1

SOLID STATE

INTRODUCTION

Matter can exists in three physical states namely ; solid, liquid and gas. Matter consists of tiny particles (atoms, ions or molecules). If the particles are very far off from one another, they behave like gases ; nearer, they behave like liquids, and nearest, like solids.

The fundamental difference between the three states of aggregation lies essentially in the difference of the relative amounts of energy possessed by the particles in the three states. The relative energies in the different states of matter are governed by two universal opposing tendencies associated with the particles:

(i) They have tendency of mutual attraction.

(ii) They have tendency of escape from one another which is known as escaping tendency.

Whether a given system would exist as a solid, liquid or gas depends upon the relative strength of these opposing tendencies. If the escaping tendency is greater than the attraction between them, the molecules will be carried far from each other to distances which are large as compared with their diameters, the system will exists in gaseous state. But in the liquid state the molecular attraction exceeds the escaping tendency and in the solid state the forces of attraction are so much greater than those of escaping tendency that each particles is bound into a definite place in a rigid position by the mutual attraction of molecules.
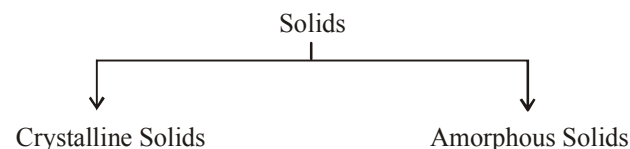
SOLIDS

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

Properties of Solids :

(a) In solid state the particles are not able to move randomly.

(b) They have definite shape and volume.

(c) Solids have high density.

(d) Solids have high and sharp melting point which is depend on the strength or value of binding energy.

(e) They are very low compressible.

(f) They show very slow diffusion.

Types of Solids :

Solids

Crystalline Solids   Amorphous Solids

Crystalline solids : A crystalline solid has a definite melting point at which it becomes liquid, bounded by well defined plane faces, having same geometry irrespective of the source from which they have been obtained.

Amorphous solids : Amorphous solids have no precise melting point but when heated, become increasingly pliable until they assume the properties usually associated with liquids; they are supercooled liquids in which the force of attraction holding the molecules together is so great that the material is rigid but there is no regularity of structure.

Difference between crystalline and amorphous solids :

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

CLASSIFICATION OF CRYSTALS

Crystal : A crystal is a homogeneous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

(i) Ionic Crystals :
(a) The lattices in ionic crystal consists of alternative positive and negative ions in equivalent amount arranged in an order so that the potential energy of the ions in the lattice is minimum.
(b) Such crystal are normally found in ionic compound. e.g. $NaCl \rightarrow Na^+ + Cl^-$

(ii) Covalent Crystals :
(a) In covalent crystals, atoms at their lattice point are held together by shared pairs of electrons between them.
(b) The covalent bonding extends through out the crystals in spatial direction and has no small molecules in the conventional sense.   e.g. Diamond, Graphite.

(iii) Molecular Crystals :
(a) In molecular crystals, the repeating unit is chemically identifiable atoms or molecules which do not carry a net charge.
(b) Molecular bonds are formed for those elements or compounds whose electronic configuration is such that there is little transfer of electrons between their atoms. e.g. Noble gases.
(c) The molecules having H-atom attached on N, O or F give H-bonding crystals. The existence of H-bonding in the crystal lattice is beyond doubt. e.g. Ice Crystal etc.

(iv) Metallic Crystals :
In metallic crystals, the lattice consists of assemblage of positive ions immersed in a sea of mobile electrons. The binding force is due to -
(a) Attraction between positive ions or ion cores of the metal and electron cloud.
(b) The mutual repulsion of free electrons.
(c) The mutual repulsion of ion cores.

Table : Classification of crystalline solids

Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic	NaCl, KCl, CaO, MgO, LiF, ZnS, $BaSO_4$ and K_2SO_4 etc.	Hard but brittle	High (1000K)	High (2000K)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO_2 (Quartz), SiC, C (diamond), C(graphite) etc.	Hard Hard Soft	Very high (4000K)	Very high (5000K)	Insulator except graphite
Molecular (i) Non-polar (ii) Polar (iii) Hydrogen bonded	Molecules	(i) Dispersion or London forces (ii) Dipole-dipole interactions (iii) Hydrogen bonding	Ar, CCl_4, H_2, I_2, CO_2 HCl, SO_2 H_2O (ice)	Soft Soft Hard	Very low (300K to 600K) Low (400K) Low	Low (450 to 800K) Low (373K to 500K) Low	Insulator Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium , Au, Cu, magnesium, metals and alloys	Hard Ductile malleable	High (800K to 1000 K)	High (1500K to 2000K)	Conductor

Network structure of diamond and graphite:
* Diamond and graphite are covalent crystals.

Figure : Network structure of diamond

Figure : Structure of graphite
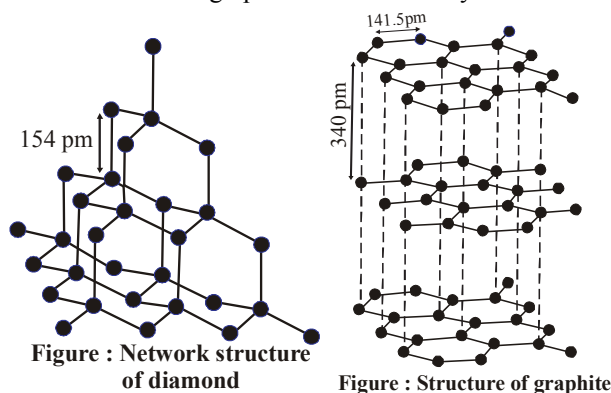
* In diamond, the carbon atoms are in tetrahedral arrangement while graphite has two dimensional array of covalent bonds and has two dimensional sheet like structure.
* In graphite carbon is sp^2 hybridised, while in diamond carbon is sp^3 hybridised.
* Covalent bonds are stronger than metallic bonds.

Graphite structure :
* Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure.
* Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about.
These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

Example 1 :
Iodine crystal are –
(A) Metallic Solid   (B) Ionic solid
(C) Molecular solid   (D) Covalent solid
Sol. (C). Molecular solids are the substances having molecules as constituent units having interparticle forces such as Vander Waal's forces or hydrogen bonds.

Example 2 :
Which of the following is molecular crystal -
(A) Noble gas   (B) Ice
(C) 1 and 2 both   (D) None
Sol. (C). Noble gas and Ice are molecular crystal.

STUDY OF CRYSTALS

Space lattice : The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

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

Face : The plane surface of the crystal are called faces.

Edge : An edge is formed by the intersection of two adjacent faces.

Interfacial angles : The angle between the perpendiculars two intersecting faces called interfacial angles.

UNIT CELL

* A units cell is obtained by joining the lattice points. The choice of lattice points to draw a unit cell is made on the basis of the external geometry of the crystal, and symmetry of the lattice.

* Unit cells can be broadly divided into two categories, primitive and centred unit cells.

(A) Primitive or simple cubic (sc) : Atoms are arranged only at the corners of the unit cell.

(B) Centred Unit Cells : When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types:

(1) Body centred cubic (bcc) : Atoms are arranged at the corners and at the centre of the unit cell.

(2) Face centred cubic (fcc) : Atoms are arranged at the corners and at the centre of each faces of the unit cell.

(3) End centered : Atoms are arranged at the centre of only one set of faces in addition to the atoms at the corner of the unit cell. In all, there are seven types of primitive unit cells.

CRYSTAL SYSTEM

Bravais showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged. Thus, there can be only 14 different space lattices. These 14 types of lattices are known as Bravais Lattices. But on the other hand Bravais showed that there are only seven types of crystal systems.
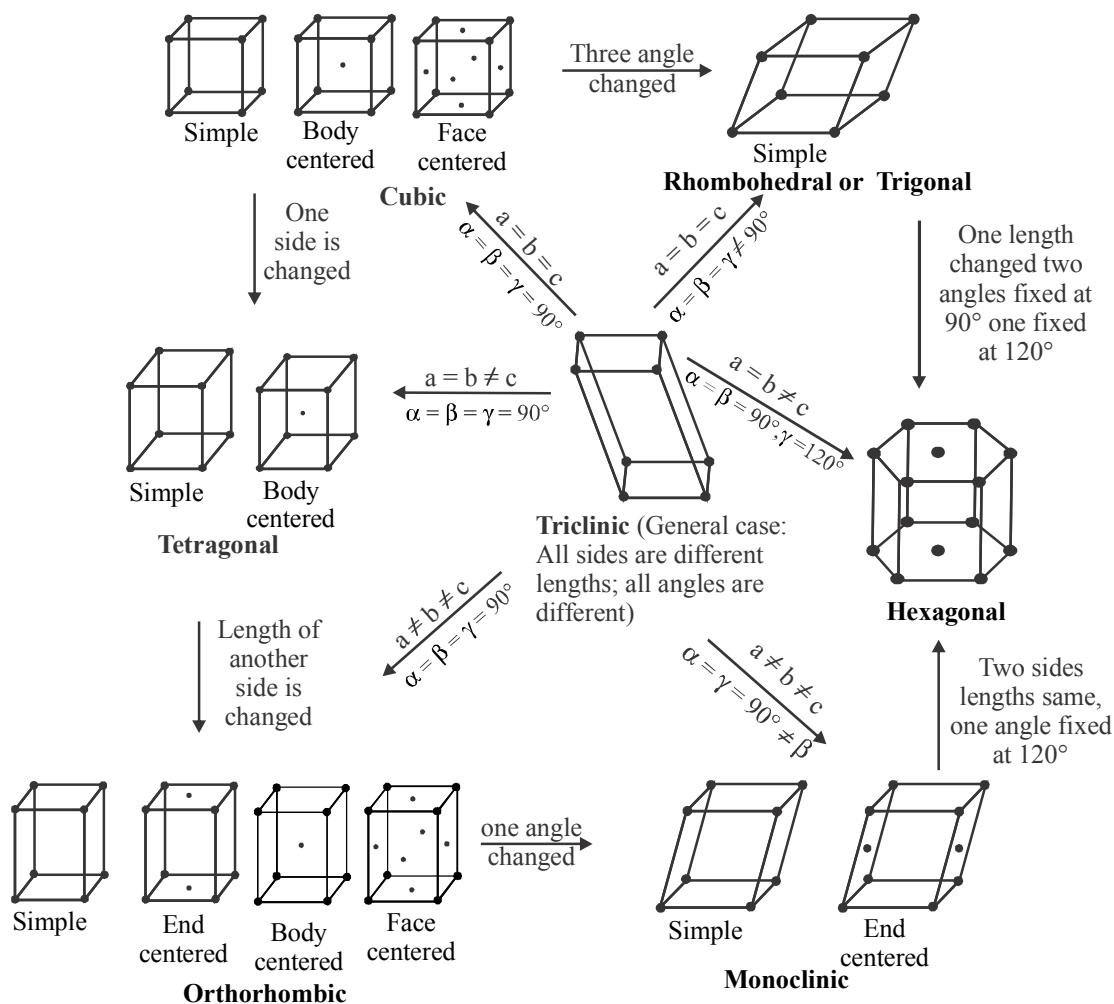
Figure : Bravais lattices

Table : Types (Bravais lattice) of unit cells their edge lengths, angles and example

No.	Crystal system	Type	Edge length	Angle	Example
1	Cubic	Simple/primitive	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Polonium
2	Cubic	Body centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Fe, Rb, Na, Ti, W, U, Zr
3	Cubic	Face centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cu, Al, Ni, Au, Ag, Pt
4	Tetragonal	Primitive	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	SnO_2
5	Tetragonal	Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2, $CaSO_4$
6	Orthorhombic	Primitive	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur
7	Orthorhombic	Body centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3
8	Orthorhombic	Face centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$BaSO_4$
9	Orthorhombic	End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$MgSO_4$, $7H_2O$
10	Monoclinic	Primitive	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Monoclinic sulphur
11	Monoclinic	End centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Na_2SO_4, $10H_2O$
12	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, H_3BO_3
13	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	ZnO, BeO, CoS, SnS, Graphite
14	Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite, $NaNO_3$, $FeCO_3$

Example 3 :

The lattice parameters of a given crystal are a = 5.62 Å, b = 7.41 Å and c = 9.48 Å. The three coordinate axes are mutually perpendicular to each other. The crystal is –
(A) tetragonal   (B) orthorhombic
(C) monoclinic   (D) trigonal

Sol. **(B).** $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ the crystal system is orthorhombic.

**MATHEMATICAL ANALYSIS OF CUBIC SYSTEM (TYPES AND ANALYSIS)**

Simplest crystal is to be studied in cubic system. Three types of cubic systems are following.
(a) **Simple Cubic (SC) :** Atoms are arranged at the corners of the cube.
(b) **Body Centered Cubic (BCC) :** Atoms are arranged at the corners and at the centre of the cube.
(c) **Face Centered Cubic (FCC) :** Atoms are arranged at the corners and at centered of the each faces.
Atomic radius : It is defined as the half of the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.
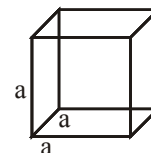
(a) **Simple cubic structure [S.C.]**
Radius of atom 'r' = a/2
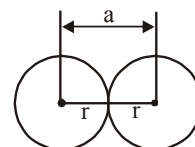
(b) **Face centered cubic structure (fcc)** 'r' = $\dfrac{a}{2\sqrt{2}}$

(c) **Body centered cubic structure (bcc)**

'r' = $\dfrac{\sqrt{3}a}{4}$

$a = b = c$

$\alpha = \beta = \gamma = 90°$

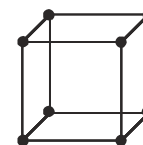

Number of atoms per unit cell / unit cell contents :

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

(a) **Simple cubic structure (sc) :**
∵ Each corner atom is shared by eight surrounding cubes.

Therefore, it contributes for $\dfrac{1}{8}$ of an atom.
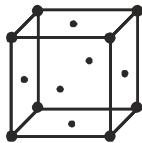
∴ $Z = 8 \times \dfrac{1}{8}$

(b) Face centered cubic structure (fcc) :

(i) The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell.

(ii) Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. Means
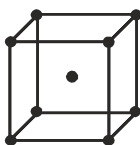
$6 \times \frac{1}{2} = 3$ atom per unit cell.

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

(c) Body centered cubic structure (bcc) :

(i) Eight Corner atoms contribute one atom per unit cell.

(ii) Centre atom contribute one atom per unit cell.

(iii) So, total 1 + 1 = 2 atoms per unit cell.

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

Number of Atoms in Unit Cell

It can be determined by the simplest relation

$$= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$$

where n_c = number of atoms at the corners of the cube

n_f = number of atoms at six faces of the cube

n_i = number of atoms inside the cube

Cubic unit cell	n_c	n_f	n_i	Total atom in per unit cell
1. Simple cubic	8	0	0	1
2. Body centered cubic	8	0	1	2
3. Face centered cubic	8	6	0	4

Co-ordination number (C.N.) :

(a) It is defined as the number of nearest neighbours or touching particles with other particle present in a crystal is called its co-ordination number.

(b) It depends upon structure of the crystal.

(c) For simple cubic system CN = 6.

(d) For bcc CN = 8.

(e) For fcc CN = 12.

Density of lattice matter :

(a) It is defined as the ratio of mass per unit cell to the total volume of unit cell.

(b) Density of lattice matter

$$= \frac{\text{mass per unit cell}}{\text{volume of unit cell}} = \frac{Z \times \text{At. wt.}}{N \times \text{volume of unit cell}}$$

Where Z is the number of atoms per unit cell and N is the Avogadro number.

Packing fraction (P.F.) : It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

(a) Simple cubic unit cell :

Let the radius of atom in packing = r

Atoms are present at the corner of the cube, each of the eight atom present at the eight corners shared amongst eight unit cells. Hence number of atoms per unit cell
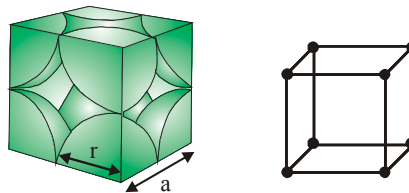
$$= 8 \times (1/8) = 1$$

Figure : Simple cubic cell

Again, $r = \frac{a}{2}$ therefore, P.F. $= \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.52$, % P.F. = 52%,

Void fraction = 1 – packing fraction = 1 – 0.52 = 0.48

(b) Body centered cubic unit cell :
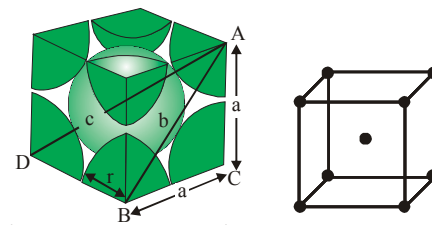
Figure : Body centered unit cell

Number of atoms per unit cell = $8 \times (1/8) + 1 = 2$

$$r = \frac{\sqrt{3}a}{4} \quad ; \quad \text{P.F.} = \frac{2 \times \frac{4}{3}\pi r^3}{(4r/\sqrt{3})^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

% P.F. = 68% ; % of void = 100 – 68 = 32%

(c) Face centered cubic unit cell :

Figure : Face centered cubic unit cell :

Number of atoms per unit cell = 4

$$r = \frac{\sqrt{2}a}{4} \quad ; \quad \text{P.F.} = \frac{4 \times \frac{4}{3}\pi r^3}{(4r/\sqrt{2})^3} = \frac{\sqrt{2}\pi}{6} = 0.74$$

% P.F. = 74% ; % of void = 100 – 74 = 26%

Note : Order of packing fraction : FCC > BCC > SC

IONIC RADII

X-ray diffraction or electron diffraction techniques provides the necessary information regarding unit cell. From the dimensions of the unit cell, it is possible to calculate ionic radii. Let, cube of edge length 'a' having cations and anions say NaCl structure. Then, $r_c + r_a = a/2$, where r_c and r_a are radius of cation and anion.

Radius of Cl⁻

$$= \sqrt{\frac{(a/2)^2 + (a/2)^2}{2}} = \frac{a}{4}$$

For body centered lattice say CsCl.

$$r_c + r_a = \frac{\sqrt{3}a}{2}$$

Limiting Radius Ratio and Structure

Limiting radius ratio $(r+)/(r-)$	C.N.	Shape	Example
0.155 – 0.225	3	Planar triangle	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 0.999	8	Body-centred cubic	CsCl

Example 4 :

A metallic element exists as cubic lattice. Each edge of the unit cell is 2.88 Å. The density of the metal is 7.20 g cm⁻³. How many unit cell will be present in 100 g of the metal.

Sol. The volume of the unit cell $= (2.88 \text{ Å})^3 = 23.9 \times 10^{-24}$ cm³

The volume of 100 g of the metal $= \dfrac{m}{\rho} = \dfrac{100}{7.20} = 13.9$ cm³.

Number of unit cells in this volume

$$= \frac{13.9 \text{ cm}^3}{23.9 \times 10^{-24} \text{ cm}^3} = 5.82 \times 10^{23}$$

Example 5 :

Fraction of total volume occupied by atoms in a simple cube is -

(A) $\dfrac{\pi}{2}$ (B) $\dfrac{\sqrt{3}\pi}{8}$ (C) $\dfrac{\sqrt{2}\pi}{6}$ (D) $\dfrac{\pi}{6}$

Sol. (D). In a simple cubic system, number of atoms

$a = 2r$

∴ Packing fraction

$$= \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

Example 6 :

A compound formed by elements X and Y crystalises in the cubic structure, where Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?

Sol. Y atoms are at the corners of the cubic unit cell and contribution of each is 1/8.
So, the total number of Y atoms per unit cell = 8 × 1/8 = 1.
X atoms are on alternate faces and contribution of each=1/2.
So, the number of X atoms per unit cell is 2 × 1/2 = 1. Hence, the formula is XY.

Example 7 :

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

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

$$\therefore \quad a = \frac{2}{\sqrt{3}} \times 2r = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm} \quad ; \quad M = 23$$

For bcc structure, z = 2 ;

$$d = \frac{z \times M}{a^3 \times N_0} = \frac{2 \times 23}{(422.5 \times 10^{-10}) \times 6.023 \times 10^{23}} = 1.51 \text{g/cm}^3.$$

Example 8 :

Potassium crystallizes in body centered cubic lattice with a unit cell length a = 5.2 Å

(a) What is the distance between nearest neighbours.
(b) What is the distance between next nearest neighbours.
(c) How many nearest neighbours does each K atom have.
(d) How many next nearest neighbours does each K have.
(e) What is calculated density of crystalline K.

Sol. (a) $2r = \dfrac{\sqrt{3}a}{2} = \dfrac{\sqrt{3} \times 5.2}{2} = 4.5$ Å

(b) Distance $= a = 5.2$ Å

(c) 8

(d) 6

(e) $d = \dfrac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92$ g / ml

TRY IT YOURSELF - 1

Q.1 Sodium crystallises in a body centred cubic unit cell with edge length 4.29 Å. What is the radius of the sodium atom?

