+

Metal excess defect due to interstitial cations

#### (ii) Metal Deficiency Defect

This type of defect generally occurs when metal shows variable valency. The defect arises due to the missing of cation from its lattice site or due to the presence of extra anions in the interstitial spaces of the crystal. e.g. ferrous oxide, 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 a crystal 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.

# **Electrical Properties of Metal**

In most of the metals conduction is through electrons, however in some ionic solids the conduction is through ions. In metals, conductivity strongly depends upon the number of valence electrons available per atom. The atomic orbitals form molecular orbitals which are so close to each other as to form a band.

The conductivity of solids can be better explained on the basis of energy gap present between the conduction band and the valence band (By band theory of metal).

# Conductors

In conductors, the conduction band is almost overlapping with the valence band, i.e. there is no energy gap present between these two bands or valence band is not completely filled. Then, electrons can flow easily under the influence of electric field, in both the cases.

Semiconductors

In the case of semiconductors, the gap between valence band and conduction band is small and therefore some of the electrons may jump from valence band to conduction band and some conductivity is observed.

It is of two types:

Semiconductor

Conductor

#### (i) Intrinsic Semiconductors

These are those semiconductors whose electrical conductivity of semiconductors increases with rise of temperature. e.g. Silicon and germanium.

#### (ii) Extrinsic Semiconductor

For practical purposes the conductivity of pure Si and Ge is very low at room temperature. In order to increase their conductance, the pure substances are doped introduced with small amount of impurities.

This process is known as **doping** and such conductance is called **extrinsic conductance**. Depending upon the nature of the elements used for doping, the extrinsic semiconductor can be of two types, *viz*, *n*-types semiconductors and *p*-type semiconductors.

#### Insulators

In case of insulators, the energy gap between valence band and conduction band is so large that it cannot even covered up by supplying energy in the form of heat.



# **Magnetic Properties of Solids**

Magnetic properties of solids is due to the movement of electrons in an atom. As electron is a charged particle, thus its motions generates magnetic field. It behaves like a tiny bar magnet and possess magnetic moment. Magnitude of this magnetic moment is very small and its unit is **Bohr magneton**  $\mu_B$ , which is equal to  $9.27 \times 10^{-24}$  A m<sup>2</sup>. On the basis of magnetic properties, substances can be classified into five categories:

# 1. Diamagnetic

Diamagnetic substances are weakly repelled by an external magnetic field and this property is called diamagetism. They are weakly magnetised in a magnetic field in opposite direction. Such substances possesses all the paired electrons. Pairing of electrons cancel their magnetic moments and they lose their magnetic character, e.g. NaCl,  $H_2O$ ,  $TiO_2$ ,  $C_6H_6$ , etc.

# 2. Paramagnetic

These substances are weakly attracted by the external magnetic field and this property is called **paramagnetism**. They are magnetised in a magnetic field in the same direction and they lose their magnetism in the absence of magnetic field. They have one or more unpaired electrons which are attracted by the magnetic field and gives rise to paramagnetism, e.g.  $O_2$ ,  $Fe^{3^+}$ ,  $Cr^{3^+}$ ,  $Cu^{2^+}$ , etc.

# 3. Ferromagnetic

These substances are strongly attracted by the external magnetic field and this property is called ferromagnetism. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains which acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance, the domains are randomly oriented, thus their magnetic moments get cancelled. When such a substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field as shown below and a strong magnetic effect is produced. This ordering of domains persist even when the magnetic field is removed and they become a permanent magnet, e.g. Fe, Co, Ni, Gd, CrO<sub>2</sub>, etc.

 $\uparrow \uparrow \uparrow \uparrow \uparrow$ Ferromagnetism

# 4. Anti-ferromagnetic

These substances have domain structure similar to ferromagnetic substances but almost half number of domains is oppositely oriented and thus cancel out each others magnetic moment. e.g. MnO

 $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ Anti - ferromagnetism

#### 5. Ferrimagnetic

In ferrimagnetic substances, the magnetic moments of the domains are aligned in parallel and antiparallel directions in unequal number, the net magnetic moment is small. Thus, ferrimagnetic substances are weakly attracted by magnetic field than ferromagnetic substances and this property is called ferrimagnetism. They also lose ferrimagnetism on heating and become paramagnetic. e.g.  $Fe_3O_4$  and ferrites, like  $ZnFe_2O_4$  and  $MgFe_2O_4$ .

 $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$ Ferrimagnetism

# **PRACTICE** QUESTIONS

# Exams', Textbook's Other Imp. Questions

# **1 MARK** Questions

#### **Exams'** Questions

- Choose the correct option (Q.Nos 1 to 6)
  - **Q.1** What type of crystal defect is indicated in the diagram below?

