Unit

1

Solid State

1.0   Introduction

You have gained information about five states, in previous standards. They are solid, liquid, gas, plasma and BEC (Bose-Einstein Condensate). We are more familiar with first three states. You have studied about liquid and gas in standard-11, in the units on liquid state and gaseous state. You have also studied the characteristic properties of liquids, etc. In this unit, we shall study in detail the solid state. The study of structure of solids and their properties etc. is called Solid State Chemistry.

We know that solid substance has definite shape and volume. In addition to this we shall study about many phenomena associated with chemistry including this statement. We are familiar with solid substances, because our life and everyday life are associated with solid. Different solid substances are used for different uses. In solids, their different compositions and properties are associated. If we study solid, information about its properties and by carrying out changes in it, we can have many uses of solids viz. substances used in superconductors and plastics for packing can be prepared. Solid substance differs from liquid and gas in one aspect and that is fluidity. Hence, liquid and gas are called fluids but in solid, the ions, molecules are in some definite form and arranged in a systematic manner. Hence, they have definite shape and so it is not a fluid. There can be two types in soild-crystalline and amorphous. In a crystalline soild, arrangement of atoms or ions is systemetic.

We shall study in this unit, the arrangement of atoms or ions and their relationship with their properties and what changes we can make in these properties so that desired and useful innumerable solid substances can be obtained.

1.1   Classification of Compounds on the basis of Binding Forces (Molecular, Ionic, Covalent, Metallic)

Most of the solid substances are crystalline viz. metals like copper, iron, silver, etc., non metals like phosphorus, sulphur, and in ionic form-crystals of sodium chloride, potassium chloride and moleculer solid like naphthalene.

The classification of solid substances on the basis of intermolecular attraction forces involved in them, can be made into four classes (1) Molecular solids (2) Ionic solids (3) Metallic solids and (4) Covalent network solids.

(1) **Molecular solids** : The molecules present in the molecular solid are its constituent particles. They can be classified into three parts as below :

(a) **Nonpolar molecular solids** : Elements like argon, helium or molecules formed by nonpolar covalent bonds. Elements like dihydrogen, dichlorine, diiodine etc. can be included in this type of solids. The atoms or molecules in this type of solid possess the weak dispersion forces or London forces. You have studied about these types of forces in standard-11. Solids of this type possess low melting points and they are soft and non conductor of electricity. At normal temperature and pressure, they are in liquid or gaseous state.

(b) **Polar molecular solids** : The solids like SO_2 etc. generally possess polar covalent bond. The molecules of such solids are bound by relatively strong polar-polar interactions. They are also soft and nonconductor of electricity. Their melting points are higher than those of nonpolar molecular solids. Even then, they are in gaseous or liquid state at normal temperature. Soild SO_2 and solid NH_3 are solids of this type.

(c) **Molecular solids containing hydrogen bond** : In this type of solids, atoms like H form polar covalent bond by combining with electronegative atoms like F, O or N. The strong hydrogen bonding in them, keep them in bound state. Substance like ice is the example of this. They are also non-conductors of electricity. At room temperature and pressure they are volatile liquids or soft solids. In the molecule of ice, four molecules of water are attracted by hydrogen bond. It gets separated from the hydrides of other elements of the same group because of hydrogen bond.

(2) **Ionic solids** : The constituent particles of ionic solids are ions. The cations and anions of such substances are attracted by strong Coulombic forces and so they possess forced molecules in three dimensional directions. They are hard and brittle. Their melting points and boiling points are higher because of strong attraction between positive and negative ions in the solid. Though ions are present in such substances, even then, they do not conduct heat or electricity because they are bound by strong attraction forces between positive and negative ions. But if they are dissolved in water or are melted in solid state, their ions get separated and so they conduct electricity.

(3) **Metallic solids** : Most of the metals are in solid state and so metal possesses positively charged nucleus around which free electrons are arranged. They are arranged in a systematic way. Electrons are spread in the form electron sea around the nucleus of atom of the metal. These electrons do not remain confined to any nucleus but are moving around the nuclei like the flow of water in the sea and these free electrons allow electricity and heat to conduct. When electric field is applied, they move, but in the new situation electron makes its arrangement around the nuclei. When heat is supplied to metal, the thermal energy is spread everywhere by the free electrons. In addition, metals have lustre and in some cases have colours. This is due to the presence of free electrons. They are ductile and malleable.

