

## CHAPTER 2



# SOLID STATE

- \* Types of Solids
- \* Defects in Solids
- \* Crystal Lattices
- \* Properties of Solids

## TYPES OF SOLIDS

### 2.1.1

#### Characteristics of solids

Matter has three main states. They are solids, liquids and gases. Temperature changes primarily cause substances to go into these states. The difference between the three states is explained in terms of kinetic molecular theory.

The particles present in solids are atoms, molecules or ions. In a solid these particles are arranged in an orderly way, due to strong binding forces. This orderly arrangement is repeated in all the three dimensions. Thus solids have definite shape and structure. Due to the rigid structures, the effect of pressure on the volume occupied by a solid is negligible.

Solids have generally high density and low compressibility. This is due to close packing of particles, which eliminates free space between particles. Solids have very slow or no diffusion. The vapour pressure of solids is generally much less than that of liquids at a definite temperature.

*Solids have high density and low compressibility*

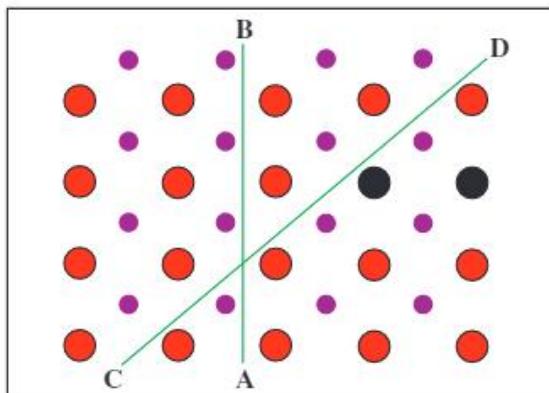
Solids are mainly divided into two classes on the basis of arrangement of the constituent particles. Amorphous solids have haphazard arrangement of building constituents. Crystalline solids have regular arrangement of the particles throughout the entire three dimensional network. Properties of crystalline and amorphous solids are presented in Table 2.1.

Table 2.1 Properties of solids

S.No.	Property	Crystalline solids	Amorphous solids
1.	Condition of formation	Slow cooling without causing disturbance	Rapid cooling with chuning or disturbance
2.	Nature	True solids	Super cooled liquids or pseudo solids
3.	Shape	Definite geometrical configuration with long range order of particles	Particles are arranged in short range order and not in a very regular order
4.	Melting points	Sharp and heat of fusion is characteristic of the substance	Not sharp. Solid melts over a range of temperature
5.	Plane surfaces	Possess plane surfaces	Not bound by plane surfaces
6.	X-ray diffraction	Characteristic X-ray diffraction bands are given	Diffraction bands are not given
7.	Anisotropy	Anisotropic	Isotropic

  
**Crystalline solids  
are anisotropic**  


Crystalline solids are anisotropic in nature. Some of their physical properties like electrical resistance or refractive index show different values when measured along different dimensions in the same crystal. This arises from different arrangement of particles in different directions as shown in Fig 2.1.

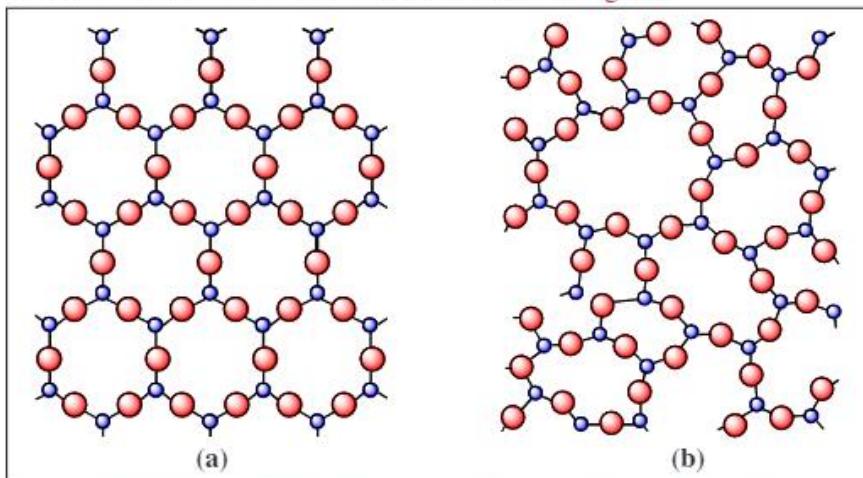


**Fig 2.1 Anisotropy in crystals**

  
**Amorphous  
solids are  
isotropic**  


Amorphous solids are isotropic in nature. There is no long range order in them and arrangement is irregular along all the directions. Therefore, value of the physical property would be same along any direction.

Silica has both crystalline and amorphous forms. Quartz is a crystalline form of silica. It has an infinite chain of regular  $\text{SiO}_4$  tetrahedra. If quartz is melted and rapidly cooled, amorphous solid results. In amorphous state,  $\text{SiO}_4$  chains are irregular both in size and orientation of the chain as shown in Fig 2.2.



**Fig 2.2 Crystalline silicon (a) and amorphous silicon (b)**

Amorphous materials may have applications in a variety of spheres like domestic construction or appliances like photovoltaic cells where the sun rays are transformed into electricity.

### 2.1.2

#### Classification of crystalline solids

Majority of solid substances are crystalline in nature. All metals, except mercury, are solids and are crystalline. Ionic substances are also crystalline. Non-metallic elements like carbon, sulphur and iodine and compounds like naphthalene, sucrose and zinc sulphide are crystalline.

## CHEMISTRY IID

  
**Crystalline  
solids are 4 types  
based on the  
nature of forces  
between particles**  


  
**Ionic solids  
do not conduct  
electricity**  


  
**Constituent  
particles of  
metallic and  
covalent solids  
are atoms**  


A crystal is defined as a solid figure which has a definite geometrical shape and has a sharp melting point.

Crystalline solids can be classified on the basis of the nature of forces operating between the constituent particles. They are of four types.

**Molecular solids :** Molecules are the constituent particles of molecular solids. Non-polar molecular solids comprise dispersion or London forces between atoms or molecules. The covalent bonds between the atoms of non-polar molecular solids are not polar. Examples include iodine, solid chlorine, solid argon, etc.

Polar molecular solids have molecules held together by dipole-dipole interactions in particular and dipole-induced dipole dispersion interaction in general.

Examples of polar molecular solids are solid sulphur dioxide, solid ammonia, ice, etc. Solids like glucose, sucrose, urea, ice have relatively stronger hydrogen bonds between H atom and F, O or N atoms of their molecules. These are called hydrogen bonded molecular solids.

**Ionic solids :** The constituent particles of ionic solids are ions. Oppositely charged ions of an ionic solid are held together by strong electrostatic (coulombic) forces. Examples include ionic substances like sodium chloride, calcium carbonate, potassium sulphate, caesium iodide, etc.

Ionic solids are hard and brittle. They have high melting points. Since the ions are not free to move, ionic solids do not conduct electricity in the solid state. However, they conduct electricity in molten or in aqueous state, due to the mobility of free ions.

**Metallic solids :** The constituent particles of metallic solids are atoms. Atoms are held together by inter atomic attraction forces called metallic bond. Examples include metals like sodium, magnesium, aluminium, iron, copper, silver, etc. and alloys like brass, bronze, elektron, german silver, etc.

Each atom in a metallic solid contributes one or more free and mobile electrons. Hence metals are good conductors of heat and electricity. These mobile electrons are also responsible for the characteristic luster and also colour in some metals. Metals are highly malleable and ductile. The hardness of metals depend upon the strength of the metallic bond.

**Covalent solids :** The constituent particles of covalent solids are atoms. Adjacent atoms of non-metals are joined with covalent bonds in a net-work structure leading to the formation of giant molecules. Examples include, silicon, silica, diamond, carborundum, beryllium chloride, etc.

Covalent solids are also called giant molecules. All bonds are covalent and are directional. Atoms of covalent solids are held very strongly at their positions and hence these solids are very hard. They have extremely high melting points and may even decompose before melting.

Covalent solids in general are insulators. Diamond as shown in Fig 2.3 has no free electrons and does not conduct electricity.

Though graphite is also a covalent solid, it is soft and conduct electricity. Carbon atom in graphite is bonded with three neighbouring atoms in layer lattice structure as shown in Fig 2.4. The fourth valence electron of each carbon atom is free to move. This movement of free electrons among atoms of a layer is the reason for the electrical conductivity of graphite.

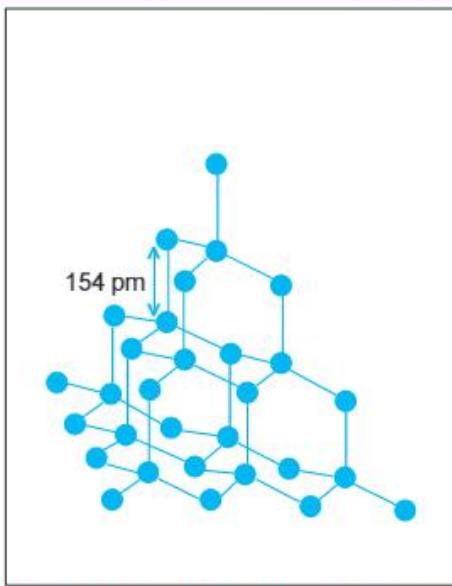


Fig 2.3 Net work structure of diamond

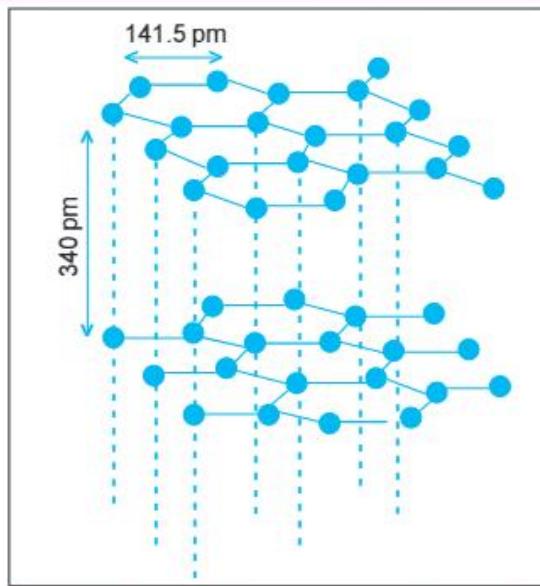


Fig 2.4 Layer lattice structure of graphite

Different properties of four types of crystalline solids along with examples are listed in Table 2.2.

Table 2.2 Types of crystalline solids and their properties

Types of solid	Constituent particles	Bonding or attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
Molecular solids (i) Non polar (ii) Polar (iii) Hydrogen bonded	Molecules	London or Dispersion forces Dipole-dipole interactions Hydrogen bonding	I <sub>2</sub> , CO <sub>2</sub> (s), Ar(s) HCl(s), SO <sub>2</sub> (s) H <sub>2</sub> O (ice)	Soft	Insulator	Very low Low Low
Ionic solids	Ions	Coulombic or electrostatic forces	NaCl, MgO, ZnS, CaF <sub>2</sub>	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg, Sn, Au, K, Zn	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
Covalent or Network solids	Atoms	Covalent bonding	SiO <sub>2</sub> (quartz) SiC, AlN, BN, C (diamond) C (graphite)	Hard Soft	Insulators Conductor (exception)	Very high High

**2.1.3****Metallic bond**

Metallic bond is the interatomic attraction force between atoms of a metal or an alloy. The concept of metallic bond must explain the following:

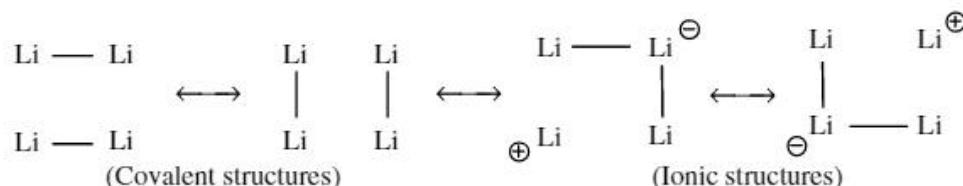
1. Bonding between atoms of the same element in a metal.
2. Bonding between atoms of different elements of an alloy.
3. The mobility of electrons in conductors.
4. The properties of metals in liquid state or in solutions.
5. The non-directional nature of bonding.

Three theories are familiar in explaining bonding in metallic solids.

1. Electron sea model of Drude and Lorentz
2. Valence bond theory of Linus Pauling
3. Molecular orbital theory of Hund and Mulliken

According to Drude and Lorentz, a metallic solid comprises of rigid spheres of metal ions. Each metal atom contributes its valence electrons to form electron sea. These electrons move freely in the lattice free spaces. Cohesive forces result from electrostatic attractions between positive metal ions and electron cloud. The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond. The electron sea model explains qualitatively the model of a metal lattice but fails in quantitative calculations of lattice energies and difference in the properties of different metals.

Pauling's valence bond theory of metals is also called resonance theory. The metallic bond is regarded as covalent bond which involves resonance between a number of structures having one electron and electron pair bond. The resonance not only involves covalent bonds, but also ionic linkages. For example, the resonance structures of lithium in a plane is a combination of covalent and ionic linkages.



