



LESSON AT A GLANCE

- **Solid:** The state of the substance in which it has definite mass, volume and shape.
- **Amorphous solids:**
 - A substance whose constituent particles do not possess a regular orderly arrangement.
 - They behave like super cooled liquids consequently.
 - Glass, plastics, rubber, starch, etc. are amorphous solids.
- **Crystalline solids:**
 - There is long range order in the arrangement of their constituent particles.
 - They have sharp melting points.
 - They are anisotropic in nature.
- **Crystal:** A solid with a regular polyhedral shape.
- **Crystal Lattice:** The regular pattern of atoms, ions or molecules in a crystalline substance. A crystal lattice can be regarded as produced by repeated translations of a unit cell of the lattice.
- **Bravais Lattice:** There are fourteen different types of lattices which are called as Bravais lattices.
- **Unit cell:** For each crystal lattice it is possible to select a group of lattice points which is repeated again and again.
- **Close packing:** Close packing of particles results in two highly efficient lattices
 - Hexagonal close-packed (hcp)
 - Cubic close-packed (ccp)In both of the packing 74% are space filled.
- **Body-centred cubic lattice:** 68% are space filled.

- **Cubic lattice:** 52.4% are space filled.
- **Photovoltaic substances:** The material which converts sunlight into electricity is called photovoltaic substances, *e.g.* amorphous silicon.
- **Crystallinity:** The degree of internal order in a crystal is called crystallinity.
- **Anisotropic:** It denotes a medium in which certain physical properties are different in different directions. Wood, for example, is an anisotropic material: its strength along the grain differs from that perpendicular to the grain.
- **Covalent solids:** Covalent bonds are formed by sharing of valence electrons rather than by transfer. For instance, hydrogen atoms have one outer electron ($1s^1$).
Covalent solids have covalent bonds throughout the solid. They are also known as network solids.
- **Crystalline solids:** The solid which has a regular internal arrangements of atoms, ions or molecules is called crystalline solid.
- **Crystallography:** The study of geometry and symmetry of crystal form and structure is called crystallography.
- **Unit cell:** The group of particles (atoms, ions, or molecules) in a crystal that is repeated in three dimensions in the crystal lattice, is called a 'unit cell'.
- **Primitive cubic unit cell:** Primitive cubic unit cell has atoms only at its corner. Since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom.
- **Body-centred Cubic Unit Cell:** A unit cell having a lattice point at the centre of the body, in addition to the lattice points at the corners, is called body-centred unit cell. Each corner atom makes $1/8$ contribution and the atom at the body centre belongs only to the particular unit cell.
- **Face-centred Cubic Unit Cell:** A face-centred cubic (*fcc*) unit cell contains one atom at each corner (there are eight corners of a cube) and one atom at the centre of each face (six faces of a cube) of the cube. That each atom located at the face centre is shared between two adjacent unit cells and makes a contribution of only $1/2$ to a particular unit cell.

- **Close-packed structure:** When the constituent particles are packed most efficiently within a crystal, so that the empty space is minimum, the arrangement is referred to as 'close-packed structure'.
- **Packing Efficiency:** The percentage of total space filled by the constituent particles (atoms, molecules or ions) is called packing efficiency.
- **Conductors:** The solids with conductivities ranging between 10^4 to $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ are called conductors. Metals have conductivities in the order of $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ are called good conductors.
- **Insulators:** These are the solids with very low conductivities ranging between 10^{-20} to $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$.
- **Semiconductors:** These are the solids with conductivities in the intermediate range from 10^{-6} to $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$.
- **Paramagnetism:** These materials are weakly attracted by a magnetic field. They can be magnetised in a magnetic field in the same direction. Paramagnetism is due to the presence of one or more unpaired electrons which are attracted by the magnetic field.
 O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} are some examples of such substances. They loss their magnetism in the absence of magnetic field.
- **Diamagnetism:** Diamagnetic substances are weakly repelled by a magnetic field.
They do not have unpaired electrons. Pairing of electrons cancels their magnetic moments and they loss their magnetic character. Some examples of such substances are H_2O , NaCl and C_6H_6 .
- **Ferromagnetism:** They have strong attraction towards the magnetic field. These substances can be permanently magnetised.
- **Antiferromagnetism:** In these substances their domains are aligned in such a way that net magnetic moment is zero. This type of magnetism is called antiferromagnetism. For example, MnO has antiferromagnetism.
- **Ferrimagnetism:** When the magnetic moments of the domains in the substance are aligned in parallel and antiparallel direction in unequal numbers.