(4) **Covalent solids** : In the whole crystal, the adjoining atoms form covalent bond in larger proportion and so it results into different crystalline solids. They are called 'Giant molecules'. Many diversities are found in these compounds because they possess covalent bond-directional properties. Their molecules are bound tightly and hence they possess very high boiling points. Some decompose before being melted. They are not conductors of electricity. Diamond and graphite are the examples of this type. Graphite is soft and good conductor of electricity because its structure is specific. Three atoms of carbon in graphite form three covalent bonds by sp^2 hybridisation and the fourth electron remains free. It keeps

one layer of graphite combined with other layer. Thus layers consisting of hexagonal structure having sp^2 hybridisation are formed in graphite and the fourth electron keeps distance of 340 pm between the layers and it conducts electricity because it is free. The different layers of graphite can move creating friction with each other and so graphite is a good solid lubricant. In contrast to this, tetrahedral structure is formed by sp^3 hybridisation in diamond and all its four corners are combined with other carbon atoms of diamond and spread in three dimension. Hence, it is very hard. It cannot conduct electricity because it has no free electrons. Thus, it can be seen that in the two allotropes of the same element, if intermolecular forces and hybridisations formed are different, there is a great change in their properties.

In the folloiwng table 1.1, four types of solids and their properties are shown.

Table 1.1 Different types and properties of solids

Type of solid	Constituent particles	Attraction forces	Example	Physical nature	Melting point	Electrical conductivity
(1) Molecular solid (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4 H_2, I_2, CO_2	Soft	Very low	Non conductor
(ii) Polar	Molecules	Dipole-Dipole-inter attraction	HCl, SO_2, NH_3	Soft	Low	Non conductor
(iii) Hydrogen bond possessing	Molecules	Hydrogen bond	H_2O (ice)	Hard	Low	Non-conductor
(2) Ionic solid	Ions	Coulombic or Electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	High	Solid state, non-conducting but molten or aqueous solution conductor.
(3) Metallic solid	Positive ion in sea of delocalised electrons	Metallic bond	Fe, Ca, Mg, Ag	Hard but ductile and malleable	Compara-tively very high	Conductors in solid and molten states
(4) Covalent or Network solids	Atoms	Covalent bond	SiO_2 (Quartz) SiC (Carbo-randum C (Dimond) C (Graphite)	Hard	Very high	Non conductor Conductor (Exception)

1.2 Crystalline and Amorphous solid substances

Solid substances are available in crystalline and amorphous forms. There is difference in their structure and formation.

Crystalline solid substances are rigid and incompressible. They have definite shape. Their geometrical structures are systematic and definite. The reason for this is the regular and definite arrangement of molecules or ions in three dimensional space. They have got definite and sharp melting points. The examples of this type of crystalline solid are NaCl, KCl etc.

Amorphous substances are also rigid and incompressible but they have no definite geometrical shapes. The periodicity of the definite formation or geometry of amporphous substances is not observed

even when the atoms or ions are bound very tightly. Their melting points are not sharp, they possess some range of temperatures. The examples of such amorphous substances are glass, rubber etc. In the following table 1.2, the differences between crystalline and amorphous solids are given.