Metallic bond will be more stronger if the number of valence electrons is more and the atomic size is less. Lattice energy is more if bond is stronger. Valence bond theory does not explain the conduction of heat in solids and their lustres. The theory does not explain the relation of metallic properties in liquid state.

**P.2.1**

How is a crystalline solid different from an amorphous solid?

**Solution** Crystalline solid has sharp and distinct melting point. Melting point is not sharp in amorphous solid.

Crystalline solid gives characteristic X-ray diffraction bands, but not amorphous solid.

**P.2.2**

Amorphous solids have unit cells in them. Comment.

**Solution** Recent investigations report that all amorphous solids contain minute crystals.

But apparently they do not have unit cells.



**P.2.3** What type of crystalline solid is boron nitride? Why?



**Solution** Boron nitride is an example of covalent crystal.

Boron nitride has network polymeric structure like in carbon, silica and silicon carbide.



**P.2.4** Compare the metallic bond strengths in Mg, Ca and Al.



**Solution** Bond strength is highest in Al, due to the presence of three valence electrons. In Mg and Ca, two valence electrons each are present. But due to large size, bond is weaker in Ca than in Mg.  
Order of metallic bond strength : Ca < Mg < Al.



**P.2.5** Classify the following solids and mention the type of intermolecular forces operating in each of them : (a) urea, (b) tin, (c) zinc sulphide and (d) silicon carbide.



**Solution** (a) Urea is a molecular solid. Between molecules of urea van der waal's forces and hydrogen bonds are present.

(b) Tin is a metallic solid. Metallic bonds are present between atoms of tin.

(c) Zinc sulphide is an ionic solid. Electrostatic attraction forces are present between zinc ion and sulphide.

(d) Silicon carbide is a covalent solid. It has network structure like in diamond. The atoms are bound by covalent bonds.



**P.2.6** How does the inter-particle forces help in characterising the properties of (a) potassium metal and (b) solid argon?



**Solution** (a) Potassium is a metallic solid. Atoms of potassium are held by metallic bonds. Since the size of atom is more and number of valence electrons is less, the metallic bonds are weak. Hence it is a soft solid with low heat of vapourisation. It is a good electrical conductor.

(b) Solid argon is a molecular solid. Argon atoms are held by weak van der waal's forces. It is soft solid with low melting point. It is not an electrical conductor, because of absence of free electrons.



### EXERCISE - 2.1.1

1. Write the main differences between crystalline solids and amorphous solids.
2. Discuss the metallic bonding.
3. What are (a) ionic solids and (b) covalent solids ? Write examples
4. Mention the forces that operate in molecular solids. Discuss.
5. Ionic solids are insulators, but conduct electricity in molten state. Explain.
6. Show that crystalline silica (quartz) and amorphous silica are different.
7. Explain anisotropy in crystalline solids.
8. Explain the following and give reasons :
  - (a) diamond is hard, but graphite is soft ; (b) diamond is insulator, but graphite is a conductor.

## CRYSTAL LATTICES

### 2.2.1

#### Space lattice

Crystal structure can be best described and systematised in terms of lattices. The internal structure of a solid is described by certain factors. A crystal contains a structural unit called structural motif or basis. This basis is repeated in three dimensions to generate crystal structure. The basis may be a single atom or molecule or ion or group of ions. Each repeated basis group has the same structure and spatial orientation.

In silver metal, the basis is an atom, Ag.

In sodium chloride, the basis is an ion pair,  $\text{Na}^+\text{Cl}^-$ .

A space lattice is a two-dimensional regular repeating arrangement of an atom, molecule or ion, called a sphere. In the space lattice each characteristic point has the same environment. However, the space lattice may not be the same as crystal structure. In sodium chloride, two space lattices are present, one representing  $\text{Na}^+$  ions and another  $\text{Cl}^-$  ions. These space lattices, when joined together, the crystal lattice of sodium chloride is formed. The space lattices of the components may be simple or complex. Inspite of the complexity, the components of the lattice arrange themselves in a regular order. An example of space lattice is present in Fig 2.5.

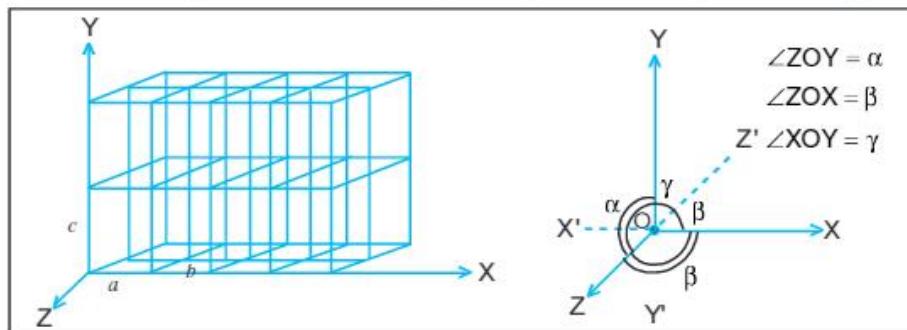


Fig 2.5 Space lattice - three dimensional figure

### 2.2.2

#### Unit cell

*Unit cell is the smallest part of crystal that generates the entire lattice*

*Unit cell is characterised by 6 parameters*

A crystal lattice is a regular three dimensional arrangement of spheres in space. There are 230 crystal forms possible and may be divided into 32 classes on the basis of their symmetry. These different types are condensed into 7 systems of crystal structures.

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

Unit cell in a specific crystal lattice appears again and again. This fundamental unit structure is a parallelepiped. This parallelepiped is characterised by six parameters, 3 edges and 3 angles.

Dimensions along the three edges : 'a' 'b' and 'c'. These edges may or may not be mutually perpendicular. Angles between the edges : ' $\alpha$ ', ' $\beta$ ' and ' $\gamma$ '. The angle ' $\alpha$ ' is labelled between edges 'b' and 'c', angle ' $\beta$ ' between edges 'a' and 'c' and angle ' $\gamma$ ' between edges 'a' and 'b'. These parameters of unit cell are illustrated in Fig 2.6.

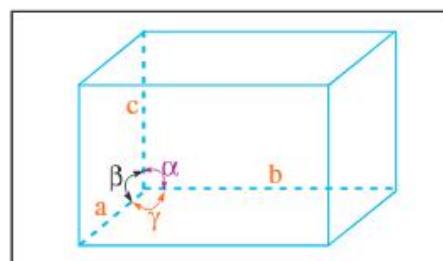


Fig 2.6 Illustration of parameters of a unit cell

  
**Primitive unit cell has particles only on corners**

  
**Number of crystal structures is 7 and Bravais lattices is 14**

  
**Rhombic system has all 4 types of lattices**

Unit cells can be broadly divided into two types: primitive unit cells and centered unit cells.

A primitive unit cell is that in which the constituent particles are present only on the corner positions of the unit cell. This is also called simple unit cell.

A centred unit cell is that in which the constituent particles are present at positions other than corners in addition to those at corners. Centered unit cells are again classified into three types.

A unit cell contains one constituent particle at its body center, besides the ones that are at its corners is called body centered unit cell.

A unit cell contains one constituent particle at the centre of each face, besides the ones present at its corners is called face centered unit cell. A unit cell contains one constituent particle at the center of any two opposite faces, besides the ones present at its corners is called end centred unit cell. Seven primitive units cells and their possible variations are presented in Table 2.3. One can observe that there are only 14 possible three dimensionally arranged lattices for crystalline solids. These are called Bravais lattices.

Every lattice has its own special features and certain characteristics. The important characteristics of a crystal lattice are:

1. Each point in a crystal lattice is called lattice site.
2. Each point in a lattice represents one constituent particle (atom or an ion or a molecule)
3. Lattice points are joined by straight lines to bring out the geometry of the lattice.

Space lattices of crystal systems and unit cells of 14 types of Bravais lattices are shown diagrammatically in Fig 2.7.

Table 2.3 Seven primitive cells and their possible variations as centred unit cells

Crystal system	Symmetry elements	Axial distances or edge lengths	Axial angles	Examples
Cubic three 2 fold axis	four 3 fold axis	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, ZnS, CaF <sub>2</sub> , Cu, Ag, Diamond
Tetragonal	one 4 fold axis	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO <sub>2</sub> , TiO <sub>2</sub> , CaSO <sub>4</sub> , K <sub>4</sub> [Fe(CN) <sub>6</sub> ]
Rhombic or Orthorhombic	three 3 fold axis one 2 fold axis two planes	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO <sub>3</sub> , BaSO <sub>4</sub> , Epsom
Hexagonal	one 6 fold axis	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, Quartz, CdS, HgS
Rhombohedral or Trigonal	one 3 fold axis HgS (cinnabar)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite KMnO <sub>4</sub> , HgS (cinnabar)
Monoclinic	one 2 fold axis	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ$	Monoclinic sulphur, Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O, Gypsum
Triclinic	no symmetry	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Boric acid, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , CuSO <sub>4</sub> .5H <sub>2</sub> O

Crystal system	Primary	Body-centered	Face-centered	End-centered
Cubic				
Tetragonal				
Orthorhombic (or Rhombic)				
Hexagonal				
Rhombohedral (or Trigonal)				
Monoclinic				
Triclinic				

Fig 2.7 Fourteen types of Bravais lattices

**2.2.3****X - ray study of crystal structure**

X-rays constitute a type of electromagnetic radiation, whose wavelengths are in the order of  $\text{A}^{\circ}$ . The inter particle space in the solids is also in the same order. Hence solid crystals act as diffractive gratings for X-rays.

Electromagnetic radiation propagates in space in the form of waves. The wavelength ( $\lambda$ ) and the corresponding frequency ( $\nu$ ) are related with velocity of propagation ( $c$ ) as,  $c = \lambda\nu$ .

Waves in phase leads to constructive interference

Let us assume that X-rays are originated from two separate points. The two waves interfere with one another. If a wave reinforces the second, then they are said to have constructive interference and if they nullify each other, they are said to have destructive interference. Waves in the same phase leads to constructive interference and waves in out of phase leads to destructive interference as shown in Fig 2.8.

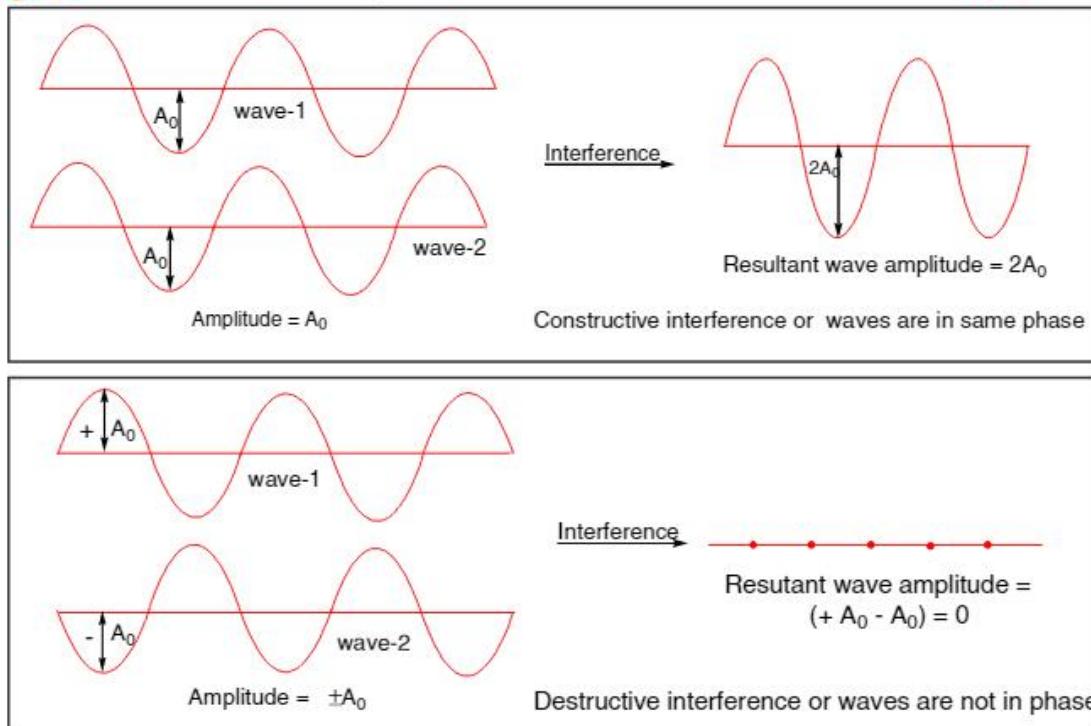


Fig 2.8 Constructive and destructive interference of waves

Any crystal serves as a 3d-grating to radiation

Solid crystal acts as reflection grating to X-rays

The arrangement of particles in a crystalline solid is determined indirectly by X-ray diffraction. Van Laue showed that any crystal could serve as a three dimensional grating to the incident electromagnetic radiation.

A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence  $\theta$ . At various angles, strong beams of detected X-rays strike photographic plate forming spots. Different kinds of crystals produce different arrangement of spots.

Bragg found that Laue photographs are easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. X-ray reflection from crystals is shown in Fig 2.9 and Fig 2.10.