TEXTBOOK QUESTIONS SOLVED

1.1 Define the term 'amorphous'. Give a few examples of amorphous solids.

Ans. Amorphous solids are those which have irregular shapes, do not have sharp melting point or definite heat of fusion and are isotropic in nature. The arrangement of their constituent particles has only short-range order but no long-range order.

Example : Glass, rubber and plastics.

1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

Ans. Glass is an amorphous solid while quartz is crystalline in nature. The constituent particles in glass have only short-range order while those in quartz have short range as well as long range order. Quartz can be converted into glass by melting it and then cooling it rapidly.

1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

- | | |
|--|--------------|
| (i) Tetraphosphorus decoxide (P_4O_{10}) | |
| (ii) Ammonium phosphate ($(NH_4)_3PO_4$) | |
| (iii) SiC | (iv) I_2 |
| (v) P_4 | (vi) Plastic |
| (vii) Graphite | (viii) Brass |
| (ix) Rb | (x) LiBr |
| (xi) Si | |

Ans. Ionic solids: $(NH_4)_3PO_4$ and LiBr

Metallic solids: Brass and Rb.

Molecular solids : P_4O_{10} , I_2 and P_4

Network (Covalent) solids : Graphite, SiC, Si

Amorphous solids: Plastics

1.4 (i) What is meant by the term 'coordination number'?

(ii) What is the coordination number of atoms:

(a) in a cubic close packed structure?

(b) in a body-centred cubic structure?

Ans. (i) The coordination number of a constituent particle is the number of its nearest neighbouring constituent particles in a crystal.

(ii) (a) 12 (b) 8

1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

Ans. Atomic mass of an unknown metal can be determined with the help of the relation

$$\text{Atomic mass} = \frac{\rho \times a^3 \times N_A}{z}$$

where ρ is the density of the metal, a is the side of the cubic unit cell, N_A is the Avogadro constant and z is the number of atoms per unit cell.

1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Ans. (a) Melting point of a solid is a measure of intermolecular forces in it. Stronger the intermolecular forces in a solid, higher is the melting point and more stable is the solid.

(b) Melting point of the given solids are:

Water = 273K; ethyl alcohol = 155.7 K; diethyl ether = 156.8 K and methane = 90.5 K. Water and ethyl alcohol have hydrogen bonding in them. That is why their melting points are high. Of the two, the lower melting point of ethyl alcohol indicates that the hydrogen bonding in it is much weaker than in water.

Diethyl ether is a polar molecular compound and there are dipole-dipole interactions in it which are quite strong as indicated by its reasonably high melting point.

Methane is a non-polar molecular compound and only the weak London forces operate in it as is indicated by its very low melting point.

1.7 How will you distinguish between the following pairs of terms:

(i) Hexagonal close packing and cubic close packing?

(ii) Crystal lattice and unit cell?

(iii) Tetrahedral void and octahedral void?

