Chapter

15

The Solid State

SOLIDS

Solids are characterised by the state of matter in which particles are closely packed and held together by strong intermolecular attractive forces.

Types of Solids :

A solid can be classified as

Solids

↓ Crystalline Solids

↓ Amorphous Solids

Crystalline solids :

A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape.

Amorphous solids :

Amorphous solids have no precise melting point but when heated, become increasingly pliable until they assume the properties usually associated with liquids.

Difference Between Crystalline and Amorphous Solids :

Property	Crystalline Solids	Amorphous Solids
Shape	Definite, Characteristic geometrical shape	Irregular shape
Melting Point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	Give plain and smooth surfaces on cutting with a sharp edged tool	Give irregular surfaces when cut with a sharp edged tool
Heat of fusion	Definite and characteristic	Not definite
Nature	True solids	Pseudo solids or supercooled liquids
Order in arrangement of particles	Long range order	Only short range order
Anisotropy and Isotropy	Anisotropic in nature, crystalline solids show different values of physical properties along different directions and hence they are anisotropic in nature.	Isotropic in nature, Amorphous solids are isotropic in nature because some of their properties like electrical resistance, refractive index, thermal exapansion, etc., are same in all the directions.
Examples	Crystalline solids:- All solids elements (metals and non-metals) and compounds exist in this form.	Amorphous solids:- rubber, glass, fused silica, plastics, etc.

Note :

(a) Glass is considered a super cooled liquid because glass is a amorphous solid and hence, it shows the property to flow, though slowly. This is supported by the fact that glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top.

(b) Any material can be made amorphous or glassy either by rapidly cooling its melt or freezing its vapours. For example : Silica (SiO_2) which crystallises as quartz can be converted into amorphous silica (i.e. silica glass) by melting and rapid cooling.

(c) Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

CLASSIFICATION OF CRYSTALLINE SOLIDS

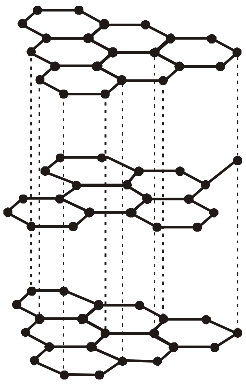
Crystalline solids are classified on the basis of nature of intermolecular forces operating in them into four categories, viz. molecular, ionic, metallic and covalent solids. The different properties of the four types of solids are given in the table below:

Type of Solid	Constituent Particles	Nature of Binding Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular Solids (i) Non-Polar	Atoms of noble gas or non-polar molecules	Dispersion or London forces	Ar, H_2, I_2, CH_4, Solid CO_2	Soft	Insulator	Very low
(ii) Polar	Polar molecules	Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded	Molecules containing H linked to F, O or N	Hydrogen bonding	H_2O (ice), NH_3	Hard	Insulator	Low
(2) Ionic Solids	Ions	Coulombic or electrostatic forces	NaCl, LiF, Zns, CaF_2, $MgBr_2$	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solution state	High
(3) Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic bonding	All metals and alloys	Hard but malleable and ductile	Conductors in solid as well as in molten state	Fairly High
(4) Covalent or Network Solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C(diamond), AlN, C(graphite)	Hard Soft	Insulators Conductor (exception)	Very High

Note :

(a) Ionic solids are insulators in the solid state because ions are not free to move. However, in the molten state, when dissolved in water, the ions become free to move about and they conduct electricity.

(b) **Exceptional behaviour of graphite :** Graphite is soft, conductor of electricity and a good solid lubricant because of 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 the layers and is free to move. This imparts graphite the above mentioned properties.



Structure of graphite

CRYSTAL LATTICES AND UNIT CELLS

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.

Space Lattice :

The arrangement of constituents particles like atoms, ions or molecules in different sites in three dimensional space is called space lattice.

There are only 14 possible three dimensional lattices and these are called **Bravais Lattices.** The characteristics of a crystal lattice are:

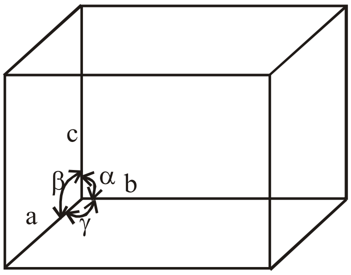
(i) Each point in a lattice is called lattice point or lattice site.

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

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

Unit Cell :

It is the smallest portion of the crystal lattice which when repeated in different directions, generates the entire lattice. A unit cell is characterised by six parameters, i.e., a, b, c, α, β and γ; where a, b and c are its dimensions along the edges while α, β and γ are the angles between the edges. These are depicted in the figure given below:



Unit cells can be broadly divided into two categories:

Primitive unit cells :

Unit cell in which constituent particles are present only on the corner positions of a unit cell.

Centred or non-primitive unit cells :

Unit cell in which constituent particles are present at positions other than corners in addition to those at corners

Types of Non-Primitive Unit Cells :

(i) Body-centred unit cells (*bcc*) :
Unit cell in which besides corners, one constituent particle is present at the body-centre.

(ii) Face-centred unit cells (*fcc*) :
Unit cell in which besides corners, one constituent particle is present at the centre of each face.

(iii) End-centred unit cells :
Unit cell in which besides corners, one constituent particle is present at the centre of any two opposite faces.

Contribution of Atoms Present at Different Lattice Sites :

In a crystal, atoms located at the corners and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell

(i) A point that lies at the corner of unit cell is shared among eight unit cells and thus, it contributes for 1/8 of each such point to unit cell.

(ii) A point along an edge is shared by four unit cells and thus contribute for 1/4 of each such point to unit cell.

(iii) A face-centred point is shared by two unit cells and thus contributes for 1/2 of each such point to unit.

(iv) A body-centred point lies entirely within the unit cell and thus contributes for one each such point to unit cell.

Calculation Number of Atoms in a Unit Cell

Primitive cubic/simple cubic unit cell :

Total number of atoms in one unit cell is $8\times\frac{1}{8}=(1)$

(8 corners × each corner is shared by 8 particles)

bcc unit cell :

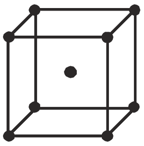
Total number of atoms per unit cell

(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.

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



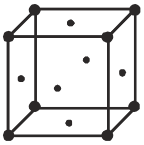
fcc unit cell :

Total number of atoms per unit cells

(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

$$6\times\frac{1}{2} = 3 \text{ atom per unit cell.}$$



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

CLOSE PACKING IN CRYSTALS :

Close-packing of particles results in two highly efficient lattices, hexagonal close packed (*hcp*) and cubic close packed (*ccp*). The latter is also called face centered cubic (*fcc*) lattice.

Hexagonal Close Packing :

In *hcp*, the pattern of spheres is repeated in alternate layers and is often written as ABAB _ _ _ _ pattern.

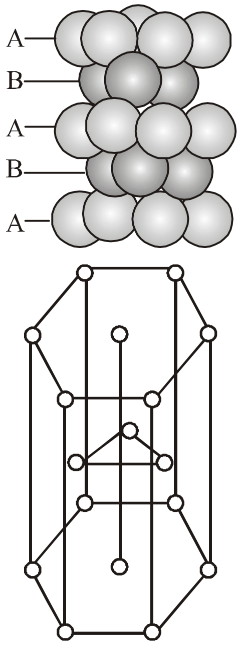


Fig. Hexagonal close-packed structure showing set of parallel planes

Here each atom is surrounded by 12 others and is said to have co-ordination number of 12.

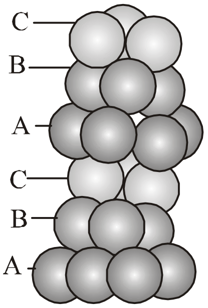
The *hcp* arrangement of atoms occupies 74% of the available space and thus has 26% vacant space.

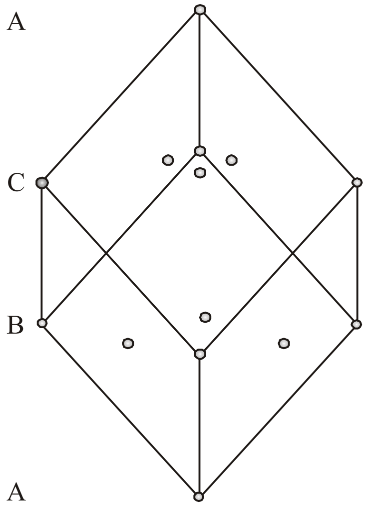
It has only one set of parallel close packed layers.

Hexagonal close packed structure is found in Be, Cd, Li, Ca, Cr, Mo, V, Mg, Zn, Ce, Zr, Os, Ru, He, etc.

Cubic Close Packing :

In *ccp*, the pattern of layers is often written as ABCABC _ _





As in *hcp*, each atom in *ccp* arrangement has 12 nearest neighbours. In other words, the co-ordination number of the atom is 12.

The *ccp* arrangement of atoms occupy 74% of the available space and thus has 26% vacant space.

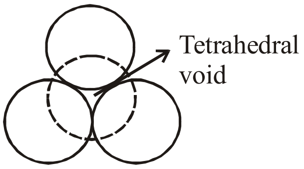
It has four sets of parallel close packed layers. Hence the chances for slipping of one layer over the other are more in the *ccp* arrangement than in the *hcp* arrangement. Hence metals having *ccp* structure (e.g. Cu, Ag, Au and Pt) are highly malleable and ductile.

Cubic close-packed structure is found in Al, Cr, Co, Cu, Au, Ag, Fe, Pb, Mn, Ni, Ca, Sr, Pt, all noble gases except He.

Type and Number of Voids

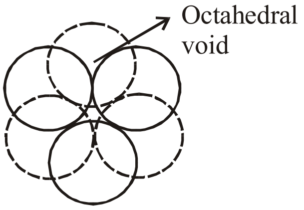
Close-packing of particles in hcp or ccp results in two types of voids : octahedral and tetrahedral.