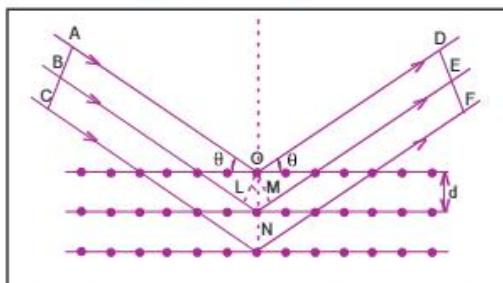


Fig 2.9 X-ray reflection from crystals

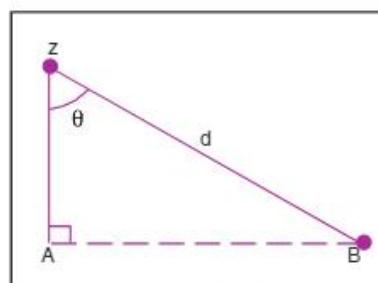


Fig 2.10 Angle (for  $\sin \theta$ )

X-rays of single wave length ( $\lambda$ ) strike the parallel planes of the crystal at angle  $\theta$ . Some of the rays are reflected from the upper plane, some from the second plane and some from the lower planes. The waves reflected by different layer planes will be in phase if the difference in the paths length of the waves reflected from the successive planes is equal to an integral number of wave lengths.

OL and OM are perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, triangles OLN and OMN are congruent, hence  $LN = NM$

$$\text{Path difference} = 2 LN.$$

As  $LN = d \sin \theta$ , where  $d$  is the distance between two planes,

$$\text{Path difference} = 2 d \sin \theta.$$

Hence the condition for maximum reflection is,  $n\lambda = 2 d \sin \theta$

This is called Bragg's equation.

*Bragg's  
equation is,  
 $n\lambda = 2d \sin \theta$*

**Debye-Scherrer method :** A monochromatic X-ray beam from source 'S' is made incident on a crystal powder sample filled in a thin walled glass capillary tube 'C'. As a result of diffraction from all sets of lattice planes diffraction maxima arise which are recorded with a detector placed on the circumference of a circle centred on the powder specimen. The essential features of a diffractometer are shown in Fig 2.11. A powder specimen C is supported on a table H, which can be rotated about an axis O perpendicular to the plane of the drawing. The X-ray source S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis O. X-rays diverge from the source S and diffracted beam which comes to a focus at the slit F and then enters the ionisation chamber or photograph plate G. The ionization chamber contains methyl bromide vapours. The energy of the X-rays causes ionization so that there is a flow of current. The current is measured with electro-meter E. The extent ionization in the vapours is shown by the electrometer reading. As the intensity of the diffracted X-rays increase, the degree of ionization also increases.

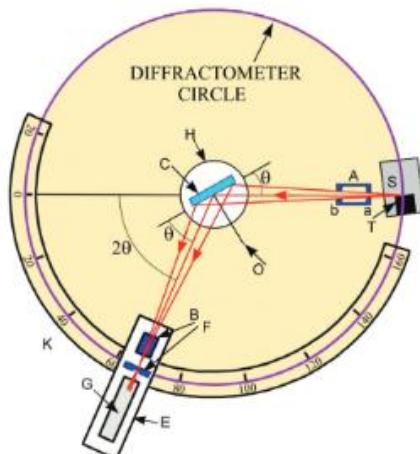


Fig 2.11 X-ray diffractometer (schematic)

  
*The flow of current due to ionisation by x-rays is measured on electrometer*  


For a set of parallel planes making an angle ' $\theta$ ' with the incident beam of X-rays that satisfy Bragg's equation, the intensity of diffracted beam will be maximum. The angle  $2\theta$  between diffracted beam and undiffracted beam is measured. In Debye-Scherrer powder method the angle  $2\theta$  for the diffracted X-rays corresponding to each and every lattice plane is measured along with the intensities of diffracted X-rays.

The values of 'd' calculated in the direction of different coordinate axes in sodium chloride crystal are in the ratio, 1 : 0.703 : 1.134. This ratio is a confirmation of face centred cubic system of sodium chloride.

#### 2.2.4

#### Packing of particles in crystal

  
*Coordination number of 'C' in diamond is 4*  


**Coordination number :** Every crystalline solid is characterised by a certain coordination number for its constituent particle. Coordination number of an atom or ion in a solid crystal is the number of nearest neighbours.

The coordination number of carbon in diamond is 4, silicon in silica is 4, oxygen in silica is 2, and chloride ion in sodium chloride is 6. Low coordination numbers 3 and 4 are observed in covalent crystals. Medium numbers 4, 6 and 8 in electrovalent crystals and high numbers 8 and 12 are observed in metallic crystals.

**Radius ratio :** The radius ratio of particles is useful in determining the structures of covalent solids, ionic solids and alloys. Radius of smaller ion to that of larger ion is called radius ratio. It is denoted by the symbol ' $\rho$ '.

$$\rho = \frac{r_{\text{small}}}{r_{\text{large}}} \quad (\text{or}) \quad \rho = \frac{r_{\text{cation}}}{r_{\text{anion}}}$$

The minimum ratio of radii that can give a specific coordination number and hence the shape of crystal is 0.15. In chloride crystals, the shape of the crystal is octahedral for sodium chloride with  $\rho$  value 0.53 and body centred cubic for caesium chloride with  $\rho$  value 0.92.

Radius ratio of ions, coordination numbers and shapes of ionic crystals are given in Table 2.4.

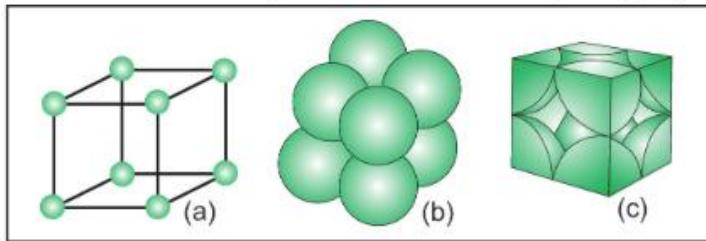
**Table 2.4 Radius ratio, the shape of the molecule and coordination number**

S.No.	Radius ratio ( $r_{\text{small}}/r_{\text{large}}$ )	Geometric shape of the crystal formed	Coordination number of the ion
1	upto 0.15	Linear	2
2	0.15 to 0.22	Trigonal planar	3
3	0.22 to 0.41	Tetrahedral	4
4	0.41 to 0.73	Square planar	4
5	0.41 to 0.73	Octahedral	6
6	0.73 to 0.99	Cubic	8

## 2.2.5

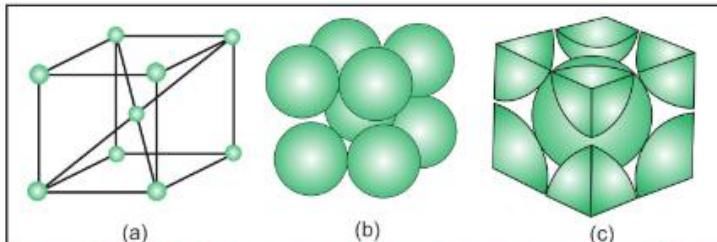
## Cubic structures

The simplest of the seven crystal structures is cubic. Three types of cubic unit cells are known in metallic crystals. Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells. Only one-eighth of an atom at the corner actually belongs to a particular unit cell. A primitive cubic unit cell is depicted in three different ways in Fig 2.12; open structure (a), space filling structure (b) and actual position of atoms in unit cell (c). The coordination number is 6. The total number of spheres in one unit cell is,  $8 \times (1/8) = 1$ .



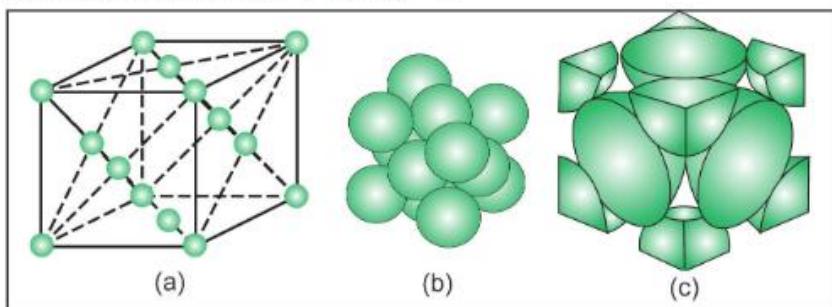
**Fig 2.12** Cubic unit cell: (a) open structure, (b) space filling structure and (c) actual positions of atoms in unit cell

Body centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre. A bcc unit cell is depicted in three different ways in Fig 2.13. The atom at the centre of the body wholly belongs to the unit cell in which it is present. The coordination number is 8. The total number of spheres in one unit cell is,  $8 \times (1/8) + 1 = 2$ .



**Fig 2.13** A body-centred cubic unit cell: (a) open structure, (b) space filling structure and (c) actual positions of atoms belonging to one unit cell

Face centred cubic (fcc) unit cell has an atom at each of its corners and also at the centre of all the faces of the cube. A fcc unit cell is depicted in three different ways in Fig 2.14. Only one half of the atom at the centre of the face belongs to a particular unit cell. The coordination number is 12. The total number of spheres in one unit cell is  $8 \times (1/8) + 6 \times (1/2) = 4$ .



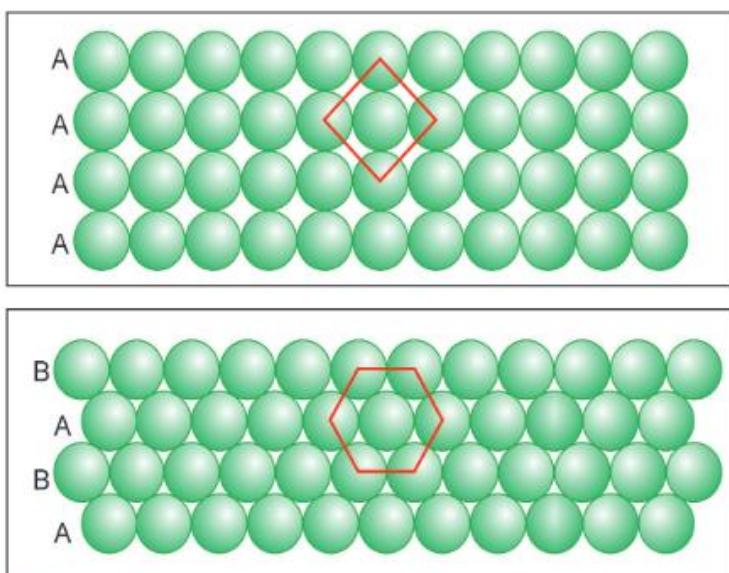
**Fig 2.14** A face centered cubic unit cell: (a) open structure, (b) space filling structure and (c) actual positions of atoms belonging to one unit cell

## 2.2.6

**Close packing  
in solids**

*Closest packing  
in crystals is  
that atoms touch  
each other*

The constituent particles of a crystal are close packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres. There is only one way of arranging spheres in an one dimensional close packed structure, that is to arrange them in a row and touching each other. The two dimensional close packed structure can be generated by stacking the rows of close packed spheres. This can be done in two ways as shown in Fig 2.15.



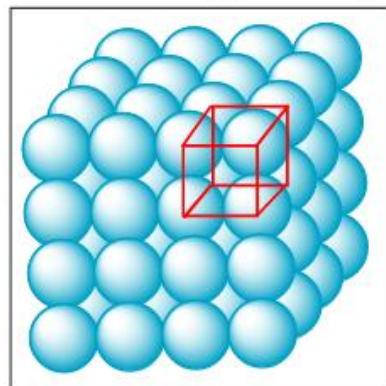
**Fig 2.15 Square close packing (AAAA) and hexagonal close packing (ABAB) of spheres in two dimensions**

a. **Square close packing**

The spheres can be arranged in a layer such that each metal atom is in touch with four other atoms. The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically.

b. **Simple cubic system**

If we call the first row as 'A' type row, the second row is also 'A' type. We may place more rows to obtain AAA..... type of arrangement as shown in Fig 2.16.



**Fig 2.16 Simple cubic lattice**

  
**Polonium metal**  
**crystallises in**  
**simple cubic**  
**system**  


  
**Body centred**  
**cube structure**  
**fills 68% of the**  
**space**  


  
**In cubic close**  
**packing atoms**  
**occupy 74% of**  
**the space**  


  
**Tetrahedral and**  
**octahedral voids**  
**are two types of**  
**interstices**  


This arrangement is called square close packing or simple cubic system. The coordination number of sphere is 6.

This structure has the spheres occupying about 52% of the volume of the cube.  
eg. Polonium.

#### c. Hexagonal closed packing (hcp)

In any layer of spheres every sphere is in contact with six other spheres. The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, in the second row it may be called 'B' type. When third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also 'A' type. The spheres of the fourth row will be aligned with those of the second 'B' type. We may place more rows to obtain ABAB..... type of arrangement as shown in Fig 2.15. This arrangement is called hexagonal close packing. In this arrangement atoms occupy 74% of the available space and thus has 26% vacant space. The co-ordination number is 12.

eg. Be, Mg, Ti, Cd, Co, Zn, Ce, Ti, Os, Ru, etc.