- Ans.** (i) *Hexagonal close packing* results from *ABAB...* stacking of layers and results in hexagonal unit cell. *Cubic close packing* results from *ABCABC...* stacking of layers and results in *face-centred cubic unit cells*.
- (ii) *Crystal lattice* is a three dimensional array of points in space, each one of which gives the location of the constituent particles in the crystal. *Unit cell* is the smallest portion of the crystal lattice with the help of which the whole crystal lattice can be generated by repeating it along different axes.
- (iii) A *tetrahedral void* is a void formed by four close packed spheres (particles), three of which are in a plane and the fourth one over the depression (triangular void) formed by the three. The centres of these spheres when joined make a regular tetrahedron and therefore, the void is called a tetrahedral void. An *octahedral void* is formed by six close packed spheres, three of which are in one plane and the remaining three in the adjoining plane. They are so placed that the triangular void of one set of 3 spheres is above that of the other set, but their vertices point in opposite directions. The centres of these six spheres, when joined, make a regular octahedron. That is why this type of void is called octahedral void.

1.8 How many lattice points are there in one unit cell of each of the following lattice?

- (i) *Face-centred cubic*
(ii) *Face-centred tetragonal*
(iii) *Body-centred*

- Ans.** (i) Lattice points in face-centred cubic unit cell = 8 corners + 6 face centres = 14
- (ii) Lattice points in face-centred tetragonal unit cell = 8 corners + 6 face centres = 14.
- (iii) Lattice points in body-centred cubic unit cell = 8 corners + 1 body centre = 9.

(Although one lattice point may be part of many adjacent unit cells, it cannot be divided since it only represents the location of particle in a crystal. However, the particles located at the corners, edges on face centres are shared between adjoining unit cells and the number of particles present per unit cell would be less than the number of lattice points.)

1.9 Explain

(i) *The basis of similarities and differences between metallic and ionic crystals.*

(ii) *Ionic solids are hard and brittle.*

Ans. (i) (a) The *similarities* between metallic and ionic crystals are due to the facts that electrostatic forces operate in both—between oppositely charged ions in ionic crystals and between positively charged kernels and negatively charged valence electrons in metallic crystals and the bonds (ionic and metallic) are non-directional.

(b) The *differences* between these crystals are due to the fact that in metallic crystals the strength of electrostatic forces can vary depending upon the number of valence electrons and the size of kernels. Also, all the lattice points are occupied by similar particles—the kernels. On the other hand, the electrostatic forces of attraction in ionic crystals are quite strong. Also, the lattice points are occupied by dissimilar particles—cations and anions.

(ii) The ionic solids are hard due to very strong electrostatic forces of attraction between oppositely charged ions. They are brittle because they consist of two different types of constituent particles namely, positively charged cations and negatively charged anions, when any force or stress is applied, a cation tries to occupy the position of an anion and becomes surrounded by other cations. The strong repulsive forces are set up and these would break the crystal structure, making it brittle.

1.10 Calculate the efficiency of packing in case of a metal crystal for

(i) *simple cubic*

(ii) *body-centred cubic*

(iii) *face-centred cubic (with the assumptions that atoms are touching each other).*

Ans. (i) **Packing efficiency in simple cubic lattice:** In a simple cubic lattice the atoms are located only on the corners of the cube.

The particles touch each other along the edge, thus the edge length or side of the cube ' a ' and the radius of each particles, r are related as:

$$a = 2r$$

The volume of the cubic unit cell

$$= a^3 = (2r)^3 = 8r^3$$

Since a simple cubic unit cell contains only 1 atom.

The volume of the occupied space = $\frac{4}{3}\pi r^3$

∴ Packing efficiency

$$\begin{aligned} &= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100 \\ &= \frac{\frac{4}{3}\pi r^3 \times 100}{8r^3} \\ &= \frac{\pi}{6} \times 100 = 52.4\% \end{aligned}$$

(ii) **Packing efficiency in body-centred cubic structures:** It is clear that atom at the centre will be in touch with the order two atoms diagonally arranged.

In ΔEFD

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

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

Now in ΔAFD

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

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

The length of the body diagonal c is equal to $4r$, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

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

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

Also we can write, $r = \frac{\sqrt{3}}{4}a$

In this type of structure, total number of atoms is 2

and their volume is $2 \times \frac{4}{3}\pi r^3$

Volume of the cube,

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

Packing efficiency

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

(iii) **Packing efficiency in face-centred cubic** (with the assumptions that atoms are touching each other):

Let us calculate the efficiency in *ccp* or *fcc* structure.