Q.2 A compound formed by elements A and B crystallises in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centres. What is the formula of the compound ?

(A) AB_3 (B) AB_2
(C) A_2B_3 (D) A_2B

Q.3 Aluminium metal forms a ccp structure. Its atomic radius is 125×10^{-12}m. Calculate the length of the side of unit cell.

Q.4 The radius of A⁺ is 66pm and the radius of B⁻ is 140pm. Predict the probable co-ordination number of A⁺ ions.

(A) 3   (B) 4
(C) 5   (D) 6

Q.5 A unit cell consists of a cube in which B atom are present at each corners and A atoms are present at alternate face centre of the unit cell. Find the simplest formula of the unit cell.

Q.6 A solid AB has ZnS structure. If the radius of cation A is 100pm, what is the radius of anion B ?

Q.7 A compound contains, A, B and C. On crystallization A spheres are present at all corners and B at all face centres except one, the C spheres are present at alternating edge centres. Find out molecular formula of compound.
(A) ABC
(B) $A_2B_5C_2$
(C) AB_5C
(D) A_2B_5C

Q.8 A compound formed by elements X and Y, crystallizes in the cubic structure, where X is at the corners of the cube and Y is at the six face centres. If side length is 5 Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Q.9 What is the two dimensional coordination number of a molecule in square close-packed layer?

Q.10 In a crystalline solid $B^{\ominus}$ forms ccp lattice while $A^{\oplus}$ are present at all edge centre and at body centre. If all the ions along one of the axes passing through face centre are removed, find the formula of the solid.

ANSWERS

(1) 1.86 Å **(2)** (A) **(3)** 354×10^{-12} m
(4) (D) **(5)** AB
(6) between 241.6 pm and 444.4 pm.
(7) (B) **(8)** 4.38 gm/cm^2
(9) 4 **(10)** AB

PACKING OF CONSTITUENTS IN CRYSTALS

In order to understand the packing of the constituent particles in a crystal, it is assumed that these particles are hard spheres of identical size. The packing of these spheres takes place in such a way that they occupy the maximum available space and hence the crystal has maximum density. This type of packing is called close packing. It is of two types :

Close packing in two dimensions : The two possible arrangements of close packing in two dimensions.

Square close packing : In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. Each sphere in this arrangement is in contact with four other spheres.
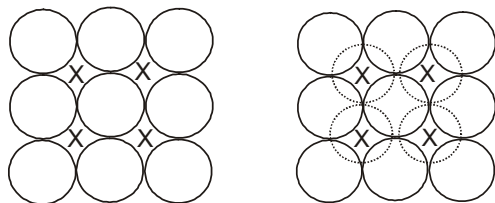
Fig. One and two surfaces of square lattice.

Hexagonal close packing : In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with sphere in first row. The similar pattern is noticed throughout the crystal structure.
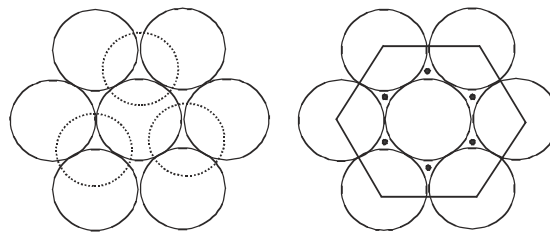
Fig. One and two surfaces of hexagonal lattice.

Comparison between Hexagonal Close Packing and Square Close Packing :

1. Hexagonal close packing is more dense than square close packing.

2. In hexagonal close packing about 60.4% of available space is occupied by spheres. Whereas, square close packing occupies only 52.4% of the space by spheres.

3. In square close packing the vacant spaces (voids) are between four touching spheres, whose centres lie at the corners of a square are called square voids. While in hexagonal close packing the vacant spaces (voids) are between three touching spheres, whose centres lie at the corners of an equilateral triangle are called triangular voids.

Close packing in three dimensions : There are also two different ways to arrange spheres in three dimensional close packing.

Hexagonal close packing : To arrange the spheres vertically above those in the first layer so that each sphere of the third layer lies strictly above a sphere of the first layer. This arrangement if continued indefinitely in the same sequence is represented as AB AB AB ....
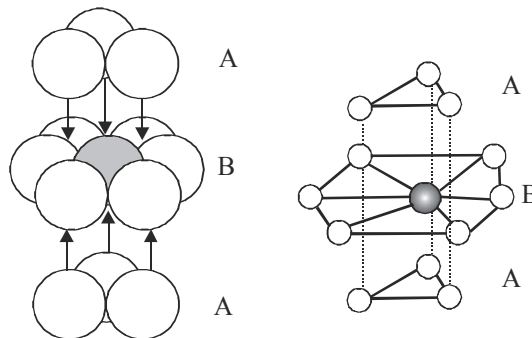
Fig. Hexagonal close packing (HCP) structure.

The arrangement is found to represent hexagonal close packing (hcp) symmetry which means that whole structure possesses one six fold of symmetry.

Hexagonal primitive unit cell : Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be 1/6. Number of atoms per unit cell = 6.
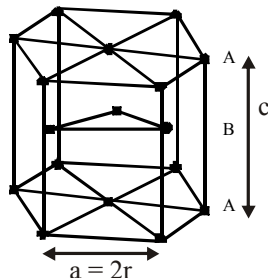
The coordination number of each atom is 12. The fraction of volume of unit cell occupied by the atoms is given by

$$PF = \frac{6 \times \frac{4}{3}\pi r^3}{\text{Area of the base} \times \text{height of unit cell (c)}}$$

Height of the unit cell is given by

$$\frac{c}{2} = \sqrt{(2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2} = \sqrt{\frac{2}{3} \times 4r^2} \qquad \therefore \ c = 4r\sqrt{\frac{2}{3}}$$

Area of the base is calculated by the area of six equilateral triangles.

$$\therefore \ \text{Area of the base} = 6 \times \frac{\sqrt{3}}{4}a^2 = 6 \times \frac{\sqrt{3}}{4}(2r)^2$$

$$\therefore \ PF = \frac{6 \times \frac{4}{3}\pi r^3}{6 \times \frac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{\frac{2}{3}}} = \frac{\sqrt{2}\pi}{6} = 0.74$$

Note :

(i) Effective no. of atoms (Z) = $3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 6$

(ii) Coordination number = 12

Cubic close packing : To arrange the spheres on the other set of hollow marked B. In this way the spheres in fourth layer will correspond with those in the first layer. This arrangement, If continued indefinitely in the same sequence, is represented as ABC ABC ABC .... This arrangement possesses cubic close packing (CCP).
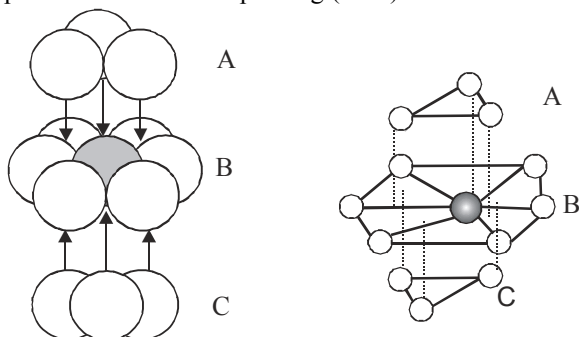
Fig. Cubic close packing (CCP) structure

Packing fraction :

$$P.F. = \frac{4 \times \frac{4}{3}\pi R^3}{4 \times 4 \times 4R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 \ (74\%)$$

NOTE

(i) Effective no. of atoms per unit cell (Z) :

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

(ii) Coordination number, (CN) = 12

Body centred cubic arrangement :
This structure will be obtained if the spheres in first layer (marked A) of cubic closed packing are slightly opened up and thus none of these is in contact with each other. One can put the second layer of the spheres (marked B) on the top of the first layer in such a way that each sphere of the second layer is in contact with four spheres of the layer below it.

Comparison of hcp, ccp, bcc and simple cubic

Property	hcp	ccp	bcc	Simple cubic
Arrangement of packing	Close packed	Close packed	Not close packed	Not close packed
Type of packing	AB AB A...	ABC ABC A...	AB AB A...	AAAA.....
Available space occupied	74%	74%	68%	52%
Coordination number	12	12	8	6
Malleability and ductility	Less malleable, hard, brittle	Malleable and ductile		

GOLDEN TIPS

Table : Crystal structures of some elements

Crystal structure	Examples
BCC	Li, Na, K, Rb, Cs, Ba
HCP	Zn, Mo, Cd, V, Be, Mg
CCP or FCC	Ni, Cu, Ag, Au, Pt

Example 9 :
A metal crystallizes in two cubic phases i.e., FCC and BCC whose unit cell lengths are 3.5Å and 3.0Å respectively. The ratio of their densities is –

(A) 3.12   (B) 2.04
(C) 1.26   (D) 0.2

Sol. (C). $d = \dfrac{ZM}{a^3 N_A}$; $\dfrac{d_1}{d_2} = \dfrac{4}{(3.5)^3} \times \dfrac{(3)^3}{2} = 1.26$

Example 10 :
An fcc lattice has lattice parameter a = 400pm. Calculate the molar volume of the lattice including all the empty space –

(A) 10.8 mL   (B) 96 mL
(C) 8.6 mL   (D) 9.6 mL
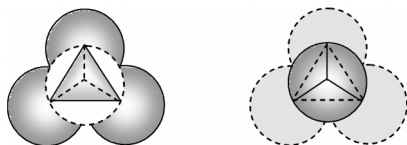
Sol. (D). Volume of 4 atoms = $a^3 = (4 \times 10^{-8})^3$ cm^3.

Volume of N_A atoms

$$= \frac{(4 \times 10^{-8})}{4} \times 6.023 \times 10^{23} = 9.6 \text{ ml}$$

VOID

The empty space in the crystal lattice is called site or void or hole.

Tetrahedral void : A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower layer.
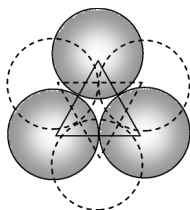

The number of tetrahedral voids is double the number of spheres in the crystal structure.

Radius ratio = $\dfrac{r_{void}}{r_{sphere}} = 0.225$

Octahedral void : This type of void is surrounded by six closely packed spheres, i.e. it is formed by six spheres. The number of octahedral voids is equal to the number of spheres.

Radius ratio = $\dfrac{r_{void}}{r_{sphere}} = 0.414$

Octahedral voids are larger than tetrahedral voids.

Formula of a Compound and Number of Voids Filled:

* In ionic solids, the bigger ions (usually anions) form the close packed structures and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough, then tetrahedral voids are occupied, if bigger, then octahedral voids. Not all octahedral or tetrahedral voids are occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound.
* If anions B form cubic close-packed structures and cations A occupy octahedral voids, then formula will be AB.
* If the anions B form cubic closed lattice and cations A occupy all the tetrahedral voids then formula of compound will be A_2B.
* Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids then the formula of the compound is A_4B_3.

Location of void :

(i) FCC or CCP unit cell :

(a) Tetrahedral void :

* FCC unit cell has 8 tetrahedral void per unit cell. Just below every corner of the unit cell.
* As unit cell has 8 corner that's why FCC unit cell has 8 tetrahedral void per unit cell.

* Distance of tetrahedral void form corner is $\dfrac{\sqrt{3}a}{4}$ and distance between two tetrahedral void is $\dfrac{\sqrt{3}a}{2}$.

* FCC unit cell has 4 body diagonal and each body diagonal contain 2 tetrahedral void that's why total tetrahedral void = 8.

* If a large size cube is divided in 8 minicube than center of each minicube contain one tetrahedral void and distance of center of minicube from corner is $\dfrac{\sqrt{3}a}{4}$.

* For FCC unit cell Z = 4 and tetrahedral void = 8 so tetrahedral void = 2Z.

(b) Octahedral void (OV) :

* Each edge center of FCC unit cell have one octahedral void and body center also contain 1 OV.

* Number of octahedral void per unit cell (Z) = 12 [Edge center] $\times \dfrac{1}{4}$ + 1 [Body center] = 4

* For FCC unit cell (Z) = 4 and octahedral void = 4. So octahedral void = Z.

(ii) Hexagonal close packing (HCP) unit cell :

(a) Tetrahedral void :

* HCP unit cell have total 12 tetrahedral void per unit cell.
* Out of which 8 are completely inside the unit cell and 12 are shared, which are present on edge center and contribution of each sphere present on edge center is 1/3 so, Tetrahedral void (TV) = 8 [Inside body]

$$+ 12 \text{ [Edge center]} \times \frac{1}{3} = 12.$$

For HCP unit cell (Z) = 6
So, tetrahedral void = (Z × 2) = 12

(b) Octahedral void : HCP unit cell have total 6 octahedral void, which are completely inside the unit cell. So octahedral void = 6.

Note :

Unit cell	Z	Tetrahedral void = Z × 2	Octahedral void = Z × 1
CCP (FCC)	4	8	4
HCP	6	12	6

Example 11 :

In a force centred cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?

(A) 0.543   (B) 0.732
(C) 0.414   (D) 0.637

Sol. (A). $\dfrac{r_{tetrahedral}}{r_{octahedral}} = \dfrac{0.225\,R}{0.414\,R} = 0.543$

IONIC COMPOUNDS

* For any ionic solid of the general formula A_xB_y, in which the molar ratio of cation and anion is x : y, the ratio of coordination number of cation to anion would be y : x. Thus using the coordination number ratio of cation and anion, the molar ratio of cation and anion in 1 mole of ionic solid can be obtained, i.e., their general formula can be obtained. The general formula of an ionic structure can also be calculated by finding the number of effective cations and anions per unit cell.

Structure of NaCl – Rock-salt structure (AB type) :

* Chloride ions are considered as having cubic close packed structure.
* Sodium ions occupy octahedral holes.
* There are six octahedral holes around each chloride ion.
* The co-ordination no. of Na^+ & Cl^- is 6 : 6.
* The ionic radii ratio = 0·414 (actual = 0·525).
* The no. of NaCl units per unit cell = 4.

* $r_c + r_a = \dfrac{a}{2}$ where r_c is the radius of Na^+ ion, r_a is the radius of Cl^- ion and 'a' is the edge length of unit cell.
* Alkali metal halides : NaCl, LiCl, KBr, RbI, AgCl, AgBr
* Oxides of alkaline earth metals : MgO, CaO, TiO, FeO, NiO

Cesium chloride structure : (AB Type)

* Cl^- ions are at the corners of a cube whereas Cs^+ ion is at the centre of the cube and vice versa.

○ Cs⁺
● Cl⁻
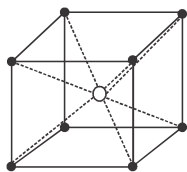
* The co-ordination is 8 : 8
* The radius ratio = 0·93 (actual = 0·732).
* The no. of CsCl units per unit cell is 1. CsBr, CsI also have this structure.
* At 760K CsCl structure changes into NaCl structure.
* The co-ordination no. of ionic solids changes with influencing temperature and pressure.
* High pressure increases the co-ordination number.
*• High temperature decreases the co-ordination number.

* NaCl-type structure $\underset{760\,K}{\overset{Pressure}{\rightleftharpoons}}$ CsCl-type structure
(6 : 6 coordination)   (8 : 8 coordination)

Zinc Blende Structure (Zinc Sulphide) : (AB type)

* Sulphide ions have ccp lattice and zinc ions occupy half of tetrahedral voids.
* Co-ordination is 4 : 4.
* Radius ratio is 0·40 (actual ·225). 4 ions per unit cell.

* $r_c + r_a = \dfrac{\sqrt{3}a}{4}$, where r_c is the radius of Zn^{2+} ion, r_a is the radius of S^{2-} ion and 'a' is the edge length of unit cell.
* CuCl, CuBr, CuI, AgI have this type of structure.

Structure of Calcium fluoride or fluorite : (AB₂ type)

* Ca^{+2} ions have FCC lattice & Fluoride ions occupy all the tetrahedral voids in lattice.
* The co-ordination of calcium and fluoride ions in CaF_2 is 8 : 4. No. of CaF_2 units per cell is 4.

* $r_c + r_a = \dfrac{\sqrt{3}a}{4}$, where r_c is the radius of Ca^{2+} ion, r_a is the radius of F^- ion and 'a' is the edge length of unit cell.
* SrF_2, CdF_2 have the same structure.

Antifluorite structure or structure of Na₂O:

* O^{-2} ions have ccp lattice and Na^+ ions occupy all tetrahedral voids.
* Co-ordination of Na_2O is 4 : 8.
* Li_2O, K_2O, Rb_2O have this type of structure.

Structure of Fe₃O₄ (Magnetite) :

* Fe^{+3} and Fe^{+2} ions are present in the ratio of 2 : 1.
* In Fe_3O_4 oxide ions are arranged in ccp
* Fe^{+2} ions occupy octahedral voids.
* Fe^{+3} ions are distributed equally between octahedral and tetrahedral voids.
* $MgFe_2O_4$ have same structure as Fe_3O_4.

Normal spinel structure : MgAl₂O₄

* AB_2O_4

$A^{+2} = \dfrac{1}{8}$ of tetrahedral voids

$B^{+3} = \dfrac{1}{2}$ of octahedral voids

O^{-2} = FCC packing

* In this mineral oxide ions are arranged in ccp.

* Mg^{+2} ions occupy $\dfrac{1}{8}$ of tetrahedral voids.

* Al^{+3} ions are arranged in a set of $\dfrac{1}{2}$ of octahedral voids.

* Ferrites $(ZnFe_2O_4)$ and magnetite also possess spinel structure.

Inverse spinel structure :

* In an inverse spinel structure, O^{-2} ions form FCC lattice, A^{2+} ions occupy one-eight of the tetrahedral voids and trivalent cation occupies one-eight of the tetrahedral voids and one-four of the octahedral voids.

In inverse spinel structure
* O^{-2} ions = FCC packing

* A^{+2} ions (divalent ions) = $\dfrac{1}{8}$ of tetrahedral voids

* B^{+3} ions (trivalent ions) = $\left(\dfrac{1}{8} \text{ of TV}\right) + \left(\dfrac{1}{4} \text{ of OV}\right)$

Fe_3O_4 has an inverse spinel structure
* O^{-2} = FCC packing = 4

* $Fe^{+2} = \dfrac{1}{8}$ of TV $= \dfrac{1}{8} \times 8 = 1$

* $Fe^{+3} = \left(\dfrac{1}{8} \text{ of TV}\right) + \left(\dfrac{1}{4} \text{ of OV}\right) = 1 + 1 = 2$

  $\therefore$ General formula = $Fe_1^{+2} Fe_2^{+3} O_4^{2-} = Fe_3O_4$

Corundum structure :
* The general formula of compounds crystallizing in corundum structure is A_2O_3.
  The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-third of the octahedral voids are filled with trivalent cations.
  Examples are : Fe_2O_3, Al_2O_3, Mn_2O_3 and Cr_2O_3.

Pervoskite structure (ABO_3) :
* This type of structure is exhibited by $CaTiO_3$ and is a prototype of the ABO_3 type of solids, with A as a divalent cation and B as tetravalent cation.
* The bivalent ions (A^{2+}) are present in primitive cubic lattice with O^{2-} ions on all the face centres.
* A^{2+} and O^{2-} ions in combination form FCC-like structure. The tetravalent cation (B^{4+}) occupy the central octahedral void (in the centre of the unit cell). So, the general formula is ABO_3. Other examples include $BaTiO_3$, $SrTiO_3$ etc.

TRY IT YOURSELF - 2

Q.1 Find out formula of compound having spheres A, B and C. A is present at all corner, B at alternate faces and C at 50% of tetrahedral voids.

Q.2 The compound CuCl has zinc blends (ZnS) fcc structure. Its density is 3.4 g cm^{-3}. What is the length of the edge of the unit cell ?

Q.3 An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3 kg^{-3}, what is the nature of the cubic unit cell?

Q.4 Ferric oxide crystallises in a hexagonal close packed array of oxide ions with 2 out of every 3 octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Q.5 If the radius of the octahedral void is r and radius of the atoms in close packing is R, find relation between r & R.

Q.6 Name the type of structure possessed by a unit cell of CsCl.

Q.7 What is the total number of atoms per unit cells in a face-centred cubic (fcc) structure?

Q.8 An element occurs in the bcc structure with a cell edge of 288pm. The density of the element is 7.2g cm^3. How many atoms of the elements do 208g of the element contian?

ANSWERS

(1) ABC_4.   (2) 578 pm   (3) ccp
(4) Fe_2O_3 (5) r = 0.414 R   (6) bcc
(7) 4   (8) 24.16×10^{23} atoms.