#### d. Body centred cubic

It is having points at all the corners as well as the centre of the cube. The coordination number in the arrangement is 8. This structure fills 68% of the space. This lattice is quite common for metals.

eg. Na, K, Rb, Cs, Ba, Cr, Mo, W

#### e. Face centred cubic (or) Cubic closed packing arrangement

In this arrangement second layer spheres are arranged at the dips of first layer. Third layer spheres are arranged in a manner such that it cover the octahedral void.

Then no longer third layer is similar to first or second layer. Third layer gives different arrangement. Fourth layer spheres are similar to first layer. If the first, second and third layers are represented as A, B, C. then this type of packing gives the arrangement of layers as ABC ABC..... (ie). The first three layers do not resemble each other but fourth, fifth, sixth layers resemble first, second and third layers respectively and the sequence is repeated with the addition of more layers.

In this arrangement atoms occupy 74% of the available space and thus has 26% vacant space. The co-ordination number is 12.

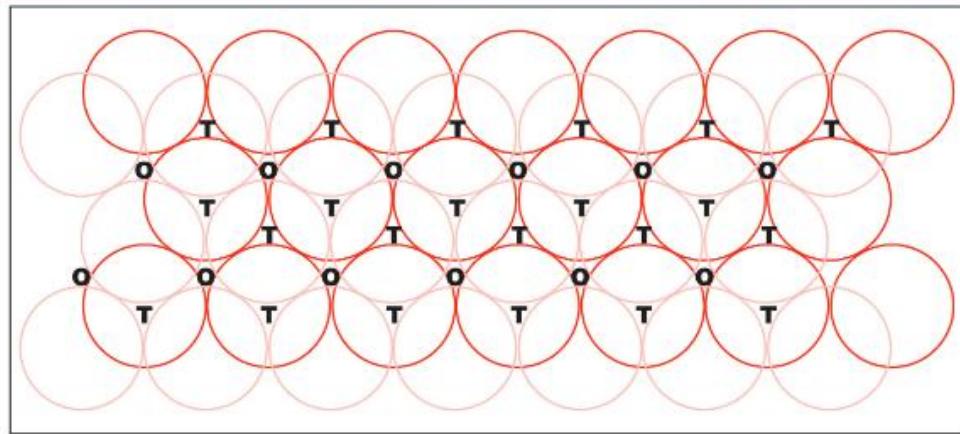
eg. Al, Cu, Au, Pb, Pt, Pd, Ni, Ca, Mn, Fe, Co, etc.

Some metals undergo changes in structures as temperature and pressure changes.

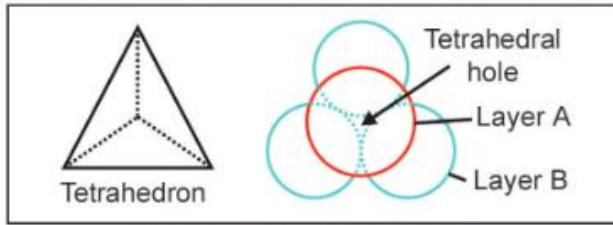
#### Voids

The empty spaces between the three dimensional layers are known as voids or holes. There are two types of common voids possible. They are called tetrahedral and octahedral voids. These are also called interstices. These voids are shown in Fig 2.17.

**Tetrahedral void :** A hole formed by three spheres of a layer in contact with each other and also with a sphere on the top or bottom layer is a hole between four spheres. The spheres are arranged at the vertices of a regular tetrahedron as shown in Fig 2.18. Such a hole is called tetrahedral void.

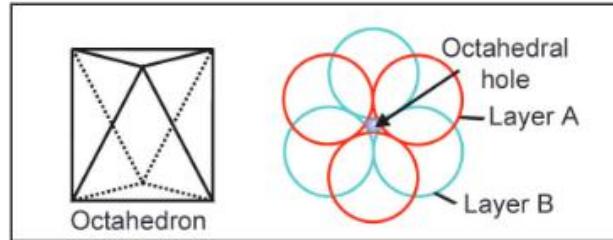


**Fig 2.17** A stack of two hexagonal close packed layer, shown different type of voids (T = Tetrahedral void; O = Octahedral void)



**Fig 2.18** Tetrahedral void

**Octahedral void :** A hole formed by three spheres of a hexagonal layer and another three spheres of the adjacent layer is a hole between six spheres. The spheres are arranged at the vertices of a regular octahedron as shown in Fig 2.19. Such a hole is called octahedral void.



**Fig 2.19** Octahedral void

**Close packed structures have both tetrahedral and octahedral voids**

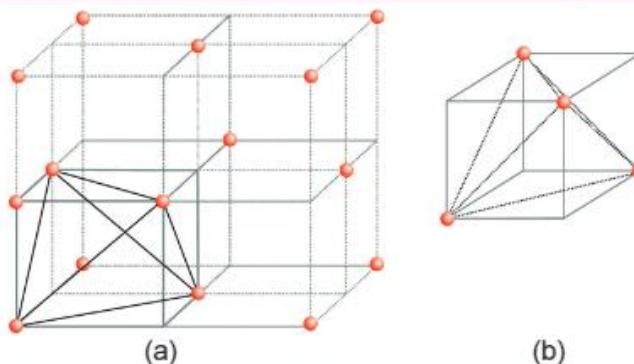
**Number of tetrahedral voids is twice the number of atoms in fcc**

#### Locating Voids

We know that close packed structures have both tetrahedral and octahedral voids. Let us take CCP (or FCC) structure and locate these voids in it.

**Locating Tetrahedral Voids :** Let us consider a unit cell of CCP or FCC lattice as shown in Fig 2.20(a). The unit cell is divided into eight small cubes.

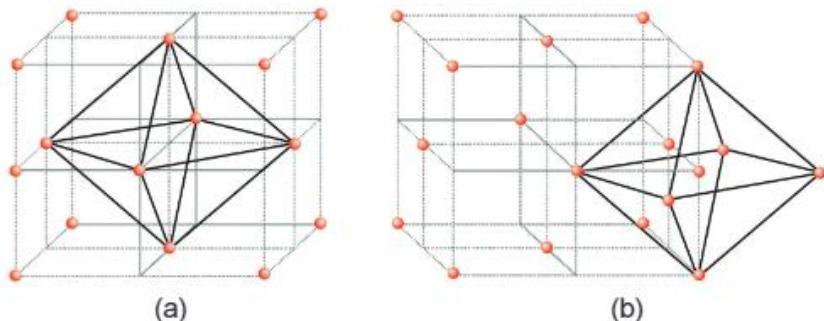
Each small cube has atoms at alternate corners. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of CCP structure. We know that CCP structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.



**Fig 2.20 (a) Eight tetrahedral voids per unit cell of ccp structure and (b) One tetrahedral void showing the geometry**

**Locating Octahedral Voids :** Let us again consider a unit cell of CCP or FCC lattice as shown in Fig 2.21(a). The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. Fig 2.21(b). It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only 1/4th of each void belongs to a particular unit cell.



**Fig 2.21 Location of octahedral voids per unit cell of CCP or FCC : (a) at the body centre of the cube and (b) at the centre of each edge (only one void is shown)**

If there are ‘n’ atoms present in the unit cell of close packed structure the number of tetrahedral voids are ‘2n’ and the number of octahedral voids are ‘n’.

The hexagonal close packed and cubic close packed structures of metallic crystals are shown in Fig 2.22.

### 2.2.7

#### Analysis of unit cells

In a simple cubic lattice the atoms are located only on the corners of the cube. The atoms touch each other along the edge. The edge length, also called the side of a cube ( $a$ ) is twice of the radius of atom ( $r$ ).

$$a = 2r \quad (\text{or}) \quad r = a/2$$

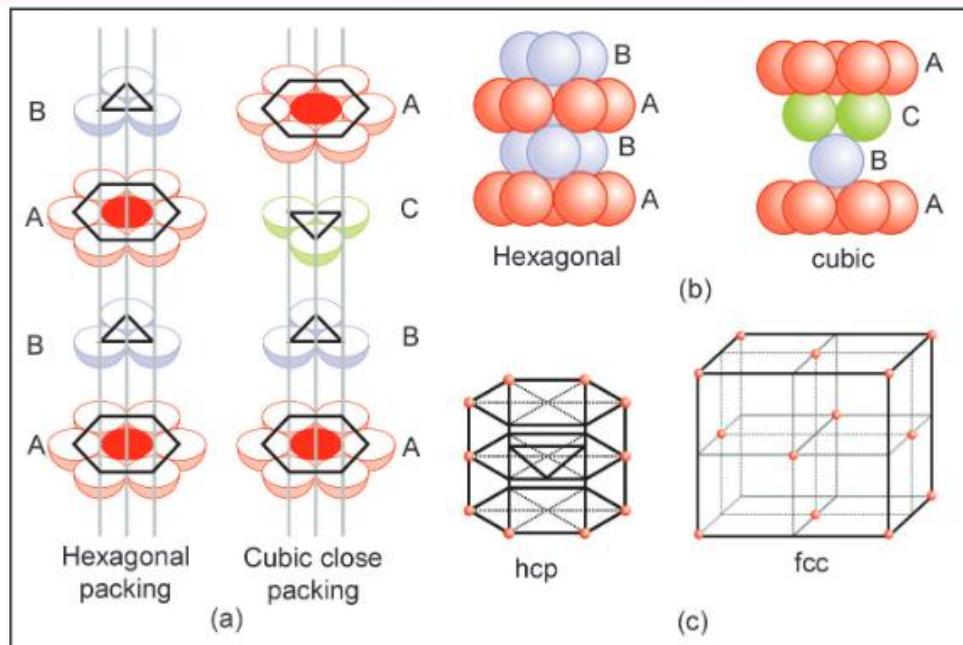


Fig 2.22 Close packing structure

In a fcc structure, the atoms of the corners do not touch each other in an edge. Instead the atoms in the opposite corner of a face and the atom in the centre of the face touch each other. The face diagonal in terms of the edge length (a) is  $\sqrt{2} a$

$$4r = \sqrt{2} a \quad (\text{or}) \quad r = \frac{a}{2\sqrt{2}}$$

In a bcc structure, the atoms in the opposite corners of a body and the atom in the body centre touch each other. The body diagonal in terms of edge length (a) is  $\sqrt{3} a$ .

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

Face diagonal and body diagonal are shown in Fig 2.23.

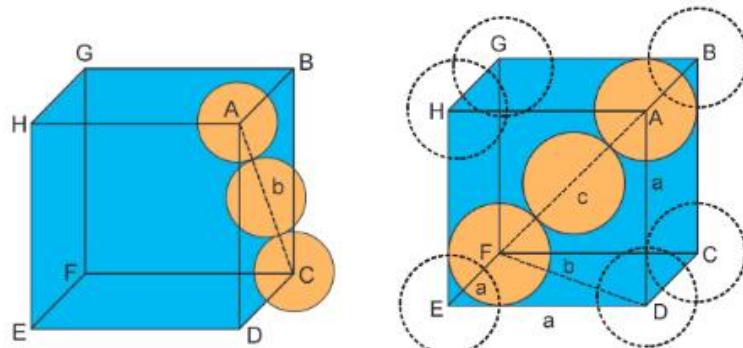


Fig 2.23 (a) Face diagonal in fcc and (b) Body diagonal in bcc

The ratio of volume of atoms in unit cell to the volume of the unit cell is called packing fraction of the unit cell.

$$\text{Packing efficiency} = \frac{n \times v}{V} \times 100$$

where n is the number of atoms in unit cell,

v is the volume of atom ( $v = \frac{4}{3}\pi r^3$ ) and

V is the volume of unit cell ( $V = a^3$ ).

If M is the molar mass or gram atomic weight of a metal, mass of an atom (m),  
 $m = M/N_0$

Here  $N_0$  is the number of atoms present in one gram atom of metal, called Avogadro number.

The density (d) of the unit cell is given as,

$$d = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{n \times m}{a^3} = \frac{n \times M}{a^3 N_0}$$

Here n is the number of metal atoms present in the unit cell.

Analysis of different properties of three cubic crystals of metal lattices is summarised in Table 2.5.

**Table 2.5 Dimensions of three types of cubic unit cells**

Property	Simple cube	Body centred cube	Face centred cube
Edge length	a	a	a
Radius of atom (r)	$\frac{a}{2}$	$\frac{\sqrt{3}a}{4}$	$\frac{a}{2\sqrt{2}}$
Volume of atom (v)	$\frac{\pi a^3}{6}$	$\frac{\pi a^3}{12\sqrt{2}}$	$\frac{\pi \sqrt{3} a^3}{16}$
Coordination number	6	8	12
Number of atoms per each unit cell	1	2	4
Packing fraction of atoms	0.52	0.68	0.74
Percentage of Packing in unit cell	52%	68%	74%
Percentage of voids in unit cell	48%	32%	26%



**P.2.7** How many symmetry elements are there for a cubic structure or a crystal?

**Solution** There are 3 types of symmetry elements. They are :

(a) centre of symmetry, (b) axis of symmetry and (c) plane of symmetry.

A cube has 1 centre of symmetry.

A cube has 3 axis of four fold symmetry, 4 axis of three fold symmetry and 6 axis of two fold symmetry.