(i) **Tetrahedral void :** Tetrahedral voids are formed when centres of four spheres are joined, i.e,



If the number of close packed spheres is N, then the number of tetrahedral voids generated = 2N

(ii) **Octahedral void :** A void surrounded by six spheres (i.e. when triangular voids in the second layer are above the triangular voids in the first layer) is called octahedral void, i.e.,



If the number of close packed spheres is N, then the number of octahedral voids generated = N and, the number of tetrahedral voids generated = 2N

Note : In ionic compounds anions are present in the packing whereas cations occupy the voids if the cations are small, they may occupy tetrahedral voids while if cations are large they occupy octahedral voids. Further, it is not necessary that all voids must be occupied. The formula of the compound can be calculated by knowing the fraction of voids occupied.

COORDINATION NUMBER :

In every ionic compound, positive ions are surrounded by negative ions and *vice versa*. Normally each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number**. The coordination number of positive and negative ions of a compound are same when the two types of ions are equal in number (e.g., NaCl, ZnS, etc.). On the other hand, when an ionic compound contains different number of positive and negative ions (as in $CaCl_2$, Na_2S etc.), the coordination numbers of positive and negative ions are different. For example, in $CaCl_2$ since Cl^- ions are twice the number of Ca^{2+} ions, the coordination number of calcium ion is twice the coordination number of chloride ion.

RADIUS RATIO RULES :

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

$$\text{Radius ratio } = \frac{r}{R} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}}$$

Table shows the relationship of radius ratio, co-ordination number and the geometrical shapes of some ionic crystals.

Limiting radius ratio $(r^+)/(r^-)$	C.N.	Shape
<0.155	2	Linear
$0.155-0.225$	3	Planar triangle
$0.225-0.414$	4	Tetrahedral
$0.414-0.732$	4	Square planar
$0.414-0.732$	6	Octahedral
$0.732-0.999$	8	Body-centred cubic

EFFECT OF PRESSURE AND TEMPERATURE ON CRYSTAL STRUCTURE

Effect of Pressure

Increase of pressure increases the co-ordination number during crystallization e.g., by applying high pressure, the NaCl crystal structure having 6 : 6 co-ordination number changes to CsCl crystal structure having co-ordination number 8 : 8.

$$\underset{(6\,:\,6\text{ co-ordination})}{\text{NaCl type crystal}} \underset{\text{heat, 760 K}}{\overset{\text{high pressure}}{\rightleftharpoons}} \underset{(8\,:\,8\text{ co-ordination})}{\text{CsCl type crystal}}$$

Effect of Temperature

Increase of temperature, however, decreases the co-ordination number e.g., upon heating to 760 K, the CsCl crystal structure having co-ordination of 8 : 8 changes to NaCl crystal structures having co-ordination 6 : 6.

PACKING EFFICIENCY

It is the percentage of total space filled by the particles.

Type of structure	Relation between 'a' and 'r' a : edge length r : radius of sphere	Packing Efficiency
hcp and ccp(fcc)	$r = \frac{a}{2\sqrt{2}}$	74%
bcc	$r = \frac{\sqrt{3}}{4}a$	68%
Simple cubic lattice	$r = \frac{a}{2}$	52.4%

Relationships between the nearest neighbour distance (d) and the edge (a) of unit cell of a cubic crystal.

Simple	Face-centred	Body-centred
$d = a$	$d = \frac{a}{\sqrt{2}}$ $= 0.707\ a$	$d = \frac{\sqrt{3}}{2}a$ $= 0.866\ a$

DENSITY OF A UNIT CELL

For cubic crystals of elements

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} \text{ g/cm}^3$$

For cubic crystals of ionic compounds

$$\rho = \frac{ZM}{a^3 N_A} \text{ g/cm}^3 \text{ or kg m}^{-3}$$

where $\rho \rightarrow$ density of the unit cell
$Z \rightarrow$ no. of atoms present in one unit cell
$M \rightarrow$ molar mass
$a \rightarrow$ edge length of the unit cell
$N_A \rightarrow$ Avogadro's number

BRAGG EQUATION :

According to Bragg, a crystal (composed of series of equally spaced atomic planes) could be employed not only as a **transmission grating** (as suggested by Laue) but also as a reflection grating. When X-rays are incident on a crystal face, these penetrate into the crystal and strike the atoms in successive planes. From each of these planes the X-rays are reflected like the reflection of a beam of light from a bundle of glass plates of equal thickness. Based on this model, Bragg derived a simple relation between the wavelength (λ) of the X-rays used, the distance (d) between the successive atomic planes and the angle of incident X-rays or the angle of reflection (θ).

$$n\lambda = 2d\sin\theta \qquad (\text{where } n = 1, 2, 3, ...)$$

The equation is known as **Bragg's equation or Bragg's law.** The reflection corresponding to $n = 1$ (for a given family of planes) is called *first order reflection*; the reflection corresponding to $n = 2$ is the *second order reflection* and so on.

IMPERFECTIONS IN SOLIDS

Point Defects and Line Defects :

Broadly the defects in crystals are of two types point and line defects. Point defects are irregularities from ideal arrangement around a point or an atom in lattice. However, when the deviation from the ideal arrangement exist in the entire row of lattice points, the defect is called line defect.

Points defect is of 3 types :

(i) Stoichiometric Defects :

Those point defects that do not disturb the stochiometry of the solid.

(a) **Vacancy defect :** This defect arises when some lattice sites are vacant. Thus generally arises due to absorption of heat from the surroundings. It decreases the density of a substance.

(b) **Interstitial defect :** This defect arises when some constituent particles occupy an interstitial site. It increases the density of the substance.

The above two types of defects are generally shown by **non-ionic solids**. Ionic solids do not show simple vacancy and interstitial defects. Instead, they show these defects as Schottky and Frenkel defects, as explained below:

(c) **Frenkel defect :** This defect arises when an ion is missing from its lattice site and it occupies the interstitial site. It does not change the density of the crystal.

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.

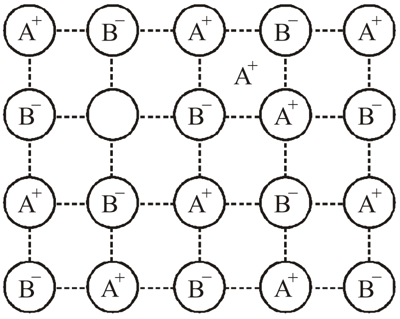


Fig. Frenkel defect

Eg. ZnS, AgCl, AgBr, AgI etc.

(d) **Schottky defect :** This defect arises when equal number of cations and anions are missing from their lattice sites. It decreases the density of substance.

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.

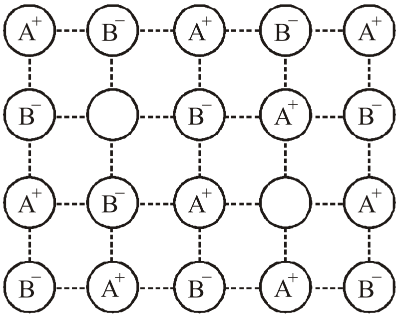


Fig. Schottky defect

Eg. NaCl, KCl, CsCl, KBr etc.

Note : AgBr shows both i.e., Frenkel and Schottky defect.

(ii) Impurity defects :

These defects arise when foreign atoms are present at lattice site (in place of host atoms) or at vacant interstitial sites.

(iii) Non-stoichiometric defects :

As a result of these defects, the ratio of cations to anions becomes different from that indicated by ideal chemical formula.

Example : VO_x (where x can vary between 0.6 to 1.3)

Two types of non-stoichiometric defects are :

(a) **Metal excess defect :**

Metal excess defects due to anion vacancies

It occurs due to *anionic vacancies* i.e. anions diffuse to the surface of the crystal resulting in anionic sites which are occupied by unpaired electrons. These sites are called F-centres. The e^{-1}s absorb energy from the visible light and impart colour to crystal

Examples :

(1) The excess sodium in NaCl makes the crystal appears yellow.
(2) Excess potassium in KCl makes it violet.
(3) Excess lithium in LiCl makes it pink.

Note : Greater the number of F-centres, greater is the intensity of colour.

Metal excess defects due to interstitial cations :

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

Example : When ZnO is heated, it loses oxygen and turns yellow due to:

$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess of Zn^{2+} ions get trapped into vacant interstitial sites.

(b) **Metal Deficiency defect :**

It occurs due to missing of cation from its lattice site and presence of higher charge cation in adjacent site. It occurs when metals show variable valency, Example : FeO, FeS and NiO.

ELECTRICAL PROPERTIES OF SOLIDS

On the basis of conductivity, solids are classified as:

(i) **Conductors :** The solids having conductivities ranging between 10^4 to 10^7 Ω^{-1} m^{-1}. Metals are good conductors.

(ii) **Insulators :** The solids having very low conductivities ranging between 10^{-20} to 10^{-10} Ω^{-1} m^{-1}. Example : plastic, rubber, non-metals etc.

(iii) **Semiconductors:** The solids having conductivities in the intermediate range from 10^{-6} to 10^4 Ω^{-1} m^{-1}.

Band Theory :

The behaviour of conductors, insulators and semiconductors are explained on the basis of band theory. The atomic orbitals of metals overlap to form a large number of molecular orbitals and this set is called **a band.** Two bands are formed:

Valence band (lower energy) and conduction band (higher energy)

If valence band is partially filled or overlaps with higher energy conduction band, e^{-1}s can easily flow under the influence of electric field. Thus, metals conduct electricity.

If gap between filled valence band and unoccupied conduction band is large, e^{-1}s cannot jump from valence band to conduction band. Hence, the substance has extremely low conductivity and it behaves as an insulator.

If the gap between valence band and conduction band is small, some e^{-1}s may jump from valence band to conduction band. Hence, the substance shows some conductivity and it acts as a semi conductor. Electrical conductivity of semiconductor increases with temperature as more electrons can jump to conduction band. Pure substances like Si and Ge show this type of behaviour and are called **intrinsic semiconductor**.

Extrinsic semiconductors are obtained by adding impurity to a semiconductor so as to increase its conductivity.

The process of adding impurities to a crystalline substance so as to change its properties is called doping.