Table 1.2 Differences between crystalline and Amorphous solid substances

| Property	Crystalline solid	Amorphous solid
(1) Shape	Definite shape and possessing characteristic geometry.	Irregular shape
(2) Melting point	Definite and sharp melting point which is the characteristic of the crystal of solid.	Becomes soft grandually during the small temperature range i.e. have no definite and sharp melting point.
(3) Fusion enthalpy	Definite and characteristic fusion enthalpy	Not definite and characteristic fusion enthalpy
(4) Cleavage property	Divided into two parts by cutting the crystal with sharp tool like knife. The surface of the new part obtained is plain and soft i.e. it is as original one	Divided into two parts cutting the crystal with sharp tool like knife but the surface of new part obtained is not as the original one. It is irregular.
(5) Nature	True solid	Pseudo solid or supercooled liquids
(6) Order of Arrangement of constituent particles.	The order is maintained till a long range	The order is maintained in a short range
(7) Effect of temperature	The graph (temperature → time) obtained on cooling after heating is not a curvature. The temperature remains definite during crystallisation	The graph (temperature → time) obtained on cooling after heating is a curvature. Temperature range is obtained during crystallisation.
(8) Properties	Their properties like electrical conductivity, thermal conductivity, mechanical strength and refractive index are different in different directions.	Their properties like electrical conductivity, thermal conductivity, mechanical strength and refractive index are same in all directions
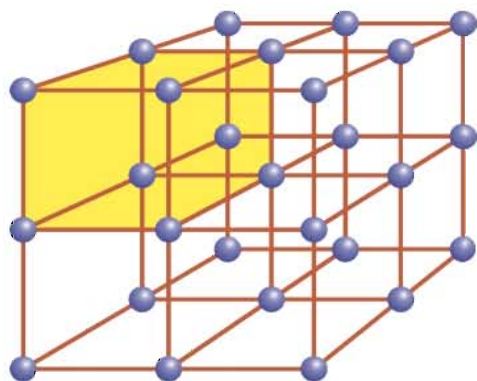
Fig. 1.1 Part of the three dimensional cube lattice and its unit cell.

1.3 Unit cell (Two Dimensional and Three Dimensional Lattice)

The smallest particle of a substance is known as atom or molecule. Similarly the smallest portion to know crystal of solid is called the unit cell; thus the smallest portion possessing the chief characteristics of a crystalline solid is called unit cell. Such unit cells are arranged with each other in three dimensional directions and the formation of crystal results. This type of arrangement is called crystal lattice (word 'Jalak' is used in Gujarati for lattice). As shown in fig 1.1 each particle is shown as point. Thus the systematic three dimensional arrangement of points in space is called

crystal lattice. In fig 1.1 the part of the crystal lattice is shown. There are 14 possibilities of such three dimensional lattices called Bravais lattice. Some of the characteristics of crystal lattice are as follows :

(1) Each point in the lattice is called lattice point or lattice position (location).

(2) Each point in the crystal lattice represents one constituent particle which can be an atom, molecule or ion.

(3) The lattice points are connected by straight lines, so that the geometry of the lattice can be indicated.

Unit cell is the smallest part of the crystal lattice, which is repeated in different directions in three dimensions and the complete lattice is formed.

The characteristics of unit cell are as follows :

(1) Its dimensions are on its three edges a,b and c. These edges may be perpendicular to one another or may not be perpendicular.

(2) The angles between the edges are α (between edges b and c.), β (between edges a and c) and γ (between edges a and b). Thus unit cell becomes characteristic by parameters a,b,c and α, β and γ. These parameters are shown in fig 1.2

It is necessary to note here, that we can show two dimensional figures in book but it is difficult to show three dimensions. Hence, this structure can be well understood by the use of models.
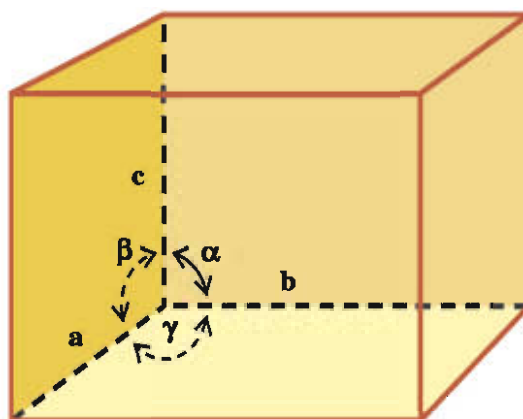
Fig. 1.2 Dimensions of Unit Cell

Primitive and Centred Unit Cells : The unit cell can be divided into two parts : (a) Primitive unit cell (b) Centred unit cell.

(a) Primitive Unit cell : When constituent particles are arranged on the four points of four corners of the unit cell, it is called primitive cell.

(b) Centred Unit cell : When one or more constituent particles are arranged at other places (sites) in addition to the sites of the corners, it is called **centred unit cell.** Centered unit cells are of three types (1) Face centred unit cell (2) Body centred unit cell (3) End centred unit cell.

(1) Face centred unit cell : In this type of unit cell one particle is arranged in the centre of each face (side) in addition to particles arranged on each corner of the unit cell.