A cube has 3 rectangular planes of symmetry and 6 diagonal planes of symmetry

The total number of symmetry elements of a cube =  $1 + (3 + 4 + 6) + (3 + 6) = 23$ .



- P.2.8** In a cubic structure, atoms of 'X' occupy the corners, atoms of 'Y' occupy the centre of the body and atoms of 'Z' occupy the centres of all six faces. Write the composition of the unit cell.

**Solution** Position of 'X' is corners of cube. Number of corners = 8

Contribution of atom as 'X' to unit cell =  $1/8$ . Number of atoms of 'X' =  $8 \times 1/8 = 1$

Position of 'Y' is centre of the body. Number of body centres = 1

Contribution of atom of 'Y' to unit cell = 1. Number of atoms of 'Y' =  $1 \times 1 = 1$

Position of 'Z' is centre of the face. Number of face centres = 6

Contribution of atom of 'Z' to unit cell =  $1/2$ . Number of atoms of 'Z' =  $6 \times 1/2 = 3$

The composition of unit cell containing atoms of X, Y and Z =  $\text{XYZ}_3$



- P.2.9** How many carbon atoms are present in one unit cell of diamond?

**Solution** The coordination number of carbon in diamond is 4. It has fcc structure similar to that of zinc sulphide.

Unit cell of  $\text{ZnS}$  has 4 zinc cations and 4 sulphide anions.

In diamond all lattice points are occupied by carbon atoms.

Hence, number of carbon atoms in unit cell of diamond = 8



- P.2.10** The packing fraction of a simple cubic structure is  $\frac{\pi}{6}$ . Prove.

**Solution** In a simple cube, the face edge length,  $a = 2r$ . Number of atoms present in one unit cell = 1

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of the unit cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{3(2r)^3} = \frac{\pi}{6} = 0.524$$



- P.2.11** An alloy of copper and zinc solidifies in ccp structure, where copper occupies lattice points and zinc occupies 50% of the tetrahedral voids and all octahedral voids. Calculate the weight percentage of copper in the alloy.

**Solution** Lattice points of fcc are, corners of the cube (8) and centre of the faces (6)

$$\text{Number of copper atoms present in the unit cell} = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4$$

Number of tetrahedral voids = 8 and number of octahedral voids = 4

$$\text{Number of zinc atoms in the unit cell} = \left(8 \times \frac{50}{100}\right) + 4 = 4 + 4 = 8$$

Atoms of Cu and Zn are in the ratio, which is the mole ratio = 4:8 = 1:2

Mass of Cu = 63.5g. Mass of Zn =  $2 \times 64.5 = 129$  g

$$\text{Percentage weight of Cu} = \frac{\text{weight of copper}}{\text{weight of alloy}} \times 100 = \frac{63.5}{63.5 + 129} \times 100 = \frac{63.5}{192.5} \times 100 = 33\%.$$



- P.2.12** A metal forms hexagonal close-packed structure? How many voids are present in 0.5 mol of it?

**Solution** Number of atoms in 0.5 mol of the given metal =  $3 \times 10^{23}$

If there are 'n' atoms, number of tetrahedral voids is '2n' and number of octahedral voids is 'n'

Number of tetrahedral voids present in 0.5 mol of metal =  $6 \times 10^{23}$

Number of octahedral voids present in 0.5 mol of metal =  $3 \times 10^{23}$

Total number of voids present in the given metal =  $9 \times 10^{23}$



**P.2.13** An alloy of metals M and N, crystallises in ccp. Atoms of N occupy lattice points and atoms of M occupy one-third of tetrahedral voids. What is the composition of the unit cell?

**Solution** Unit cell of ccp has 8 atoms of N at corners and 6 atoms of N at face centres.

$$\text{Number of atoms of N} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$$

$$\text{Number of tetrahedral voids} = 2 \times 4 = 8$$

$$\text{Number of atoms of M} = 8 \times \frac{1}{3} = \frac{8}{3}$$

$$\text{Ratio of number of atoms of M and number of atoms of N} = \frac{8}{3} : 4 = \frac{8}{3} : \frac{8}{2} = 2 : 3$$

Composition of alloy is  $M_2N_3$



**P.2.14** An X-ray beam ( $\lambda = 70.9$  pm) was scattered by a crystalline solid. The angle ( $2\theta$ ) of the diffraction for a second order reflection is  $14.66^\circ$ . Calculate the distance between parallel planes of atoms of the crystalline solid.

**Solution** The Bragg's equation is given as,  $n\lambda = 2d \sin \theta$

$$n = \text{order of reflection} = 2$$

$$\lambda = \text{wave length of X-rays} = 7.09 \times 10^{-11}\text{m}$$

$$\theta = \text{Angle of reflection} = 7.33^\circ$$

$$d = \text{distance between parallel planes}$$

$$\text{Distance between parallel planes} = d = \frac{\lambda}{\sin \theta} = \frac{7.09 \times 10^{-11}}{\sin 7.33^\circ} = 6.18 \times 10^{-10}\text{m}$$



**P.2.15** Calculate the density of unit cell of sodium, if the edge length of cubic structure is 4.24 angstroms.

**Solution**  $n = \text{Number of atoms per unit cell} = 2$  (since Na crystallise in bcc lattice)

$$M = \text{Gram atomic mass of sodium} = 23 \text{ g mol}^{-1}$$

$$N_0 = \text{Avogadro number} = 6.023 \times 10^{23}$$

$$a = \text{Edge length} = 4.24 \text{ angstroms} = 4.24 \times 10^{-10}\text{m}$$

$$\text{Density, } d = \frac{n \times M}{a^3 N_0} = \frac{2(23 \times 10^{-3})}{6.023 \times 10^{23} \times (4.24 \times 10^{-10})^3} = 1.002 \times 10^3 \text{ kg m}^{-3}$$



**P.2.16** Length of a face edge in lithium chloride crystal is  $5.11 \text{ \AA}^0$ . What is the radius of anion of the crystal?

**Solution** LiCl is assumed to have the structure of NaCl face centred cubic lattice, in which face diagonal has anions touching each other.

$$\text{Face diagonal length} = \sqrt{2}a = 4 \times \text{radius of chloride}$$

$$\text{Face edge length of LiCl} = a = 5.11 \text{ \AA}^0$$

$$\text{Radius of chloride} = \frac{\sqrt{2}}{4}a = \frac{1.414}{4} \times 5.11 = 1.81 \text{ \AA}^0$$

### EXERCISE - 2.1.2

- Define (a) space lattice, (b) crystal lattice, (c) unit cell and (d) coordination number.
- What are the parameters to characterise a unit cell?
- Draw the three cubic lattices of metallic crystals.
- Derive the Bragg's equation useful for X-ray diffraction of crystals.
- Discuss the close packing in crystal structures.

6. Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice? (Ans : hcp, 74%)
7. A grating has  $5.7 \times 10^3$  lines per cm. If X-rays of wavelength 546 nm are incident on the grating, find the angle of reflection for the first order diffraction maximum. (Ans :  $9.95^\circ$ )
8. A bcc lattice is made up of two elements X and Y. Atoms of X occupy two corners and atoms of Y occupy the remaining lattice points. Derive the composition of the compound. (Ans :  $XY_7$ )
9. Atomic weight of silver is 107.8. Silver crystallises in fcc lattice with edge length of unit cell is  $4.086 \text{ \AA}^0$ . Calculate the density of unit cell of silver and radius of silver atom. (Ans :  $1.05 \times 10^4 \text{ kgm}^{-3}$ ,  $1.4 \text{ \AA}^0$ )
10. An element with molar mass  $2.7 \times 10^{-2} \text{ kgmol}^{-1}$  forms a cubic unit cell with edge length 405 pm. If its density is  $2.7 \times 10^3 \text{ kgm}^{-3}$ , what is the nature of the cubic unit cell? (Ans : ccp)
11. A compound is formed by two elements X and Y. Atoms of the element Y (as atoms) make ccp and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound? (Ans :  $XY$ )
12. Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B? (Ans :  $A_4B_3$ )
13. The edge length of a face of crystalline barium is 0.42 nm. Calculate the diameter of an atom of the metal. (Ans : 0.36nm)
14. The edge length of sodium chloride  $5.64 \text{ \AA}^0$ . Calculate is the density of sodium chloride. (Ans :  $2.16 \text{ g cc}^{-1}$ )
15. A metal crystallises in body centred cubic lattice with edge length of the cube 287 pm. Calculate the radius of metal atom. (Ans :  $1.86 \text{ \AA}^0$ )

## DEFECTS IN SOLIDS

### 2.3.1

#### Imperfections

*Imperfections  
in crystals are  
called defects*

All crystalline solids are assumed to possess systematic structures. However, there will be imperfections. These imperfections are called defects. The defects may be structural or may be in the compositions. Because of the imperfections in the crystals, properties like density, entropy and heat capacity are slightly affected. Properties like mechanical strength, chemical activity, catalytic activity and electrical conductivity are largely affected due to these defects.

The defects are basically irregularities in the arrangement of constituent particles of crystals. Thermodynamically all solids have a tendency to become defective because of the increase in the disorderliness and hence an increase in their entropy.

Crystal defects may be intrinsic or extrinsic. Intrinsic defects are seen in pure crystals. Extrinsic defects are due to the impurities in the solids. Broadly speaking, defects are of two types, namely point defects and line defects. Irregularities around a sphere in a crystal are point defects, while deviation from ideal arrangement in entire rows of lattice points called line or extended defects.

Point defects are three types. They are: stoichiometric defects, non-stoichiometric defects and impurity defects. The stability of crystal decreases, because of the defects.

### 2.3.2

#### Stoichiometric defects

Stoichiometric defects are the point defects that do not disturb the stoichiometry of the solid. They are also called thermodynamic defects or intrinsic defects. Basically point defects are vacancy defects or interstitial defects. When few lattice points are vacant, the crystal is said to have vacancy defect. Vacancy defect a thermodynamic defect. The defect can also develop when a substance is heated. Vacancy defect results in the decrease in the density of the solid. When few constituent particles occupy void, the crystal is said to have interstitial defect. This defect results in the increase in the density of the solid.

Vacancy and interstitial defects are shown in Fig 2.24.

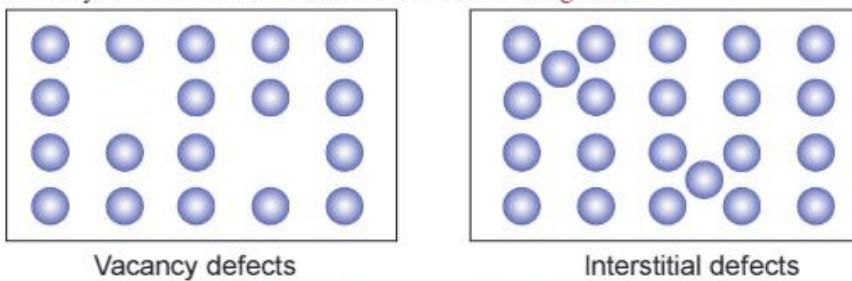


Fig 2.24 Two type of point defects

**Schottky defect :** It is a vacancy defect in ionic solids. The crystal is said to have vacancy defect when some of the lattice points are vacant. In order to maintain electrical neutrality, the number of missing cations and anions are equal. In sodium chloride about one million Schottky pairs per  $\text{cm}^3$  are defected at room temperature. Since one cc has about  $10^{22}$  ion pairs, there is one Schottky defect per  $10^{16}$  ion pairs.

Schottky defect was observed in ionic substances in which cation and anion are of similar size. This was shown by ionic crystals of high coordination number. Examples include  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CsCl}$ ,  $\text{AgBr}$ , etc. As a result of Schottky defect density decreases and conductivity increases.

Schottky defect of ionic crystal is shown in Fig 2.25.

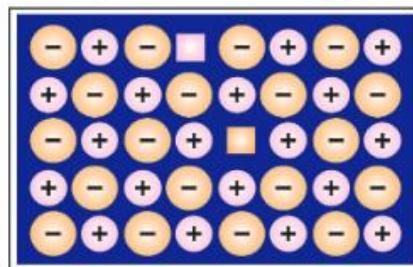


Fig 2.25 Schottky defect

**Frenkel defect  
is a combined  
effect of vacancy  
and interstitial  
defects**

**Frenkel defect :** It is a combined effect of vacancy and interstitial defects. This is also called dislocation defect. Generally the smaller cation is dislocated from its normal site to an interstitial site.

Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions. It is observed in ionic substances of low coordination number. Examples include  $ZnS$ ,  $AgCl$ ,  $AgBr$ ,  $AgI$ , etc.

As a result of Frenkel defect, the density does not change, but the conductivity increases.

It may be noted that silver bromide shows both Schottky and Frenkel defects. Stability of the crystal decreases in stoichiometric defect, as entropy increases.

Frenkel defect of ionic crystals is shown in Fig 2.26, respectively.

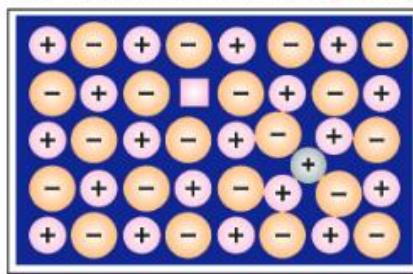


Fig 2.26 Frenkel defect

### 2.3.3

#### Non-stoichiometric defects

**Stoichiometry is  
not maintained  
due to excess  
metal or metal  
deficiency**

A large number of non-stoichiometric inorganic solids are known which contain constituents in non-stoichiometric ratio due to defects. Stoichiometry is not maintained due to excess metal or metal deficiency.