IMPERFECTIONS IN SOLIDS
* Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. Imperfection not only modify the properties of solids but also give rise to new properties.
* If an atom is missing from a lattice site, it creates a vacancy. Due to vacancy, density of the crystal decreases. Due to absence of atoms from lattice sites, the occupancy of the lattice sites decreases and the percentage occupancy of such crystals can be determined as,
  Percentage occupancy

  $= \dfrac{\text{No. of atoms actually present at the lattice site}}{\text{No. of atoms theoretically present at the lattice site assuming no vacancy defect}}$

  $= \dfrac{\text{Observed density}}{\text{Theoretical density}} \times 100$
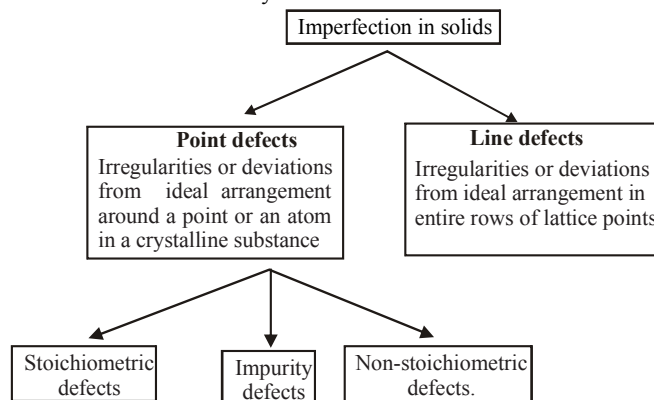
(a) Stoichiometric Defect :
* Defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects.
* These are of two types, vacancy defects and interstitial defects.

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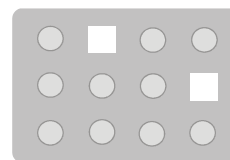
Figure : Vacancy defects

(ii) **Interstitial Defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect . This defect increases the density of the s~~u~~
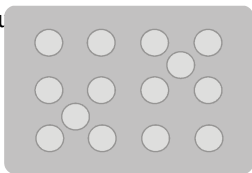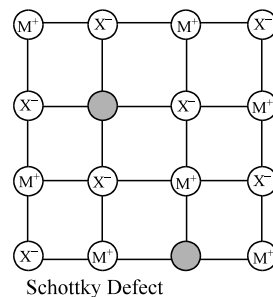

Figure : Interstitial defects

Vacancy and interstitial defects can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and Schottky defects.
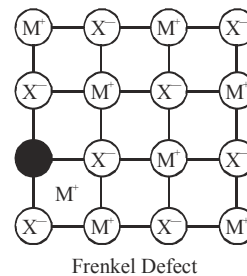
(iii) **Schottky defect :**

* This type of defect is created when same number of positive ion and negative ion are missing from their respective positions leaving behind a pair of holes.
* Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal.
* The presence of large number of schottky defects in crystal results in significant decrease in its density.
  Ex. NaCl, KCl, CsCl, KBr etc.

Schottky Defect

(iv) **Frenkel Defect :**

* This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site.
* Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions.
* Makes solid crystals good conductor.
* In Frenkel defect ions in interstitial sites increases the dielectric constant.
* **Ex.** ZnS, AgCl, AgBr, AgI etc.

Frenkel Defect

Vacancy Defect:	Interstitial Defect	Frenkel defect	Schottky Defect:
(i) Some of the lattice sites are vacant	(i) Some constituent particles (atoms or molecules) occupy an interstitial site	(i) 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.	(i) when same number of positive ion and negative ion are missing from their respective positions leaving behind a pair of holes.
(ii) Density decreases	(ii) Density increases	(ii) Density unchanged.	(ii) Density decreases
(iii) This defect can also develop when a substance is heated.	(iii) Shown by non-ionic solid.	(iii) Shown by ionic substance. for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^{+} ions.	(iii) Shown by ionic substance. Ex. NaCl, KCl, CsCl, KBr etc.

GOLDEN TIPS

* Frenkel defect is also called dislocation defect.
* Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
* Frenkel defect is not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. In AgBr both Schottky and Frenkel defects occur simultaneously.

* Schottky defect is more common in ionic compounds which have high co-ordination number and where the size of positive and negative ions are almost equal.
* Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions.

(b) **Impurity Defects :** If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions.

It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Thus, one can say that these defects arise when foreign atoms are present at the lattice site (in place of lost atoms) or at the vacant interstitial sites.

(c) **Non-Stoichiometric Defects :** There are many compound in which the ratio of positive and negative ions present in the compound differs from that required by ideal formula of the compound. Such compounds are called Non-stoichiometric compounds.

For example, VO_x (Where x can very between 0.6 to 1.3). In these compounds balance of positive and negative charges is maintained by having extra electrons or extra positive charge. So, these defects are of following types:

(i) **Metal Excess Defect :**

Metal excess defects due to anion vacancies

* A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole which is occupied by electron to maintain electrical neutrality.
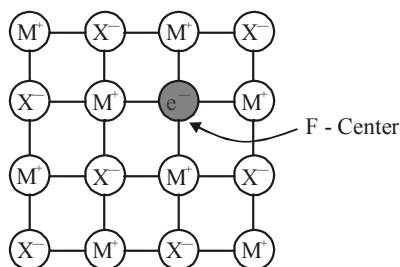
Metal excess defects due to anion vacancies

* The holes occupied by electrons are called **F-centres** (from the German word Farbenzenter for colour centre) and are responsible for the colour of the compound. F-centres are responsible for paramagnetic nature of solids.
* **Ex. :** The excess sodium in NaCl makes the crystal appears yellow. Excess potassium in KCl makes it violet. Excess lithium in LiCl makes it pink. Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky defects.

Metal excess defect due to the presence of extra cations at interstitial sites:

* It may occur if an extra positive ion is present in an interstitial site. Electrically neutrality is maintained by the presence of an electron in the interstitial site.
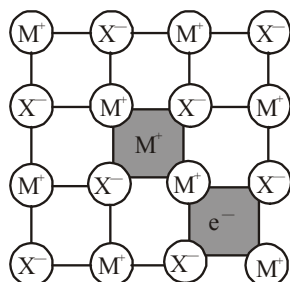

Metal excess defects due to interstitial cation

* This type of defects are exhibited by the crystals which are likely to exhibit "Frenkel defects."
* **Ex.** Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
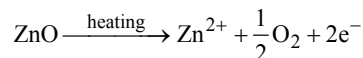
Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) **Metal Deficiency Defect :**

* This defect occurs when the metal shows variable valency i.e., transition metals.
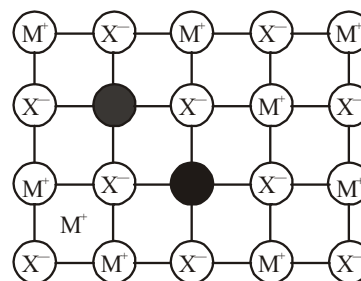
Metal deficiency due to cation vacancies

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

Example 12 :

What is the nature of crystal defect produced when sodium chloride is doped with $MgCl_2$?

Sol. Cation vacancy is created

Example 13 :

Why are Frenkel defects not found in pure alkali halides ?

Sol. Due to appreciable difference between the size of cation and anion, the cation cannot occupy interstitial position.

Example 14 :

In a crystal both ions are missing from normal sites in equal number. This is an example of -
(A) F - centres   (B) Interstitial defect
(C) Frenkel defect   (D) Schotty defect

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

Example 15 :

Frenkel defect is noticed in -
(A) AgBr   (B) ZnS
(C) AgI   (D) All

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

BRAGG'S LAW

In solid crystals, atoms are arranged in fairly regular pattern with interatomic gaps of the order of 0.1 nm. Common salt is an example of a crystalline solid. Almost all the metals at ordinary temperature are crystalline. These metals may act as a natural three-dimensional gratings for the diffraction of X-rays.

X-ray reflection from crystals
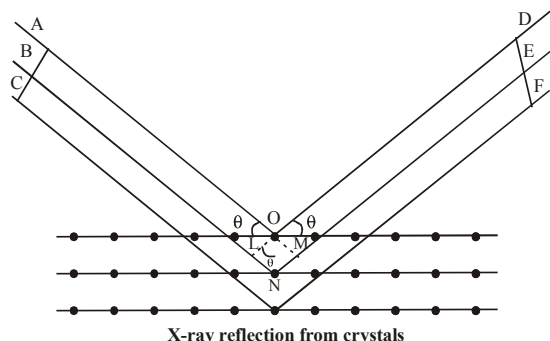
This method is based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes, as represented by the lines XX', YY', ZZ' etc.   **2d sin θ = nλ**
This equation is called **Bragg's equation.**
For monochromatic X - rays, λ is constant and there are some specific angles $\theta_1, \theta_2, \theta_3$......etc, corresponding to n = 1, 2, 3,...... etc, in the above equation. Thus, if the X-rays are incident at one of these, they are reflected ; otherwise they are absorbed. When they are reflected, the laws of reflection are obeyed i.e. (a) the angle of incidence is equal to the angle of reflection and (b) the incident ray, the reflected ray and the normal to the reflecting plane are coplanar.
The interplanar spacing d and several informations about the structure of the solid can be obtained with the help of monochromatic X-ray beam.

Example 16 :
When an electron in an excited Mo atom falls from L to K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64Å. What is the difference in energy between K-shell and L-shell in Mo assuming a first order diffraction. (sin 7.75 = 0.1349)

Sol. $n\lambda = 2d \sin \theta$
$1 \times \lambda = 2d \sin \theta = 2 \times 6.64 \times 10^{-10} \times \sin 7.75$
$\therefore \ \lambda = 7.123 \times 10^{-11}$m

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{7.123 \times 10^{-11}} = 27.88 \times 10^{-16} \text{ J}$$

PROPERTIES OF SOLIDS

Electric Properties : On the basis of electrical conductivity the solids can be broadly classified into the three types:
(a) Metals (conductors) (b) Insulators (c) Semi-conductors.

Electrical conductivity of solids may arise through the motion of electrons and positive holes (electronic conductivity) or through the motion of ions (ionic conductivity). The conduction through electrons is called **n-type conduction** and through positive holes is called **p-type conduction.** Pure ionic solids where conduction can take place only through motion of ions are insulators. However, the presence of defects in the crystal structure increases their conductivity. Unlike metals, the conductivity of semi-conductors and insulators is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections. The conductivity of semiconductors and insulators increases with increase in temperature while that of metals decreases.
The electrical behaviour of some oxides of transition metals:
Electrical Properties of Some Transition Oxides

TiO(M)	VO(M)	MnO(I)	FeO(I)
		CoO(I) NiO(I) CuO(I)	
Ti_2O_3(M-I)	V_2O_3M(I) Cr_2O_3(I)	Mn_2O_3(I)	Fe_2O_3(I)
TiO_2(I)	VO_2(M-I) CrO_2(M)	MnO_2(I)	
	V_2O_5(I)		

M = Metal ; I = Insulator ; M-I = shows a transition from metal to insulator behaviour at a certain temperature.

Example 17 :
Name an element with which silicon can be doped to give an n-type semiconductor.
Sol. Phosphorus

MAGNETIC PROPERTIES

On the basis of magnetic properties, substances are classified into the following three types.
(i) Paramagnetic substances : Substances which are weakly attracted into the magnetic field are called paramagnetic. These substances lose their magnetism on removing the magnetic field. Paramagnetism is caused by the presence of unpaired electrons and since most of the transition metal atoms have unpaired d-electrons, they are paramagnetic in behaviour.
(ii) Diamagnetic substances : Substances which are repelled by magnetic field are called diamagnetic. It is the property of the completely filled electronic subshells.
Since most of the transition metal ions have unpaired d-electrons, they show paramagnetic behaviour. The exceptions are Sc^{3+}, Ti^{4+}, Zn^{2+}, Cu^+, etc. which do not contain any unpaired d-electrons & hence these are diamagnetic. The presence of an unpaired electron in an element causes it to behave like a permanent magnet. As a result of permanent magnet, a paramagnetic substances when placed in an applied magnetic field, takes up a parallel position to the field. It is important to note that diamagnetic substances show a decrease in weight while paramagnetic substances show an increase in weight in presence of a magnetic field.
(iii) Ferromagnetic substances : The substances possessing unpaired electrons are further classified in three different groups based on the alignment of magnetic moments of unpaired electrons.

(a) Ferromagnetic substances : The substances which are strongly attracted by magnetic field are termed as ferromagnetic substances. This type of substance have alignment of all the unpaired electrons in the same direction (orientation) These substances are permanently magnetised i.e. these substances show magnetism even in the absence of magnetic field. Examples are Ni, Fe, Co and CrO_2.

(b) Antiferromagnetic substances : When equal number of unpaired electrons are aligned in opposite directions, their magnetic moment (electron spin) will compensate each other magnetic moment. Such substances are termed as antiferromagnetic substances. For example, MnO, Mn_2O_3 and MnO_2.

(c) Ferrimagnetic substances : When unequal number of unpaired electrons are aligned in opposite directions, the net magnetic moment is not zero. Such substances are termed as ferrimagnetic substances e.g. ferrite Fe_2O_3. It has been observed that the ferro-magnetic, ferrimagnetic and antiferromagnetic substances show paramagnetic nature at higher temperatures. This arises due to randomisation of spins at higher temperature e.g. Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K.

Magnetic Properties of Some Transition Metal Oxides

TiO(p)   VO(p)   MnO(af)   FeO(af)
                        CoO(af)NiO(af) CuO(p)
Ti_2O_3(p) V_2O_3 (af) Cr_2O_3(af) Mn_2O_3(af) Fe_2O_3(af)
Ti_2O_2(p) VO_2(p) CrO_2(f) MnO_2(af) Fe_3O_4(fe)
          V_2O_5(d)

p = paramagnetic ; af = anti-ferromagnetic ;
fe = ferrimagnetic; f = ferromagnetic ; d = diamagnetic.

DIELECTRIC PROPERTIES

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

(i) Piezoelectricity : A dielectric crystal which has a resultant dipole moment can produce electricity or show electrical property when external pressure is applied. Such a crystal is known as piezoelectric crystal and this property is called piezoelectricity. The mechanical stress caused by the applied pressure results in electric current because of the displacement of the ions in the crystals.

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

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

(iii) Ferroelectricity : In certain piezoelectric crystals, the dipoles are permanently polarised even in the absence of applied electric field. However, the direction of polarisation may change on applying current. This phenomenon is known as ferroelectricity and the effect involved is called ferroelectric effect. The examples of some ferroelectric solids are: Potassium dihydrogen phosphate (KH_2PO_4) Potassium tartrate or Rochelle's salt (KOOCCH(OH)CH(OH)COOK) and barium titanate ($BaTiO_2$).

(iv) Anti-ferroelectricity : When the dipoles in alternate lattices point up and down, the two dipoles cancel on another so that there is no resultant dipole moment. Such crystals are known as antiferroelectric crystals and the phenomenon is called antiferroelectricity. For example, lead zirconate ($PbZrO_3$) is an antiferroelectric solid.

TRY IT YOURSELF - 3

Q.1 In a solid lattice the cation has left a lattice site and is located at an interstitial position. Name the lattice defect

Q.2 Calcium crystallizes in a face-centred cubic unit cell with a = 0.556 nm. Calculate the density if it contains 0.1% Schottky defects.

Q.3 Name the type of point defect that occurs in a crystal of zinc sulphide

Q.4 Which point defect may lower the density of an ionic crystal?

Q.5 Name the class of magnetic substances in which the following alignments of magnetic moments holds.

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

Q.6 What other element may be added to silicon to make electrons available for conduction of an electric current?

Q.7 Name a substance which on addition to AgCl causes cation vacancy in it.

Q.8 Name an element with which germanium can be doped to produce an n-type semiconductor.

Q.9 What makes the crystal of KCl appear sometimes violet?

Q.10 Which point defect in crystals of a solid decreases the density of the solid?

ANSWERS

(1) Frenkel defect   **(2)** 1.5439 g/cm^3. **(3)** Frenkel defect
(4) Schottky defect.**(5)** ferrimagnetic **(6)** Phosphorus or Boron
(7) Cadmium or strontium chloride. **(8)** Arsenic.
(9) F centre   **(10)** Vacancy defect

USEFUL TIPS

* The space occupied by hard spheres in fcc and hcp is 74%, in bcc it is 68%, in simple cubic it is 52% and in diamond it is 34%. Thus only fcc and hcp are close packed structures.

* Out of the seven crystal system triclinic is the most unsymmetrical system (a ≠ b ≠ c, α ≠ β ≠ γ ≠ 90°).

* In NaCl crystal, if there are 14 Na^+ ions, then there are 13 Cl^- ions. Out of 14 Na^+ ions, 8 are on the corners and 6 are on the face-centres.Then 12 Cl^- ions are on the edge centres and 1Cl^- at the body-centre. It can be vice-versa also.

* Halides of all alkali metals (except those of Cs) and those of NH_4^+, oxides and sulphides of alkaline earths (except BeS) and halides of silver (except AgI) have rock-salt (NaCl) type structure.

* CsBr, CsI, CsCN, TlCl, TlBr, TlI and TlCN have CsCl structure.
* CuCl, CuBr, CuI, AgI, BeS have zinc blende (ZnS) structure.
* SrCl$_2$, SrF$_2$, BaCl$_2$, BaF$_2$, CdF$_2$, HgF$_2$ have fluorite (CaF$_2$) structure.
* Na$_2$O, K$_2$O, Na$_2$S, K$_2$S have antifluorite (Li$_2$O type) structure.
* BCC is present in all alkali metals.
* All noble gases have ccp structure except. He which has hcp structure.
* The conductivity of insulators is of the order of 10^{-22} ohm^{-1} cm^{-1} whereas conductivity of semiconductors lies in the range 10^{-9} to 10^2 ohm^{-1} cm^{-1}.
* Beryl (Be$_3$Al$_2$Si$_6$O$_{18}$) is a cyclic/ring silicate, pyroxenes and asbestos are chain silicates, clay is a sheet silicate and quartz is a three dimensional silicate.
* TiO$_2$, NaCl and benzene are diamagnetic, Fe, Ni, Co, CrO$_2$ are ferromagnetic, MnO is anti ferromagnetic, ferrites are ferrimagnetic,
* Barium titanate (BaTiO$_3$), sodium potassium tartrate (Rochelle salt) and potassium dihydrogen phosphate (KH$_2$PO$_4$) are ferroelectric solids.
* Lead zirconate (PbZrO$_3$) is an example of anti-ferroelectric crystal.
* Piezoelectric crystals are used as pick ups in record players.
* Amorphous silica is used for making photovoltaic cell (used for converting sunlight into electricity).

ADDITIONAL EXAMPLES

Example 1 :
An element crystallises in a structure having a fcc unit cell of an edge 200 pm. Calculate its density if 200g of this element contains 24×10^{23} atoms ?

Sol. Molar mass = $\dfrac{200}{24 \times 10^{23}} \times 6.023 \times 10^{23} = 50.19$ gm / mol

For FCC, n = 4, V = a^3 ; V = $(200 \times 10^{-10})^3$

Apply crystal density = $\dfrac{n \times M}{V \times N_A}$ = 4.166 gm/cm^3

Example 2 :
Potassium metal crystallizes in a face-centred arrangement of atoms where the edge of the unit cell is 0.574mm. Determine the shortest separation of any two potassium nuclei.

Sol. n = 4, a = 0.574 mm

$$\dfrac{\sqrt{2}a}{2} = \dfrac{4r}{2} \; ; \; 2r = \dfrac{a}{\sqrt{2}} = \dfrac{0.574}{1.414} \text{mm} = 0.4059 \text{ mm}$$

Example 3 :
Sodium crystallises in a body-centred cubic unit cell (bcc) with edge length 4.29 Å. What is the radius of the sodium atom ? What is the length of the body-diagonal of the unit cell

Sol. For a body centred cubic unit cell (bcc)

Radius (r) = $\dfrac{a \times \sqrt{3}}{4} = \dfrac{(4.29\text{Å}) \times 1.732}{4} = 1.86$ Å

Length of the body diagonal = 4r = 4 × 1.86 = 7.44 Å

Example 4 :
Niobium crystallizes in body centred cubic structure. If density is 8.55g cm^{-3}, calculate atomic radius of niobium. (M$_w$ of niobium = 93)

Sol. For bcc, n = 2 ; Mw of niobium = 93

∵ Crystal density = $\dfrac{n \times M_w}{V \times N_A}$ ∴ V = $\dfrac{2 \times 93}{8.55 \times 6.023 \times 10^{23}}$

$= 3.6 \times 10^{-23}$ cm^3

or a^3 = 36×10^{-24} cm^3 ∴ a = 3.3×10^{-24} cm

For bcc, 4r = $\sqrt{3}$a ; r = $\dfrac{1.732 \times 3.3 \times 10^{-8}}{4} = 1.43 \times 10^{-8}$ cm.

Example 5 :
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.