- (a) Frenkel defect (b) Schottky defect
- (c) Interstitial defect
- (d) Frenkel and Schottky defects
- **Sol** (b) As number of missing cations and anions are equal. Thus, it is a Schottky defect.
- Q.2 The substances, which shows permanent magnetism even in the absence of magnetic field are called
  - (a) ferrimagnetic (b) ferromagnetic
  - (c) diamagnetic (d) paramagnetic
- **Sol** (b) The substances which shows permanent magnetism even in the absence of magnetic field are called ferromagnetism.
- **Q.3** Which of the following has the highest value of energy gap ?
  - (a) Aluminium (b) Silver

(c)	Germanium	(d)	Diamond

- Sol. (d) Diamond has the highest value of energy gap.
- **Q.4** The *n*-type semiconductor is obtained when Si is doped with
  - (a) Al (b) Ge (c) B (d) As
- **Sol.** (d) The *n*-type semiconductor is obtained when Si (Silicon) is doped with As (Arsenic).
- **Q.5** What type of defect will arise when a solid is heated? Which physical property is affected by it and in what way?
- **Sol.** On heating a solid, vacancy defect arises. As a result of this defect, the density of the substance decreases.

- Q.6 What type of stoichiometric defect is shown by (i) ZnS? (ii) AgBr?
- Sol. (i) ZnS shows Frenkel defect.
  - (ii) AgBr shows both Frenkel defect and Schottky defect.
- Fill in the blank (Q.Nos 7-9)
- **Q.7** The type of point defect that occurs in a crystal of zinc sulphide is .......
- *Sol.* Frenkel defect.
- **Q.8** The density of a crystal ...... due to Schottky defect.
- Sol. decreases
- **Q.9** ..... is an example of ionic compound which shows Schottky defect.
- Sol. NaCl.
- **Q.10** Why does Frenkel defect not change the density of AgCl crystal?
- **Sol.** There is only displacement of Ag<sup>+</sup> from its site. Number of particles in a unit volume remains the same. Hence, the density of AgCl crystal remains unchanged.
- **Q.11** What type of defect is produced when NaCl is doped with SrCl<sub>2</sub>?
- **Sol.** Impurity defect is produced when NaCl is doped with SrCl<sub>2</sub>.

# **2 MARK** Questions

#### **Exams' Questions**

**Q.12** Account for the following.

- (i) Schottky defects lower the density of related solids.
- (ii) Conductivity of silicon increases on doping it with phosphorus.
- Sol (i) In Schottky defects, equal number of cationic sites and anionic sites are vacant, thus decreases the density of the substance. (1)
  - (ii) Conductivity increases due to the extra free delocalised electrons. (1)

Q.13	(i)	What change occurs when AgCl is doped	
		with CdCl <sub>2</sub> ?	

(ii) What type of semiconductor is produced when silicon is doped with boron?

		*	
Sol	(i)	When AgCl is doped with CdCl <sub>2</sub> , two Ag	<sup>+</sup> ions
		will be replaced by one $Cd^{2+}$ ion to main	ıtain
		electrical neutrality. Thus, a noie is cre	ated at
		the lattice site for every Cd <sup>2+</sup> ion introd	uced.
		Hence, the crystal becomes conductor.	(1)
	(ii)	p-type semiconductor is obtained, when	ı Si is
		doped with boron.	(1)
Q.14	Exp	lain the following: [T	extbook]

**Q.14** Explain the following:

(i) Ferromagnetism	(ii) Paramagnetism
(iii) Antiferromagnetism	(iv) Ferrimagnetism

- Sol Refer to text on pages 14 and 15. (2)
- Q.15 Explain the difference between conductor and semiconductor. [Textbook]
- Sol Refer to text on page 14
- **Q.16** Ionic solids which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.
- Sol. Metal excess defect is due to anionic vacancies. When crystals of an ionic solid, like NaCl are heated in an atmosphere of sodium vapours, sodium atoms are deposited on the surface of the crystal. The Cl<sup>-</sup> ions diffuse to the surface of the crystal and combine with Na<sup>+</sup> ions to form NaCl. The Na<sup>+</sup> ions are formed by the loss of electrons. These released electrons diffuse into the crystals and occupy anionic sites. The anionic sites occupied by the electrons are known as *F*-centres. They impart yellow colour to the crystal. (2)
- Q.17 (i) What change occurs when AgCl is doped with CdCl<sub>2</sub>?
  - (ii) What type of semiconductor is produced when silicon is doped with boron?
- (i) When AgCl is doped with  $CdCl_2$ , two Ag<sup>+</sup> ions Sol will be replaced by one Cd<sup>2+</sup> ion to maintain electrical neutrality. Thus, a hole is created at the lattice site for every Cd<sup>2+</sup> ion introduced. Hence, the crystal becomes conductor. (1)
  - (ii) *p*-type semiconductor is obtained, when Si is doped with boron. (1)

# 3 MARK Questions

#### **Exams' Questions**

Q.18 How does Schottky defect arise? In which type of ionic compounds does this defect arise? [2019]

Sol Refer to text on page 13.