Thus, the impurities added may be electron rich or electron deficit. Each of these is briefly described below :

(i) Doping with electron rich impurities : Group 14 element like silicon or germanium has 4 electrons in the valence shell. When it is doped with Group 15 element like P or As, the silicon or germanium atoms at some lattice sites are substituted by atoms of P or As. Now, as these atoms have 5 electrons in the valence shell, after forming normal four covalent bonds with the neighbouring silicon atoms, the fifth extra electron is free and gets delocalized. These delocalized electrons increase the conductivity of silicon or germanium, the silicon or germanium crystals doped with electron rich impurities are called **n-type semiconductors**.

(ii) Doping with electron deficit impurities : When Group 14 element like Si or Ge is doped with Group 13 element like B, Al or Ga, the Si or Ge atom at some lattice sites are substituted by those of B, Al or Ga. Now, as Group 13 elements have only three valence electrons, they can form three covalent bonds with the neighbouring silicon atoms. Thus, a hole is created at the site where fourth electron is missing. This is called electron hole or electron vacancy. Electron deficit doped silicon or germanium are called **p-type semiconductors**.

MAGNETIC PROPERTIES OF SOLIDS

Magnetic properties of materials are studied in terms of magnetic moments which arise due to orbital motion and spinning motion of electrons.

Based on their behaviour in the external magnetic field, substances are classified as below :

Diamagnetic Substances :

Those substances which are weakly repelled by external magnetic field. It is shown by substances which contain fully-filled orbitals. For ex: TiO_2, H_2O, NaCl, benzene, etc.

Paramagnetic Substances :

Which are weakly attracted by external magnetic field. It is shown by substances which contain unpaired e^{-1}s. Example : O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}. However, they loose their magnetism in the absence of magnetic field.

Ferromagnetic Substances:

The substances which are strongly attracted by magnetic field are termed as ferromagnetic substances. This type of substance has 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.

Anti-Ferromagnetic Substances :

Substances which possess zero net magnetic moment. It is due to presence of equal number of electrons in opposite directions. For ex: MnO, Mn_2O_3. Their magnetic moment will compensate each others magnetic moment.

Ferrimagnetic Substances :

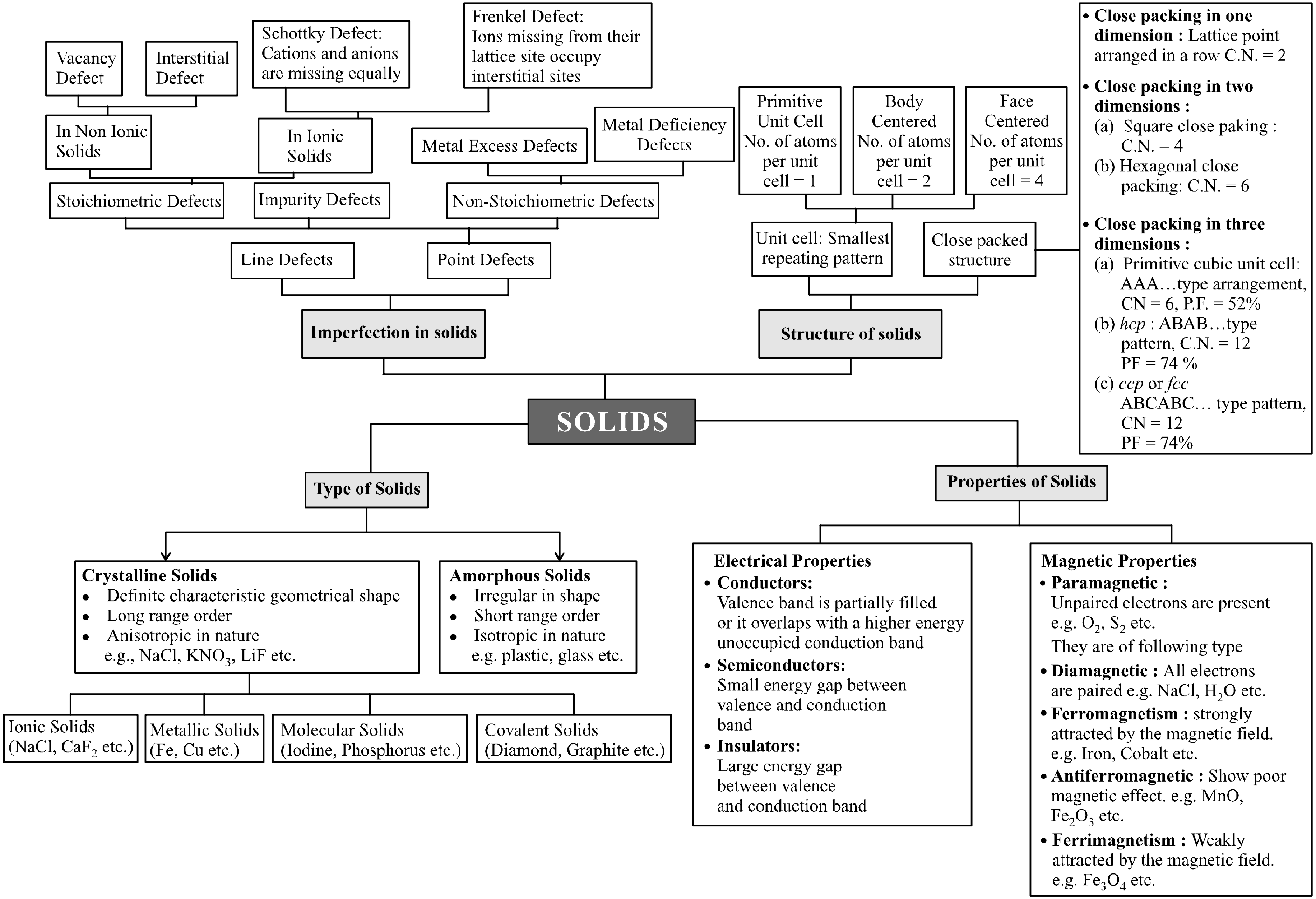
When unequal number of unpaired electrons are aligned in opposite directions, the net magnetic moment is not zero. Such substances are termed as ferrimagnetic substances e.g., ferrite Fe_2O_3.

Note :

(i) All magnetically ordered substances, i.e., ferromagnetic and anti-ferromagnetic solids change into paramagnetic at high temperature. This is due to randomisation of domains (spins) on heating. For ex: ferrimagnetic substance, Fe_3O_4, becomes paramagnetic at 850 K.

(ii) Each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie temperature**.

CONCEPT MAP



Schottky Defect: Cations and anions are missing equally

Frenkel Defect: Ions missing from their lattice site occupy interstitial sites

Primitive Unit Cell No. of atoms per unit cell = 1

Body Centered No. of atoms per unit cell = 2

Face Centered No. of atoms per unit cell = 4

- **Close packing in one dimension :** Lattice point arranged in a row C.N. = 2
- **Close packing in two dimensions :**
  - (a) Square close paking : C.N. = 4
  - (b) Hexagonal close packing: C.N. = 6
- **Close packing in three dimensions :**
  - (a) Primitive cubic unit cell: AAA…type arrangement, CN = 6, P.F. = 52%
  - (b) *hcp* : ABAB…type pattern, C.N. = 12 PF = 74 %
  - (c) *ccp* or *fcc* ABCABC… type pattern, CN = 12 PF = 74%

Crystalline Solids
- Definite characteristic geometrical shape
- Long range order
- Anisotropic in nature e.g., NaCl, KNO_3, LiF etc.

Amorphous Solids
- Irregular in shape
- Short range order
- Isotropic in nature e.g. plastic, glass etc.

Electrical Properties
- **Conductors:** Valence band is partially filled or it overlaps with a higher energy unoccupied conduction band
- **Semiconductors:** Small energy gap between valence and conduction band
- **Insulators:** Large energy gap between valence and conduction band

Magnetic Properties
- **Paramagnetic :** Unpaired electrons are present e.g. O_2, S_2 etc. They are of following type
- **Diamagnetic :** All electrons are paired e.g. NaCl, H_2O etc.
- **Ferromagnetism :** strongly attracted by the magnetic field. e.g. Iron, Cobalt etc.
- **Antiferromagnetic :** Show poor magnetic effect. e.g. MnO, Fe_2O_3 etc.
- **Ferrimagnetism :** Weakly attracted by the magnetic field. e.g. Fe_3O_4 etc.

EXERCISE - 1

Conceptual Questions

1. Frenkel and Schottky defects are :
(a) nucleus defects (b) non-crystal defects
(c) crystal defects (d) nuclear defects

2. Which of the following compounds is a good conductor of electricity in solution state ?
(a) Covalent (b) Molecular
(c) Metallic (d) Ionic

3. Most crystals show good cleavage because their atoms, ions or molecules are
(a) weakly bonded together
(b) strongly bonded together
(c) spherically symmetrical
(d) arranged in planes

4. Certain crystals produce electric signals on application of pressure. This phenomenon is called :
(a) pyroelectricity (b) ferroelectricity
(c) piezoelectricity (d) ferrielectricity

5. A solid with high electrical and thermal conductivity is
(a) Si (b) Li
(c) NaCl (d) Ice

6. Solid CH_4 is
(a) ionic solid (b) covalent solid
(c) molecular solid (d) does not exist

7. An example of a covalent crystalline solid is:
(a) Si (b) Al
(c) NaF (d) Ar

8. The pure crystalline substance on being heated gradually first forms a turbid liquid at constant temperature and still at higher temperature turbidity completely disappears. The behaviour is a characteristic of substance forming
(a) Allotropic (b) Liquid
(c) Isomeric (d) Isomorphous

9. Na and Mg crystallize in the bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is :
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

10. For *fcc* if AB is just like the rock salt like structure then, A^+ and B^- are located at –
(a) A^+ - Tetrahedral voids ; B^- - Corner
(b) A^+ - Corner and faces ; B^- - Octahedral voids
(c) A^+ - Octahedral voids ; B^- - Corner and faces
(d) A^+ - Corner and faces ; B^- - Octahedral and tetrahedral voids

11. The ionic radii of X^+ and Y^- ions are 146 and 216 pm respectively. The probable type of structure shown by it is
(a) CsCl type (b) Rock salt type
(c) Zinc blend type (d) CaF_2 type

12. The element which is used as semiconductor is
(a) Al (b) Bi
(c) Cr (d) Si

13. A solid has a structure in which 'W' atoms are located at the corners of a cubic lattice 'O' atoms at the centre of edges and Na atoms at the centre of the cube. The formula for the compound is
(a) Na_2WO_3 (b) Na_2WO_2
(c) $NaWO_2$ (d) $NaWO_3$

14. A solid is made of two elements X and Z. The atoms Z are in *ccp* arrangement while the atoms X occupy all the tetrahedral sites. What is the formula of the compound?
(a) XZ (b) XZ_2
(c) X_2Z (d) X_2Z_3

15. The radius ratio in CsCl is 0.93. The expected lattice structure is
(a) tetrahedral (b) square planar
(c) octahedral (d) body-centred cubic

16. In NaCl crystal each Cl^- ion is surrounded by
(a) 4 Na^+ ions (b) 6 Na^+ ions
(c) 1 Na^+ ions (d) 2 Na^+ ions

17. Edge length of a cube is 400 pm, its body diagonal would be
(a) 566 pm (b) 600 pm
(c) 500 pm (d) 693 pm

18. In stoichiometric defects, the types of compound exhibit Frenkel defects have/has
(a) Low co-ordination nos.
(b) High co-ordination.
(c) Small difference in the size of cations and anions
(d) None of these.