Let the unit cell edge length be '*a*' and face diagonal

AC = *b*

In $\triangle ABC$

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

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

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

If *r* is the radius of the sphere

We find $b = 4r$

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

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

We know that in *fcc* structure has effectively 4 spheres.

Total volume of the four spheres is equal to $4 \times \frac{4}{3} \pi r^3$

and the volume of the cube $a^3 = (2\sqrt{2}r)^3$

Therefore, Packing efficiency

$$\begin{aligned}
 & \text{Volume occupied by four spheres} \\
 & \quad \text{in unit cell} \times 100 \% \\
 = & \frac{\text{Total volume of the unit cell}}{\text{Total volume of the unit cell}} \%
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{4 \times \frac{4}{3} \pi r^3 \times 100}{(2\sqrt{2}r)^3} \% \\
 &= \frac{16/3 \pi r^3 \times 100}{16\sqrt{2}r^3} \% = 74\%
 \end{aligned}$$

1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.

Ans.
$$M = \frac{\rho \times a^3 \times N_A}{z}$$

Given $\rho = 10.5 \text{ g cm}^{-3}$; $a = 4.07 \times 10^{-8} \text{ cm}$; $z = 4$ (FCC lattice)

$$\begin{aligned}
 \therefore M &= \frac{(10.5 \text{ g cm}^{-3}) \times (4.07 \times 10^{-8} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{4} \\
 &= 107.09 \text{ g mol}^{-1}
 \end{aligned}$$

1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Ans. Since atoms of the element P are present at the body centre of bcc unit cell, the number of atoms of P per unit cell = 1 atom. The atoms of the element Q are present at the corners of the bcc unit cell. There are 8 corners per unit cell and the contribution of each in the unit cell is 1/8, the number of atoms of Q present per unit cell = $8 \times 1/8 = 1$ atom. Thus in each unit cell the ratio of atoms of P and Q is 1 : 1; the formula of the compound = PQ. In bcc unit cell the coordination number = 8 for atoms of P and Q both.

1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium using its atomic mass 93 u.

Ans. (a) Calculation of 'a' the edge length of the unit cell

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

Given $M = 92.9 \text{ g mol}^{-1}$, z (bcc unit cell) = 2

$$\rho = 8.55 \text{ g cm}^{-3}; N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$a^3 = \frac{(92.9 \text{ g mol}^{-1}) \times 2}{(8.55 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = 36.1 \times 10^{-24} \text{ cm}^3$$

$$a = (36.1 \times 10^{-24})^{1/3} = 3.304 \times 10^{-8} \text{ cm} = 3.304 \times 10^2 \text{ pm}$$

(1 pm = 10^{-10} cm)

(b) *Calculation of atomic radius 'r'*

In a body-centred cubic unit cell

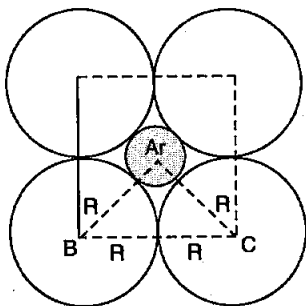
$$r = \frac{\sqrt{3}}{4} a = 0.433a$$

$$= 0.433 \times 3.304 \times 10^2 \text{ pm}$$

$$= 143.1 \text{ pm}$$

1.14 *If the radius of the octahedral void is r and radius of the atoms in close packing is R , derive relation between r and R .*

Ans.



A sphere fitting into the octahedral void is shown by shaded circle. ABC is a right angle triangle. Applying Pythagoras theorem,

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

$$(2R)^2 = (R + r)^2 + (R + r)^2$$

$$= 2(R + r)^2$$

or $\frac{(2R)^2}{2} = (R + r)^2$

or $\sqrt{\frac{(2R)^2}{2}} = R + r$

or $\sqrt{\frac{2R^2}{2}} = R + r$

or $\sqrt{2}R = R + r$

$$r = \sqrt{2}R - R$$

$$r = R(\sqrt{2} - 1)$$

$$= R(1.414 - 1)$$

$$= 0.414 R$$

- 1.15** Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .

Ans.
$$\rho = \frac{M \times z}{a^3 \times N_A}$$

Given $a = 3.61 \times 10^{-8}$ cm ; $z = (\text{FCC lattice}) = 4$
 $\therefore M = 63.5 \text{ g mol}^{-1}$

$$\rho = \frac{(63.5 \text{ g mol}^{-1}) \times 4}{(3.61 \times 10^{-8} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 8.97 \text{ g cm}^{-3}$$

This value is in agreement with the measured value 8.92 g cm^{-3} .

- 1.16** Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

Ans. Formula $\text{Ni}_{0.98}\text{O}$ indicates that with every 100 O^{2-} ions, 98 Ni-ions are present in nickel oxide. Let x be the number of Ni^{2+} ions then the number of Ni^{3+} ions = $(98 - x)$.

Since total positive charge on 98Ni ions = total negative charge on 100 O^{2-}

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

$$2x + 294 - 3x = 200$$

$$-x = 200 - 294 = -94$$

$$x = 94$$

\therefore There are 94 Ni^{2+} and 4 Ni^{3+} ions per 100 O^{2-} ions

$$\text{Fraction of } \text{Ni}^{2+} \text{ ions} = \frac{94}{98} = 0.96 \text{ or } 96\%$$

$$\text{Fraction of } \text{Ni}^{3+} \text{ ions} = \frac{4}{98} = 0.04 \text{ or } 4\%$$

- 1.17** What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

Ans. Semiconductors are the materials whose conductance lies in between that of conductors and insulators. There are two main types of semiconductors:

(i) ***n*-type semiconductors:** Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised.

These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron with impurity is called *n*-type semiconductor.

(ii) ***p*-type semiconductor:** Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called *electron hole* or *electron vacancy*. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductors are called *p*-type semiconductors.

1.18 *Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a *p*-type semiconductor?*

Ans. Since ratio of Cu to O in non-stoichiometric cuprous oxide Cu_2O is less than 2 : 1, some Cu^+ ions have been replaced by Cu^{2+} ions. To maintain the charge balance, two Cu^+ ions are replaced by only one Cu^{2+} ion that leaves one position

vacant (a hole). The conduction of electricity would be due to the presence of such holes which behave as if they are positively charged and make the substance a *p*-type semiconductor.

1.19 Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Ans. Let the number of oxide ions constituting the *hcp* lattice be N .

\therefore Number of octahedral voids generated = N

Number of octahedral voids filled by ferric ions = $\frac{2}{3}N$

\therefore Number of Fe^{3+} ion = $\frac{2}{3}N$

Number of Fe^{2+} ions : Number of O^{2-} ions

$$\frac{2}{3}N : N$$

or $2 : 3 \quad \therefore$ Formula = Fe_2O_3

1.20 Classify each of the following as being either a *p*-type or a *n*-type semiconductor:

(i) Ge doped with In (ii) B doped with Si.

Ans. (i) Since Ge, a group 14 element is doped with In, a group 13 element, an electron deficit hole is created and thus makes it a *p*-type semiconductor.

(ii) Since B, a group 13 element is doped with Si, a group 14 element, there will be free electrons in it and would thus make it an *n*-type semiconductor.

1.21 Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

Ans. Given atomic radius, r of gold atom = 0.144 nm and it makes face-centred unit cell.

$$\begin{aligned} \text{For FCC} \quad a &= 2\sqrt{2}r = 2 \times 1.414 \times 0.144 \text{ nm} \\ &= 0.407 \text{ nm} \end{aligned}$$

1.22 In terms of band theory, what is the difference

- (i) between a conductor and an insulator
(ii) between a conductor and a semiconductor?

Ans. (i) *Difference between a conductor and an insulator.* In a conductor, the valence band and conduction band either overlap or have only very small energy gap, while in an insulator there is a large energy gap between them.