Q.19 Examine the given defective crystal.

$X^+$	$Y^{-}$	$X^+$	$Y^{-}$	$X^+$
$Y^{-}$	0	$Y^{-}$	$X^+$	$Y^-$
$X^+$	$Y^-$	$X^+$	0	$X^+$
$Y^{-}$	$X^+$	$Y^{-}$	$X^+$	$Y^{-}$

Answer the following questions:

- (i) Is the above defect stoichiometric or non-stoichiometric?
- (ii) Write the term used for this type of defect. Give an example of the compound which shows this type of defect.
- (iii) How does this defect affect the density of the crystal?
- Sol (i) The above defect is stoichiometric because equal number of cations and anions are missing from lattice sites. (1)
  - (ii) The term used for this type of defect is Schottky defect. These defects are interstitial defects shown by ionic solids in which the anion and cation are nearly of the same size. e.g. NaCl and KCl show Schottky defect. (1)
  - (iii) The presence of the Schottky defect in a crystal lattice lowers its density appreciably. (1)

#### Important Questions

(2)

(3)

- **Q.20** Explain the following giving suitable example in each:
  - (i) Schottky defect (ii) Frenkel defect (iii) F-centre
  - **Sol** (i) and (ii) refer to text on page 13.
    - (iii) *F***-centres** The anionic sites occupied by unpaired electrons are called F-centres or Farbenzenter (German word for colour centre). F-centres impart colour to crystals. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystal. They impart yellow colour to NaCl crystals. Violet colour to KCl crystal and pink colour to LiCl crystal are imparted due to excess of metals K and Li, respectively. (3)

# 7 MARK Questions

#### **Exams' Questions**

- Q.21 Explain the difference between conductor and insulator. [Textbook]
- Sol Refer to text on page 14. (7)
- **Q.22** What is a semiconductor? What are *n*-type and *p*-type semiconductors? [2018]
- Sol. The solids which exhibits intermediate conductivities ranging from  $10^{-6}$  to  $10^{-4} \Omega^{-1} m^{-1}$  are known as semiconductors. In this case, the gap between the valence band and conduction band is small. Therefore, some of the electrons may jump from valence band to conduction band and some conductivity is observed. Pure substances like silicon and germanium exhibit conducting behaviour and are called intrinsic semiconductors. On the

basis of impurities added for doping, semiconductors are of two types. (3)

(a) WhypenSilinicconductor germanium crystal is doped with group 15 elements like P or As, the dopant atoms with five valence electrons occupy some of the lattice sites normally occupied by silicon atom.



The dopant atom uses four of its electrons for covalent bonding but the

fifth extra electron becomes delocalised and this extra electron increases the conductivity of Si crystal.

Hence, silicon doped with electron rich impurity is called *n*-type semiconductor.

- (b) *p*-type Semiconductor
  - When a silicon or germanium crystal is doped with group 13 elements like B, Al or Ga which contains only three valence electrons, the dopant atoms occupy some of the lattice sites normally occupied by silicon atoms.

P (r	ositive no ele	e ho ctro	ole on)			
0:	0	?	0	:	0	:
	••				••	
0:		: (	В	:		:
	••		••		••	
0:		:(		:		:
			••		••	
0:		:		:		:

#### The place, where the fourth valence electron is missing is called electron hole or electron vacancy. These holes can move through the crystal like a positive charge and increase the conductivity of Si crystal.

Hence, silicon doped with electron deficient impurity is called *p*-type semiconductor. (4)

- **Q.23** What is a semiconductor? Describe the two main types of semiconductors and explain mechanism for their conduction.
- Sol Semiconductors In semiconductors, the gap between the valence and conduction bands is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature. These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4$  ohm<sup>-1</sup>m<sup>-1</sup>.

Types of semiconductors Refer to text on page 14. (7)

- Q.24 Explain the crystal defects and their origin in the crystal. [Textbook]
  - Sol Refer to text on page 13. (7)

Q.25 Explain the following with suitable examples:

(i) Ferromagnetism	(ii) Paramagnetism
(iii) Ferrimagnetism	(iv) Anti-ferromagnetism
(v) Diamagnetism	(vi) <i>n</i> -type semiconductor
(vii) <i>p</i> -type semiconductor	(7)

Sol. Refer to text on pages 14 and 15 and Q.22.