19. For orthorhombic system axial ratios are $a \neq b \neq c$ and the axial angles are
(a) $\alpha = \beta = \gamma \neq 90°$ (b) $\alpha = \beta = \gamma = 90°$
(c) $\alpha = \beta = \gamma = 90°, \beta = 90°$ (d) $\alpha \neq \beta \neq \gamma = 90°$

20. In the fluorite structure, the coordination number of Ca^{2+} ion is :
(a) 4 (b) 6
(c) 8 (d) 3

21. Na and Mg crystallize in *bcc* and *fcc* type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

22. In the solid state, MgO has the same structure as that of sodium chloride. The number of oxygens surrounding each magnesium in MgO is
(a) 6 (b) 1
(c) 2 (d) 4

23. Equal number of atoms or ion missing from normal lattice point creating a vacancy due to

(a) Frenkel defect (b) Mass defect
(c) Schottky defect (d) Interstitial defect

24. When molten zinc is converted into solid state, it acquires *hcp* structure. The number of nearest neighbours of Zn will be

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

25. Hexagonal close packed arrangement of ions is described as

(a) ABC ABA (b) ABC ABC
(c) ABABA (d) ABBAB

26. CsBr has *bcc* structure with edge length 4.3. The shortest interionic distance in between Cs^+ and Br^- is

(a) 3.72 (b) 1.86
(c) 7.44 (d) 4.3

27. Schottky defect generally appears in :

(a) NaCl (b) KCl
(c) CsCl (d) all of these

28. 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]

(a) 5.14×10^{21} unit cells (b) 1.28×10^{21} unit cells
(c) 1.71×10^{21} unit cells (d) 2.57×10^{21} unit cells

29. In a solid '*AB*' having the *NaCl* structure, '*A*' atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

(a) AB_2 (b) A_2B
(c) A_4B_3 (d) A_3B_4

30. A solid AB crystallises as NaCl structure and the radius of the cation is 0.100nm. The maximum radius of the anion can be:

(a) 0.137 nm (b) 0.241 nm
(c) 0.274 nm (d) 0.482 nm

31. Edge length of a cube is 400 pm. Its body diagonal would be

(a) 500 pm (b) 566 pm
(c) 600 pm (d) 693 pm

32. In the calcium fluoride structure, the coordination number of the cation and anion are respectively

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

33. The limiting radius ratio for tetrahedral shape is:

(a) 0 to 0.155 (b) 0.225 to 0.414
(c) 0.155 to 0.225 (d) 0.414 to 0.732

34. The second order Bragg diffraction of X-rays with = 1.00 Å from a set of parallel planes in a metal occurs at an angle 60º. The distance between the scattering planes in the crystal is

(a) 0.575 Å (b) 1.00 Å
(c) 2.00 Å (d) 1.15 Å

35. For a cubic geometry the limiting $\frac{r^+}{r^-}$ is :

(a) 0.414 (b) 0.155
(c) >0.731 (d) 0.731

36. CsBr crystallises in a body centered cubic lattice. The unit cell length is 436.6 pm. 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 density of CsBr is

(a) 0.425 g/cm^3 (b) 8.5 g/cm^3
(c) 4.25 g/cm^3 (d) 82.5 g/cm^3

37. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is

(a) 5.96×10^{-3} (b) 5.96×10^4
(c) 5.96×10^{-2} (d) 5.96×10^{-1}

38. Potassium fluoride has NaCl type structure. What is the distance between K^+ and F^- ions if cell edge is 'a' cm.

(a) 2a cm (b) a/2 cm
(c) 4a cm (d) a/4 cm

39. In the Bragg's equation for diffraction of X-rays, n represents for

(a) quantum number (b) an integer
(c) Avogadro's numbers (d) moles

40. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5Å which crystallizes in cubic lattice. If the density is 2g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm.

(a) 217 pm (b) 210 pm
(c) 220 pm (d) 205 pm

41. An element occuring in the bcc structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cells will be

(a) 24.16×10^{23} (b) 36.18×10^{23}
(c) 6.04×10^{23} (d) 12.08×10^{23}

42. The number of atoms in 100 g of an *fcc* crystal with density, $d = 10\ g/cm^3$ and cell edge equal to 100 pm, is equal to

(a) 1×10^{25} (b) 2×10^{25}
(c) 3×10^{25} (d) 4×10^{25}

43. Pottasium has a bcc structure with nearest neighbour distance 4.52 Å. Its atomic weight is 39. Its density (in kg m^{-3}) will be

(a) 454 (b) 804
(c) 852 (d) 910

44. 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

45. The cubic unit cell of a metal (molar mass = 63.55g mol^{-1}) has an edge length of 362 pm. Its density is 8.92g cm^{-3}. The type of unit cell is

(a) primitive (b) face centered
(c) body centered (d) end centered

46. Coordination numbers of Zn^{2+} and S^{2-} in the crystal structure of wurtzite are
(a) 4, 4 (b) 6, 6
(c) 8, 4 (d) 8, 8

47. Each of the following solids show, the Frenkel defect except
(a) ZnS (b) AgBr
(c) AgI (d) KCl

48. Doping of silicon (Si) with boron (B) leads to :
(a) *n*-type semiconductor (b) *p*-type semiconductor
(c) metal (d) insulator

49. Schottky defect defines imperfection in the lattice structure of
(a) solid (b) gas
(c) liquid (d) plasma

50. On doping Ge metal with a little of In or Ga, one gets
(a) p-type semi conductor (b) n-type semi conductor
(c) insulator (d) rectifier

51. If *Z* is the number of atoms in the unit cell that represents the closest packing sequence ..... ABC ABC ......, the number of tetrahedral voids in the unit cell is equal to :
(a) Z (b) $2Z$
(c) $Z/2$ (d) $Z/4$

52. Schottky defect in crystals is observed when
(a) an ion leaves its normal site and occupies an interstitial site
(b) unequal number of cations and anions are missing from the lattice
(c) density of the crystal increases
(d) equal number of cations and anions are missing from the lattice

53. The appearance of colour in solid alkali metal halides is generally due to
(a) Schottky defect (b) Frenkel defect
(c) Interstitial positions (d) F-centre

54. The crystal system of a compound with unit cell dimensions "$a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90°$ and $\gamma = 120°$" is
(a) cubic (b) hexagonal
(c) orthorhombic (d) rhombohedral

55. Crystal defect indicated in the diagram below is
$Na^+Cl^-Na^+Cl^-Na^+Cl^-$ Cl^- □ Cl^-Na^+ □ Na^+
Na^+Cl^- □ $Cl^-Na^+Cl^-$ $Cl^-Na^+Cl^-Na^+$ □ Na^+
(a) Interstitial defect
(b) Schottky defect
(c) Frenkel defect
(d) Frenkel and Schottky defects

56. Schottky defect generally appears in :
(a) NaCl (b) KCl
(c) CsCl (d) all of these

57. Which defect causes decrease in the density of crystal
(a) Frenkel (b) Schottky
(c) Interstitial (d) F – centre

58. What is the coordination number of sodium in Na_2O?
(a) 6 (b) 4
(c) 8 (d) 2

59. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.02 \times 10^{23}$ mol^{-1})
(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}

60. The fraction of total volume occupied by the atoms present in a simple cube is
(a) $\frac{\pi}{3\sqrt{2}}$ (b) $\frac{\pi}{4\sqrt{2}}$
(c) $\frac{\pi}{4}$ (d) $\frac{\pi}{6}$

61. 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,
(a) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (b) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{3}}{2}a$ (d) $1a : \sqrt{3}a : \sqrt{2}a$

62. With which one of the following elements silicon should be doped so as to give *p*-type of semiconductor ?
(a) Germanium (b) Arsenic
(c) Selenium (d) Boron

63. AB; crystallizes in a body centred cubic lattice with edge length '*a*' equal to 387 pm. The distance between two oppositely charged ions in the lattice is :
(a) 335 pm (b) 250 pm
(c) 200 pm (d) 300 pm

64. Among the following which one has the highest cation to anion size ratio?
(a) NaF (b) CsI
(c) CsF (d) LiF

65. A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y^-) will be :
(a) 275.1 pm (b) 322.5 pm
(c) 241.5 pm (d) 165.7 pm

66. A metal crystallizes with a face-centered cubic lattice. The edge length of the unit cell is 408 pm. The diameter of the metal atom is :
(a) 288 pm (b) 408 pm
(c) 144 pm (d) 204 pm

67. In a compound, atoms of element Y form *ccp* lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be
(a) X_4Y_3 (b) X_2Y_3
(c) X_2Y (d) X_3Y_4

68. Copper crystallises in *fcc* with a unit cell length of 361 pm. What is the radius of copper atom?
(a) 127 pm (b) 157 pm
(c) 181 pm (d) 108 pm

69. 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
(a) 288 pm (b) 398 pm
(c) 618 pm (d) 144 pm