Metal excess defect is commonly observed in alkali metal halides. This is generally due to anionic vacancies. When sodium chloride is heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The chloride ions diffuse to the surface and react with metal atoms to give sodium chloride. This happens by the loss of electron by sodium atoms to form sodium cations.



The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal has excess sodium ions. The larger size anionic sites are occupied by smaller size unpaired electrons called F-centres. An F-centre in a metal chloride crystal is shown in Fig 2.27.

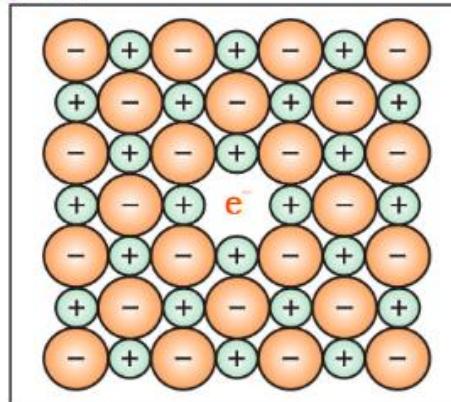


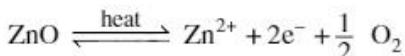
Fig 2.27 F-centre in a crystal

  
**F-centre is  
large anionic site  
occupied by  
small electron**  


F–centre imparts colour to the crystal. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the solid. Excess sodium in sodium chloride imparts yellow colour. Similarly excess potassium in potassium chloride gives lilac blue (violet) and excess lithium in lithium chloride gives crimson red (pink) colours. These F–centers are also responsible for the increased conductivity of the ionic crystal.

Zinc oxide is white at room temperature. On heating it turns yellow. This is explained based on the loss of oxygen by zinc oxide reversibly.

This is referred to metal excess defect and is due to the presence of extra cations at interstitial sites.



Zinc oxide is a stoichiometric compound with  $\text{Zn}^{2+}$  and  $\text{O}^{2-}$  ions in the ratio  $n : n$ . Due to the excess of zinc ion, the ratio of ions becomes,  $n + 1 : n$ . The excess  $\text{Zn}^{2+}$  ions move to the interstitial site and the electrons to the neighbouring interstitial sites.

  
**Non-stoichiometric  
ionic solid  
contains less  
amount of metal**  


There are many metal oxides, metal sulphides and metal hydrides difficult to prepare in the stoichiometric composition. They generally contain less amount of metal as compared to the stoichiometric ratio.

A typical example of non-stoichiometric iron oxide is  $\text{Fe}_{0.94}\text{O}$ , actually ranging between  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ . Stoichiometric iron oxides are ferrous oxide ( $\text{FeO}$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ). The non-stoichiometry may be explained as missing of some of  $\text{Fe}^{2+}$  cations in the crystals of  $\text{FeO}$  and the loss of positive charge is compensated by the presence of appropriate number of  $\text{Fe}^{3+}$  ions.

### 2.3.4

#### Impurity defects

Impurity defects arise when a salt of metal of higher valency is added in the crystallisation of a salt of metal of lower valency.

If molten sodium chloride containing a little amount of strontium chloride is crystallised, some of the sites of sodium cations are occupied by strontium cations. Each  $\text{Sr}^{2+}$  ion replaces two  $\text{Na}^+$  ions, in order to conserve net charge. Introduction of another material leading to impurity defect is shown in Fig 2.28.

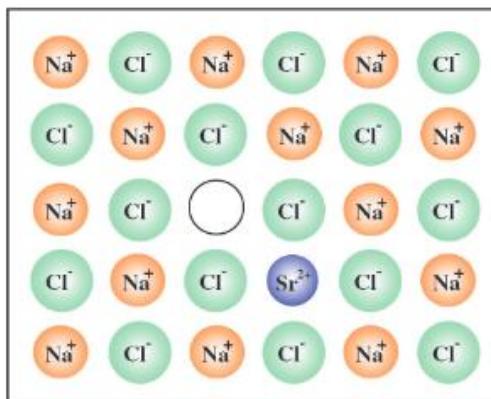


Fig 2.28 Impurity ( $\text{SrCl}_2$ ) defect in crystalline ionic solid ( $\text{NaCl}$ )

When a divalent ion occupies the site of one monovalent ion, another site of monovalent ion remains vacant. This leads to variation in the density and increase in the conductivity.

Similar examples of solid solutions of impurity defects are a solution of  $\text{CaCl}_2$  in  $\text{AgCl}$ , a solution of  $\text{ZnCl}_2$  in  $\text{Cu}_2\text{Cl}_2$ , etc.



- P.2.17** Density of ionic substance is unchanged in Frenkel defect, but the conductivity of ionic crystalline solid increases. Comment.

**Solution** In Frenkel defect the cations missing at lattice points appear at interstitial sites. The total number of ions is conserved and hence density is constant.

However conductivity increases because of the lattice vacancy and interstitial occupancy of the ions in the lattice of the crystal.



- P.2.18** Differentiate between vacancy defect and interstitial defect.

**Solution** Vacancy defect and interstitial defect are examples of point defects.

Missing of a point in the lattice of crystal is called vacancy defect.

Presence of a point in the interstitial site of crystal is interstitial defect.



- P.2.19** On cooling hot zinc oxide, the yellow colour become white. Why ?

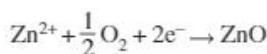
**Solution** The composition of  $\text{Zn}^{2+}$  and  $\text{O}^{2-}$  ions in stoichiometric  $\text{ZnO}$  is  $n : n$ .

On heating  $\text{ZnO}$ , oxygen is lost reversibly.

A non - stoichiometric compound with excess  $\text{Zn}^{2+}$  ions is formed possessing a composition of  $\text{Zn}^{2+}$  and  $\text{O}^{2-}$  ions  $n : n - x$ .

Due to excess metal in the interstices, it is yellow.

On cooling the non-stoichiometric zinc oxide, it gains oxygen. A stoichiometric zinc oxide is formed and hence it is white.



- P.2.20** Crystal stability decreases, upon stoichiometric defects. Why ?

**Solution** Solid crystals are very stable because of orderly arranged particles in systematic lattices.

Eventhough stoichiometry is maintained, due to point defects, systematicity is lost and crystal stability decreases.



- P.2.21** The non - stoichiometric iron oxide has a composition  $\text{Fe}_{0.94}\text{O}$ . Find the ratio of ferrous and ferric ions present in it.

**Solution** Say one hundred ions of each  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  present in the stoichiometric  $\text{FeO}$ . Some of  $\text{Fe}^{2+}$  ions ( $x$ ) are replaced by  $\text{Fe}^{3+}$  ions ( $y$ ).

In view of the conservation of ions in an ionic crystal,  $x + y = 94$  ... (1)

In view of the conservation of positive charge of cations in a crystal,

$$2x + 3y = 200 \dots (2)$$

Solving, for 'x' and for 'y',  $y = 12$  and  $x = 82$

$$\begin{aligned} \text{The ratio of } \text{Fe}^{2+} \text{ and } \text{Fe}^{3+} \text{ ions present in } \text{Fe}_{0.94}\text{O} &= 82 : 12 \\ &= 41 : 6 \end{aligned}$$



**P.2.22** In the crystallisation of 71.75 grams of  $\text{AgCl}$ , in molten state  $1 \times 10^{-4}$  mole of cadmium chloride is added to cause impurity defect. Calculate (a) the number of  $\text{Ag}^+$  ions present, (b) the number of  $\text{Cd}^{2+}$  ions present and (c) the number of lattice vacancy defects.

**Solution** Number of moles of  $\text{Ag}^+$  = number of moles of  $\text{AgCl}$  =  $\frac{71.75}{143.5} = 0.5$

Original number of  $\text{Ag}^+$  ions in the given crystalline substance

$$= 0.5 \times 6.023 \times 10^{23} = 3.0115 \times 10^{23}$$

Number of  $\text{Cd}^{2+}$  ions added

$$= 1 \times 10^{-4} \times 6.023 \times 10^{23} = 6.023 \times 10^{19}$$

Number of  $\text{Ag}^+$  ions removed

$$= 2 \times 6.023 \times 10^{19} = 1.2046 \times 10^{20}$$

Number of lattice vacancies created in the given crystal

$$= 6.023 \times 10^{19}$$

Number of  $\text{Ag}^+$  ions present in the defected crystal

$$= 3.0115 \times 10^{23} - 1.2046 \times 10^{20} = 3.0103 \times 10^{23}$$

### EXERCISE - 2.1.3

- How do the properties of crystals vary with imperfections?
- How are the properties of crystals vary upon point defects?
- State and explain Schottky defect. Write examples.
- What is Frenkel defect? Discuss.
- Differentiate between stoichiometric and non-stoichiometric defects.
- Write on metal excess defect.
- Illustrate with a suitable example, the impurity defects in ionic crystal.

## PROPERTIES OF SOLIDS

Properties of solids vary depending on the nature of bonding or cohesive forces present between constituent particles. Crystal structures, cohesive forces and chemical reactivity of solids throw much light on a variety of properties of crystalline solids. The important properties of solids are of three types.

- Electrical properties.
- Magnetic properties.
- Dipolar properties.

### 2.4.1

#### Electrical properties

Solids exhibit an amazing range of electrical conductivities. Based on their conductivities, solids can be classified into three types, namely insulators, conductors and semi-conductors.

**A. Insulators :** Insulators are very poor conductors of electricity. They are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$ . Diamond is the best familiar insulator.

*Conductivity in metals is due mobility of free electrons. In electrolytes it is due to free ions*

**B. Conductors :** The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are known as conductors. Metals have conductivities in the order of  $10^6$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ . They are good conductors.

**C. Semiconductors :** The solids with intermediate conductivity ranging between  $10^{-6}$  to  $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$  are called semiconductors.

Electrical conductors are of two types. They are electrolytic conductors and metallic conductors. Electrolytes conduct electricity through mobility of free ions. Metallic solids conduct electricity through movement of free electrons. Metallic conductors are called electronic conductors.

Metals conduct electricity in solid state as well as in molten state. Conductivity of metals and alloys depend upon the number of valence electrons available per atom.

The atomic orbitals of metal atoms form molecular orbitals. The energy gap between bonding and anti-bonding molecular orbitals keeps on decreasing with the increase of number of atoms of atomic orbitals. A stage comes when the gap between the molecular orbitals is so small that these orbitals can be considered as a continuous one. The collection of these so closed molecular orbitals are called bands. The highest filled band of orbitals is called valence band. The lowest unfilled band of orbitals is called conduction band. Conductivity of solids can be explained based on the band theory shown in Fig 2.29.

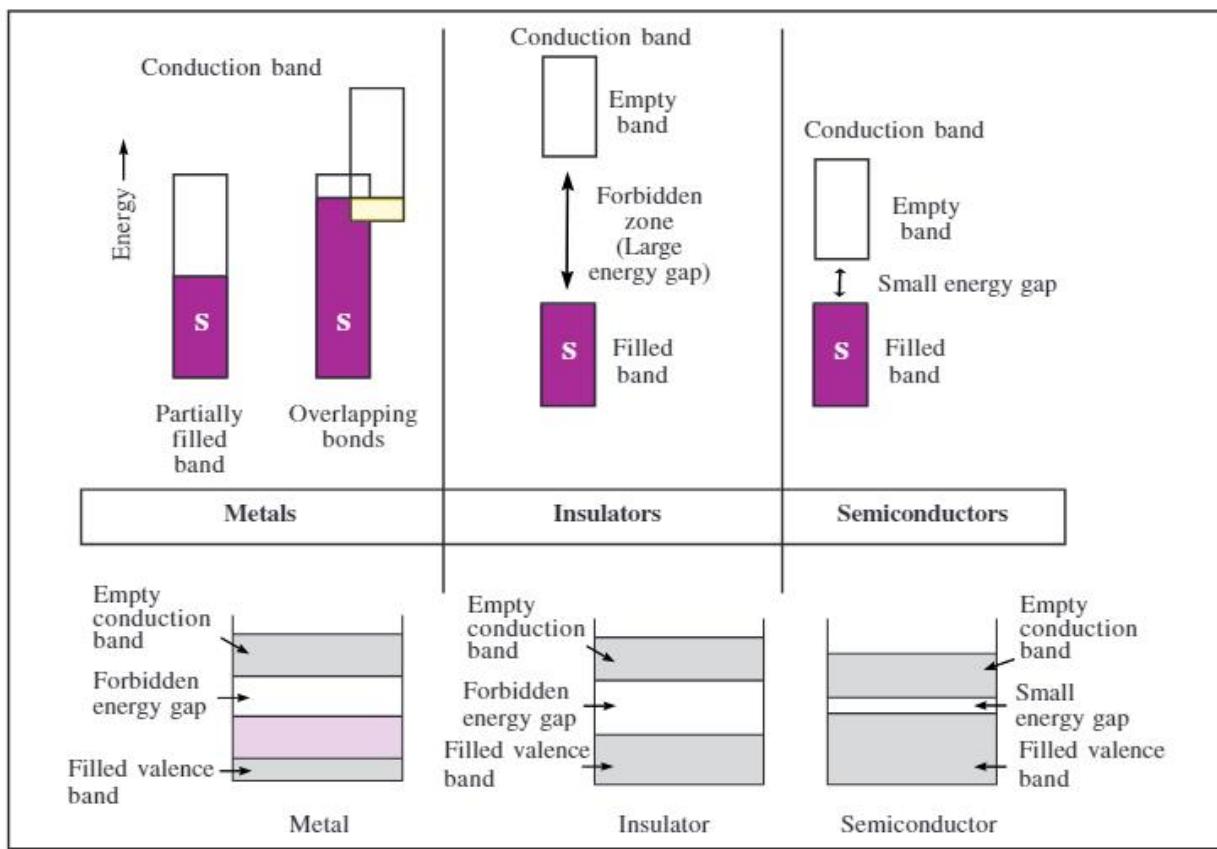


Fig 2.29 Valence and conduction bands in solids

If the valence band is partially filled or it overlaps with the conduction band, the electrons can flow easily under an applied electric field and metal shows good conductivity.