Sol. For fcc, n = 4 ; M$_w$ of Cu = 63.5

∵ Crystal density = $\dfrac{n \times M_w}{V \times N_A}$ = 8.96 g/cm^3

It is agreement with measured value of 8.92 g/cm^3

Example 6 :
Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(a) What is the length of the side of the unit cell ?
(b) How many unit cells are there in 1.00 cm^3 of aluminium?

Sol. For fcc n = 4

(a) 4r = $\sqrt{2}$a ∴ a = $\dfrac{4r}{\sqrt{2}} = \dfrac{4 \times 125 \times 10^{-10}}{1.414} = 3.53 \times 10^{-8}$ cm.

(b) No. of unit cell = Total volume/Volume of a unit cell

$= \dfrac{1.00}{V} = \dfrac{1}{(3.53 \times 10^{-8})^3}$ [V = a^3]

$= 2.27 \times 10^{22}$

Example 7 :
A solid A$^+$B$^-$ has a sodium-chloride-type close-packed structure. If the anion has a radius of 250pm, what should be the radius of the cation? Can a cation C$^+$ having a radius of 180pm be slipped into the tetrahedral site of the crystal A$^+$B$^-$

Sol. As A$^+$B$^-$ has a sodium-chloride-type packing, A$^+$ ions will be present in octahedral voids. The ideal radius of the cation will be equal to the radius of the octahedral void as then the cation will touch the anions and the arrangement will be close packed.

Radius of octahedral void = r_{A^+} = $0.414 \times r_{B^-}$

Therefore, r_{A^+} = 0.414×250 pm = 103.4 pm

The radius of tetrahedral site = $0.225 \times r_{B^-}$

$= 0.225 \times 250$ pm = 56.25 pm

Obviously, cation C$^+$ of 180 pm dimension cannot be slipped into the tetrahedral site.

# QUESTION BANK   CHAPTER 1 : SOLID STATE

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART - 1 : GENERAL CHARACTERISTICS OF SOLID STATE

Q.1 Which of the following statement{s} is not true about the properties of solids?
(A) They are compressible and rigid.
(B) Intermolecular distances are short.
(C) Intermolecular forces are strong.
(D) They have definite shape, volume and mass.

Q.2 Which of the following conditions favours the existence of a substance in the solid state?
(A) High temperature
(B) Low temperature
(C) High thermal energy
(D) Weak cohesive forces

Q.3 ____ tends to keep the solid molecules apart by making them move faster.
(A) Low temperature
(B) Intermolecular forces
(C) Thermal energy
(D) Both (B) and (C)

PART - 2 : AMORPHOUS AND CRYSTALLINE SOLIDS

Q.4 Solids can be classified as
(A) crystalline
(B) amorphous
(C) Both (A) and (B)
(D) Neither (A) nor (B)

Q.5 Which of the following is not a characteristic of a crystalline solid?
(A) Definite and characteristic heat of fusion
(B) Isotropic nature
(C) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
(D) A true solid

Q.6 When cut with a sharp edged tool, crystalline solids split into two pieces and the newly generated surfaces are plain and smooth. This property is known as
(A) anisotropy
(B) isotropy
(C) cleavage property
(D) None of these

Q.7 A crystalline solid have –
(A) Long range order
(B) Short range order
(C) Disordered arrangement
(D) None of these

Q.8 Which one is an example of amorphous solid
(A) Glass
(B) Salt
(C) Cesium chloride
(D) Calcium fluoride

Q.9 Glass is –
(A) Supercooled liquid
(B) Crystalline solid
(C) Amorphous solid
(D) Both (A) and (C)

Q.10 Figure of a solid shows the arrangement of particles. Which is the most appropriate term used for the figure?
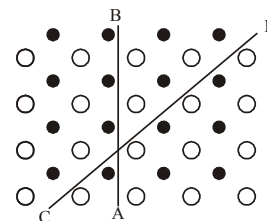
(A) Isotropy
(B) Anisotropy
(C) Irregular shape
(D) Amorphous nature

Q.11 Which of the following statements is not true about amorphous solids?
(A) On heating they may become crystalline at certain temperature.
(B) They may become crystalline on keeping for long time.
(C) Amorphous solids can be moulded by heating.
(D) They are anisotropic in nature.

Q.12 The word 'amorphous' has been derived from greek word.
(A) Amorphos
(B) Amorphous
(C) Omorphos
(D) Omorphous

Q.13 Which of the following is an amorphous solid?
(A) Graphite (C)
(B) Quartz glass (SiO_2)
(C) Chrome alum
(D) Silicon carbide (SiC)

Q.14 Which of the following statement{s} is/are correct?
(A) Crystalline solids have sharp melting points.
(B) Crystalline solids are called true solids.
(C) Amorphous solids have irregular shape.
(D) All of the above

Q.15 Which of the following are the examples of crystalline solid?
(A) NaCl
(B) Quartz
(C) Both (A) and (B)
(D) Neither (A) nor (B)

Q.16 Which of the following is true about the value of refractive index of quartz glass?
(A) Same in all directions
(B) Different in different directions
(C) Cannot be measured
(D) Always zero

Q.17 Some of the physical properties of crystalline solids like refractive index show different values on measuring along different directions in the same crystals. This property is called
(A) isotropy
(B) cleavage property
(C) anisotropy
(D) None of these

PART - 3 : CLASSIFICATION OF CRYSTALLINE SOLIDS

Q.18 Which of the following statements is not correct about molecular crystals?
(A) They are generally soft and easily compressible.

(B) They are good conductors of electricity as the electrons are delocalised in the bonds.
(C) They have low melting and boiling points.
(D) They consist of polar or non-polar molecules.

Q.19 Graphite is a good conductor of electricity due to the presence of –
(A) lone pair of electrons   (B) free valence electrons
(C) cations   (D) anions

Q.20 Iodine crystal are –
(A) Metallic Solid   (B) Ionic solid
(C) Molecular solid   (D) Covalent solid

Q.21 Solid SO_2 and NH_3 are the examples of –
(A) polar molecular solids
(B) non-polar molecular solids
(C) hydrogen bonded molecular solids
(D) None of the above

Q.22 Iodine molecules are held in the crystals lattice by
(A) London forces
(B) dipole-dipole interactions
(C) covalent bonds
(D) coulombic forces

Q.23 Solid X is a very hard solid which is electrical insulator in solid as well as in molten state and has extremely high melting point. Solid X is –
(A) Ionic solid   (B) Covalent solid
(C) Metallic solid   (D) Molecular solid

Q.24 Which of the following is molecular crystal -
(A) Noble gas   (B) Ice
(C) 1 and 2 both   (D) None

Q.25 Graphite **CANNOT** be classified as –
(A) conducting solid   (B) network solid
(C) covalent solid   (D) ionic solid

Q.26 Identify the network solids
(A) I_2 (B) SO_2 (solid)
(C) diamond   (D) H_2O (ice)

Q.27 Ionic solids conduct electricity in molten state but not in solid state because
(A) in molten state free ions are furnished which are not free to move in solid state.
(B) in solid state ionic solids are hard, brittle and become soft in molten state.
(C) all solids conduct electricity in molten state.
(D) in solid state ions are converted to atoms which are insulators.

Q.28 Which of the following cannot be regarded as molecular solid?
(A) AIN   (B) SiC
(C) I_2 (D) Diamond

Q.29 Which of the statement is incorrect? In metallic solids
(A) Positive ions are surrounded by a sea of free electrons.
(B) These electrons are mobile.
(C) Covalent bonds are strong and directional.
(D) These are highly malleable and ductile.

Q.30 Major binding force in diamond, silicon and quartz is
(A) electrostatic force   (B) electrical attraction
(C) covalent bond force   (D) van der Waals forces.

Q.31 Which of the following is not the characteristic of ionic solids?
(A) Very low value of electrical conductivity in the molten state.
(B) Brittle nature
(C) Very strong forces of interactions
(D) Anisotropic nature

Q.32 Iodine molecules are held together in the crystal lattice by –
(A) London forces
(B) dipole-dipole interactions
(C) coulombic forces
(D) covalent bonds

PART - 4 : CRYSTAL LATTICES AND UNIT CELLS

Q.33 How many three dimensional lattices are possible?
(A) 12   (B) 13
(C) 14   (D) 15

Q.34 Monoclinic sulphur is an example of monoclinic crystal system. What are the characteristics of the crystal system?
(A) $a \neq b \neq c, \alpha = \beta = \gamma = 90°$
(B) $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$
(C) $a = b \neq c, \alpha = \beta = \gamma = 90°$
(D) $a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$

Q.35 The lattice parameters of a given crystal are $a = 5.62$ Å, $b = 7.41$ Å and $c = 9.48$ Å. The three coordinate axes are mutually perpendicular to each other. The crystal is –
(A) tetragonal   (B) orthorhombic
(C) monoclinic   (D) trigonal

Q.36 Cinnabar is an example of ____ crystal system.
(A) cubic   (B) monoclinic
(C) trigonal   (D) triclinic

Q.37 Which type of crystals contain more than one Bravais lattice?
(A) Hexagonal   (B) Triclinic
(C) Rhombohedral   (D) Monoclinic

Q.38 When constituent particles are present only on the corner positions of a unit cell, it is called
(A) primitive unit cell
(B) centred unit cell
(C) body-centred unit cell
(D) face-centred unit cell

Q.39 Which of the following primitive cells show the given parameters? $a \neq b \neq c, \alpha = \beta = \gamma = 90°$
(A) Cubic   (B) Tetragonal
(C) Orthorhombic   (D) Hexagonal

Q.40 A unit cell is characterised by
I. its dimensions along the edges, a, b and c.
II. angle(s) between the edges, a, b and c.
(A) Only I   (B) Only II
(C) Both I and II   (D) Neither I nor II

PART - 5 : NUMBER OF ATOMS IN A UNIT CELL

Q.41 In a simple cubic unit cell, each corner atom is shared between ____ unit cells.
(A) 5   (B) 6
(C) 7   (D) 8

Q.42 A crystal is formed by two elements X and Y in cubic structure. X atoms are at the corners of a cube while Y atoms are at the face centre. The formula of the compound will be –
(A) XY   (B) XY_2
(C) X_2Y_3 (D) XY_3

Q.43 In a bcc unit cell ___ atom is present at its body centre.
(A) two   (B) four
(C) three   (D) one

Q.44 How much part of any constituent particle actually belongs to a particular unit cell?
(A) $(1/4)^{th}$ (B) $(1/6)^{th}$
(C) $(1/8)^{th}$ (D) $(1/10)^{th}$

Q.45 I. Space-filling representation of the unit cell depicts the actual particle size.
II. The arrangement of particles is easier to follow in open structures.
Which of these statement(s) is/are true?
(A) Only I   (B) Only II
(C) Both I and II   (D) None of these

PART - 6 : CLOSE PACKED STRUCTURES

Q.46 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

Q.47 Coordination numbers of Cs^+ and Cl^- in CsCl crystal are
(A) 8, 8   (B) 4, 4
(C) 6, 6   (D) 8, 4

Q.48 Hexagonal close packing is found in crystal lattice of
(A) Na   (B) Mg
(C) Al   (D) None

Q.49 Tetrahedral voids are called so because
(A) tetrahedron is formed on joining the centres of the four spheres.
(B) an octahedron is formed.
(C) a trigonal structure is formed.
(D) Either (A) or (B)

Q.50 Number of nearest neighbours of a particle is called its –
(A) coordination number
(B) neighbouring number
(C) Neither (A) nor (B)
(D) None of these

Q.51 In NaCl crystal each Cl^- ion is surrounded by
(A) 4 Na^+ ions   (B) 6 Na^+ ions
(C) 1 Na^+ ion   (D) $2Na^+$ ions

Q.52 Which of the following statements is not true about the voids?
(A) Octahedral void is formed at the centre of six spheres which lie at the apices of a regular octahedron.
(B) There is one octahedral site for each sphere.
(C) There are two tetrahedral sites for each sphere.
(D) Octahedral voids are formed when the triangular voids in second layer exactly overlap with similar voids in the first layer.

Q.53 Name the two types of voids present in a crystal
(A) tetrahedral ; octahedral   (B) hexagonal ; trigonal
(C) diagonal ; octahedral   (D) None of these

Q.54 A metal crystallises into a lattice containing a sequence of layers as AB AB AB .... What percentage of voids are left in the lattice?
(A) 72%   (B) 48%
(C) 26%   (D) 32%

Q.55 In the cubic close packing, the unit cell has
(A) 4 tetrahedral voids each of which is shared by four adjacent unit cells.
(B) 4 tetrahedral voids within the unit cell.
(C) 8 tetrahedral voids each of which is shared by four adjacent unit cells.
(D) 8 tetrahedral voids within the unit cells.

Q.56 In AAA type arrangement, each sphere is in contact with ____ of its neighbours.
(A) two   (B) three
(C) four   (D) five

Q.57 If the number of close packed sphere be N then, the number of octahedral and tetrahedral voids generated are ____ and ____ respectively.
(A) 2N; N   (B) N; 3N
(C) 3N; N   (D) N; 2N

Q.58 In ccp arrangement the pattern of successive layers can be designated as
(A) AB AB AB   (B) ABC ABC ABC
(C) AB ABC AB   (D) ABA ABA ABA

Q.59 The coordination number of Al in the crystalline state of $AlCl_3$ is –
(A) 2   (B) 4
(C) 6   (D) 8

Q.60 The coordination number of metal crystallising in a hexagonal close packing is
(A) 12   (B) 4
(C) 8   (D) 6

Q.61 If the second row is placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. This arrangement is, in general, called
(A) AAA type arrangement   (B) A type arrangement
(C) ABAB type arrangement   (D) B type arrangement

PART - 7 : PACKING EFFICIENCY

Q.62 ___ is the percentage of total space filled by the particles.
(A) Packing efficiency   (B) Interstices
(C) Either (A) or (B)   (D) None of these

Q.63 Copper crystallises in fcc with a unit cell length of 361 pm. What is the radius of copper atom?
(A) 157 pm (B) 181 pm
(C) 127 pm (D) 108 pm

Q.64 Formula for calculating the packing efficiency of simple cubic lattice is

(A) $PE = \dfrac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$

(B) $PE = \dfrac{\text{Volume of two atom}}{\text{Volume of cubic unit cell}} \times 100\%$

(C) $PE = \dfrac{\text{Volume of cubic unit cell}}{\text{Volume of one atom}} \times 100\%$

(D) $PE = \dfrac{\text{Volume of cubic unit cell}}{\text{Volume of two atom}} \times 100\%$

Q.65 Fraction of total volume occupied by atoms in a simple cube is -

(A) $\dfrac{\pi}{2}$ (B) $\dfrac{\sqrt{3}\pi}{8}$ (C) $\dfrac{\sqrt{2}\pi}{6}$ (D) $\dfrac{\pi}{6}$

Q.66 Packing efficiency in bcc structures can be calculated by the formula

(A) $PE = \dfrac{\text{Volume occupied by a sphere in the unit cell}}{\text{Total volume of the unit cell}}\%$

(B) $PE = \dfrac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of unit cell}}\%$

(C) $PE = \dfrac{\text{Volume occupied by three spheres in the unit cell}}{\text{Total volume of the unit sphere}}\%$

(D) $PE = \dfrac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume occupied by the unit cell}}\%$

Q.67 The fraction of the total volume occupied by the atoms present in a simple cube is
(A) $\pi/4$ (B) $\pi/6$
(C) $\pi/3\sqrt{2}$ (D) $\pi/4\sqrt{2}$

Q.68 Packing efficiency of simple cubic lattice is –
(A) 50.4% (B) 52.4%
(C) 54.4% (D) 56.4%

Q.69 In face centred cubic unit cell, edge length is

(A) $4r/\sqrt{3}$ (B) $4r/\sqrt{2}$

(C) $2r$ (D) $\sqrt{3}\, r/2$

PART - 8 : CALCULATIONS INVOLVING UNIT CELL DIMENSIONS

Q.70 How many lithium atoms are present in a unit cell with edge length 3.5 Å and density 0.53 g cm^{-3}? (Atomic mass of Li = 6.94)

(A) 2 (B) 1
(C) 4 (D) 6

Q.71 A metal crystallizes in two cubic phases i.e., FCC and BCC whose unit cell lengths are 3.5Å and 3.0Å respectively. The ratio of their densities is
(A) 3.12 (B) 2.04
(C) 1.26 (D) 0.2

Q.72 Which is the correct expression for the density of the unit cell?

(A) $d = \dfrac{ZM}{a^3 N_A}$ (B) $d = \dfrac{ZN_A}{a^3 M}$ (C) $d = \dfrac{MN_A}{Za^3}$ (D) $d = \dfrac{Ma^3}{ZN_A}$

Q.73 A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?
(A) 3.89 g cm^{-3} (B) 2.16 g cm^{-3}
(C) 3 g cm^{-3} (D) 1.82 g cm^{-3}

PART - 9 : IMPERFECTIONS IN SOLIDS

Q.74 I. A solid consists of an aggregate of large number of small crystals.
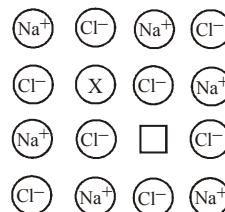II. These small crystals have some defects in them.
III. When crystallisation process occurs at fast or moderate rate, these defects are produced.
Which of the above statement{s} is/are correct?
(A) I and II (B) I and III
(C) II and III (D) I, II and III

Q.75 In the given crystal structure what should be the cation X which replaces Na$^+$ to create a cation vacancy?
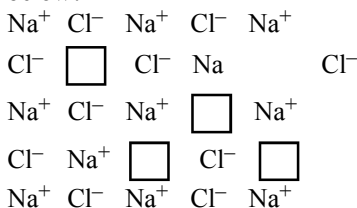

(A) Sr^{2+} (B) K$^+$
(C) Li$^+$ (D) Br$^-$

**Q.76** Metal excess defect and metal deficiency defect are the two types of
(A) stoichiometric defects
(B) impurity defects
(C) non-stoichiometric defects
(D) None of the above

Q.77 What type of crystal defect is shown in the figure given below?

(A) Frenkel defect (B) Schottky defect
(C) Interstitial defect (D) Cation excess defect

Q.78 Find the odd one out
(A) Stoichiometric defects   (B) Interstitial defects
(C) Non-stoichiometric defects   (D) Impurity defects

Q.79 In the following figure, the blank X is known as ____ and why?

A^+ B^- A^+ B^-
B^- A^+ B^- A^+
A^+ X^- A^+ B^-
B^- A^+ B^- A^+
A^+ B^- A^+ B^-
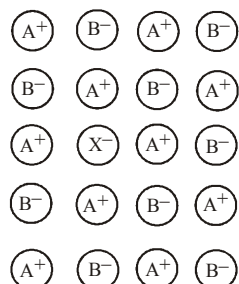
(A) Electron trap, because an electron is present here.
(B) Metal deficient centre, since negative charge is present here.
(C) F-centre, since it imparts colour to the crystal.
(D) F-centre, since it is responsible for positive charge on the crystal.

Q.80 In a Schottky defect,
(A) an ion moves to interstitial position between the lattice points.
(B) electrons are trapped in a lattice site
(C) some lattice sites are vacant
(D) some extra cations are present in interstitial spaces.

Q.81 Which of the following defects is also known as dislocation defect?
(A) Frenkel defect
(B) Schottky defect
(C) Non-stoichiometric defect
(D) Simple interstitial defect

Q.82 ____ and ____ are the two types of main defects.
(A) Vacancy and Schottky
(B) Point and impurity
(C) Point and line
(D) Schottky and Frenkel

Q.83 The anionic sites occupied by unpaired electrons are called F-centres or colour centres. They impart __X__ colour to the crystals of NaCl. Excess of lithium makes LiCl crystals __Y__ and excess of potassium makes KCl crystals __Z__. (X), (Y) and (Z) are –
(A) yellow, green and pink respectively.
(B) pink, yellow and violet (or lilac) respectively.
(C) yellow, pink and violet (or lilac) respectively.
(D) red, yellow and pink respectively.