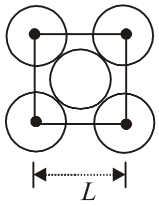
70. The Ca^{2+} and F^- are located in CaF_2 crystal, respectively at face centred cubic lattice points and in
(a) tetrahedral voids (b) half of tetrahedral voids
(c) octahedral voids (d) half of octahedral voids

71. KCl crystallises in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$. Calculate the ratio of the edge length of the unit cell for KCl to that of NaCl.
(a) 1.123 (b) 0.891
(c) 1.414 (d) 0.414

72. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively
(a) 30% and 26% (b) 26% and 32%
(c) 32% and 48% (d) 48% and 26%

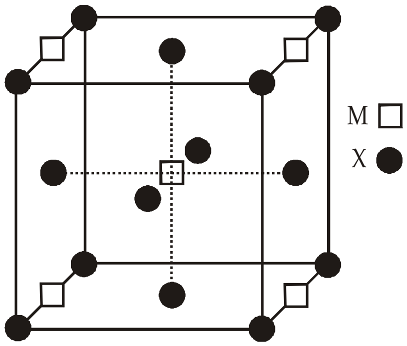
73. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :
(a) 75 pm (b) 300 pm
(c) 240 pm (d) 152 pm

74. The packing efficiency of the two-dimensional square unit cell shown below is :



(a) 39.27% (b) 68.02%
(c) 74.05% (d) 78.54%

75. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is



(a) MX (b) MX_2
(c) M_2X (d) M_5X_{14}

EXERCISE - 2
Applied Questions

1. The correct statement regarding F– centre is
(a) electron are held in the voids of crystals
(b) F – centre produces colour to the crystals
(c) conductivity of the crystal increases due to F – centre
(d) All of these

2. The anions (*A*) form hexagonal closest packing and the cations (*C*) occupy only 2/3 of octahedral holes. The simplest formula of the ionic compound is :
(a) CA (b) C_3A_2
(c) C_4A_3 (d) C_2A_3

3. Certain crystals produce electric signals on application of pressure. This phenomenon is called
(a) Pyroelectricity (b) Ferroelectricity
(c) Piezoelectricity (d) Ferrielectricity

4. For a cubic geometry the limiting $\frac{r^+}{r^-}$ is :
(a) 0.414 (b) 0.155
(c) >0.731 (d) 0.731

5. Which of the following has maximum value of cation/anion ratio?
(a) KCl (b) NaCl
(c) CaF_2 (d) $MgCl_2$

6. What is the number of tetrahedral voids per atom in a crystal?
(a) 1 (b) 2
(c) 6 (d) 8

7. Fe_3O_4 contains the magnetic dipoles of cations oriented as
(a) ↑↓↑↓ (b) ↑↑↑↓↓
(c) ↑↑↑↑↑ (d) ↑↑↑↓↓↓

8. The intermetallic compound LiAg crystallizes in a cubic lattice in which both lithium and silver atoms have coordination number of eight. To what crystal class does the unit cell belong
(a) Simple cubic (b) Face-centred cubic
(c) Body-centred cubic (d) None of these

9. A compound is formed by elements A and B. The crystalline cubic structure has the A atoms at the corners of the cube and B atoms at the body centre. The simplest formula of the compound is
(a) AB (b) A_6B
(c) AB_6 (d) A_8B_4

10. A compound formed by elements X and Y crystallizes in a cubic structure in which the X atoms are at the corners of a cube and the Y atoms are at the face centres. The formula of the compound is

(a) XY_3 (b) X_3Y
(c) XY (d) XY_2

11. Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

12. A match box exhibits
(a) Cubic geometry
(b) Monoclinic geometry
(c) Orthorhombic geometry
(d) Tetragonal geometry

13. Olive oil when allowed to cool slowly gets solidified and forms a solid over a wide range of temperature. Best description of the solid based on above observation is
(a) Ionic solid (b) covalent network solid
(c) metallic solid (d) molecular solid

14. A crystalline solid
(a) changes abruptly from solid to liquid when heated
(b) has no definite melting point
(c) undergoes deformation of its geometry easily
(d) has an irregular 3-dimensional arrangements

15. Which of the following statements about amorphous solids is incorrect ?
(a) They melt over a range of temperature
(b) They are anisotropic
(c) There is no orderly arrangement of particles
(d) They are rigid and incompressible

16. To get a n- type semiconductor, the impurity to be added to silicon should have which of the following number of valence electrons
(a) 1 (b) 2
(c) 3 (d) 5

17. Which set of following characteristics for ZnS crystal is correct?
(a) Coordination number (4 : 4); *ccp*; Zn^{++} ion in the alternate tetrahedral voids
(b) Coordination number (6 : 6); *hcp*; Zn^{++} ion in all tetrahedral voids.
(c) Coordination number (6 : 4); *hcp*; Zn^{++} ion in all octahedral voids
(d) Coordination number (4 : 4); *ccp*; Zn^{++} ion in all tetrahedral voids.

18. In p-type semiconductor, the added impurity to silicon is -----and conduction of electric current is due to the movement of-----
(a) As, electrons (b) P, holes
(c) Ga, holes (d) Ga, electrons & holes

DIRECTIONS for Qs. 19 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation of Statement-1
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation of Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

19. **Statement-1 :** In crystal lattice, the size of the tetrahedral hole is larger than an octahedral hole.
Statement-2 : The cations occupy less space than anions in crystal packing.

20. **Statement-1 :** In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.
Statement-2 : Equal number of cation and anion vacancies are present.

21. **Statement-1 :** Space or crystal lattice differ in symmetry of the arrangement of points.
Statement-2 : $n\lambda = 2d\sin\theta$, is known as Bragg's equation.

22. **Statement-1 :** Crystalline solids have long range order.
Statement-2 : Amorphous solids have short range order.

23. **Statement-1 :** In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.
Statement-2 : A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.

24. **Statement-1 :** Electrical conductivity of semiconductors increases with increasing temperature.
Statement-2 : With increase in temperature, large number of electrons from the valence band can jump to the conduction band.

25. **Statement-1 :** On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.
Statement-2 : The electrons change their spin on heating.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

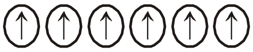
Exemplar Questions

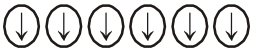
1. Which of the following conditions favours the existence of a substance in the solid state?
(a) High temperature (b) Low temperature
(c) High thermal energy (d) Weak cohesive forces

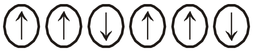
2. Which of the following is not a characteristic of a crystalline solid?
(a) Definite and characteristic heat of fusion
(b) Isotropic nature
(c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
(d) A true solid

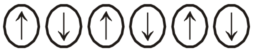
3. Which of the following is an amorphous solid?
(a) Graphite (C) (b) Quartz glass (SiO_2)
(c) Chrome alum (d) Silicon carbide (SiC)

4. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?

(a) 

(b) 

(c) 

(d) 

5. 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

6. Which of the following statement 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

7. 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.

8. Iodine molecules are held in the crystals lattice by......... .
(a) London forces
(b) dipole – dipole interactions
(c) covalent bonds
(d) coulombic forces

9. Which of the following is a network solid?
(a) SO_2 (solid) (b) I_2
(c) Diamond (d) H_2O (ice)

10. Which of the following solids is not an electrical conductor?
1. Mg(s) 2. TiO (s)
3. I_2(s) 4. H_2O(s)
(a) Only 1 (b) Only 2
(c) 3 and 4 (d) 2, 3 and 4

11. 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

12. 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

13. Which of the following oxides behaves as conductor or insulator depending upon temperature?
(a) TiO (b) SiO_2
(c) TiO_3 (d) MgO

14. Which of the following oxides shows electrical properties like metals?
(a) SiO_2 (b) MgO
(c) SO_2(s) (d) CrO_2

15. The lattice site in a pure crystal cannot be occupied by .....
(a) molecule (b) ion
(c) electron (d) atom

16. Graphite cannot be classified as ....
(a) conducting solid (b) network solid
(c) covalent solid (d) ionic solid

17. Cations are present in the interstitial sites in ....
(a) Frenkel defect (b) Schottky defect
(c) vacancy defect (d) metal deficiency defect

18. 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

19. Which of the following is true about the charge acquired by *p* – type semiconductors?
(a) Positive
(b) Neutral
(c) Negative
(d) Depends on concentrations of *p* impurity

20. To get a *n*-type semiconductor from silicon, it should be doped with a substance with valency ....
(a) 2 (b) 1
(c) 3 (d) 5

21. The total number of tetrahedral voids in the face-centred unit cell is ....
(a) 6 (b) 8
(c) 10 (d) 12

22. Which of the following points defects are shown by AgBr(s) crystals?
1. Schottky defect
2. Frenkel defect
3. Metal excess defect
4. Metal deficiency defect
(a) 1 and 2 (b) 3 and 4
(c) 1 and 3 (d) 2 and 4

23. In which of the following pair, most efficient packing is present?
(a) hcp and bcc
(b) hcp and ccp
(c) bcc and ccp
(d) bcc and simple cubic cell

24. The percentage of empty space in a body centred cubic arrangement is ....
(a) 74 (b) 68
(c) 32 (d) 26

25. Which of the following statement is not true about the hexagonal close packing?
(a) The coordination number is 12
(b) It has 74% packing efficiency
(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
(d) In this is arrangement spheres of the fourth layer are exactly aligned with those of the first layer

26. In which of the following structures coordination number for cations and anions in the packed structure will be same?
(a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell

(b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
(c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
(d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell

27. What is the coordination number in a square close packed structure in two dimensions?
(a) 2 (b) 3
(c) 4 (d) 6

28. Which kind of defects are introduced by doping?
(a) Dislocation defect (b) Schottky defect
(c) Frenkel defect (d) Electronic defect

29. Silicon doped with electron rich impurity forms..... .
(a) *p* – type semiconductor
(b) *n* – type semiconductor
(c) intrinsic semiconductor
(d) insulator

30. 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.