(ii) *Difference between a conductor and a semiconductor.* In a conductor, the valence band and conduction band either overlap or have only a very small energy gap, there is always a small energy gap in case of a semiconductor.

1.23 *Explain the following terms with suitable examples:*

- (i) *Schottky defect* (ii) *Frenkel defect*
(iii) *Interstitials and* (iv) *F-centres.*

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

Like simple vacancy defect, schottky defect also decreases the density of the substance. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr.

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

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

(iii) **Interstitial defect:** When some constituent particles (atoms or molecules) occupy an interstitial site the crystal is said to have interstitial defect. This defect increases the density of the substance. Non ionic solids are example of this defect.

(iv) **F - centres:** Alkalihalides like NaCl and KCl show this type of defect when crystals of NaCl are heated in a atmosphere of sodium vapour the sodium atoms are deposited normal on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine

with Na atoms to give NaCl. This happens by the loss of electrons by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result crystal has now excess of sodium. The anionic sites occupied by unpaired electrons are called F-centres. They impart yellow colour to the crystal of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

Another examples are: LiCl, KCl etc.

1.24 Aluminium crystallises in a cubic close-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 cm^3 of aluminium?

Ans. (i) Given the metallic radius, r of aluminium = 125 pm.
 Nature of unit cell = FCC.

$$\begin{aligned} \text{The side of FCC unit cell} = a &= 2\sqrt{2} r \\ &= 2 \times 1.414 \times 125 \text{ pm} \\ &= 354 \text{ pm} \end{aligned}$$

(ii) Volume of one unit cell

$$\begin{aligned} &= a^3 = (354 \text{ pm})^3 = (354 \times 10^{-10} \text{ cm})^3 \\ \therefore \text{Number of unit cell in } 1 \text{ cm}^3 &= \\ &= \frac{1}{(354 \times 10^{-10})^3} = \frac{1}{4.44 \times 10^{-23}} = 2.25 \times 10^{22}. \end{aligned}$$

1.25 If NaCl is doped with 10^{-3} mol % of SrCl_2 , what is the concentration of cation vacancies?

Ans. Since NaCl is doped with 10^{-3} mol %, 100 mol of NaCl are doped with 10^{-3} mol SrCl_2 .

$$\therefore 1 \text{ mol of NaCl is doped with } \frac{10^{-3}}{100} = 10^{-5} \text{ mol SrCl}_2$$

Since each Sr^{2+} ion replaces two Na^+ ions, it creates one vacancy, number of vacancies per mol = 10^{-5} mol

$$= 10^{-5} \times 6.022 \times 10^{23} = 6.022 \times 10^{18}$$

$$\therefore \text{Concentration of vacancies (number of vacancies per mol)} = 6.022 \times 10^{18}.$$

1.26 Explain the following with suitable examples:

(i) Ferromagnetism

- (ii) *Paramagnetism*
- (iii) *Ferrimagnetism*
- (iv) *Antiferromagnetism*
- (v) *12-16 and 13-15 group compounds.*

Ans. (i) **Ferromagnetism:** A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances.

Besides strong attractions, these substances can be permanently magnetised.

- (ii) **Paramagnetism:** These substances are weakly attracted by a magnetic field. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} are some examples of such substances.
- (iii) **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 magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like MgFe_2O_4 and ZnFe_2O_4 are examples of such substances. These substances lose ferrimagnetism on heating and become paramagnetic.
- (iv) **Antiferromagnetism:** When magnetic moments are aligned in such a way that net magnetic moment is zero then magnetism is called antiferromagnetism. For example, MnO .
- (v) **12-16 compounds:** Compounds formed between group 12 elements with elements of group 16 are called 12-16 compounds *e.g.*, ZnS , Hg , Te etc.
13-15 compounds: Compounds formed between elements of group 13 with group 15 elements are called 13-15 compounds *e.g.*, GaAs , AlP , etc.

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