If the gap between valence band and conduction band is large, electrons can not jump to the next higher unoccupied band. Such a substance has very small conductivity and it behaves as an insulator.

Conductivity of metals decreases upon heating due to increased vibrations of lattice points called resistance. Electrical resistance becomes almost zero near the absolute zero. Materials in this state are said to possess super conductivity. Impurity in metals and imperfections in the lattices increase in conductivity of metals.

Pure silicon and pure germanium are called intrinsic semiconductors. The conductivity of such substances, however, increases with increase in temperature. At room temperature, the conductivity of Si or Ge is too low to be of practical use.

A number of solid state semiconductors have been prepared by a combination of elements of group 13 and group 15 or group 12 and group 16. In the substances formed by these combinations like AlP, InSb, GaAs, CdSe, ZnS, HgTe, CdS, etc., the bonds are not pure covalent bonds. Due to bond polarity even at room temperature, these substances have increased conductivity.

Some oxides of transition metals show wide variation in their electrical properties. Similar variation in properties is exhibited by sulphides also. They show marked differences in their electrical properties. Variation in the electrical properties of transition metal oxides at room temperature is presented and compared in Table 2.6.

**Table 2.6 Some transition metal oxides and variation in their electrical property**

Metallic property	Semiconductors property				Insulator property
VO	FeO	V <sub>2</sub> O <sub>5</sub>			MnO
TiO	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	Mn <sub>3</sub> O <sub>4</sub>	
CrO <sub>2</sub>	CuO	Cu <sub>2</sub> O			

TiO and NbO become superconductors at about 2K

The conductivity of intrinsic semiconductors is increased by adding an appropriate amount of suitable impurity. The process of adding impurity is called doping. Doping can be done by using an electron deficient or electron rich element as compared to the intrinsic semiconductor.

These doped impurities introduce electronic defects in the semiconducting elements. Doping of group 13 elements and group 15 elements in group 14 element silicon is illustrated in Fig 2.30.

*Doped impurities introduce electronic defects in semiconducting elements*

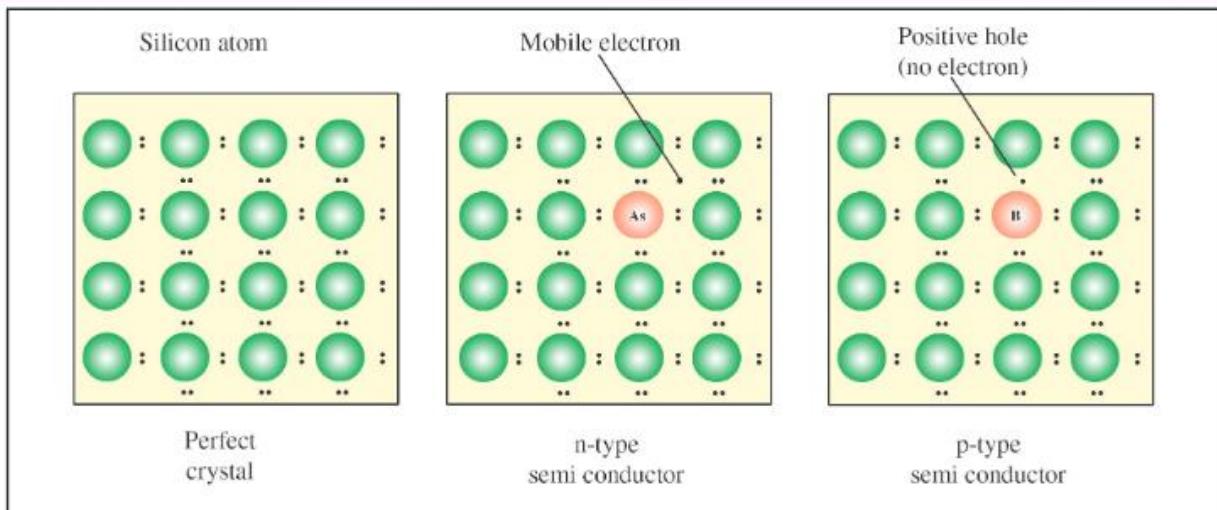


Fig 2.30 Creation of n-type and p-type semiconductors by doping

*Si doped with  
P or As  
acts as n-type  
semiconductor*

*Si doped with  
B or Al  
acts as p-type  
semiconductor*

**n-Type semiconductor :** Silicon is a group 14 element with four valence electrons. In the crystal of silicon, each atom forms four covalent bonds with its neighbours. When doped with group 15 element like phosphorus or arsenic, the element doped occupies some of the lattice sites in silicon. Four out of five valence electrons are used to form four single covalent bonds with neighbouring silicon atoms. The extra unbonded electron is delocalised. These delocalised electrons of the doped element increase conductivity of silicon. Semiconductor doped with electron rich impurity is called n-type semiconductor because increase in the conductivity is due to the negatively charged electron.

**p-Type semiconductor :** Boron, aluminum or gallium, the element of group 13 has only three valence electrons. When such an element is doped with silicon, four bonds are formed. The place where the fourth valence electron is missing is called electron vacancy or electron hole. An electron of the neighbouring atom can come and fill the electron vacancy, but in doing so it would leave an electron hole in its original position. It appears as if the electron vacancy has moved in the direction opposite to that of electron that filled it. Under the influence of electric field, the positively charged electron vacancy moves towards negatively charged plate, increasing conductivity. Semiconductor doped with electron deficient impurity is called p-type semiconductor because increase in conductivity is due to the positively charged electron hole.

**Application of semiconductors :** Various combinations of n-type and p-type semiconductors are used for making electronic components. Diode is combination of n-type and p-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germantium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond.

A large variety of solid state materials have been prepared by combination of groups 13 and 14 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

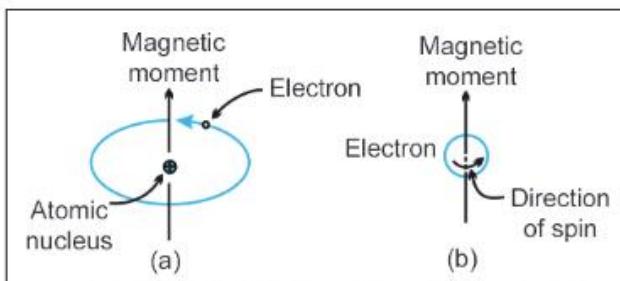
  
**TiO, CrO<sub>2</sub> and  
ReO<sub>3</sub> behave  
like metals**  


It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO<sub>2</sub> and ReO<sub>3</sub> behave like metals. Rhenium oxide, ReO<sub>3</sub> is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO<sub>2</sub>, VO<sub>3</sub> and TiO<sub>3</sub> show metallic or insulating properties depending on temperature.

#### 2.4.2 Magnetic properties

  
**One Bohr  
magneton is  
 $9.27 \times 10^{-24} \text{ JT}^{-1}$**   


According to classical thermodynamics, any charged particle moving in a circle generates magnetic field. Since the electron is a negatively charged particle, it behaves as a tiny magnet. Magnetic moment originates from two types of motions as shown in Fig 2.31. Its original motion around the nucleus and its spin around its own axis. Magnitude of the magnetic moment is very small and is measured in Bohr magneton. One Bohr magneton is equal to  $9.27 \times 10^{-24} \text{ Am}^2$ .



**Fig 2.31 Magnetic moment associated with (a) orbiting electron and (b) spinning electron**

  
**Substances  
exhibit five types  
magnetic  
behaviour**  


Substances can be classified into five types on the basis of their magnetic behaviour. Diamagnetism and paramagnetism are important in gaseous and solution state. Ferromagnetism, antiferromagnetism and ferrimagnetism are exclusively the properties of solids.

##### Diamagnetism

Diamagnetic substances are weakly repelled by a magnetic field. Sodium chloride, water, benzene, ozone, zinc oxide, vapours of alkaline earth metals are some examples of diamagnetic substances.

Diamagnetism is shown by those substances in which all the electrons are paired and no unpaired electrons are present. Pairing of electrons cancels their magnetic moments and they lose their magnetic character. Diamagnetic substances are feebly magnetised in a magnetic field in opposite direction.

##### Paramagnetism

Paramagnetic substances are weakly attracted by a magnetic field. Oxygen, nitric oxide, chlorine dioxide, vanadium dioxide, cupric copper, ferric iron, vapours of alkali metals are some examples of paramagnetic substances.

  
*Alignment of magnetic moments in the same direction gives rise to ferromagnetism*  


  
*Antiferromagnetic substances cannot be magnetised*  


  
*Ferrimagnetism is due to alignment of magnetic moments in parallel and antiparallel directions*  


Paramagnetism is shown by those substances in which one or more unpaired electrons are present. Paramagnetic substances are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field.

### Ferromagnetism

Ferromagnetic substances show permanent magnetism even after the applied magnetic field is removed. Iron, cobalt, nickel, gadolinium and chromium dioxide are examples of ferromagnetic substances.

In ferromagnetic substances, there are domains of magnetisation. Each domain acts as tiny magnet. In an unmagnetised piece of a ferromagnetic substance, the domains are randomly oriented. When the substance is placed in a magnetic field all the domains set oriented in the direction of magnetic field and a strong magnetic effect is produced.

A spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism. Parallel alignment of electrons is shown in Fig 2.32(A).

### Antiferromagnetism

Antiferromagnetic substances have no magnetic moment and cannot be magnetised. Manganese oxide and nickel oxides show antiferromagnetism. In antiferromagnetic substance, the domains are oppositely oriented in equal number and cancel out each other's magnetic moment as shown in Fig 2.32(B).

### Ferrimagnetism

Ferrimagnetic substances are weakly attracted into the magnetic field. Magnetic oxide ( $\text{Fe}_3\text{O}_4$ ) and ferrites (like  $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ , etc.) are examples of such substances.

Ferrimagnetism is observed when the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers as shown in Fig 2.32 (C). The magnetic properties of solids are listed in Table 2.7.

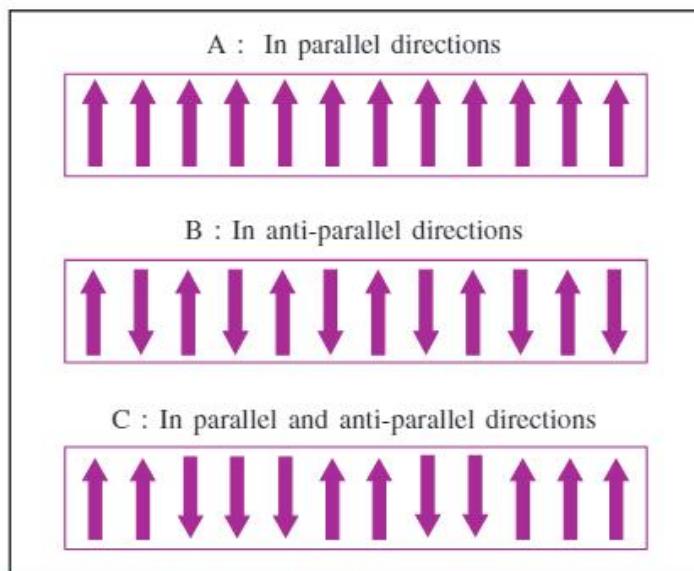


Fig 2.32 Alignment of electrons leading to different magnetic properties of crystalline solid substances

Table 2.7 Magnetic properties of crystalline solids at a glance

Property	Information	Example	Applications
Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	$C_6H_6$ , NaCl, $TiO_2$ , $V_2O_5$	Insulators
Paramagnetic	Have unpaired electrons and weakly attached in magnetic field. They cannot	$O_2$ , VO, CuO, TiO	Electronic devices
Paramagnetic	Have unpaired electrons and weakly attached in magnetic field. They cannot	$O_2$ , VO, CuO, TiO	Electronic devices
Ferromagnetic	Have unpaired electrons and strongly attracted in magnetic field. Such solids can be permanently magnetised	Fe, Ni, Co, $CrO_2$	$CrO_2$ is used in audio and video tapes
Antiferromagnetic	Unpaired electrons align themselves in such a way that resultant magnetic moments is zero	$Cr_2O_3$ , CoO, $Co_3O_4$ , $Fe_2O_3$ , MnO, $MnO_2$	Used in the instruments of magnetic susceptibility measurement
Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment	$Fe_3O_4$ , Ferrites	---

All magnetically ordered solids transform to paramagnetic state at elevated temperatures, due to randomisation of spins. Iron on oxidation, followed by dissolution in water becomes paramagnetic. Nickel oxide changes from anti-ferromagnetic phase to paramagnetic phase at 523K. Similarly  $V_2O_3$ , an antiferromagnetic substance changes to paramagnetic at 1500K.