Q.84 ____ shows both Frenkel and Schottky defects.
(A) AgCl   (B) AgBr
(C) NaCl   (D) NaBr

PART - 10 : ELECTRICAL PROPERTIES

Q.85 Electrical conductivity of semiconductors ____ with rise in temperature.
(A) increases   (B) decreases
(C) (A) or (B)   (D) remains unchanged

Q.86 Three types of bands are shown in the figures given below showing the position of the valence band and conduction band. The figures A, B and C represent –
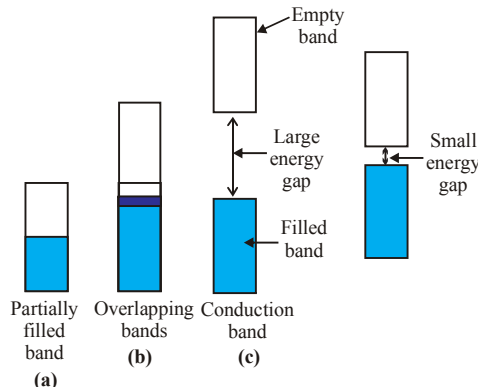
(A) a-Non-metal, b-Metal, c-Semiconductor
(B) a-Semiconductor, b-Insulator, c-Conductor
(C) a-Metal, b-Insulator, c-Semiconductor
(D) a-Insulator, b-Conductor, c-Semiconductor

Q.87 To get a n-type semiconductor from silicon, it should be doped with a substance with valence–
(A) 2   (B) 1
(C) 3   (D) 5

Q.88 Insulators are the solids with very low conductivities ranging between –
(A) 10^4 to $10^7\ \Omega^{-1}\ m^{-1}$ (B) 10^{-20} to $10^{-5}\ \Omega^{-1}\ m^{-1}$
(C) 10^{-20} to $10^{-10}\ \Omega^{-1}\ m^{-1}$ (D) 10^{-6} to $10^5\ \Omega^{-1}\ m^{-1}$

Q.89 Silicon doped with electron-rich impurity forms
(A) p-type semiconductor
(B) n-type semiconductor
(C) intrinsic semiconductor   (D) insulator

Q.90 Which of the following statements is true about semiconductors?
(A) Impurity of lower group creates n-type semiconductors.
(B) Impurity of higher group creates p-type semiconductors.
(C) Extrinsic semiconductors are formed by doping impurity.
(D) Intrinsic semiconductors become conductors when temperature is raised.

Q.91 In case of semiconductors, the gap between the valence band and conduction band is –
(A) large   (B) small
(C) Either (A) or (B)   (D) None of these

PART - 11 : MAGNETIC PROPERTIES

Q.92 Magnetic moment originates from
I. its orbital motion around the nucleus.
II. its spin around its own axis.
Which of the above fact(s) is/are true?
(A) Only I   (B) Only II
(C) Both I and II   (D) Neither I nor II

Q.93 Match the column I with column II and mark the appropriate choice.

Column I	Column II
(a) Ferromagnetic	(i) ↑↑↓↑↑↓↑↑
(b) Ferrimagnetic	(ii) ↑↓↑↓↑↓↑↓
(c) Antiferromagnetic	(iii) ↑↑↑↑↑↑↑↑
(d) Diamagnetic	(iv) ⇅ ⇅ ⇅ ⇅ ⇅
(e) Paramagnetic	(v) ↖ ↙ → ↑ ↘ ↗

(A) (a) – (iii), (b) – (i), (c) – (ii), (d)– (iv), e–(v)

(B) (a) – (i), (b) – (ii), (c) – (iii), (d) –(iv), e–(v)

(C) (a) – (iv), (b) – (i), (c) – (iii), (d)–(ii), e– (v)

(D) (a) – (v), (b) – (iv), (c) – (iii), (d)–(ii), e– (i)

Q.94 Which of the following represents correct order conductivity in solids?

(A) $K_{metals} >> K_{insulators} < K_{semiconductors}$

(B) $K_{metals} << K_{insulators} < K_{semiconductors}$

(C) $K_{metals} < K_{semiconductors} > K_{insulators}$ = zero

(D) $K_{metals} < K_{semiconductors} > K_{insulators}$ ≠ zero

Q.95 Which of the following statements is not true?

(A) Paramagnetic substances are weakly attracted by magnetic field.

(B) Ferromagnetic substances cannot be magnetised permanently.

(C) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.

(D) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.

Q.96 The value of Bohr magneton, μ_B is

(A) $9.27 \times 10^{-24}\,Am^2$ (B) $9.27 \times 10^{-22}\,Am^2$

(C) $11.27 \times 10^{-22}\,Am^2$ (D) $11.27 \times 10^{-24}\,Am^2$

Q.97 A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because

(A) all the domains get oriented in the direction of magnetic field.

(B) all the domains get oriented in the direction. opposite to the direction of magnetic field.

(C) domains get oriented randomly.

(D) domains are not affected by magnetic field.

Q.98 Those substances which show permanent magnetism even in the absence of magnetic field are called –

(A) ferrimagnetic (B) ferromagnetic

(C) diamagnetic (D) paramagnetic

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 What is the necessary condition for the existence of solids?

(A) Intermolecular forces should be weaker than thermal energy.

(B) Intermolecular forces should be stronger than thermal energy.

(C) Intermolecular forces should be equal to the thermal energy.

(D) No definite relationship between them.

Q.2 I. Packing efficiency of bcc structure is 74%.
II. Packing efficiency of hcp structure is 68%.
Which of the above statement(s) is/are correct?

(A) Only I (B) Only II

(C) Both I and II (D) Neither I nor II

Q.3 Which oxides behaves as conductor or insulator depending upon temperature?

(A) TiO (B) SiO_2

(C) TiO_3 (D) MgO

Q.4 Pure silicon and germanium behave as –

(A) conductors (B) semiconductors

(C) insulators (D) piezoelectric crystals

Q.5 Number of atoms per unit cell of bcc is –

(A) 1 (B) 2

(C) 8 (D) 4

Q.6 A cubic solid is made up of two elements P and Q. Atoms of P are present at the corners of the cube and atoms of Q are present at body centre. What is the formula of the compound & what are coordination numbers of P and Q

(A) PQ_2, 6 : 6 (B) PQ, 6 : 6

(C) P_2Q, 6 : 8 (D) PQ, 8 : 8

Q.7 Consider the following characteristic of a crystal lattice.

I. Each point in a lattice is called lattice point.

II. Each point in a lattice represents one constituent particle (atom, molecule or ion).

III. Lattice points are joined by straight lines to bring out the geometry of the lattice.

Which of the above statement(s) is/are true?

(A) I and II (B) II and III

(C) I and III (D) I, II and III

Q.8 A crystal lattice with alternative +ve and -ve ions has radius ratio 0.524. The coordination number of lattice is

(A) 4 (B) 6

(C) 8 (D) 12

Q.9 Examples of few solids are given below. Find out the example which is not correctly matched.

(A) Ionic solids - NaCl, ZnS

(B) Covalent solids - H_2, I_2

(C) Molecular solids - $H_2O(s)$

(D) Metallic solids - Cu, Sn

Q.10 Which of the following crystals does not exhibit Frenkel defect?

(A) AgBr (B) AgCl

(C) KBr (D) ZnS

Q.11 Match the column I with column II and mark the appropriate choice.

Column I	Column II
(a) Fe in solid state	(i) Electrolytic conductor
(b) NaCl in molten state	(ii) p-type semiconductor
(c) CO_2 in solid state	(iii) Electronic conductor
(d) Si doped with aluminium	(iv) Non-polar insulator

(A) (a) – (iv), (b) – (ii), (c) – (i), (d) – (iii)

(B) (a) – (ii), (b) – (iii), (c) – (i), (d) – (iv)

(C) (a) – (iii), (b) – (i), (c) – (iv), (d) – (ii)

(D) (a) – (i), (b) – (iv), (c) – (iii), (d) – (ii)

Q.12 The percentage of empty space in a body centred cubic arrangement is –
(A) 74 (B) 68
(C) 32 (D) 26

Q.13
I. NaCl and KCl show metal excess defect due to anionic vacancies.
II. F-centres are the anionic sites occupied by unpaired electrons.
III. F-centres is derived from the German word 'Farbenzenter' for colour centre.
IV. F-centres impart yellow colour to the NaCl crystals.
Which of the above statement{s} is/are correct?
(A) II, III, IV (B) I, III, IV
(C) I, II, III (D) All of these

Q.14 Which type of semiconductor is formed when germanium is doped in the gallium as indicated in the figure?

Ge Ge Ge Ge

Ge Ge (Ga) Ge

Ge Ge Ge Ge
Ge Ge Ge Ge

(A) p-type semiconductor
(B) n-type semiconductor
(C) No change in conductivity
(D) It becomes superconductor.

Q.15 What is the coordination number in a square close packed structure in two dimensions?
(A) 2 (B) 3
(C) 4 (D) 6

Q.16 Consider the following statement(s).
I. Diode is a combination of n-type and p-type semiconductors.
II. Diode is used as rectifier.
III. n-p-n and p-n-p are the types of rectifier.
IV. n-p-n and p-n-p are used to detect or amplify radio or audio signals.
Identify the correct ones.
(A) I, II and III (B) I, II and IV
(C) II, III and IV (D) I, II, III and IV

Q.17 Which of the following statements is not correct regarding diamond and graphite?
(A) In diamond, each carbon atom is covalently bonded to four other carbon atoms.
(B) In graphite, each carbon atom is covalently bonded to three other carbon atoms in the same plane.
(C) The C – C bond length in graphite is intermediate between single and double bond distance.
(D) Diamond is a layered structure, the two layers joined by van der Waals' forces.

Q.18 In a face centre cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face-centred points, the formula of the compound is –
(A) A_2B (B) AB_2
(C) A_2B_2 (D) A_2B_5

Q.19 Which of the following is not true about the ionic solids?
(A) Bigger ions form the close packed structure.

(B) Smaller ions occupy either the tetrahedral or octahedral voids depending upon their size.
(C) Occupation of all the voids is not necessary.
(D) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.

Q.20 The radii of Na^+ and Cl^- ions are 95 pm and 181 pm respectively. The edge length of NaCl unit cell is –
(A) 276 pm (B) 138 pm
(C) 552 pm (D) 415 pm

Q.21 An element with atomic mass 100 has a bcc structure and edge length 400 pm. The density of element is
(A) $10.37\ g\ cm^{-3}$ (B) $5.19\ g\ cm^{-3}$
(C) $7.29\ g\ cm^{-3}$ (D) $2.14\ g\ cm^{-3}$

Q.22 Total volume of atoms present in a fcc unit cell of a metal with radius r is
(A) $(12/3)\,\pi r^3$ (B) $(16/3)\,\pi r^3$
(C) $(20/3)\,\pi r^3$ (D) $(24/3)\,\pi r^3$

Q.23 Consider the following statements regarding ferromagnetism.
I. In solid, metal ions of such substances are grouped together in domains.
II. Each domain acts as a tiny magnet.
III. In the absence of magnetic field, these domains are randomly oriented whereas in magnetic field, these get oriented in the direction of the magnetic field.
IV. This ordered arrangement persist even after the removal of magnetic field.
V. These substances act as permanent magnet.
Which of the above statement(s) is/are true?
(A) I, III and IV (B) II, IV and V
(C) I, IV and V (D) All of these

Q.24 The lattice site in a pure crystal cannot be occupied by
(A) molecule (B) ion
(C) electron (D) atom

Q.25 If three elements X, Y and Z crystallise in a ccp lattice with X atoms at the corners, Y atoms at the cube centre and Z atoms at the edges, the formula of the compound will be –
(A) XYZ (B) XYZ_2
(C) XYZ_3 (D) X_2Y_2Z

Q.26 An element crystallises in a structure having a fcc unit cell of an edge 200 pm. If 200 g of this element contains 24×10^{23} atoms then its density
(A) $41.66\ g\ cm^{-3}$ (B) $313.9\ g\ cm^{-3}$
(C) $8.117\ g\ cm^{-3}$ (D) $400\ g\ cm^{-3}$

Q.27
I. Deviations from ideal arrangement in entire rows of lattice points are called point defects.
II. Deviations from ideal arrangement around a point or an atom in crystalline substance are called line defects.
III. These irregularities are called crystal defects.
Which of these statement (s) is/are correct?
(A) I and II (B) II and III
(C) Only I (D) Only III

Q.28 In zinc blende structure,
(A) zinc ions occupy half of the tetrahedral sites.
(B) each Zn^{2+} ion is surrounded by six sulphide ion.
(C) each S^{2-} ion is surrounded by six Zn^{2+} ions
(D) it has fcc structure.

Q.29 Fe_3O_4 is ferrimagnetic at room temperature but at 850 K, it becomes –
(A) diamagnetic   (B) ferrimagnetic
(C) paramagnetic   (D) anti-ferromagnetic.

Q.30 Which of the following statement is false?
(A) Non-polar molecular solids are formed by non-polar covalent bonds.
(B) In these solids, the atoms or molecules are held by weak dispersion forces or London forces.
(C) These solids are soft and non-conductors of electricity.
(D) HCl, SO_2 are formed by non-polar covalent bonds.

Q.31 The radii of Na^+ and Cl^- ions are 95 pm and 181pm respectively. The edge length of NaCl unit cell is
(A) 276 pm   (B) 138 pm
(C) 552 pm   (D) 415 pm

Q.32 Zinc oxide loses oxygen on heating according to reaction,

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

It becomes yellow on heating because
(A) Zn^{2+} ions and electrons move to interstitial sites and F-centres are created
(B) oxygen and electrons move out of the crystal and ions become yellow.
(C) Zn^{2+} again combine with oxygen to give yellow oxide.
(D) Zn^{2+} are replaced by oxygen.

Q.33 The sharp melting point of crystalline solids is due to __
(A) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.
(B) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.
(C) same arrangement of constituent particles in different directions.
(D) different arrangement of constituent particles in different directions.

Q.34 Ferrimagnetism is observed when the magnetic moments of the domains in the substance are –
(A) oppositely oriented and cancel each other's magnetic moment.
(B) aligned in parallel and anti-parallel directions in unequal numbers.
(C) randomly oriented and their magnetic moments get cancelled.
(D) in same direction and get aligned in a magnetic field.

Q.35 A crystalline structure has radius ratio (r_{c^+} / r_{a^-}) in the range of 0.225 – 0.414. The coordination number and arrangement of anions around the cations are –
(A) 3, plane triangular   (B) 6, octahedral
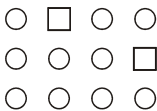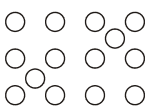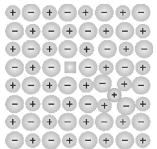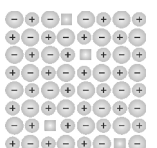(C) 4, tetrahedral   (D) 8, cubic

Q.36 In the table given below, dimensions and angles of various crystals are given. Complete the table by filling the blanks.

S.N.	Type of crystal	Dimensions	Angles
1	Cubic	a = b = c	$\alpha = \beta = \gamma = p$
2	Tetragonal	q	$\alpha = \beta = \gamma = 90°$
3	Orthorhombic	$a \neq b \neq c$	r
4	Hexagonal	s	$\alpha = \beta = 90°$, $\gamma = t$

(A) p - 90° ; q - a = b ≠ c ; r - $\alpha = \beta = \gamma = 90°$ s - a = b ≠ c, t - 120°
(B) p - 120° ; q - a = b = c ; r - $\alpha = 90°$, $\beta = \gamma = 120°$; s - a ≠ b ≠ c, t - 90°
(C) p - 90° ; q - a ≠ b = c ; r - $\alpha = \beta = \gamma = 120°$ s - a ≠ b ≠ c, t - 90°
(D) p - 120° ; q - a ≠ b ≠ c ; r - $\alpha \neq \beta \neq \gamma \neq 90°$ s - a ≠ b = c, t - 120°

Q.37 The conductivity of intrinsic semiconductors can be increased by adding a suitable impurity. This process is called (P). This can be done with an impurity which is (Q) rich or deficient as compared to the semiconductor. Such impurities introduce (R) defects in them. Electron rich impurities result in (S) type semiconductors while electron deficit impurities result in (T) type semiconductors.
(A) P-doping, Q-proton, R-point, S-p, T-n
(B) P-doping, Q-electron, R-non-stoichiometric, S-p,T-n
(C) P-energy gap, Q-charged, R-impurity, S-n, T-p
(D) P-doping, Q-electron, R-electronic, S-n,T-p

Q.38 The number of atoms contained in a fcc unit cell of a mono atomic substance is –
(A) 1   (B) 2
(C) 4   (D) 6

Q.39 Mark the incorrect pair from the following.
(A) Schottky defect - Equal number of cations and anions are missing.
(B) Frenkel defect - Dislocation of cation from its normal site to an interstitial site.
(C) Impurity defect - $CdCl_2$ in AgCl crystal to create cationic vacancy.
(D) Metal excess defect - $Fe_{0.93}O$

Q.40 I.   As regards dielectric properties, barium titanate is ferroelectric
II. As regards magnetic behaviour, magnetite is ferromagnetic.
III. Antiferromagnetic substances have maximum magnetic moment.
IV. Paramagnetic substances lose their magnetism in the absence of a magnetic field.
Which of the above statement(s) is/are correct?
(A) I, II and III   (B) I, II and IV
(C) II, III and IV   (D) I, III and IV

Q.41 Match the Column I and Column II.

Column I		Column II
a.		1. Frenkel defects
b.		2. Interstitial defects
c.		3. Vacancy defects
d.		4. Schottky defects

Codes
(A) (a) – (1), (b) – (2), (c) – (3), (d) – (4)
(B) (a) – (4), (b) – (3), (c) – (2), (d) – (1)
(C) (a) – (3), (b) – (2), (c) – (1), (d) – (4)
(D) (a) – (4), (b) – (2), (c) – (3), (d) – (1)

Q.42 For the structure shown the site marked as S is a –
(A) tetrahedral void
(B) cubic void
(C) octahedral void
(D) none of these

Q.43 Generally, photovoltaic cells
(A) convert sunlight into electricity.
(B) convert wind power into electricity.
(C) amorphous silicon is not a photovoltaic cell.
(D) quartz glass is not photovoltaic cell.

Q.44 Cations are present in the interstitial sites in –
(A) Frenkel defect   (B) Schottky defect
(C) vacancy defect   (D) metal deficiency defect

Q.45 Schottky defect is observed in crystals when –
(A) some cations move from their lattice site to interstitial sites.
(B) equal number of cations and anions are missing from the lattice.
(C) some lattice sites are occupied by electrons.
(D) some impurity is present in the lattice.

Q.46 Consider the following statements,
I. When Si is doped with P or As, four electrons of both Si and P or As are involved in covalent bond formation.
II. The fifth electron of Si is delocalised.
III. Delocalisation increases the conductivity of doped Si.
Which of these statement(s) is/are correct?
(A) I and III   (B) II and III
(C) I and II   (D) I, II and III

Q.47 Silver halides generally show
(A) Schottky defect
(B) Frenkel defect
(C) both Frenkel and Schottky defects
(D) cation excess defect.

Q.48 NaCl type crystal (with coordination no. 6 : 6) can be converted into CsCl type crystal (with coordination no. 8 : 8) by applying
(A) high temperature
(B) high pressure
(C) high temperature and high pressure
(D) low temperature and low pressure.

Q.49 Which of the following structures is not correctly matched?
(A) NaCl type –Cl^- ions in ccp structure. Na^+ ions in half octahedral holes.
(B) ZnS type – S^{2-} ions in ccp structure. Zn^{2+} ions in alternate tetrahedral voids.
(C) CaF_2 type -Ca^{2+} ions in ccp structure. F^- ions in all tetrahedral voids.
(D) Na_2O type-O^{2-} ions in ccp structure. Na^+ ions in all tetrahedral holes.

Q.50 Amorphous solids have
I. short range order.
II. structure similar to that of liquids.
III. no definite heat of fusion.
IV. glass, quartz and quartz glass are examples of amorphous solids.
Which of the above statement{s) is/are true?
(A) I, II and III   (B) II, III and IV
(C) I, III and IV   (D) I, II, III and IV
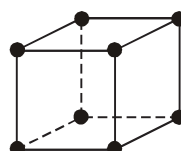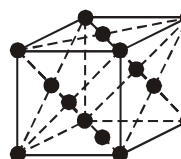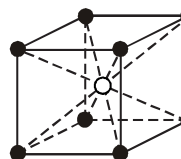
Q.51 Match the following Columns.

Column I (Open structures)		Column II (Unit cells)
a.		1. Face-centred cubic unit cell
b.		2. Primitive cubic unit cell
c.		3. Body-centred cubic unit cell

Codes
(A) (a) – (1), (b) – (2), (c) – (3)
(B) (a) – (3), (b) – (1), (c) – (2)
(C) (a) – (2), (b) – (3), (c) – (1)
(D) (a) – (2), (b) – (1), (c) – (3)

Q.52 Alkali halides do not show Frenkel defect because
(A) cations and anions have almost equal size.
(B) there is a large difference in size of cations and anions.
(C) cations and anions have low coordination number.
(D) anions cannot be accommodated in voids.

Q.53 I. Crystalline solids have definite heat of fusion whereas amorphous solids lack it.
II. Crystalline solids have definite geometrical shape whereas amorphous solids have no definite shape.
III. Crystalline solids are anisotropic whereas amorphous solids are isotropic.
IV. Crystalline solids do not have sharp melting point whereas amorphous solids have sharp melting point.
The correct statement{s} is/are
(A) I, II, IV   (B) I, II, III
(C) II, III, IV   (D) I, II, III, IV

Q.54 A unit cell of $BaCl_2$ (fluorite structure) is made up of –
(A) four Ba^{2+} ions and four Cl^- ions
(B) four Ba^{2+} ions and eight Cl^- ions
(C) eight Ba^{2+} ions and four Cl^- ions
(D) four Ba^{2+} ions and six Cl^- ions.