Fig. 1.3 Atom on each corner of a simple cubic cell is shared with 8 atoms

(2) Body centred unit cell : In this type of unit cell one particle is arranged on the centre of the body in addition to each particle arranged on the four corners of the unit cell.
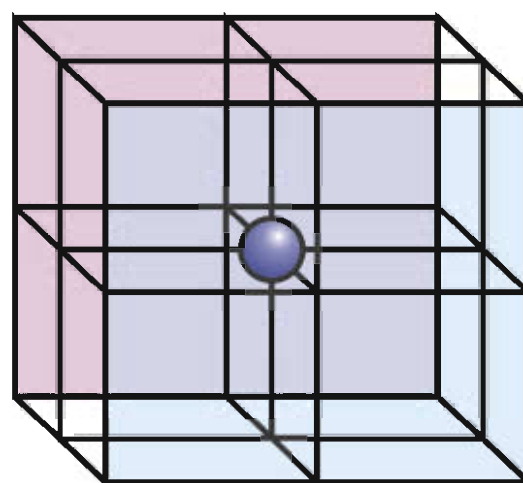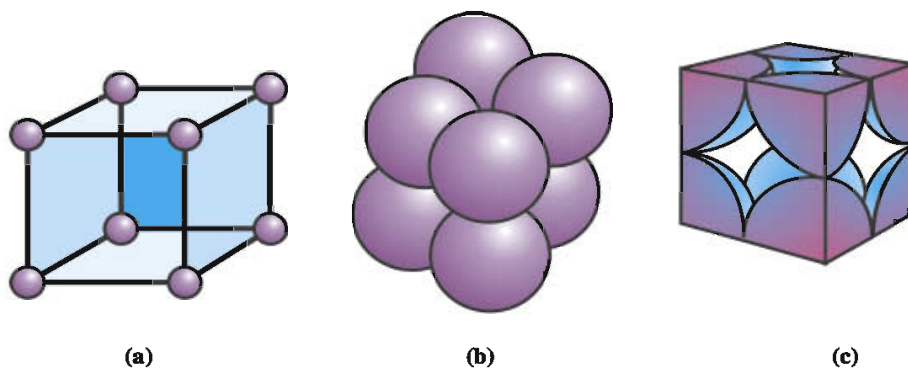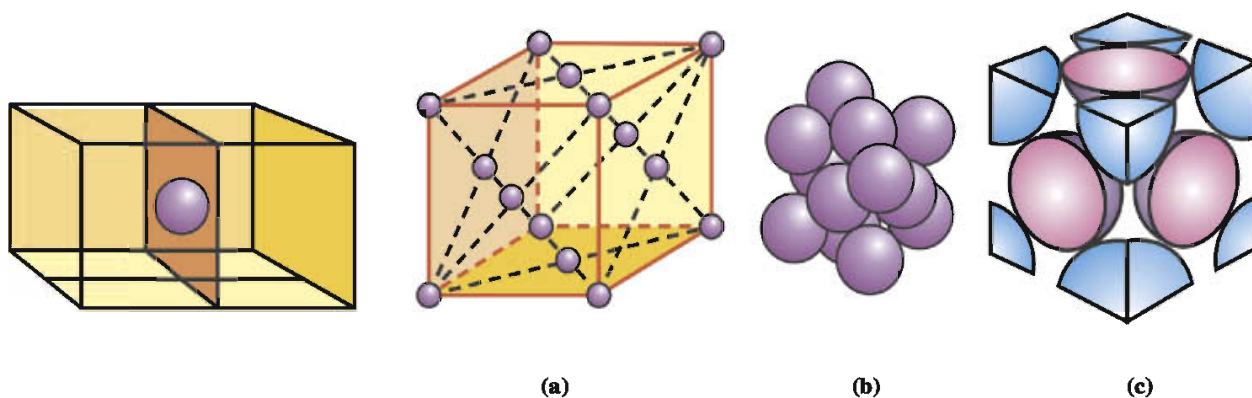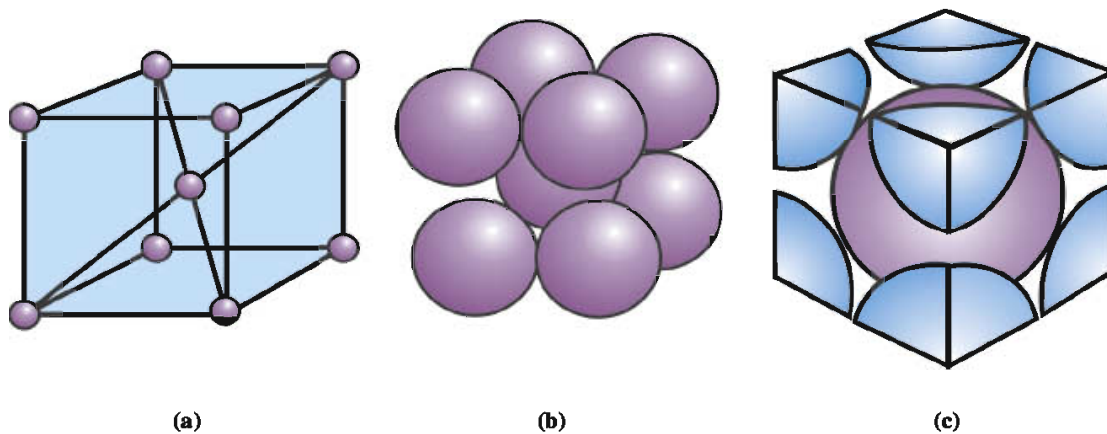
Primitive unit cell
(a) Open space filling structure (b) Space filling structure
**(c) Actual portions of atoms belonging to unit cell**