# **TOPIC TEST 3**

- 1. The substances which shows permanent magnetism even in the absence of magnetic field is called
  - (a) ferrimagnetic(c) diamagnetic

(b) ferromagnetic

- (d) paramagnetic
- 2. The type of alignment in crystal is ..... which makes them ferromagnetic (Fill in the blanks)
- **3.** How are point defects different from line defects.
- 4. Why are the defects of the crystalline solids called thermodynamic defects?
- **5.** Define piezoelectricity and give one use of piezoelectric crystals?
- 6. Why does the presence of excess of lithium makes lice crystal pink?
- 7. In terms of band theory, explain the difference between a conductor and a semiconductor. Also give one suitable example for each.

- Assign reasons for the following (Q.Nos 8-12)
  - 8. Phosphorus doped silicon is a semiconductor.
  - 9. Schottky defect lowers the density of a solid.
  - 10. Zinc oxide on heating becomes yellow.
  - 11.  $Fe_3O_4$  is ferrimagnetic at room temperature but becomes paramagnetic at 850 K.
  - **12.** Frenkel defect does not change the density of AgCl crystals.
  - 13. (i) What type of semiconductor is obtained when silicon is doped with boron?
    - (ii) What type of magnetism is shown in the following alignment of magnetic moments?
       ↑↑↑↑↑↑↑
    - (iii) What type of point defect is produced when AgCl is doped with CdCl<sub>2</sub>?

# **Chapter Test**

#### **1 MARK** Questions

1  $\text{TiO}_2$  is well known example of

(a) triclinic system

- (b) tetragonal system
- (c) monoclinic system (d) None of these
- 2 A crystal made of metal crystallises into a lattice containing a sequence of layers *ABABABA*... Packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is occupied?
  - (a) 50% (b) 26% (c) 74% (d) None of these
- **3** In which of the following crystals alternate tetrahedral voids are occupied ?
  - (a) NaCl (b) ZnS (c) CaF<sub>2</sub> (d) Na<sub>2</sub>O
- 4 How many Cs<sup>+</sup> ions occupy the second nearest neighbour locations of a Cs<sup>+</sup> ion in the structure CsCl (8 : 8 coordination)?

(a) 16 (b) 8 (c) 6 (d) 24 [Ans. 1. (b), 2. (c), 3. (b), 4. (c)]

### **2 MARK** Questions

5 The type of solid SiC is ..... [Ans. Covalent or Network solid]

6 The type of semiconductor formed when silicon is doped with N is .......

[Ans. n-type semiconductor]

- 7 Give example of a solid substance which conducts electricity even when possessing covalent bonds.
- 8 What is the formula of a compound in which the element *Y* forms ccp lattice and atoms of *X* occupy  $\frac{1}{3}$ rd of tetrahedral voids?

# **3 MARK** Questions

- **9** What are different types of voids formed in close packed structures?
- **10** In NaCl crystal, Cl ions are in fcc arrangement. Calculate the number of Cl ions in its unit cell.
- 11 Lithium iodide crystal has a face-centred cubic unit cell. If the edge length of the unit cell is 620 pm, determine ionic radius of  $I^-$  ions.

- 12 Explain by giving reasons why ionic solids conduct electricity in molten state, but not in solid state.
- 13 (i) What are *F*-centres in an ionic crystal?
  - (ii) Why are crystals having *F*-centres paramagnetic?
- **14** What are semiconductors? What is the effect of increasing temperature on the conductivity of a semiconductor?
- **15** The density of lead is 11.35 g cm<sup>-3</sup> and the metal crystallises with fcc unit cell. Estimate the radius of lead atom (Atomic mass of lead = 207 g mol<sup>-1</sup> and  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ ). [Ans.  $a\sqrt{2} = 4r,175 \text{ pm}$ ]
- 16  $C_sCl$  has cubic structure. Its density is 3.99 gcm<sup>-3</sup>. What is the distance between  $Cs^{\oplus}$  and  $Cl^s$  ions? (Atomic mass of Cs = 133)
- 17 Compare the following properties of crystalline and amorphous solids.(i) Orderly arrangement (ii) Melting points
- 18 Name the ions which form the close packed structure (along with the type of packing) and the ions which fill the voids (along with the types)
  - (i) NaCl (ii) ZnS (iii) CaF<sub>2</sub>

### **7 MARK** Questions

of voids) in the compounds:

- **19** The CsCl has cubic structure of  $Cl^{-}$  ions in which  $Cs^{+}$  ion is present in the body centre of the cube. Its density is 3.99 g cm<sup>-3</sup>.
  - (i) Calculate the length of the edge of unit cell.
  - (ii) What is the distance between  $Cs^+$  and  $Cl^$ iron? [Ans. a = 412 pm]
- **20** Show that in a cubic close packed structure, eight tetrahedral voids are present per unit cell.
- 21 (i) In reference to crystal structure, explain the meaning of the coordination number.
  - (ii) What is the number of atoms in a unit cell of(a) a face-centred cubic structure?
    - (b) a body-centred cubic structure?