Q.55 Diamagnetic substances are –
I. weakly repelled by a magnetic field.
II. weakly magnetised in a magnetic field in opposite direction.
III. those which have no unpaired electron.
IV. pairing of electrons cancels their magnetic moment.
Which of the above statement(s) is incorrect?
(A) Only I   (B) Only II
(C) Only III   (D) None of these

Q.56 Which of the following statements is not true?
(A) Silicon carbide is a covalent crystal.
(B) Molecular crystals are soft in nature.
(C) In calcium fluoride structure, coordination number of Ca^{2+} is 4.
(D) Increase in radius ratio results in increase in coordination number.

Q.57 A metal X crystallises in a face-centred cubic arrangement with the edge length 862 pm. What is the shortest separation of any two nuclei of the atom?
(A) 406 pm   (B) 707 pm
(C) 862 pm   (D) 609.6 pm

Q.58 Match the following Columns.

Column I (Cubic system)	Column II (Examples)
a. Cubic	1. $K_2Cr_2O_7$
b. Triclinic	2. NaCl
c. Tetragonal	3. ZnO
d. Hexagonal	4. TiO_2

Codes
(A) (a) – (4), (b) – (3), (c) – (2), (d) – (1)
(B) (a) – (2), (b) – (1), (c) – (4), (d) – (3)
(C) (a) – (3), (b) – (2), (c) – (1), (d) – (4)
(D) (a) – (1), (b) – (4), (c) – (3), (d) – (2)

Q.59 I. Total number of atoms per unit cell is 2 for a bcc unit cell.
II. In a fcc unit cell, total number of atoms per unit cell is 4.
Which of the above statement(s) is/are correct?
(A) Only II   (B) Only I
(C) Both I and II   (D) Neither I nor II

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 The coordination number of a metal crystallizing in a , hexagonal close-packed structure is

Q.2 The number of hexagonal faces that are present in a truncated octahedron is

Q.3 A crystalline solid of a pure substance has a face – centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3}, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is _____.

Q.4 If in diamond, there is a unit cell of carbon atoms as fcc and if carbon atom is sp^3, what will be the number of carbon atoms per unit cell ?

Q.5 A crystal formula AB_3 has A ions at the cube corners and B ions at the edge centres. The coordination numbers of
A + B is –

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

Q.1 The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively - **[AIEEE-2002]**
(A) 8, 10 (B) 2, 4
(C) 1, 2 (D) 1, 3

Q.2 How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g ?
[Atomic masses Na = 23, Cl = 35.5] **[AIEEE-2003]**
(A) 1.28×10^{21} unit cells (B) 1.71×10^{21} unit cells
(C) 2.57×10^{21} unit cells (D) 5.14×10^{21} unit cells

Q.3 What type of crystal defect is indicated in the diagram below ? **[AIEEE-2004]**

$Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-$
$Cl^- \square Cl^- Na^+ \square Na^+$
$Na^+ Cl^- \square Cl^- Na^+ Cl^-$
$Cl^- Na^+ Cl^- Na^+ \square Na^+$

(A) Frenkel defect
(B) Schottky defect
(C) Interstitial defect
(D) Frenkel & Schottky defects.

Q.4 An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be – **[AIEEE-2005]**
(A) A_2B (C) AB
(C) A_3B (D) AB_3

Q.5 Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) **[AIEEE 2006]**
(A) $\frac{24}{3}\pi r^3$ (B) $\frac{12}{3}\pi r^3$ (C) $\frac{16}{3}\pi r^3$ (D) $\frac{20}{3}\pi r^3$

Q.6 In a compound, atoms of element Y form ccp lattice and those of element X occupy $2/3^{rd}$ of tetrahedral voids. The formula of the compound will be - **[AIEEE 2008]**
(A) X_2Y_3 (B) X_2Y
(C) X_3Y_4 (D) X_4Y_3

Q.7 Copper crystallises in fcc with a unity cell length of 361pm. What is the radius of copper atom ?
[AIEEE-2009]
(A) 108 pm (B) 127 pm
(C) 157 pm (D) 181 pm

Q.8 The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is – **[AIEEE 2010]**
(A) 288 pm (B) 398 pm
(C) 618 pm (D) 144 pm

Q.9 Percentage of free space in cubic close packed structure and in body centred packed structure are respectively
[AIEEE 2010]
(A) 30% and 26% (B) 26% and 32%
(C) 32% and 48% (D) 48% and 26%

Q.10 In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is : **[AIEEE 2011]**
(A) A_2B (B) AB_2
(C) A_2B_3 (D) A_2B_5

Q.11 Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be **[AIEEE 2012]**
(A) 75 pm (B) 300 pm
(C) 240 pm (D) 152 pm

Q.12 Which of the following exists as covalent crystals in the solid state ? **[JEE MAIN 2013]**
(A) Iodine (B) Silicon
(C) Sulphur (D) Phosphorus

Q.13 Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be –
[JEE MAIN 2013]
(A) 7.01% (B) 4.08%
(C) 6.05% (D) 5.08%

Q.14 CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? **[JEE MAIN 2014]**

(A) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (B) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

(C) $r_{Cs^+} + r_{Cl^-} = 3a$ (D) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

Q.15 Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately – **[JEE MAIN 2015]**
(A) 3.22 Å (B) 5.72 Å
(C) 0.93 Å (D) 1.86 Å

Q.16 A metal crystallizes in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be:
[JEE MAIN 2017]
(A) $a / \sqrt{2}$ (B) 2a
(C) $2\sqrt{2} \, a$ (D) $\sqrt{2} \, a$

Q.17 Which type of 'defect' has the presence of cations in the interstitial sites ? **[JEE MAIN 2018]**
(A) Frenkel defect (B) Metal deficiency defect
(C) Schottky defect (D) Vacancy defect

Q.18 At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm⁻³) at this temperature ?
[Atomic Mass of Cu = 63.55u] **[JEE MAIN 2019 (Jan)]**
(A) $\frac{105}{x^3}$ (B) $\frac{211}{x^3}$ (C) $\frac{205}{x^3}$ (D) $\frac{422}{x^3}$

Q.19 Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is : **[JEE MAIN 2019 (April)]**
(A) A_2BO_4 (B) A_2B_2O
(C) A_4B_2O (D) AB_2O_4

Q.20 Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more in solid 2 than in 1. What is the approximate packing efficiency in solid 2? **[JEE MAIN 2019 (APRIL)]**

Solid 1   Solid 2
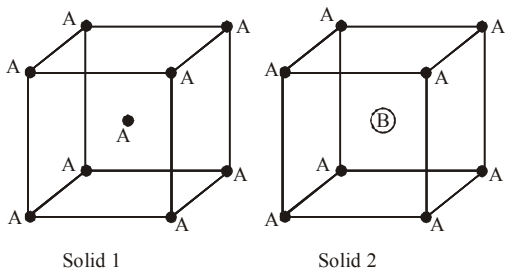
(A) 45%   (B) 65%
(C) 90%   (D) 75%

Q.21 An element has a face-centred cubic (fcc) structure with a cell edge of a. The distance between the centres of two nearest tetrahedral voids in the lattice is :
[JEE MAIN 2019 (APRIL)]
(A) a/2   (B) a
(C) (3/2) a   (D) $\sqrt{2}$a

Q.22 Which of the following exhibit both Frenkel & Schottky defect? **[JEE MAIN 2020 (JAN)]**
(A) AgBr   (B) KCl
(C) CsCl   (D) ZnS

EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 In face-centred cubic lattice, a unit cell is shared equally by how many unit cells **[AIPMT 2005]**
(A) 2 (B) 4
(C) 6 (D) 8

Q.2 The appearance of colour in solid alkali metal halides is generally due to – **[AIPMT 2006]**
(A) Schottky defect (B) Frenkel defect
(C) Interstitial positions (D) F-centres

Q.3 CsBr crystallises in a body centered cubic lattice. The unit cell length is 436.6pm. Given that the atomic mass of Cs = 133 and that of Br = 80 amu and Avogadro number being 6.02×10^{23} mol^{-1} the denisty of CsBr is **[AIPMT 2006]**
(A) 0.425 g/cm^3 (B) 8.25 g/cm^3
(C) 4.25 g/cm^3 (D) 42.5 g/cm^3

Q.4 If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentraton of cation vacancies will be –
($N_A = 6.02 \times 10^{23}$ mol^{-1}) **[AIPMT 2007]**
(A) 6.02×10^{16} mol^{-1} (B) 6.02×10^{17} mol^{-1}
(C) 6.02×10^{14} mol^{-1} (D) 6.02×10^{15} mol^{-1}

Q.5 The fraction of total volume occupied by the atoms present in a simple cube is **[AIPMT 2007]**

(A) $\dfrac{\pi}{3\sqrt{2}}$ (B) $\dfrac{\pi}{4\sqrt{2}}$

(C) $\pi/4$ (D) $\pi/6$

Q.6 If 'a' stands for the edge length of the cubic systems simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively, **[AIPMT 2008]**

(A) $1a : \sqrt{3}a : \sqrt{2}a$ (B) $\dfrac{1}{2}a : \dfrac{\sqrt{3}}{4}a : \dfrac{1}{2\sqrt{2}}a$

(C) $\dfrac{1}{2}a : \sqrt{3}a : \dfrac{1}{\sqrt{2}}a$ (D) $\dfrac{1}{2}a : \dfrac{\sqrt{3}}{2}a : \dfrac{\sqrt{2}}{2}a$

Q.7 Which of the following statement is not correct ? **[AIPMT 2008]**
(A) The number of Bravais lattices in which a crystal can be categorized is 14.
(B) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.
(C) Molecular solids are generally volatile.
(D) The number of carbon atoms in an unit cell of diamond is 4.

Q.8 Percentage of free space in a body centred cubic unit cell is: **[AIPMT 2008]**
(A) 28% (B) 30%
(C) 32% (D) 34%

Q.9 With which one of the following elements silicon should be doped so as to give p-type of semiconductor ? **[AIPMT 2008]**
(A) Boron (B) Germanium
(C) Arsenic (D) Selenium

Q.10 Lithium metal crystallises in a body centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of the lithium will be:**[AIPMT 2009]**
(A) 151.8 pm (B) 75.5 pm
(C) 300.5 pm (D) 240.8 pm

Q.11 Copper crystallises in a face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm? **[AIPMT 2009]**
(A) 157 (B) 181
(C) 108 (D) 128

Q.12 AB crystallizes in a body centred cubic lattice with edge length 'a' equal to 387 pm. The distance between two oppositively charged ions in the lattice is: **[AIPMT (PRE) 2010]**
(A) 335 pm (B) 250 pm
(C) 200 pm (D) 300 pm

Q.13 A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y$^-$) will be : **[AIPMT (MAINS) 2011]**
(A) 275.1 pm (B) 322.5 pm
(C) 241.5 pm (D) 165.7 pm

Q.14 Ametal crystallizes with a face-centered cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is: **[AIPMT (PRE) 2012]**
(A) 288 pm (B) 408 pm
(C) 144 pm (D) 204 pm

Q.15 The number of octahedral void (s) per atom present in a cubic close-packed structure is : **[AIPMT (PRE) 2012]**
(A) 1 (B) 3
(C) 2 (D) 4

Q.16 Structure of a mixed oxide is cubic close - packed (c.c.p). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is **[AIPMT (MAINS) 2012]**
(A) ABO_2 (B) A_2BO_2
(C) $A_2B_3O_4$ (D) AB_2O_2

Q.17 The number of carbon atoms per unit cell of diamond unit cell is – **[NEET 2013]**
(A) 1 (B) 4
(C) 8 (D) 6

Q.18 A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72g cm^{-3}. The molar mass of the metal is – **[NEET 2013]**
(A) 20g mol^{-1} (B) 40g mol^{-1}
(C) 30g mol^{-1} (D) 27 g mol^{-1}

Q.19 If a is the length of the side of a cube, the distance between the body centered atom and one corner atom in the cube will be **[AIPMT 2014]**

(A) $\dfrac{2}{\sqrt{3}}a$ (B) $\dfrac{4}{\sqrt{3}}a$ (C) $\dfrac{\sqrt{3}}{4}a$ (D) $\dfrac{\sqrt{3}}{2}a$

Q.20 A given metal crystallizes out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom.

[AIPMT 2015]

(A) 127 pm   (B) 80 pm

(C) 108 pm   (D) 40 pm

Q.21 The vacant space in bcc lattice unit cell is :

[RE-AIPMT 2015]

(A) 23%   (B) 32%

(C) 26%   (D) 48%

Q.22 The correct statement regarding defects in crystalline solids is –   **[RE-AIPMT 2015]**

(A) Frenkel defect is a dislocation defect.

(B) Frenkel defect is found in hallides of alkaline metals.

(C) Schottky defects have no effect on the density of crystalline solids.

(D) Frenkel defects decrease the density of crystalline solids.

Q.23 Lithium has a bcc structure. Its density is $530 \, kg \, m^{-3}$ and its atomic mass is $6.94 \, g \, mol^{-1}$. Calculate the edge length of a unit cell of Lithium metal

$(N_A = 6.02 \times 10^{23} \, mol^{-1})$ **[NEET 2016 PHASE 1]**

(A) 154 pm   (B) 352 pm

(C) 527 pm   (D) 264 pm

Q.24 The ionic radii of A^+ & B^- ions are

0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is   **[NEET 2016 PHASE 1]**

(A) 6   (B) 4

(C) 8   (D) 2

Q.25 In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are –   **[NEET 2016 PHASE 2]**

(A) 4 and 2   (B) 6 and 6

(C) 8 and 4   (D) 4 and 8

Q.26 Which is the INCORRECT statement ?   **[NEET 2017]**

(A) Density decreases in case of crystals with Schottky's defect.

(B) NaCl (s) is insulator, silicon is semiconductor, silver is conductor, quartz is piezo electric crystal.

(C) Frenkel defect is favoured in those ionic compounds in which sizes of cation and anions are almost equal.

(D) $FeO_{0.98}$ has non stoichiometric metal deficiency defect.

Q.27 Iron exhibits bcc structure at room temperature. Above 900°C, it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900°C (assuming molar mass and atomic radii of iron remains constant with temperature) is   **[NEET 2018]**

(A) $\dfrac{3\sqrt{3}}{4\sqrt{2}}$ (B) $\dfrac{4\sqrt{3}}{3\sqrt{2}}$ (C) $\dfrac{\sqrt{3}}{\sqrt{2}}$ (D) $\dfrac{1}{2}$

Q.28 A compound is formed by cation C and anion A. The anions form hexagonal close packed (hcp) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is :   **[NEET 2019]**

(A) C_2A_3 (B) C_3A_2

(C) C_3A_4 (D) C_4A_3

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	A	B	C	C	B	C	A	A	D	B	D	A	B	D	C	A	C	B	B	C	A	A	B	C	D
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	A	D	C	C	A	A	C	D	B	C	D	A	C	C	D	D	D	C	C	A	A	B	A	A
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	B	D	A	C	D	C	D	B	C	A	C	A	C	A	D	B	B	B	B	A	C	A	B	D	A
Q	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98		
A	C	B	B	C	C	A	C	C	B	A	C	D	C	B	D	B	C	A	A	B	A	A	B		

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	D	C	C	B	D	D	B	B	C	C	C	D	A	C	B	D	D	D	C	B	B	D	C	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	A	D	A	C	D	C	A	B	B	C	A	D	C	D	B	C	C	A	A	B	A	C	B	A	A
Q	51	52	53	54	55	56	57	58	59																
A	D	A	B	C	D	C	D	B	C																

EXERCISE - 3

Q	1	2	3	4	5
A	12	8	2	8	8

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
A	B	C	B	D	C	D	B	D	B	D	D	B	B	A	D	A	A	D	D	C	A	A

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	D	D	B	D	B	B	C	A	A	D	A	C	A	A	D	C	D	D	A	B	A	B	A	C
Q	26	27	28																						
A	C	A	C																						

SOLUTIONS
SOLID STATE
TRY IT YOURSELF - 1

(1) Radius (r) = $\dfrac{a \times \sqrt{3}}{4} = \dfrac{4.29\text{Å} \times 1.732}{4} = 1.86\text{Å}$

(2) **(A).** In a cube, A atoms are present at the 8 corners each shared by 8 cubes.

Therefore, the number of A atoms in the unit cell = $\dfrac{1}{8} \times 8 = 1$

Now, B atoms are at the centres of 6 faces and each face is shared by two cubes.

Therefore, the number of B atoms in the unit cell = $\dfrac{1}{2} \times 6 = 3$

Hence, the formula of the compound is AB_3.

(3) For a FCC unit cell, $r = \dfrac{a}{2\sqrt{2}}$

$a = r \times 2\sqrt{2} = 125 \times 10^{-12} \times 2\sqrt{2}\,\text{m}$
$= 125 \times 2 \times 1.414 \times 10^{-12}\,\text{m} = 354 \times 10^{-12}\,\text{m}$

(4) **(D).** Radius of $A^+ = 66\,\text{pm}$
Radius of $B^- = 140$ pm

Radius ratio, $\left(\dfrac{r^+}{r^-}\right) = \dfrac{rA^+}{rB^-} = \dfrac{66}{140} = 0.471$

As the radius ratio lies between 0.732 and 0.414, therefore the co-ordination number of A^+ must be 6.

(5) Number of B atoms per unit cell = $8 \times \dfrac{1}{8} = 1$

Number of A atoms per unit cell = $2 \times \dfrac{1}{2} = 1$

Formula of the compound = AB

(6) Since solid AB has ZnS structure, therefore, radius ratio must be between 0.414 and 0.225.

Now, $\dfrac{\text{Radius of cation A}}{\text{Radius of anion B}} = 0.225$

(Taking the lower limit of radius for ideal lattice)

i.e., $\dfrac{100}{\text{Radius of anion B}} = 0.225$

or Radius of anion B = $\dfrac{100}{0.225} = 444.4$ pm

Similarly, by taking the upper limit of radius ratio,

$\dfrac{100}{\text{Radius of anion B}} = 0.414\text{pm}$

or Radius of anion B = $\dfrac{100}{0.414} = 241.6\text{pm}$

Thus, the radius of anion B lies between 241.6 pm and 444.4 pm.

(7) **(B).** The contribution of corner, face centre and edge centre is $\dfrac{1}{8}, \dfrac{1}{2}$ and $\dfrac{1}{4}$.

$A = 8 \times \dfrac{1}{8} = 1$; $B = 5 \times \dfrac{1}{5} = 2.5$ [one face is missing]

$C = 4 \times \dfrac{1}{4} = 1$ [At alternating edge centre only]

(8) From eight corner atoms, one atom (X) contributes to one unit cell.
From six face centres, three atoms (Y) contribute to one unit cell.
So, the formula of the compound is XY_3.

As we know that, $\rho = \dfrac{Z \times M}{N_A \times a^3}$, here $Z = 1$.

Molar mass of XY_3
$M = 60 + 3 \times 90 = 330$ gm

$\rho = \dfrac{1 \times 330}{6.023 \times 10^{23} \times (5 \times 10^{-8})^3}$ gm/cm^3 = 4.38 gm/cm^2

(9) In the two dimensional square close-packed layer, the atom touches 4 nearest neighbouring atoms. Hence, its coordination number = 4.

(10) Number of $B^\Theta = 8 \times \dfrac{1}{8} + 6 \times \dfrac{1}{2} = 4$

Number of $A^\oplus = 12 \times \dfrac{1}{4} + 1 = 4$

Hence, formula of solid is AB.
After removing ions lying along one axis passing through face centre C_4-axis or tetrad axis, then

Number of $B^\Theta = 8 \times \dfrac{1}{8} + 4 \times \dfrac{1}{2} = 3$

Number of $A^\oplus = 12 \times \dfrac{1}{4} = 3$

Formula is AB.

TRY IT YOURSELF - 2

(1) Sphere A = $\dfrac{1}{8} \times 8 = 1$; Sphere B = $\dfrac{1}{2} \times 2 = 1$

Spheres C = $1 \times 4 = 4$
Hence, formula of unit cell = ABC_4.