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

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

A body centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

(3) End-centred unit cell : In such a unit cell one constituent particle is present at the centre of any two oppositive faces besides the ones present at its corners.

Cubic   Tetragonal   Orthorhombic

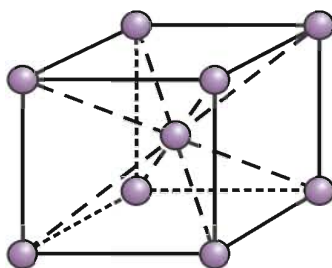Monoclinic   Hexagonal   Rhombohedral   Triclinic
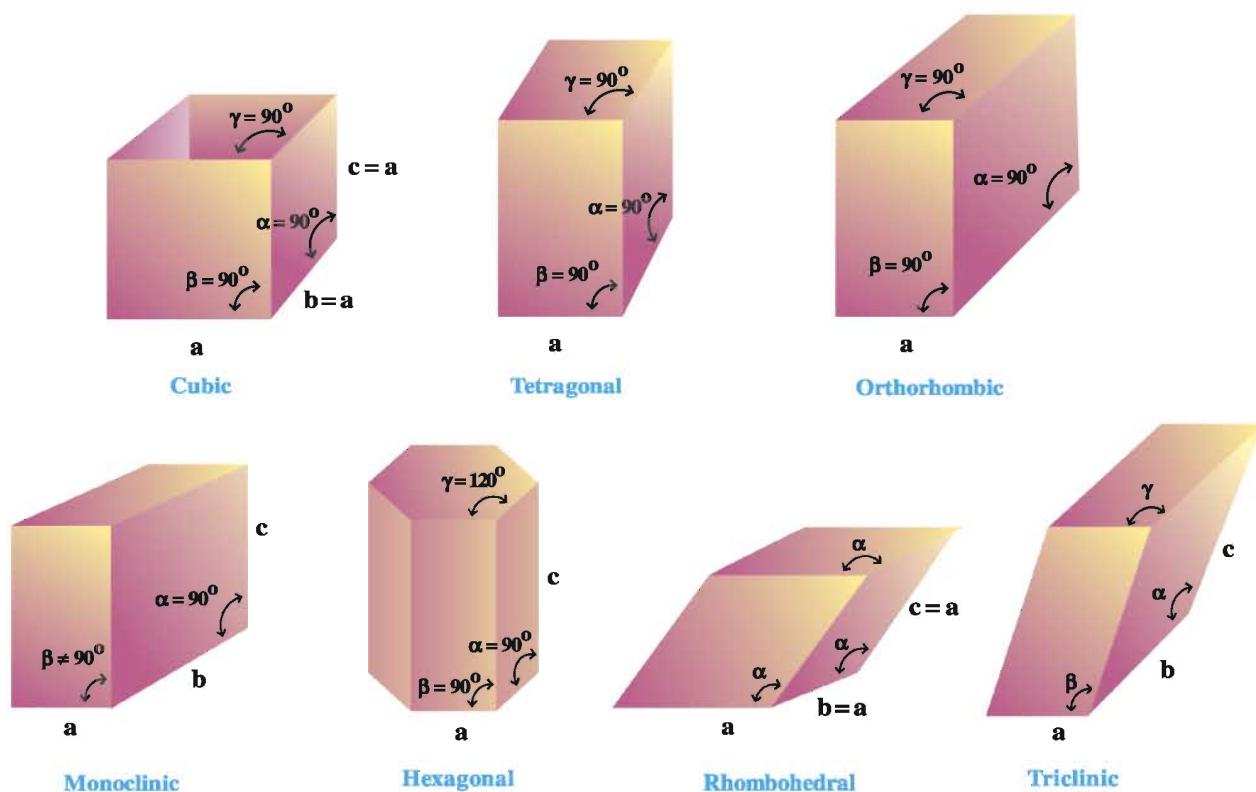
Primitive Cells