Every substance has some type of magnetic properties associated with it. The magnetic properties are measured in terms of magnetic moment ( $\mu$ ).

Magnetic moment,  $\mu = \sqrt{n(n+2)}$ , where n is the number of unpaired electrons.

Magnetic properties are also measured in terms of magnetic susceptibility, expressed in molar susceptibility and gram susceptibility.



**P.2.23** What is the significance of resistance ratio,  $\rho_{300K}/\rho_{4.2K}$ ?

**Solution** Resistance to the flow of electrons decreases the conductivity of metals. Conductivity of metal decreases with increase in temperature. But presence of impurity in metals increases conductivity.

The resistance ratio, at room temperature and at liquid helium temperature, is a measure of the purity of metal.



**P.2.24** Graphite is a non-metal, but its electrical behaviour is like metals. Explain.

**Solution** Graphite consists of a layer structure having an hexagonal arrangement of carbon atoms. Each carbon atom is  $sp^2$  hybridized and connected to three more carbon atoms by sigma bonds. Hexagonal structures in each layer are connected to each other through the weak overlap of fourth electron present on each carbon atom perpendicular to the molecular plane.

Weak overlap leads to the formation of band structure which is half filled and half empty, thus responsible for free motion of electron.

Hence graphite acts an electrical conductor. However it may be noted that metal is a 3D-conductor, but graphite is a 2D-conductor.



**P.2.25** Write the conductivity order of aluminium phosphide, silicon and cadmium sulphide.

**Solution** At room temperature, conductivity will be more if the polarity of the covalent bond is more. Si – Si bond is non-polar, Al – P bond is slightly polar and Cd – S bond is more polar.

Increasing order of conductivity :

Silicon < Aluminium phosphide < Cadmium sulphide.



**P.2.26** Sodium vapour is paramagnetic, but cations of sodium are diamagnetic, while magnesium vapour as well as cations of magnesium are diamagnetic. Explain.

**Solution** Atoms or ions with unpaired electrons are paramagnetic. Diamagnetism is due to the absence of unpaired electrons

Number of electrons in Na is 11. Na vapour has unpaired electrons. Hence, paramagnetic.

Number of electrons in  $\text{Na}^+$  is 10. Na cations have no unpaired electrons. Hence, diamagnetic.

Both Mg and  $\text{Mg}^{2+}$  have no unpaired electrons. Hence, they are diamagnetic.



**P.2.27** NiO is antiferromagnetic. But on heating at  $250^\circ\text{C}$ , it becomes paramagnetic. Why?

**Solution** In solid state, the magnetic moments of NiO are aligned in such a fashion, such that the net moment is zero. So, NiO is antiferromagnetic.

On heating, the alignment is disturbed. The domains are randomized.  $\text{Ni}^{2+}$  has  $d^8$  configuration with unpaired electrons, hence, exhibits paramagnetism.

### EXERCISE - 2.1.4

1. Distinguish between conductors, insulators and semiconductors.
2. What are n-type and p-type semiconductors?
3. Discuss on diamagnetism and paramagnetism with suitable examples.
4. What are ferromagnetic, antiferromagnetic and ferrimagnetic substances?
5. An element of group 14 is to be converted into n-type semiconductor by doping it with a suitable impurity. Discuss. (Hint : doping with group 15 elements)
6. What type of defect can arise when a solid is heated ? Which physical property is affected by it and in what way?
7. What type of stoichiometric defect is shown by : a) ZnS ; b) AgBr
8. Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.
9. Write applications of n- and p- type semi conductors.
10. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic? Justify your answer.



1. Solid state of matter has definite shape and structure.
2. Amorphous solids are isotropic. Crystalline solids are anisotropic.
3. Crystalline solids have long range of order in the arrangement of constituent particles and have sharp melting points.

## CHEMISTRY IID

4. Crystalline solids are four types: Metallic, ionic, covalent and molecular solids.
5. The force of attraction between atoms of a metal or alloy is called metallic bond. The strength of the metallic bond is more, if the number of valence electrons is more.
6. Unit cell is the smallest part of crystal when repeated in different directions generates entire lattice.
7. There are seven types of crystal structures and 14 types of Bravais lattices.
8. The distance ( $d$ ) between rows of adjacent layers of crystal can be calculated using Bragg's equation.  $n\lambda = 2d \sin \theta$ , where ' $\lambda$ ' is the wave length of X-rays and  $\theta$  is the angle of maximum diffraction.
9. Coordination number of a sphere in a solid is the number of nearest neighbours. Covalent crystals have low coordination numbers and closed packed metals have high coordination numbers.
10. Radius ratio is the ratio of smaller ion to the larger ion in an ionic crystal. The minimum ratio of radii of cation and anion is 0.15.
11. The simple among all structures is cubic and the simplest cubic structure is primitive cube.
12. The inter atomic spaces in a solid are called voids. If the number of spheres in a closed packed structures is  $x$ , the number of tetrahedral voids is  $2x$  and the number of octahedral voids is  $x$ .
13. The density ( $d$ ) of unit cell in terms of Avagadro number ( $N_0$ ), number of atoms per unit cell ( $n$ ), edge length ( $a$ ) and gram atomic weight ( $M$ ) is,  $d = n \times M / a^3 N_0$ .
14. The imperfections in crystal are called defects. The solids have a tendency to become defective because of the increase in their entropy.
15. Schottky defect is a vacancy defect, due to which density decreases and conductivity increases.
16. Frenkel defect is dislocation of a cation from lattice point to interstitial vacancy. Density of solid does not change due to Frenkel defect.
17. Non-stoichiometric defects are metal excess defects or containing less amount of metal.
18. Insulators are very poor conductors, metals are good conductors and substances with intermediate conductivity are called semiconductors.
19. Semiconductors doped with electron rich impurity are called n-type semiconductors and with electron deficient impurities are called p-type semiconductors.
20. Substances with no unpaired electrons are diamagnetic and with unpaired electrons are paramagnetic.
21. A spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism.
22. Alignment of magnetic moments in opposite directions in equal number gives antiferromagnetism and in unequal number gives ferrimagnetism.
23. Magnetic solids on heating transform to paramagnetic state due to randomisation of electronic spins.

**EXERCISE - 2.2**

1. Mention various types of crystalline solids. Give examples.
2. Mention different examples of molecular solids.
3. What are anisotropy and isotropy?
4. Discuss the band theory of solids, to account for their conductivity properties.
5. How the elements of group 12, 13, 15 and 16 are used in order to get substances of electrical importance?
6. Distinguish between square and hexagonal two dimensional packing of metal atoms
7. Distinguish between hcp and ccp lattices with suitable examples.
8. A compound of two elements P and Q crystallises in cubic structure. If P occupies corners and Q occupies face centres, what is the composition of the compound? If atoms of Q along with one direction are removed, what is the composition? **(Ans :  $PQ_3 : PQ_2$ )**
9. An alloy of Au and Cu crystallises with atoms of Au occupying all lattice points at the corners of cubic and atoms of Cu occupying the centres of all faces. Write the empirical formula of the alloy. **(Ans :  $AuCu_3$ )**
10. Unit cell of silver (at wt. 108) has a density  $10.5 \text{ g cc}^{-1}$ . The crystal is cubic with edge length  $4.09 \text{ \AA}^0$ . How many silver atoms are present in unit cell of the metal? **(Ans : 4)**
11. Discuss the symmetry elements of crystal line solids.
12. The density KBr cubic crystal is  $2.75 \text{ g cm}^{-3}$  with an edge length of cube  $654 \text{ pm}$ . How many mass points are present in the unit cell? **(Ans : 4)**
13. A crystal was examined with X - rays of wave length  $1.53 \text{ \AA}^0$  with a maximum reflection at  $15^\circ 36'$ . What is the interplanar spacing ? If X - rays of wave length  $2.29 \text{ \AA}^0$  was used, what will be angle of reflection? **(Ans :  $3.2 \text{ \AA}^0 ; 28^\circ 2'$ )**
14. Density of silver is  $10.5 \text{ g cc}^{-1}$ . Calculate the edge length of the unit cell of silver. **(Ans : 409 pm)**
15. Density of potassium is  $2.64 \times 10^6 \text{ g m}^{-3}$ . What is the radius of metal atom? **(Ans :  $1.76 \text{ \AA}^0$ )**
16. Silicon crystallises in fcc lattice, a single crystal of high purity like diamond. Gram atomic weight of silicon is  $28 \text{ g mol}^{-1}$ . Edge length of unit cell is  $0.543 \text{ nm}$ . Calculate the number of silicon atoms per unit cell and density of unit cell. **(Ans : 8;  $2.33 \text{ g cc}^{-1}$ )**
17. In a close packed structure of mixed oxide, the lattice is composed of  $O^{2-}$  ions. One eighth of tetrahedral voids are occupied by divalent cations  $A^{2+}$  and one half of octahedral voids by trivalent cations  $B^{3+}$ . What is the formula of oxide? **(Ans :  $AB_2O_4$ )**
18. A metal crystallises in fcc lattice with edge length of unit cell  $3.5 \text{ \AA}^0$  and also in bcc lattice with edge length of unit cell  $3 \text{ \AA}^0$ . Calculate the ratio of the densities of fcc and bcc lattices. **(Ans : 1.26)**

## CHEMISTRY IID

19. Metallic chromium crystallises in bcc lattice. The edge length of unit cell is  $2.87 \text{ \AA}^0$ . Calculate (a) atomic radius and (b) density.   
  
(Ans :  $1.24 \text{ \AA}^0$ ;  $7.3 \text{ g cm}^{-3}$ )
20. For a cubic lattice edge length of unit cell is  $5\text{\AA}^0$  and density is  $2\text{gcm}^{-3}$ . Calculate the radius of an atom, if gram atomic weight is  $75 \text{ g mol}^{-1}$ .   
  
(Ans :  $2.17\text{\AA}^0$ )
21. What is the ratio of lengths of face edge, face diagonal and body diagonal of cube ?  
  
(Ans :  $1:\sqrt{2}:\sqrt{3}$ )
22. Which of the crystal structures has no symmetry elements? Why?   
  
(Hint : Triclinic)
23. The interplanar distance in a crystal used for X - ray diffraction is  $2\text{\AA}^0$ . The angle of incidence for first order diffraction is  $9^\circ$ , what is the wave length of X - rays?   
  
(Ans :  $0.63\text{\AA}^0$ )
24. An alloy is made up of metals X and Y. Atoms of X are in ccp arrangement. Atoms of Y occupy half of the tetrahedral and all octahedral voids. Write the composition of the alloy.  
  
(Ans :  $\text{XY}_2$ )
25. An element crystallises in the fcc lattice having edge length  $400 \text{ pm}$ . Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure.  
  
(Ans :  $117 \text{ pm}$ )
26. In a compound AB, the ionic radii of  $\text{A}^+$  and  $\text{B}^-$  are  $88 \text{ pm}$  and  $200 \text{ pm}$  respectively. Write the coordination number of  $\text{A}^+$ .  
  
(Ans : 6)
27. Edge length of unit cell of KCl is  $629 \text{ pm}$  and density is  $1.989 \text{ g cm}^{-3}$ . Calculate Avagadro's number based on this X-ray diffraction data.   
  
(Ans :  $6 \times 10^{23}$ )
28. Formula of nickel oxide is  $\text{Ni}_{0.98}\text{O}$ . Calculate the fractions of nickel that exists as  $\text{Ni}^{3+}$  ions and  $\text{Ni}^{2+}$  ions.   
  
(Ans : 0.04, 0.96)
29.  $\text{NH}_4\text{X}$  crystallises in bcc lattice with edge length  $383 \text{ pm}$ . If the radius of  $\text{NH}_4^+$  ion is  $154 \text{ pm}$ , calculate the radius of halide ( $\text{X}^-$ ).   
  
(Ans :  $178 \text{ pm}$ )
30. Discuss the non-stoichiometric imperfections in crystalline solid substances.
31. During the crystallisation one fourth mole of  $\text{Cu}_2\text{Cl}_2$  in molten state one millimole of zinc chloride is added. How many cuprous ions are removed? Calculate the number of lattice vacancies created in the crystal.   
  
(Ans :  $1.2 \times 10^{21}$ ;  $6 \times 10^{20}$ )
32. Solids containing F-centres are paramagnetic and coloured. Why?
33. Differentiate between intrinsic semiconductors and extrinsic semiconductors.
34. Explain different magnetic properties of solids. What happens when these substances are heated?
35. Ferrites are ferrimagnetic substances. Substantiate.
36. Magnetically ordered solids transform to paramagnetic state upon heating. Explain.