(2) Since CuCl has ZnS structure (fcc). Therefore, the number of CuCl present per unit cell = 4.
Let the length of each edge = a cm (to be found)
∴ Volume of the cube = a^3 cm^3
Density of cell = 3.4 g cm^{-3} (given)

Now, density of unit cell = $\dfrac{\text{mass of the unit cell}}{\text{volume of the unit cell}}$ .... (1)

Mass of unit cell = (Mass of one molecule)
× (Number of molecules present per unit cell) ..... (2)

Mass of a molecule = $\dfrac{\text{Molecular mass}}{\text{Avogadro's number}}$

$= \dfrac{99}{6.023 \times 10^{23}}$ (Molecular mass of CuCl = 99)

Substituting this value in (2), we get

Mass of unit cell = $\dfrac{99}{6.023 \times 10^{23}} \times 4$

Putting various values in eq. (1), we get

$3.4 = \dfrac{99 \times 4}{6.023 \times 10^{23} \times 3.4}$

or $a^3 = \dfrac{99 \times 4}{6.023 \times 10^{23} \times 3.4} = 193.3 \times 10^{-24}\,cm^3$

or $a = 5.78 \times 10^{-8}\,cm = 578\,pm$

Thus, edge of each unit cell = 578 pm

(3)   We know that $Z = \dfrac{d \times a^3 \times N_A}{M}$

Given : density $d = 2.7 \times 10^{-2}\,kg\,mol^{-1}$,
$a = 405\,pm = 405 \times 10^{-12}\,m$
$N_A = 6.022 \times 10^{23}$, $M = 2.7 \times 10^3\,kg\,mol^{-1}$
The number of atoms per unit cell, $Z = ?$

$Z = \dfrac{2.7 \times 10^3 \times (405 \times 10^{-12})^3 \times 6.022 \times 10^{23}}{2.7 \times 10^{-2}}$

$Z = \dfrac{2.7 \times 405 \times 405 \times 405 \times 6.022 \times 10^{-8}}{2.7} = 4.0$

Because number of atoms per unit cell is four, hence it would be ccp (cubic close-packed) unit cell.

(4)   There is only one octahedral hole for every one sphere (or particle) in the structure.
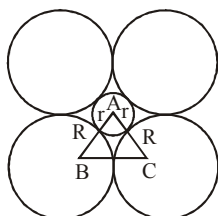No. of oxygen atoms = No. of octahedral holes = 3 (say).
and no. of iron (ferric) ions = 2
(only 2 out of 3 are occupied by ferric ions)
Therefore, formula of ferric oxide = $2Fe + 3O = Fe_2O_3$

(5)   Suppose octahedral void A is formed which has radius r. The atoms in close packing has the radius R.

In $\triangle\,ABC$, $BC^2 = (AC)^2 + (BA)^2$
or $2R^2 = (R + r)^2 + (R + r)^2 = 2\,(R + r)^2$

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

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

or $r = R\,(1.414 - 1)$ $(\because \sqrt{2} = 1.414)$

or $r = 0.414\,R$

(6)   Body centred cubic structure.

(7)   Total number of atoms per unit cell in a fcc structure = 4 atoms.

(8)   Length of the cell edge = 288 pm (given)
Volume of the unit cell $= (288pm)^3 = (288 \times 10^{-12}\,m)^3$
$\qquad\qquad\qquad\qquad\qquad = 23.9 \times 10^{-24}\,cm^3$.

Volume pf 208g of the element $= \dfrac{208g}{7.2g\,cm^{-3}} = 28.88\,cm^3$

No. of unit cells in this volume

$= \dfrac{28.88}{23.9 \times 10^{-24}} = 12.08 \times 10^{23}$ unit cells

Since each bcc cube contains 2 atoms, therefore, the total number of atoms in 208g = $2 \times 12.08 \times 10^{23}$
$\qquad\qquad\qquad\qquad = 24.16 \times 10^{23}$ atoms.

TRY IT YOURSELF - 3

(1)   When cation shifts from lattice to interstitial site, the defect is called Frenkel defect.

(2)   Since the crystal contains 0.1% Schottky defect (in which the atoms are missing from lattice site), so the mass of crystal decreases by 0.1% assuming the volume of crystal remain same. Thus, the density of the crystal also decreases by 0.1%

$\therefore \;\; \rho' = \rho\left(1 - \dfrac{0.1}{100}\right) = 0.999\rho = 0.999 \times 1.5455$

$\qquad = 1.5439\,g/cm^3$.

(3)   Frenkel defect

(4)   Schottky defect.

(5)   Because the magnetic moments are aligned in parallel and antiparallel directions in unequal numbers, resulting the net moment, therefore, it is ferrimagnetic substance.

(6)   Phosphorus or Boron may be added.

(7)   Cadmium chloride or strontium chloride.

(8)   Arsenic.

(9)   It is due to presence of F centre, the electrons present at the site of anion which absorb light from visible region and radiate complementary colour.

(10)   Vacancy defect decreases the density of a substance. Vacancy defect in ionic solids is known as Schottky defect.

CHAPTER-1 : SOLID STATE
EXERCISE-1

(1) **(A).** Properties of solid
(i) They have shorter intermolecular distance.
(ii) They possess stronger intermolecular distances.
(iii) They are incompressible and rigid.
(iv) They have definite shape, mass and volume.

(2) **(B).** At sufficiently low temperature, the thermal energy is low and intermolecular forces bring the particles so close that they cling to one another and occupy fixed positions. The particles can still oscillate about their mean positions and the substance exists in solid state.

(3) **(C).** Thermal energy tends to keep the solid molecules by making them move faster.

(4) **(C).** Solids can be classified as crystalline and amorphous solids.

(5) **(B).** Crystalline solids are anisotropic in nature.

(6) **(C).** On cutting a crystalline solid with a sharp edge tool, it splits into two pieces and the newly generated surfaces are plain and smooth. This property is called cleavage property.

(7) **(A).** Crystalline solids have regular arrangement of constituent particles, sharp melting points and are anisotropic.

(8) **(A).** Amorphous solids neither have ordered arrangement (i.e. no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids.
It is therefore they are regarded as super-cooled liquids.

(9) **(D).** Amorphous solids neither have ordered arrangement (i.e. no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.

(10) **(B).** Crystalline solids are anisotropic in nature due to different arrangement of particles in different directions.

(11) **(D).** Amorphous solids are isotropic in nature.

(12) **(A).** The word 'amorphous' has been derived from greek word 'amorphos' which means 'no form'.

(13) **(B).** Quartz glass (SiO_2) is an amorphous solid.

(14) **(D).** Crystalline solids have sharp melting points and are called true solids. Amorphous solids have irregular shape.

(15) **(C).** Both NaCl and quartz are the examples of crystalline solid.

(16) **(A).** Quartz glass is amorphous solid i.e., isotropic in nature. Therefore, value of any physical property (e.g., refractive index) would be same along any direction.

(17) **(C).** Some of the physical properties of crystalline solids like refractive index show different values on measuring along different directions in the same crystals. This property of crystalline solids is known as anisotropy.

(18) **(B).** Molecular crystals are bad conductors of electricity as the electrons are localised in the bonds.

(19) **(B).** Graphite is a good conductor of electricity due to the presence of free valence electrons.

(20) **(C).** Molecular solids are the substances having molecules as constituent units having interparticle forces such as Vander Waal's forces or hydrogen bonds.

(21) **(A).** Solid SO_2 and NH_3 are polar molecular solids.

(22) **(A).** Iodine molecules are held in the crystals lattice by london forces.

(23) **(B).** Covalent solids or network solids are very hard with high melting point and are insulators in solid as well as in molten state.

(24) **(C).** Noble gas and Ice are molecular crystal.

(25) **(D).** Graphite cannot be classified as ionic solid.

(26) **(C).** Diamond is the network solid.

(27) **(A).** Ionic solids conduct electricity in molten state since in molten state ionic solids dissociate to give free ions which in solid state are not free to move and are held together by, strong electrostatic forces of attraction.

(28) **(D).** Diamond is a covalent solid.

(29) **(C).** In metallic solids, positive ions are surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread throughout the crystal. These are highly malleable and ductile. Covalent bonds are strong and directional in covalent solids.

(30) **(C).** In covalent solids, the forces of attraction are covalent bond forces.

(31) **(A).** Ionic solids:
* Brittle nature
* Very strong forces of interactions
* Anisotropic nature

(32) **(A).** Iodine molecules are held together by London forces in the crystal lattice.

(33) **(C).** There are only 14 possible three dimensional lattices. These are called Bravais Lattices (after the French mathematician who first described them).

(34) **(D).** For monoclinic crystal system,
$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$

(35) **(B).** $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ the crystal system is orthorhombic.

(36) **(C).** Cinnabar is an example of trigonal crystal system.

(37) **(D).** Monoclinic crystals have two Bravais lattices- Primitive and end centred.

(38) **(A).** When constituent particles are present only on the corner positions of a unit cell, it is called primitive unit cell.

(39) **(C).** In orthorhombic crystal system,
$a \neq b \neq c$ but axial angles α, β and γ are equal at 90°.

(40) **(C).** A unit cell is characterised by (i) its dimensions along the three edges, (a, b & c). These edges may or may not be mutually perpendicular. (ii) angle(s) between the edges, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters a, b, c, α, β and γ.

(41) **(D).** In a simple cubic unit cell, each corner atom is shared between 8 unit cells. Hence, the total number of atoms in one unit cell is

$$8 \times \frac{1}{8} = 1 \text{ atom.}$$

(42) **(D).** No. of X atoms (at the corners)$= \frac{1}{8} \times 8 = 1$

No. of Y atoms (fcc) $= 6 \times \frac{1}{2} = 3$

Hence, the formula is XY_3.

(43) **(D).** In a bcc unit cell one atom is present at its body centre.

(44) **(C).** $\frac{1}{8}$ th part of a constituent particle actually belongs to a particular unit cell.

(45) **(C).** In open structures, each small sphere represents only the centre of the particle occupying that position and not its actual size. The arrangement of particles is easier to follow in open structures.

(46) **(A).** When the centres of the four immediate neighbouring spheres are joined, a square is formed. Thus, this packing is called square close packing.

(47) **(A).** CsCl has a bcc structure. Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by $8 Cs^+$ ions. Thus, the structure has 8 : 8 coordination number.

(48) **(B).** Co-ordination number in HCP =12
Co-ordination number in Mg is also = 12

(49) **(A).** Tetrahedral voids are called so because a tetrahedron is formed on joining the centres of the four spheres.

(50) **(A).** Number of nearest neighbours of a particle is called its coordination number.

(51) **(B).** In NaCl crystal, Cl^- ions adopt cubic close packed arrangement and Na^+ ions occupy all the octahedral sites. Therefore, Na and Cl^- have 1 : 1 stoichiometry. In other words, each Na^+ ion is surrounded by six Cl^- ions which are disposed towards the corners of a regular octahedron. Similarly, each Cl^- ion is surrounded by six Na^+ ions.

(52) **(D).** Octahedral sites are created by overlapping two equilateral triangles with apices in opposite directions.

(53) **(A).** Two types of voids present in a crystal are tetrahedral and octahedral voids.

(54) **(C).** AB AB packing is hexagonal close packing in which all atoms occupy 74% of the total space. Hence, 26% of the space is empty or voids.

(55) **(D).** Cubic close packing is also called face centred cubic. No. of atoms per unit cell in ccp (or fcc) = 4

$\therefore$ No. of tetrahedral voids = 2 × 4 = 8

(56) **(C).** In AAA type of arrangement, each sphere is in contact with four of its neighbours.
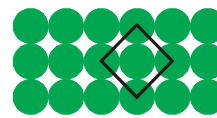
Square close packing

(57) **(D).** If the number of close packed sphere be N, then the number of octahedral and tetrahedral voids generated are N and 2N respectively.

(58) **(B).** In ccp pattern, fourth layer is identical to first layer.

(59) **(C).** Coordination number of Al in $AlCl_3$ in (solid) crystalline state is 6.

(60) **(A).** The coordination number of metal crystallising in a hexagonal close packing is 12.

(61) **(C).** If the second row is placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row, this arrangement is called ABAB type arrangement.
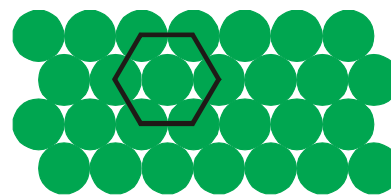
ABAB type arrangement

(62) **(A).** Packing efficiency is the percentage of total space filled by the particles.

(63) **(C).** For fcc,

$$r = \frac{\sqrt{2}}{4} a = \frac{\sqrt{2}}{4} \times 361 = \frac{1.414 \times 361}{4} = 127 \text{pm}$$

(64) **(A).** Packing efficiency of simple cubic lattice

$$PE = \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$$

(65) **(D).** In a simple cubic system, number of atoms
$a = 2r$

$\therefore$ Packing fraction

$$= \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

(66) **(B).** $PE = \dfrac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of unit cell}}\%$

(67) **(B).** The fraction of the total volume occupied by the atoms present in a simple cube is $\pi/6$.

(68) **(B).** Packing efficiency of simple cubic lattice

$$PE = \frac{\text{Volume of one atom}}{\text{Volume of cell cubic unit}} \times 100\%$$

$$= \frac{4/3\,\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% \approx 52.4\%$$

(69) **(B).** In face centred cubic unit cell, edge length is $4r/\sqrt{2}$.

(70) **(A).** $d = \dfrac{Z \times M}{N_A \times a^3}$; $Z = \dfrac{a^3 \times d \times N_A}{M}$

$$Z = \frac{(3.5 \times 10^{-8})^3 \times 0.53 \times 6.023 \times 10^{23}}{6.94} = 1.97 \approx 2$$

(71) **(C).** $d = \dfrac{ZM}{a^3 N_A}$; $\dfrac{d_1}{d_2} = \dfrac{4}{(3.5)^3} \times \dfrac{(3)^3}{2} = 1.26$

(72) **(A).** Density of the unit cell, $d = \dfrac{ZM}{a^3 N_A}$

where, Z = number of atoms present in one unit cell,
M = molar mass
a = edge length of a unit cell
N_A = Avogadro's constant.

(73) **(B).** $d = \dfrac{Z \times M}{a^3 \times N_A} = \dfrac{4 \times 58.5}{(5.64 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$

$$= 2.16 \text{ g cm}^{-3}$$

(74) **(D).** Generally, a solid consists of an aggregate of large number of small crystals. These small crystals have some defects in them. When crystallisation process occurs at fast or moderate, these defects are created.

(75) **(A).** Each Sr^{2+} in the NaCl crystal replaces two Na^+ ions. It occupies the site of one ion and the other remains vacant creating a cation vacancy.

(76) **(C).** Metal excess and metal deficiency are the two types of non-stoichiometric defects.

(77) **(B).** Equal number of cations and anions are missing from the crystal.

(78) **(B).** Stoichiometric defects, impurity defects and non-stoichiometric defects are the types of point defects. Whereas interstitial is a sub-type of stoichiometric defects.

(79) **(C).** The anionic sites occupied by the unpaired electrons are called F-centres from the German word Farbenzenter for colour centre.

(80) **(C).** In Schottky defect, some of the lattice points are unoccupied creating holes in the crystal.

(81) **(A).** Frenkel defect is also known as dislocation defect as in this the smaller ion (usually cation) is dislocated from its normal site to an interstitial site.

(82) **(C).** Point and line defects are the two types of main defects.

(83) **(C).** F-centres impart yellow colour to the crystals of NaCl when heated in an atmosphere of sodium vapour. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

(84) **(B).** Ions have Schottky defects when their cations and anions are both absent from the crystal lattice. In AgBr, the Ag^+ ions (and corresponding Br^- ions) are absent from the crystal lattice causing Schottky defects. However, Ag^+ ions are exceptionally mobile and they have a tendency to move about inside the lattice. Thus, they compliment the Schottky defects with Frenkel defects with the Ag^+ ions trapped in interstitial spaces, thus they show both Frenkel and Schottky defects. Or in short, we can say that due to the similar size of Ag^+ ions and Br^- ions and the small size of Ag^+ ions and the fact that Ag^+ ions have a property to be mobile both Schottky and Frenkel defects occur.

(85) **(A).** Electrical conductivity of semiconductors increases with rise in temperature since electrons can jump to conduction band.

(86) **(C).** In conductors there is no gap or overlapping between valence band and conduction band. The insulators have a large gap while semiconductors have a small energy gap.

(87) **(D).** n-type semiconductor is obtained when group 14 element Si or Ge having four valence electrons is doped with a group 15 element like P or As, which contains five valence electrons.

(88) **(C).** Insulators are the solids with very low conductivities, ranging between 10^{-20} to $10^{-10}\ \Omega^{-1}\ m^{-1}$.

(89) **(B).** Silicon doped with electron-rich impurity forms n-type semiconductor.

(90) **(D).** Intrinsic semiconductors are insulators at room temp. & become semiconductors when temperature is raised.

(91) **(B).** In case of semiconductors, the gap between valence band and conduction band is small.

(92) **(C).** Magnetic moment originates from its orbital motion around the nucleus and its spin around its own axis.

(93) **(A).** (a) – (iii), (b) – (i), (c) – (ii), (d) – (iv), e – (v)

(94) **(A).** $K_{metals} >> K_{insulators} < K_{semiconductors}$

(95) **(B).** Ferromagnetic substances can be magnetised permanently.

(96) **(A).** The value of Bohr magneton, μ_B is $9.27 \times 10^{-24}\ Am^2$

(97) **(A).** When ferromagnetic substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field.

(98) **(B).** Ferromagnetic substances are those which show permanent magnetism even in the absence of magnetic field.

EXERCISE-2

(1) **(B).** Intermolecular forces should be stronger than thermal energy for the existence of solids.

(2) **(D).** Packing efficiency of hcp and ccp structure is 74% packing efficiency of bcc structures is 68%.

(3) **(C).** TiO_3 behaves as conductor or insulator depending upon temperature.

(4) **(C).** Pure Si and Ge are insulators because of the absence of any hole or free electron. They show semiconductor behaviour only after doping.

(5) **(B).** In bcc 8 corners $\times \frac{1}{8}$ per corner atom $8 \times \frac{1}{8} = 1$ atom

1 body centre atom $= 1 \times 1 = 1$ atom

∴ Total number of atoms per unit cell $= 1 + 1 = 2$

(6) **(D).** No. of atoms of P $= \frac{1}{8} \times 8 = 1$

No. of atoms of Q $= 1 \times 1 = 1$

The formula of the compound is PQ.

Coordination no. of P and Q $= 8 : 8$

(7) **(D).** Characteristic features of a crystal lattice are as follows:

(i) Each point in a crystal lattice is called lattice site or lattice point.

(ii) Each point in a crystal lattice represents one constituent particle (an atom, a molecule or an ion).

(iii) These lattice points are joined by straight lines to bring out the geometry of the lattice.

(8) **(B).** Coordination no. of crystal lattices which fall in the range of $0.414 - 0.732$ is 6.

(9) **(B).** H_2 and I_2 are molecular solids.

(10) **(C).** Frenkel defect is exhibited by compound having low coordination number and compound having large difference in size of cation and anion. This defect is not found in alkali metal halides because cations and anions have almost equal size and cations cannot be accommodated in interstitial sites.

(11) **(C).** (a) – (iii), (b) – (i), (c) – (iv), (d) – (ii)

(12) **(C).** Packing efficiency (i.e., space occupied) for bcc is 68%

∴ % of empty space $= 100 - 68 = 32\%$

(13) **(D).** A large number of non-stoichiometric inorganic solids are known which contain the constituent element in non-stoichiometric ratio due to defects in their crystal structures. These are of two types (i) metal excess defect and (ii) metal deficiency defect. Alkali metals like KCl and NaCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions get diffused to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by Na atoms to form Na^+ ions.

The released electron diffused into the crystal and occupy anionic sites. Hence, the crystal now has anionic sites. Therefore, the crystal now has an excess of sodium. These anionic sites occupied by unpaired electrons are called F-centres (derived from the German word Farbenzenter for colour centre). These F- centres impart yellow colour to the crystal.

(14) **(A).** Impurity of lower group creates a positively charged hole. On applying potential difference, p-holes conduct electric current.

(15) **(C).** In such arrangement, each sphere is in contact with four of its neighbours. Thus, two dimensional coordination number is 4.

(16) **(B).** Various combinations of n-type and p-type semiconductors are used for making electronic components. Diode is a combination of n-type and p-type semiconductors and is used as a rectifier. Transistors made by sandwiching a layer of one type of semiconductor. n-p-n and p-n-p type of transistors are used to detect amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

(17) **(D).** Diamond is a rigid three-dimensional network solid resulting in extremely hard structure.

(18) **(D).** Number of atoms (A) per unit cell $= 8 \times \frac{1}{8} = 1$

Number of atoms (B) per unit cell $= (6 - 1) \times \frac{1}{2} = \frac{5}{2}$

One atom of B is missing
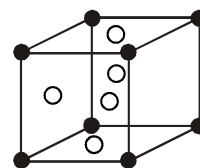
Hence, formula is $A_1 B_{5/2} = A_2 B_5$

(19) **(D).** Number of tetrahedral voids are always double than octahedral voids.