There are in all seven types of primitive cells which are shown below in table 1.3

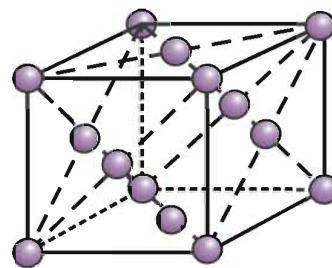**Table 1.3 Seven primitive unit cells and deviation possible as centred unit in them**

| Sr.	Crystal System	Possible variations	Axial distance or distance of edge	Axial angle	Example
1.	Cube	Primitive Body centred Face centred	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	NaCl, ZnS, (zinc blende), Cu
2.	Tetragonal	Primitive, Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	White tin, SnO_2, TiO_2, $CaSO_4$
3.	Orthorhombic	Primitive Body centred Face centred End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	Rhombic sulphur, KNO_3, $BaSO_4$
4.	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^o \, \gamma = 120^o$	Graphite, ZnO, CdS
5.	Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o < 120^o$	Calcite ($CaCO_3$) Cinnabar (HgS)
6.	Monoclinic	Primitive End centred	$a \neq b \neq c$	$\alpha = \gamma = 90^o \, \beta \neq 90^o$	Monoclinic sulphur $Na_2SO_4 \cdot 10H_2O$
7.	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
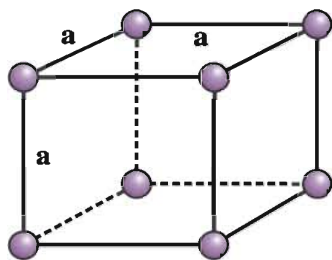
Primitive (or simple)   **Body-centred**   **Face-centred**
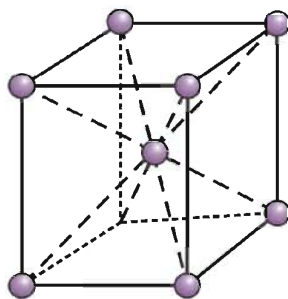
The three cubic lattice : all sides of same length, angles between face all 90°
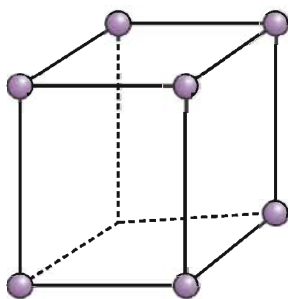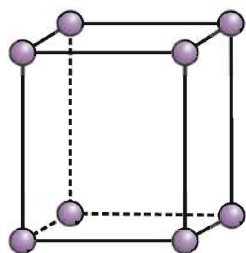