31. 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 the 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

32. 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

33. The correct order of the packing efficiency in different types of unit cells is ....
(a) fcc < bcc < simple cubic
(b) fcc > bcc > simple cubic
(c) fcc < bcc > simple cubic
(d) bcc < fcc > simple cubic

34. 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

35. 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

36. The edge lengths of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cells are respectively ....
(a) $2\sqrt{2}r, \frac{4r}{\sqrt{3}}, 2r$ (b) $\frac{4r}{\sqrt{3}}, 2\sqrt{2}r, 2r$
(c) $2r, 2\sqrt{2}r, \frac{4r}{\sqrt{3}}$ (d) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2}r$

37. Which of the following represents correct order of conductivity in solids?
(a) $\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
(b) $\kappa_{\text{metals}} << \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
(c) $\kappa_{\text{metals}\cdot} > \kappa_{\text{semmiconductors}} > \kappa_{\text{insulators}} = \text{zero}$
(d) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

NEET/AIPMT (2013-2017) Questions

38. Which of the following statements about the interstitial compounds is incorrect ? ***[NEET 2013]***
(a) They are chemically reactive.
(b) They are much harder then the pure metal.
(c) They have higher melting points than the pure metal.
(d) They retain metallic conductivity.

39. The number of carbon atoms per unit cell of diamond unit cell is : ***[NEET 2013]***
(a) 8 (b) 6
(c) 1 (d) 4

40. A metal has a *fcc* lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3}. The molar mass of the metal is : (N_A, Avogadro's constant = 6.02×10^{23} mol^{-1}) ***[NEET 2013]***
(a) 30 g mol^{-1} (b) 27 g mol^{-1}
(c) 20 g mol^{-1} (d) 40 g mol^{-1}

Hints & Solutions

EXERCISE - 1

1. (c) Frenkel and Schottky defects are crystal defects. It arises due to dislodgement of cation or anion from their places in the crystal lattice.
2. (d) Ionic compounds are dissociated in solution state and form ions. Ions are good carrier of charge which make solution conducting.
3. (d) Crystals show good cleavage because their constituent particles are arranged in planes.
4. (c) The phenomenon is called piezoelectricity.
5. (b) Out of the given substances, only Li has high electrical and thermal conductivity as Li is a metallic solid.
6. (c) Solid CH_4 is a molecular solid. In this, the constituent molecules are held together by van der Waal's forces.
7. (a) Si is an example of covalent crystalline solid among the given choices. Si atoms are covalently linked in tetrahedral manner.
8. (b) Liquid crystals on heating first become turbid and then clear.
9. (d) In a bcc cell eight atoms are located at the corners whereas one lies at the centre.

$$\therefore \quad n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

whereas in an fcc cell eight atoms are at the corners and one atom is located at each of the six faces which is shared by two unit of cell.

$$\therefore \quad n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

10. (c) AB is just like NaCl. Thus twelve A^+ are at edges and 1 within body of *fcc* i.e. in octahedral voids and six B^- at faces and 8 at corner.
11. (b) The radius ratio $\frac{r_+}{r_-} = \frac{146}{216} = 0.675$

It lies between 0.414 – 0.732. Hence, it exhibits rock salt type structure.

12. (d) Semiconductors are those solids which are good conductors of electricity at room temperature but behave as insulators at room temperature, e.g., silicon and germanium.
13. (d) In a unit cell, W atoms at the corner $= \frac{1}{8} \times 8 = 1$

O-atoms at the centre of edges $= \frac{1}{4} \times 12 = 3$

Na-atoms at the centre of the cube = 1

W : O : Na = 1 : 3 : 1

Hence, formula = $NaWO_3$

14. (c) Let the number of Z atoms in the *ccp* arrangement = 100

Thus the number of tetrahedral sites = 200

Since all the tetrahedral sites are occupied by X atoms, the number of X atoms = 200

Hence ratio of X : Z = 2 : 1

Thus the formula is X_2Z

15. (d) Since the radius ratio of CsCl is 0.93, it is expected to have a body centred cubic structure.
16. (b) In NaCl crystal, each Cl^- ion is surrounded by 6 Na^+ ions. Similarly, each Na^+ is surrounded by 6 Cl^- ions.

17. (d) For a simple cube, the relation can be obtained as under. For a cube, body diagonal = 4 r

(r = radius of sphere)

For such a cube, we have a (edge length) $= \frac{4}{\sqrt{3}} r$ or

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

Thus, body diagonal

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

$$= \sqrt{3}\, a = \sqrt{3} \times 400 \text{ pm}$$

$$= 1.73 \times 400 \text{ pm} \simeq 693 \text{ pm}.$$

18. (a) In stoichiometric Frenkel defects occurs in those compound which have
   (i) Low C.N.
   (ii) Large difference in size of cations and anions
19. (b) For orthorhombic system $\alpha = \beta = \gamma = 90°$
20. (c) In fluorite structure each F^- ion is surrounded by four Ca^{++} ions whereas each Ca^{++} is surrounded by eight F^- ions, giving a body centred cubic arrangement. Thus the co-ordination number of Ca^{++} and F^- are 8 and 4 respectively.
21. (d) The *bcc* cell consists of 8 atoms at the corners and one atom at centre. Contribution of each atom at each corner is equal to $\frac{1}{8}$.

$$\therefore n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

The *fcc* cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

22. (a) Since MgO has a rock salt structure. In this structure each cation is surrounded by six anions and vice versa.

23. (c) The vacancy created due to missing of equal no. of atoms or ions form normal lattice point is called Schottky defect. In this type of defect electrical neutrality of ionic crystal is maintained.

24. (b) *hcp* is a closed packed arrangement in which the unit cell is hexagonal and coordination number is 12.

25. (c) ABAB...... is hexagonal close packing.

26. (a) For bcc structure, atomic radius, $r = \frac{\sqrt{3}}{4}a$

$$= \frac{\sqrt{3}}{4} \times 4.3 = 1.86$$

Since, r = half the distance between two nearest neighbouring atoms.

Shortest interionic distance = 2 × 1.86 = 3.72

27. (d) Schottky defect occurs in ionic crystals of type $A^+ B^-$, when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This defect generally appears in highly ionic compounds which have high coordination number. NaCl, KCl and CsCl all have high coordination numbers i.e., 6, 6 and 8 respectively. So, Schottky defect appear in all of the given compounds.

28. (d) Since in NaCl type of structure 4 formula units form a cell.

58.5 gm. of NaCl = 6.023×10^{23} atoms

1 gm of NaCl = $\frac{6.023 \times 10^{23}}{58.5}$ atoms

4 atoms constitute 1 unit cell

$\therefore \frac{6.023 \times 10^{23}}{58.5}$ atoms constitute

$$= \frac{6.023 \times 10^{23}}{58.5 \times 4}$$

$= 2.57 \times 10^{21}$ unit cells.

29. (d) Effective number of 'A' atoms $= \left(8 \times \frac{1}{8}\right) + \left(4 \times \frac{1}{2}\right) = 3$

Effective number of 'B' atoms $= \left(12 \times \frac{1}{4}\right) + 1 = 4$

$\therefore$ Formula of the solid = $\mathbf{A_3B_4}$.

30. (b) Solid AB crystallizes as NaCl structure, so it has coordination number 6 and its r^+/r^- ranges from 0.414 – 0.732.

For maximum radius of anion, we have to take the lower limit of the range 0.414– 0.732. So, $\frac{r^+}{r^-} = 0.414$

$$\Rightarrow r^- = \frac{0.100}{0.414}\text{ nm} = 0.241\text{ nm}$$

31. (d) Body diagonal (d) of a cubic crystal of edge length (a) is given by,

$d = a\sqrt{3}$

putting a = 400 pm, we get

$d = \sqrt{3} \times 400$ pm = 692.8 pm ≈ 693 pm.

32. (b) In CaF_2, Ca^{2+} ions have ccp arrangement and F^- ions occupy the tetrahedral voids.

In ccp arrangement total no. of Ca^{2+} ions is 4 and no. of tetrahedral voids is always 2n i.e. 8. Hence for every Ca^{2+} there are $8F^-$ ions as C.N, for F^- there are 4 Ca^{2+} ions.

33. (b) For tetrahedral shape radius ratio is 0.225 – 0.414.

34. (d) Order of Bragg diffraction (n) = 2; Wavelength (λ) = 1Å and angle (θ) = 60º.

We know from the Bragg's equation

$n\lambda = 2d \sin\theta$

or $2 \times 1 = 2d \sin 60^\circ$

$$\Rightarrow 2 \times 1 = 2.d.\frac{\sqrt{3}}{2} \Rightarrow d = \frac{2}{\sqrt{3}} = 1.15\text{Å}$$

(where d = Distance between the scattering planes)

35. (c) For cubic geometry the limiting ratio is

$$\frac{r^+}{r^-} > 0.731 \text{ i.e. (c)}$$

36. (b) For body centred cubic lattice Z = 2

Atomic mass of unit cell = 133 + 80 = 213 a.m.u

Volume of cell = $(436.6 \times 10^{-10})^3$ cm^3

$$\text{Density, } \rho = \frac{ZM}{a^3N_A} = \frac{2 \times 213}{(436.6 \times 10^{-10})^3 \times 6.02 \times 10^{23}}$$

= 8.50 g/cm^3

37. (a) Fraction of unoccupied sites in NaCl crystal

$$= 1 - \frac{2.165 \times 10^3}{2.178 \times 10^3}$$

$$= \frac{2.178 \times 10^3 - 2.165 \times 10^3}{2.178 \times 10^3} = \frac{0.13 \times 10^3}{2.178}$$

$$= \frac{130}{2178} = 5.96 \times 10^{-3}$$

38. (b) Distance between K^+ and F^- $= \frac{1}{2} \times$ length of the edge

39. (b) Bragg's equation is $n\lambda = 2d \sin\theta$

where n is a positive integer i.e., 1, 2, 3, 4 etc. which stands for serial order of diffracted beams

40. (a) $\rho = \frac{ZM}{N_A V}$

$$Z = \frac{\rho N_A V}{M} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75}$$

Z = 2, which represents *bcc* structure

$$\therefore r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 5 = 2.165\text{Å} = 216.5\text{ pm}$$

≈ 217 pm

41. (a) There are two atoms in a *bcc* unit cell.

So, number of atoms in 12.08×10^{23} unit cells

$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}$ atoms.