(20) **(C).** NaCl has fcc structure

In fcc lattice, $r^+ + r^- = a/2$

where, a = edge length

$r^+ = 95$ pm, $r^- = 181$ pm

Edge length $= 2r^+ + 2r^- = (2 \times 95 + 2 \times 181)$ pm

$= 190 + 362 = 552$ pm

(21) **(B).** $d = \dfrac{Z \times M}{a^3 \times N_A} = \dfrac{2 \times 100}{(400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}$

$= 5.188$ g cm^{-3}

(22) **(B).** $a = 2\sqrt{2}r$

Volume of the cell

$= a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}\ r^3$

No. of spheres in fcc $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Volume of 4 spheres $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

(23) **(D).** In solid, metal ions of such substances are grouped together in domains in which domain acts as a tiny magnet. In the absence of magnetic field, these domains are randomly oriented whereas in magnetic field, these get oriented in the direction of the magnetic field. This ordered arrangement persist even after the removal of magnetic field so these substances act as permanent magnet.

(24) **(C).** Lattice sites in a pure crystal are occupied by the constituent units like atoms, molecules, ions but not occupied by electrons.

(25) **(C).** No. of X atoms = $\frac{1}{8} \times 8 = 1$; No. of Y atoms = 1

No. of Z atoms = $12 \times \frac{1}{4} = 3$

Formula of the compound = XYZ_3

(26) **(A).** Molar mass of the element

$= \frac{200}{24 \times 10^{23}} \times 6.023 \times 10^{23} = 50.19 \text{ g mol}^{-1}$

For fcc, Z = 4, V = $a^3 = (200 \times 10^{-10})^3$

$d = \frac{Z \times M}{N_A \times V} = \frac{4 \times 50.19}{6.023 \times 10^{23} \times (200 \times 10^{-10})^3}$

$d = 41.66 \text{ g cm}^{-3}$

(27) **(D).** Irregularities or deviations from ideal arrangement in the entire rows of lattice points are called line defects, whereas deviations or irregularities from ideal arrangement around a point or an atom in crystalline substance are called point defects. All these irregularities are called crystal defects.

(28) **(A).** ZnS has a ccp structure. S^{2-} ions are present at the corners of the cube and centre of each face. Zn^{2+} ions occupy half of the tetrahedral sites. Each Zn^{2+} ion is surrounded by four S^{2-}ions and each S^{2-} ion is surrounded by four Zn^{2+} ions.

(29) **(C).** At 850 K, Fe_3O_4 becomes paramagnetic.

(30) **(D).** Non-polar molecular solids are formed by non-polar covalent bonds. In these solids, the atoms or molecules are held by weak dispersion or London forces. These are soft and non-conductors of electricity. e.g., H_2, Cl_2 and I_2, HCl and SO_2 are formed by polar covalent bonds.

(31) **(C).** a = 2($r_+ + r_-$) = 2 (95 + 181) = 552 pm

(32) **(A).** Zn^{2+} ions and electrons move to interstitial sites and F-centres are created which impart yellow colour to ZnO.

(33) **(B).** The sharp melting point of crystalline solids is due to a regular arrangement of constituent particles observed over a long distance in the crystal lattice.

(34) **(B).** In ferrimagnetic substances the magnetic moments of the domains are aligned in parallel and antiparallel directions in unequal numbers.

(35) **(C).** 4, tetrahedral

(36) **(A).** For cubic, a = b = c, $\alpha = \beta = \gamma = 90°$

Tetragonal, a = b $\neq$ c, $\alpha = \beta = \gamma = 90°$
Orthorhombic, a $\neq$ b $\neq$ c, $\alpha = \beta = \gamma = 90°$
Hexagonal, a = b $\neq$ c, $\alpha = \beta = 90°$, $\gamma = 120°$

(37) **(D).** P-doping, Q-electron, R-electronic, S-n, T-p

(38) **(C).** In fcc, contribution of each atom present at the corner = 1/8.
In fcc, contribution of each atom present at the face centre = 1/2

∴ Total number of atoms in face= $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$

(39) **(D).** $Fe_{0.93}O$ is a metal deficiency defect. In FeO, some Fe^{2+} ions are missing and the loss of positive charge is made up by Fe^{3+} ions.

(40) **(B).** Antiferromagnetic substances have zero magnetic moment.

(41) **(C).** (a) – (3), (b) – (2), (c) – (1), (d) – (4)

(42) **(C).** Octahedral voids occupy the position of edge centre and body centre.

(43) **(A).** Generally photovoltaic cells convert sunlight into electricity and amorphous silicon is one of the best photovoltaic cells.

(44) **(A).** Frenkel defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its interstitial site.

(45) **(B).** In Schottky defect, equal number of cations and anions are missing from the crystal.

(46) **(A).** When Si is doped with P or As, four electrons of both and P or As are involved in covalent bond formation. The electron of P or As is extra and becomes delocalised. Delocalisation increases the conductivity of doped Si.

(47) **(C).** Silver halides generally show both Frenkel and Schottky defects.

(48) **(B).** Increase of pressure increases coordination number. Hence, by applying high pressure, NaCl type crystal can be changed into CsCl type crystal.

(49) **(A).** In NaCl type, Cl^- ions form ccp structures while Na^+ ions are present in all octahedral voids.

(50) **(A).** Amorphous solids possess short range order. Their structure is similar to that of liquid. Thus, they are called pseudo solids or supercooled liquids. These do not have definite heat of fusion. Glass and quartz glass are amorphous solids. Quartz is a crystalline solid.

(51) **(D).** (a) – (2), (b) – (1), (c) – (3)

(52) **(A).** Frenkel defect is not shown by alkali metals because cations and anions have almost same size and cations cannot be accommodated in interstitial sites.

(53) **(B).** Crystalline solids have definite heat of fusion while amorphous solids do not have definite heat of fusion. Crystalline solids are anisotropic while amorphous solids are isotropic.
Crystalline solids have definite geometrical shape while amorphous solids do not have any definite geometrical shape.

Crystalline solids have sharp melting point while amorphous solids do not have sharp melting point.

(54) **(C).** In fluorite structure, cations form ccp structure and anions are present in all tetrahedral holes. Hence, no. of Ba^{2+} ions = 8 and no. of Cl^- ions = 4.

(55) **(D).** Diamagnetic substances are weakly repelled by a magnetic field. H_2O, NaCl and C_6H_6 are some of diamagnetic substances. These have no unpaired electron. Pairing of electrons cancels their magnetic moment and they lose their magnetic character.

(56) **(C).** Coordination number of Ca^+ in CaF_2 is 8.

(57) **(D).** For fcc arrangement, distance of nearest neighbour

(d) is $\dfrac{a}{\sqrt{2}} = \dfrac{862}{1.414} = 609.6$ pm

(58) **(B). Cubic system   Examples**
Cubic - NaCl, zinc blende, Cu
Triclinic - $K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
Tetragonal - White tin, SnO_2, TiO_2, $CaSO_4$
Hexagonal - Graphite, ZnO, Cd

(59) **(C).** Total number-of atoms per unit cell in bcc and fcc unit cell are 2 and 4 respectively.

EXERCISE-3

(1) **12.** In a hcp structure atoms are located at the corners and centre of two hexagons placed parallel to each other; three more atoms are placed in a parallel plane midway between these two planes. Here each atom is surrounded by 12 others and is said to have coordination number of 12.

(2) **8.** The truncated octahedron is the 14-faced Archimedean solid, with 14 total faces : 6 squares and 8 regular hexagons.
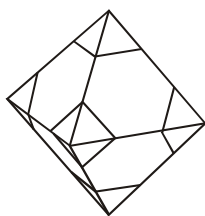
The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron.

(3) **2.** a = 400pm, d = 8 g cm^{-3}

$d = \dfrac{z \times M_0}{a^3 \times N_A}$

$M_0 = \dfrac{z \times a^3 \times N_A}{z} = \dfrac{8 \times (400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{4}$

$= 77.09$ g/mol

Number of atoms $= \dfrac{256}{77.09} \times 6.023 \times 10^{23} = N \times 10^{24}$

$2 \times 10^{24} = N \times 10^{24}$

$N = 2$

(4) **8.** Since unit cell is fcc, the number of atoms should be 4, but since carbon atoms are arranged tetrahedrally, the atoms should also be present in alternate tetrahedral voids. The number of tetrahedral voids in fcc is 8 and hence the total number of carbon atoms per unit cell

$$= 4 + 8 \times \dfrac{1}{2} = 8.$$

(5) **8.** $\dfrac{\text{Co} - \text{ordination of cation}}{\text{Co} - \text{ordination no of anion}}$

$= \dfrac{\text{charge of cation}}{\text{charge of anion}} = \dfrac{3}{1} = 3$

coordination no. of A = 6
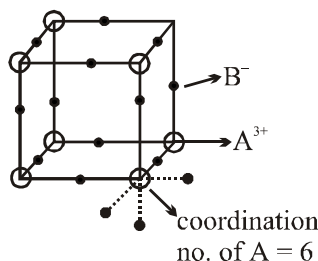
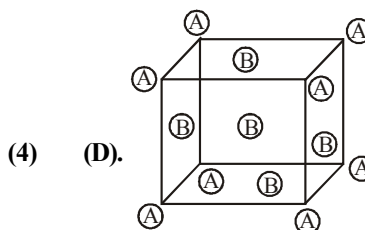Now Co-ordination no. of A is as shown so of B is 2.

EXERCISE-4

(1) **(B).** No. of atoms per unit cell in B.C.C. = 2
No. of atoms per unit cell in F.C.C. = 4

(2) **(C).** Mass per unit cell of NaCl

$= 4 \times 58.5 = 234u = \dfrac{234 \times 1}{6.02 \times 10^{23}}$ gm

No. of unit cell in 1.0gm $= \dfrac{6.02 \times 10^{23}}{234} = 2.57 \times 10^{21}$

(3) **(B).** Since equal no. of (+ve) and (−ve) ions are missing from the lattice site in questions, so, this effect is "Schottky effect".

(4) **(D).**

Number of A ion per unit cell = 8/8 = 1
Number of B ion per unit cell = 6/2 = 3
Empirical formula = AB_3.

(5) **(C).** No. of atom/unit cell $= \dfrac{8}{8} + \dfrac{6}{2} = 4$

Volume of 4-atoms $= 4 \times \dfrac{4}{3}\pi r^3 = \dfrac{16}{3}\pi r^3$

![OAL - ODM ADVANCED LEARNING] Q.B. - SOLUTIONS   STUDY MATERIAL : CHEMISTRY

(6) **(D).** From the question, $x = \dfrac{2}{3} \times 8 = \dfrac{16}{3}$, $y = 4$

So, $x : y = \dfrac{16}{3} : 4$ or $\dfrac{4}{3} : 1 = X_4Y_3$.

(7) **(B).** For FCC, $4r = \sqrt{2}\,a$

or $r = \dfrac{a}{2\sqrt{2}} = \dfrac{361}{2 \times 1.414} = \dfrac{361}{2.828} = 127.6$ pm

(8) **(D).** For an ionic substance in FCC arrangement,
$2(r^+ + r^-) =$ edge length
$2(110 + r^-) == 508$; $r^- = 144$ pm

(9) **(B).** Packing fraction of cubic close packing and body centred packing are 0.74 and 0.68 respectively.

 A B

(10) **(D).** $8 \times \dfrac{1}{8} \quad 5 \times \dfrac{1}{2}$; Formula of compound A_2B_5.

(11) **(D).** For BCC structure, $\sqrt{3}a = 4r$

$r = \dfrac{\sqrt{3}}{4}a = \dfrac{\sqrt{3}}{4} \times 352 = 152$ pm

(12) **(B).** Silicon exists as covalent crystal in solid state. (Network like structure, like diamond).

(13) **(B).** $M_{0.98}O$. Consider one mole of the oxide.
Moles of $M = 0.98$, Moles of $O^{2-} = 1$
Let moles of $M^{3+} = x \Rightarrow$ Moles of $M^{2+} = 0.98 - x$
Doing charge balance $(0.98 - x) \times 2 + 3x - 2 = 0$
$\Rightarrow 1.96 - 2x + 3x - 2 = 0 \Rightarrow x = 0.04$

$\therefore$ % of $M^{3+} = \dfrac{0.04}{0.98} \times 100 = 4.08\%$

(14) **(A).** In CsCl structure, Cs^+ ion is in contact with Cl^- ion at the nearest distance which is equal to $\sqrt{3}\dfrac{a}{2}$.
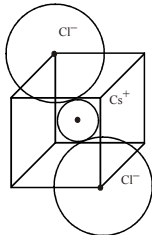
(15) **(D).** Edge length of BCC is 4.29 Å.

In BCC, edge length $= \dfrac{4}{\sqrt{3}}r$; $4.29 = \dfrac{4}{\sqrt{3}}r$

$r = \dfrac{4.29}{4}\sqrt{3} = 1.86$ Å

(16) **(A).** In FCC distance of closest approach between two atoms $= 2r$
In FCC, atoms are in close contact along face diagonal of FCC unit cell.

$\because \quad 4r = \sqrt{2}\,a$; $2r = \dfrac{\sqrt{2}\,a}{2} = \left(\dfrac{a}{\sqrt{2}}\right)$

(17) **(A).** Pressure of cation in interstitial sites is 'Frenkel' defect.

(18) **(D).** FCC unit cell $Z = 4$

$d = \dfrac{63.5 \times 4}{6 \times 10^{23} \times x^3 \times 10^{-24}}$ g / cm^3

$d = \dfrac{63.5 \times 4 \times 10}{6}$ g / cm^3 ; $d = \dfrac{422.33}{x^3} \approx \dfrac{422}{x^3}$

(19) **(D).** $Z_B = 4$, $Z_A = 4 \times \dfrac{1}{2} = 2$, $Z_O = 8$
Formula ; $A_2B_2O_8 \equiv AB_2O_4$

(20) **(C).** $\text{p.f.} = \dfrac{\left(z_{eff} \times \dfrac{4}{3}\pi r_A^3\right)_A + \left(z_{eff} \times \dfrac{4}{3}\pi r_B^3\right)_B}{a^3}$

$2(r_A + r_B) = \sqrt{3}a$; $r_B = 2\,r_A$
$2\sqrt{3}r_A = a$

$\text{p.f.} = \dfrac{1 \times \dfrac{4}{3}\pi r_A^3 + \dfrac{4}{3}\pi (8r_A^3)}{8 \times 3\sqrt{3}r_A^3} = \dfrac{9 \times \dfrac{4}{3}\pi}{8 \times 3\sqrt{3}} = \dfrac{\pi}{2\sqrt{3}}$

p. efficiency $= \dfrac{\pi}{2\sqrt{3}} \times 100 \approx 90\%$

(21) **(A).** Distance between two nearest tetrahedral void
$= a/2$

(22) **(A).** Only AgBr can exhibit both Schottky and Frenkel defect.

EXERCISE-5

(1) **(C).** Each face of the fcc cell is common to two adjacent cells. Therefore, each face centre atom contributes only half of its volume and mass to one cell. Arranging six cels each sharing the remaining half of the face centred atoms, constitutes fcc cubic lattice e.g., Cu and Al.

(2) **(D).** The appearance of colour in solid alkali metal halide is due to presence of F-centres found as defect in the crystal structure.

(3) **(D).** In body centred cubic lattice one molecule of CsBr is within one unit cell.
Atomic mass of unit cell $= 133 + 80 = 213$ amu
Volume of cell $= (436.6 \times 10^{-12})^3$

Density $= \dfrac{n \times \text{at. wt.}}{\text{Av. no.} \times \text{vol. of unit all cell}}$

$= \dfrac{213}{6.02 \times 10^{23} \times (436.6 \times 10^{-12})^3}$ $\left[\rho = \dfrac{ZM}{a^3 N_A}\right]$

$= \dfrac{213 \times 10^7}{6.02 \times (436.6)^3} = 42.5$ g/cm^3

(4) **(B).** Since each Sr^{++} ion provides one cation vacancy, hence Concentration of cation vacancies
$=$ mole % of $SrCl_2$ added $= 10^{-4}$ mole %

$= \dfrac{10^{-4}}{100} \times 6.023 \times 10^{23} = 6.023 \times 10^{17}$

40

(5) (D). Number of atoms per unit cell = 1
Atoms touch each other along edges. Hence, r = a/2
[r = radius of atom and a = edge length]

Therefore % fraction $= \dfrac{\frac{4}{3}\pi r^3}{(2r)^3} = \dfrac{\pi}{6} = 0.52$

(6) (B). S.C.C., r = a/2 ; F.C.C., $r = \dfrac{a}{2\sqrt{2}}$

B.C.C., $r = \dfrac{\sqrt{3}a}{4}$; $r_{SCC} : r_{BCC} : r_{FCC}$

$\dfrac{1}{2}a : \dfrac{\sqrt{3}}{4}a : \dfrac{1}{2\sqrt{2}}a$

(7) (B). The fraction of total volume occupied in primitive cell is 0.52.

(8) (C). Packing fraction in BCC is 68%, so free space = 32%

(9) (A). Boron is added to form p type semiconductor

(10) (A). $a\sqrt{3} = 4r$; $r = \dfrac{a\sqrt{3}}{4} = \dfrac{351 \times 1.732}{4} = 151.98$ pm

(11) (D). $a\sqrt{2} = 4r$

$r = \dfrac{a \times 1.414}{4} = \dfrac{361 \times 1.414}{4} = 128$ pm

(12) (A). For body centred cubic (bcc) lattice, distance between two oppositely charged ions,

$d = \dfrac{\sqrt{3}a}{2} = \dfrac{\sqrt{3} \times 387}{2}$ pm = 335.15 pm

(13) (C). Radius ratio of NaCl like crystal $= r_+/r_- = 0.414$

$r^- = \dfrac{100}{0.414} = 241.5$ pm

(14) (A). For CCP, $\sqrt{2}a = 4R$; $\dfrac{\sqrt{2}a \times 408}{2} = 2R$

Diameter = 288.5

(15) (A). Number of octahedral voids in ccp, is equal to effective number of atoms.
In ccp, effective number of atoms are 4 so, 4 octahedral voids. So, 1 octahedral voids per atom.

(16) $A^{2+} = \dfrac{1}{4} \times 8 = 2$; $B^+ = 4 \times 1 = 4$

$O^{2-} = 8 \times \dfrac{1}{8} + 6 \times \dfrac{1}{2} = 4$; $A_2B_4O_4 = AB_2O_2$

(17) (C). In the diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure.
∴ Number of atoms present in a diamond cubic unit cell = 1 + 3 + 4 = 8 atoms

(18) (D). $\rho = \dfrac{Z \times M}{N_A \times a^3}$ for FCC, Z = 4

$a = 404$ pm $= 404 \times 10^{-10}$ cm.

$2.72 = \dfrac{4 \times M}{6.02 \times 10^{23} \times (404 \times 10^{-10})^3}$

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

(19) (D). Half of body diagonal, $\dfrac{\sqrt{3}a}{2}$.

(20) (A). In FCC unit cell (Z = 4)

$4r = \sqrt{2}\,a$; $r = \dfrac{\sqrt{2}\,a}{4} = \dfrac{1.414 \times 361}{4} = 127.25$ Pm

(21) (B). Packing efficiency in bcc lattice = 68%
∴ Vacant space in bcc lattice = 100 – 68 = 32%

(22) (A). Frenkel defect is a dislocation defect.

(23) (B). $0.53\,g/cm^3 \times \dfrac{2 \times 6.94\,(g/mol)}{a^3 \times 6.02 \times 10^{23}\,mol^{-1}}$
On solving, a = 352 pm

(24) (A). $\dfrac{r_{(+)}}{r_{(-)}} = \dfrac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.54$

i.e., Ionic solid has octahedral geometry, thus co-ordination number of each ion in AB is 6.

(25) (C). In CaF_2, Ca^{2+} has fcc arrangement and F^- ions are present in all tetrahedral voids.
∴ Co-ordination numbers for Ca^{2+} and F^-

(26) (C). In frenkel defect the radius of cation must be very less than anion.

(27) (A). For BCC lattice : Z = 2, $a = \dfrac{4r}{\sqrt{3}}$

For FCC lattice : Z = 4, $a = 2\sqrt{2}r$

$\dfrac{d_{25°C}}{d_{900°C}} = \dfrac{\left(\dfrac{ZM}{N_A a^3}\right)_{BCC}}{\left(\dfrac{ZM}{N_A a^3}\right)_{FCC}} = \dfrac{2}{4}\left(\dfrac{2\sqrt{2}r}{\frac{4r}{\sqrt{3}}}\right)^3 = \dfrac{3\sqrt{3}}{4\sqrt{2}}$

(28) (C). Anions(A) are in hcp.
So number of anions (A) = 6
Cations(C) are in 75% O.V.

So number of cations (C) $= 6 \times \dfrac{3}{4} = \dfrac{18}{4} = \dfrac{9}{2}$

So formula of compound will be
$C_{9/2}A_6 \Rightarrow C_9A_{12}$; $C_9A_{12} \Rightarrow C_3A_4$