Primitive   **Body-centred**
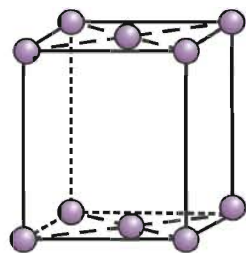
The two tetragonal : one side different in length to the other, two angles between face all 90°
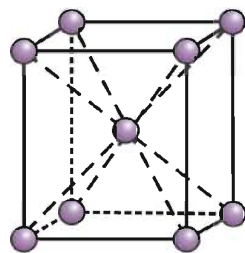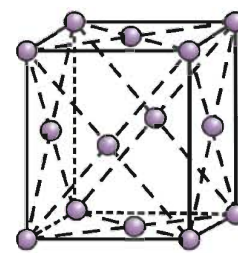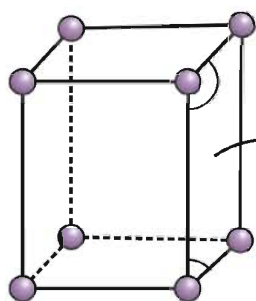

Primitive   **End-centred**   **Body-centred**   **Face-centred**

The four orthorhombic lattice : unequal sides, angles between face all 90°
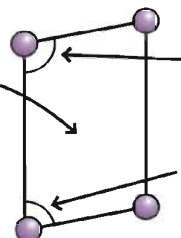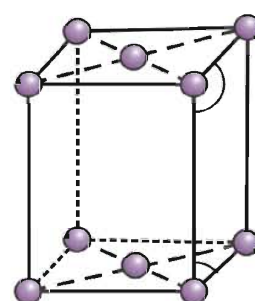

More than 90°

Less than 90°

Primitive   **End-centred**

The two monoclinic lattice : unequal sides, two faces have angles different to 90°

1.4 Calculation of Volume Occupied by Atoms in Unit cell

The arrangement of molecules atoms, or ions in unit cells of different crystals is different. We shall study about the close packing efficiency of atoms in different unit cells.

Packing efficiency : The packing of constituent particles (atoms, molecules or ions) may be of any type but some free space is left out which is called hollowness or void. The percentage of total space volume occupied by particles is called packing efficiency. We shall now carry out calculations of packing efficiency of different structures.

(1) Packing efficiency in simple cubic lattice : The atoms are only on the corners of the cube in simple cubic lattice. The particles touch each other along the edges.

The relation between the side or the edge length of a cube and the radius of each particle will be a = 2r.

The volume of cube in any unit cell $= a^3 = (2r)^3 = 8r^3$

Each cubic unit cell possesses only one atom.

Hence, the volume occupied by one atom $= \dfrac{4}{3}\pi r^3$

Now packing efficiency

$$= \dfrac{\text{Volume of one atom}}{\text{Volume of cubic unit Cell}} \times 100 \ \%$$

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

Fig. 1.4 Packing efficiency of cubic lattice unit cell

(2) Packing efficiency of body centred unit cell : As shown in figure 1.5, the atom in the centre touches two other atoms diagonally arranged. Hence, in ΔEFD,

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

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

Now, in ΔAFD,

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

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

The diagonal length of body centred cube c = 4r, where r is radius of the atom because, all the three spheres touch diagonally.

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

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

Fig. 1.5 Packing efficiency of body centred unit cell

The total number of atoms in this type of arrangement is 2 and so its volume will be $2 \times \dfrac{4}{3}\pi r^3$

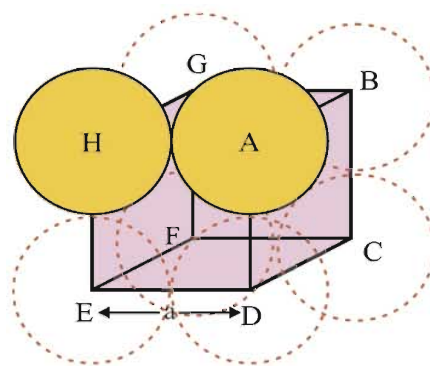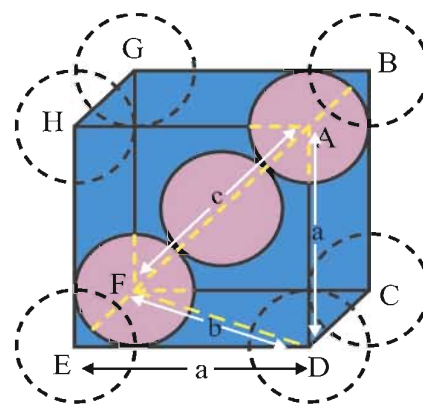Volume of cube $a^3 = \left(\dfrac{4}{\sqrt{3}}r\right)^3$