42. (d) $M = \frac{\rho \times a^3 \times N_A \times 10^{-30}}{Z}$

$$= \frac{10 \times (100)^3 \times 6.02 \times 10^{23} \times 10^{-30}}{4} = 15.05$$

$$\therefore \text{ Number of atoms in 100 g} = \frac{6.02\times10^{23}}{15.05}\times100$$

$$= 4 \times 10^{25}$$

43. (d) For *bcc*, $d = \frac{\sqrt{3}}{2}a$ or $a = \frac{2d}{\sqrt{3}} = \frac{2\times4.52}{1.732} = 5.219\text{Å}$

$$= 522 \text{ pm}$$

$$\rho = \frac{z\times M}{a^3\times N_A\times10^{-30}}$$

$$= \frac{2\times39}{(522)^3\times(6.023\times10^{23})\times10^{-30}}$$

$$= 0.91 \text{g/cm}^3 = 910 \text{ kg m}^{-3}$$

44. (c) In a *fcc* lattice, the distance between the cation and anion is equal to the sum of their radii, which is equal to half of the edge length of unit cell,

i.e. $r^+ + r^- = \frac{a}{2}$ (where a = edge length)

$r^+ = 95$ pm, $r^- = 181$ pm

Edge length $= 2r^+ + 2r^- = (2\times95 + 2\times181)$ pm

$= (190 + 362)$ pm $= 552$ pm.

45. (b) $\rho = \frac{ZM}{N_AV}$

$$Z = \frac{\rho N_A V}{M} = \frac{8.92\times6.02\times10^{23}\times(362)^3\times10^{-30}}{63.55}$$

$= 4$

$\therefore$ It has *fcc* unit cell

46. (a) Wurtzite has *face centred cubic* structure in which each Zn^{2+} ion is attached to four S^{2-} ions and each S^{2-} ion remains in contact with four Zn^{2+} ions. Hence coordination number of each ion is 4.

47. (d) In KCl, co-ordination number of cation and anion is 6 and 6 respectively. KCl is highly ionic so Schottky defect is common.

Note : Schottky defect is common in compounds having high coordination nummber while Frenkel defect is common in compounds with low coordination number.

48. (b)

49. (a) Schottky defects are found in solid.

50. (a) *p*-type of semiconductors are produced

(i) due to metal deficiency defects

(ii) by adding impurity containing less electrons (i.e., atoms of group 13)

Ge belongs to Group 14 and In to Group 13. Hence on doping, p-type semicondutor is obtained.

51. (b) In cubic closed pack system (CCP system) ....ABC ABC....... type of arrangement of layers is found. In this system, there are atoms at the corners as well as centre of the unit cell.

$\therefore$ No. of atoms per unit cell $= 8\times\frac{1}{8}+1 = 2$

Hence, the no. of tetrahedral voids in a unit cell = 2*Z*

52. (d) If in an ionic crystal of the type A^+, B^-, equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. The defect is called Schottky defect.

53. (d) The appearance of colour in solid alkali metal halide is due to presence of F-centre found as defect in the crystal structure.

54. (b) $a = b \neq c$, $\alpha = \beta = 90°, \gamma = 120°$

These are the characteristics of a hexagonal system.

55. (b) When equal number of cations (Na^+) and anions (Cl^-) are missing from their regular lattice positions, we have schottky defect.

56. (d) Schottky defect occurs in ionic crystals of type A^+ B, when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This defect generally appears in highly ionic compounds which have high coordination number. NaCl, KCl and CsCl all have high coordination numbers i.e., 6, 6 and 8 respectively. So, Schottky defect appear in all of the given compounds.

57. (b) More is the Schottky defect in crystal more is the decrease in density.

58. (b) In Na_2O there is antifluorite structure. Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion is surrounded by 8 positive ions. So coordination no. of Na^+ is 4.

59. (b) Since each Sr^{++} ion provides one cation vacancy, hence Concentration of cation vacancies = mole % of $SrCl_2$ added

$= 10^{-4}$ mole %

$$= \frac{10^{-4}}{100}\times6.023\times10^{23} = 6.023\times10^{17} \text{ mol}^{-1}$$

60. (d) Number of atoms per unit cell = 1

Atoms touch each other along edges. Hence $r = \frac{a}{2}$

(r = radius of atom and a = edge length)

$$\text{Therefore \% fraction} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

61. (a) Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length (a) of the cell and r the radius of the sphere.

For simple cubic : $a = 2r$ or $r = \frac{a}{2}$

For body centred cubic :

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

For face centred cubic :

$$a = 2\sqrt{2}r \text{ or } r = \frac{1}{2\sqrt{2}}\text{ a}$$

Thus the ratio of radii of spheres for these will be simple : bcc : fcc

$$= \frac{a}{2} : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}\text{ a}$$

i.e. option (a) is correct answer.

62. (d) The semiconductors formed by the introduction of impurity atoms containing one elecron less than the parent atoms of insulators are termed as *p*-type semiconductors. Therefore silicon containing 14 electrons is to be doped with boron containing 13 electrons to give a *p*-type semi-conductor.

63. (a) For *bcc* lattice body diagonal = $a\sqrt{3}$.
The distance between the two oppositely charged ions

$$= \frac{a}{2}\sqrt{3}$$

$$= \frac{387 \times 1.732}{2} = 335\text{pm}$$

64. (c) $\frac{M^+}{X^-}$ is highest in CsF
∴ correct choice : (c)

65. (c) Radius ratio of NaCl like crystal

$$= \frac{r^+}{r^-} = 0.414$$

$$r^- = \frac{100}{0.414} = 241.5\,\text{pm}$$

66. (a) For *ccp* $\sqrt{2}a = 4r$

$$\frac{\sqrt{2} \times 408}{2} = 2r \quad (2r = \text{Diameter})$$

Diameter = 288.5

67. (a) From the given data, we have
Number of Y atoms in a unit cell = 4
Number of X atoms in a unit cell $= 8 \times \frac{2}{3} = \frac{16}{3}$
From the above we get the formula of the compound as
$X_{16/3}Y_4$ or X_4Y_3

68. (a) For *fcc* unit cell, $4r = \sqrt{2}\,a$

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

69. (d) For an *fcc* crystal

$$r_{\text{cation}} + r_{\text{anion}} = \frac{\text{edge length}}{2}$$

$$110 + r_{\text{anion}} = \frac{508}{2}$$

$$r_{anion} = 254 - 110 = 144\text{ pm}$$

70. (a)

71. (a) $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55$ and $\frac{r_{K^+}}{r_{Cl^-}} = 0.74$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.55 + 1 \text{ and } \frac{r_{K^+}}{r_{Cl^-}} + 1 = 0.74 + 1$$

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.55 \text{ and } \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.74$$

Now edge length ratio of KCl and NaCl is

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.123.$$

72. (b) Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the total volume of the unit cell.
P.F. for *cpp* and *bcc* are 0.74 and 0.68 respectively.
So, the free space in *ccp* and bcc are 26% & 32% respectively.

73. (d) For *bcc* structure $\sqrt{3}\,a = 4r$

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351 = 152\,\text{pm}.$$

74. (d) Packing efficiency

$$= \frac{\text{Area occupied by circles within the square}}{\text{Area of square}}$$

$$= \frac{2\pi r^2}{L^2} \times 100 = \frac{2\pi r^2}{2(\sqrt{2}r)^2} \times 100 = \frac{\pi}{4} \times 100 = 78.54\%$$

75. (b) No. of M atoms $= \frac{1}{4} \times 4 + 1 = 1 + 1 = 2$

No. of X atoms $= \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$

So, formula $= M_2X_4 = MX_2$

EXERCISE - 2

1. (d) All the given statements are correct about *F*-centres.

2. (d) The number of *A* ions per unit cell $= \frac{1}{6} \times 12$ (corners)
$+ \frac{1}{2} \times 2$ (end centres) + 3 (in the body)
Number of octahedral voids per unit cell = 1× 6 = 6.
Number of cations (*C*) per unit cell $= \frac{2}{3} \times 6 = 4$
Formula : C_4A_6 or C_2A_3

3. (c) When polar crystal is subjected to a mechanical stress, electricity is produced – a case of piezoelectricity. Reversely, if electric field is applied, mechanical stress is developed. Piezoelectric crystal acts as a mechanical electrical transductor.

4. (c) For cubic geometry the limiting ratio is

$$\frac{r^+}{r^-} > 0.731 \text{ i.e., (c)}$$

5. (c) Among the three options KCl, NaCl and $MgCl_2$, the size of anion is same. So larger the cation, larger will be the cation/anion ratio i.e., KCl will have larger cation/anion ratio among the three. So, we left with two options KCl and CaF_2. Among these two CaF_2 will have maximum value of cation/anion ratio because decrease in ionic radii of anion from Cl^- to F^- does not overcome the effect of decrease in ionic radii of cation from K^+ to Ca^{2+}.

6. (b) Number of tetrahedral voids (V_T) in a crystal is twice the number of atoms (n) in a crystal i.e.,
$V_T = 2n$
So, number of tetrahedral voids per atom is given by
$V_T / n = 2$

7. (b)

8. (c) A body-centred cubic system consists of all eight corners plus one atom at the centre of cube.

9. (a) Atoms are present in the corners of cube = A and atom present at body centre = B.
We know that a cubic unit cell has 8 corners. Therefore

contribution of each atom A at the corner = $\frac{1}{8}$. Since number of atoms per unit cell is 8, therefore total contribution = $8 \times \frac{1}{8} = 1$. We also know that atoms in the body centre, therefore number of atoms of B per unit cell = 1. Thus formula of the compound is AB.

10. (a) For a face centred cubic structure,

No. of X atoms $= 8 \times \frac{1}{8} = 1$

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

$\therefore$ Formula of the compound = XY_3

11. (d) In *bcc* - 8 atoms are at corners and one in the centre of the unit cell.

Number of atoms per unit cell, $n = 8 \times \frac{1}{8} + 1 = 2$.

In *fcc* - 8 atoms are at the corners and also centre of the six faces of each cell.

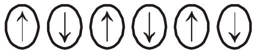
Number of atoms per unit cell , $n = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$.

12. (c) Match box exhibits orthorhombic geometry i.e., $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$
13. (d) It can best be described as molecular solid.
14. (a) In crystalline solid there is perfect arrangement of the constituent particles only at 0 K. As the temperature increases the chance that a lattice site may be unoccupied by an ion increases. As the number of defects increases with temperature solid changes into liquid.
15. (b) Amorphous solids are isotropic, because these substances show same properties in all directions.
16. (d) For n-type, impurity added to silicon should have more than 4 valence electrons.
17. (a) ZnS has cubic close packed (ccp) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, S^{2-} ion is surrounded by four Zn^{2+} ions.
18. (c)
19. (d) Tetrahedral holes are smaller in size than octahedral holes. Cations usually occupy less space than anions.
20. (a) Schottky defect is due to missing of equal number of cations and anions.
21. (b) Space or crystal lattice is a regular repeating arrangement of points in space and forms the basis of classification of all structures.
22. (b) In crystalline solids constituents are arranged in definite orderly arrangement. This regular arrangement of constituents extends throughout the three dimensional network of crystal. Thus crystalline substances said to have long range order. Whereas amorphous solids have no regular arrangement.
23. (c) Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally.
24. (a) In case of semiconductors, the gap between valence band and the conduction band is small and therefore some of the electrons may jump from valence band to conduction band and thus on increasing temperature conductivity is also increased.
25. (a) All magnetically ordered solids (ferromagnetic, ferrimagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins.

EXERCISE - 3

Exemplar Questions

1. (b) At low temperature existence of a substance in the solid state is due to slow molecular motion and strong cohesive forces.
2. (b) Crystalline solid is anisotropic in nature as it shows different physical properties such as electrical resistance, refractive index in different directions.
3. (b) Quartz glass (SiO_2) is an amorphous solid due to its short range order of constituent particles.
4. (d) Substances which have domain structure are oppositely oriented and cancel each other's magnetic field are known as antiferromagnetic substances.



Schematic arrangement of antiferromagnetic substance

5. (a) Since, quartz glass is an amorphous solid having short range order of constituents. Hence, value of refractive index is same in all directions, measurable and not to be equal to zero always.
6. (d) Amorphous solids are isotropic in nature and any of its physical property will be same in all direction.
7. (b) Crystalline solids has a regular arrangement of constituent particles observed over a long distance in the crystal lattice due to which they exhibit sharp melting point.
8. (a) Iodine molecules belongs to a class of non – polar molecular solids in which constituents molecule are held together by London or dispersion forces.
9. (c) Diamond is a giant molecule in which constituent atoms are held together by covalent bonds.
10. (c) Iodine is a non–polar molecular solid and a non–conductor of electricity. Water is a hydrogen bonded molecular solid in which H and O are held together by polar covalent bond and each water molecule is held together by hydrogen bonding. Also, due to its non-ionic nature, it also behaves as a non-conductor of electricity.
11. (a) Ionic solids get easily dissociated into its ions in molten state and show high electrical conductivity.
12. (b) In graphite, each carbon is sp^2 hybridised having one free electron and due to the presence of free electrons graphite behaves as a good conductor of electricity.

13\. (c) Certain metal oxides like VO_2, VO_3 and TiO_3 etc. show metallic or insulating property depending upon temperature which is due to variation in energy gap between conduction band and valence band.

14\. (d) Metal oxides like CrO_2, TiO and ReO_3 show electrical conductivity similar to metals while SiO_2, MgO and SO_2 do not show electrical properties.

15\. (c) Each lattice point in a pure crystal is either an atom or molecule or ion which are joined together by a straight line to bring out geometry of lattice in pure crystal constituents which are arranged in fixed stoichiometric ratio.

16\. (d) Graphite is a covalent solid which is made up of carbon atoms covalently bonded to three carbon atoms. As, the formation of covalent bond occurs throughout the crystal hence, it is a type of network solid. Also due to the presence of free electrons graphite is a conducting solid.

17\. (a) When smaller ion (usually a cation) is dislocated from its normal site in crystal and move to interstitial site, it is known as Frenkel defect.

18\. (b) Schottky defect is observed in crystal when equal number of cations and anions are missing from the lattice.

When lattice site is occupied by electron, this type of defect is known as metal excess defect.

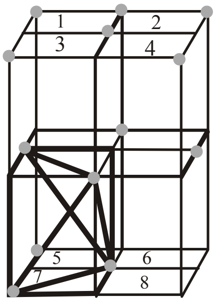
19\. (b) For the formation of *p*-type semiconductors, group 13 elements are doped with group 14 elements, which creates a hole in a molecule but the molecule as a whole remain neutral.

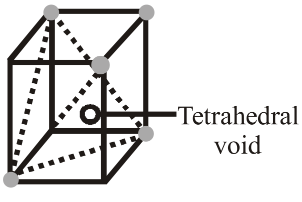
20\. (d) To get a *n* – type semiconductor from silicon, it should be doped with a substance with valency 5.

e.g., silicon is doped with phosphorus to form a *n* – type semiconductor.

21\. (b) In a fcc unit cell 8 tetrahedral voids are present at the centre of each 8 smaller cube of the unit cell.

Eight tetrahedral voids per fcc unit cell





Each cube contain one tetrahedral void at its body centre

Number of octahedral voids present = 4

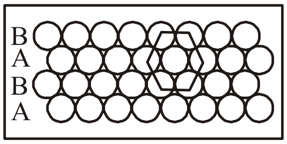
Number of tetrahedral voids present = 8

22\. (a) In AgBr, both Ag^+ and Br^- ions are absent from the lattice causing Schottky defect. Also, Ag^+ ions are mobile so they have a tendency to move from their lattice site to interstitial site which causes Frenkel defect.

23\. (b) As, packing efficiency for hcp or ccp is calculated to be 74%, it is maximum among all type of crystals.

24\. (c) Packing efficiency for bcc arrangement is 68% which represents total filled space in the unit cell. Hence empty space in a bcc arrangement will be 100 – 68 = 32%.

25\. (d) Hexagonal close packing can be diagramatically represented as :

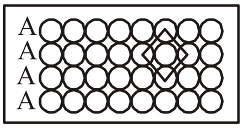


We can see that lst layer (A) and 4th layer (B) are not exactly aligned.

26\. (a) In NaCl crystal Cl^- ions are present at fcc lattice points and face centre and Na^+ occupies all the octahedral voids of the unit cell.

Thus, coordination number of Na^+ and Cl^- is 6.

27\. (c) Coordination number in a square closed packed structure in 2-D must be equal to 4 as shown :



Square closed packed structure

28\. (d) When electron rich or electron deficient impurity is added to a perfect crystal it introduces electronic defect in it.

29\. (b) Sillicon doped with electron rich impurity to form a *n* – type semiconductor.

30\. (b) Ferromagnetic substances can be permanently magnetised by applying magnetic field and they will exhibit the magnetic properties even after the removal of magnetic field.

31\. (d) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions present at the lattice points. As we know the radii of octahedral or tetrahedral void is related to radii of atoms (r) as

Radius of octahedral void $(R_o) = 0.414\ r$

Radius of tetrahedral void $(R_t) = 0.225\ r$

Where, r = radius of bigger atom involved

32\. (a) When a ferromagnetic substance is placed in a magnetic field it becomes a permanent magnet because all the domains get oriented in the direction of magnetic field even after the removal of applied magnetic field.

33\. (b) Packing efficiency in different types of unit cells is as follows :

Unit cell	Packing efficiency
fcc	74%
bcc	68%
Simple cubic	52%

Thus, the correct order of packing efficiency is: fcc (74%) > bcc (68%) > simple cubic (52%).

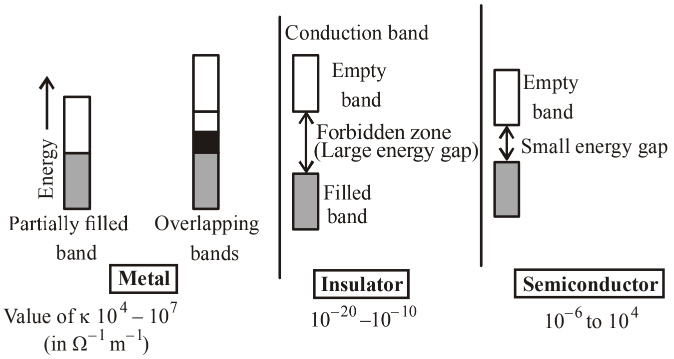
34. (a) Frenkel defect is also known as dislocation defect because in this defect atoms present in crystal lattice are dislocated to interstitial site.

35. (d) In the cubic close packing the unit cell has 8 tetrahedral voids are located at each eight smaller cube of an unit cell.

36. (a) Edge lengths for different types of unit cells are given as :

Types of unit cell	**Edge length**
fcc	$2\sqrt{2}r$
bcc	$\frac{4}{\sqrt{3}}r$
Simple cubic	$2r$

37. (a) Conductivity of metal, insulator and semiconductors can be represented in the terms of κ (Kappa) which depends upon energy gap between valence band and conduction band.



Hence, correct order of conductivity in solids is :

$$\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$$

NEET/AIPMT (2013-2017) Questions

38. (a) In interstitial compounds small atoms like H, B & C enter into the void sites between the packed atoms of crystalline metal. They retain metallic conductivity and are chemically inert.

39. (a) Diamond is like ZnS. In diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure (tetrahedral voids).
Total no. of atoms present per unit cell

$$= \underset{\text{(corners)}}{8\times\frac{1}{8}} + \underset{\text{(face centered)}}{6\times\frac{1}{2}} + \underset{\text{(inside body)}}{4} = 8$$

40. (b) Density is given by

$$d = \frac{Z\times M}{N_A a^3}$$; where Z = number of formula units present in unit cell, which is 4 for *fcc*
a = edge length of unit cell. M = Molecular mass

$$2.72 = \frac{4\times M}{6.02\times10^{23}\times\left(404\times10^{-10}\right)^3}$$

$$(\because\ 1\text{pm} = 10^{-10}\text{cm})$$

$$M = \frac{2.72\times6.02\times(404)^3}{4\times10^7} = 26.99$$

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