Now, packing efficiency $= \dfrac{\text{Volume occupied by two spheres in unit cell}}{\text{Total volume of unit cell}} \times 100$

$$= \dfrac{2 \times \frac{4}{3}\pi r^3}{\left[\left(\dfrac{4}{\sqrt{3}}\right)r\right]^3} \times 100\,\% \quad = \dfrac{\frac{8}{3}\pi r^3 \times 100}{\frac{64}{(3\sqrt{3})}r^3} = 68\,\%$$
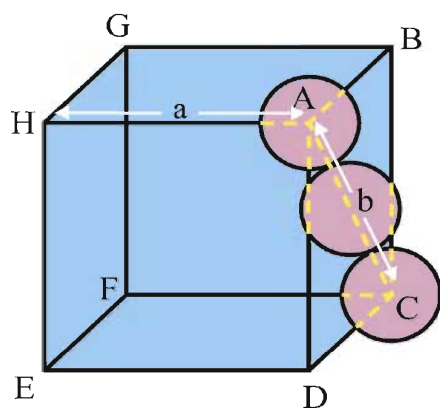

Fig. 1.6 Cubic close packing efficiency

(3) Packing efficiency in hexagonal packing (hcp) and cubic close packing (ccp) : The close packing is equally efficient in both these types. We calculate the packing efficiency of ccp structure. As shown in figure 1.6, the length of the edge of unit cell is a and the diagonal of face is AC = b

In ΔABC, $AC^2 = b^2 = BC^2 + AB^2$

$= a^2 + a^2 = 2a^2$ or $b = \sqrt{2}\,a$

Suppose the radius of the sphere is r, then $b = 4r = \sqrt{2}a$

or $a = \dfrac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$

As we know, four atoms or spheres are there in ccp structure and so the total volume of four spheres $= 4 \times \frac{4}{3}\pi r^3$ and the volume of cube will be a^3 or $(2\sqrt{2}r)^3$

Hence,

packing efficiency $= \dfrac{\text{Volume occupied by four spheres of unit cell}}{\text{Total volume of unit cell}} \times 100$

$$= \dfrac{4 \times \left(\frac{4}{3}\right)\pi r^3 \times 100}{(2\sqrt{2}r)^3}\,\%$$

$$= \dfrac{\frac{16}{3} \times \pi r^3 \times 100}{16\sqrt{2}\,r^3} = 74\,\%$$

It can be determined from the above three calculations that, there is maximum packing efficiency in ccp and hcp.

1.5	Close packed structures and their types (one dimensional, two dimensional and three dimensional)

We can accept atom, molecule or ion as spherical form and their arrangement in solid state by each other from all the adjoining sides and some space remains between them. Suppose we take small spheres in a closed tin and shake then and put, them all the small spheres will be arranged from all the sides but space will be left out between spheres. Particles (spheres) in the solid state possess close

packing and so there is very less space among them. Hence, if we consider component particles as hard spheres and think of their arrangement, the three situations can be possible (1) One dimensional arrangement (2) Two dimensional arrangement (3) Three dimensional arrangement. We shall study this in detail.

(1) One dimensional close packing : In this type of packing, as shown in figure 1.7 two other particles are arranged near one particle (sphere). The number of most nearby neighbour particles is called the **co-ordination number.** Thus, the co-ordination number is 2 in one dimensional close packing.

Fig. 1.7 Close packing of spheres in one dimension

(2) Two dimensional close packing : In this type of packing the rows having close packing are arranged as a stack. This arrangement can be of two types.
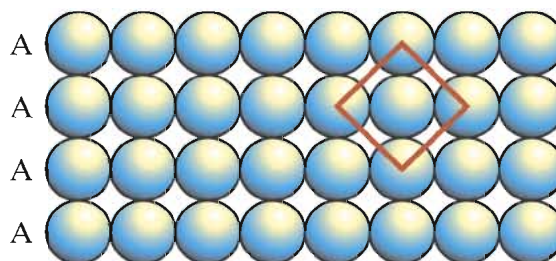
(a) In this arrangement the other particles are exactly arranged on the particles arranged in the row below them and forms a stack. Thus, the particles in the rows are aligned with each other vertically and horizontally. If we call first row as A, the second row is similar to it and so it will also be called A. Thus, one by one, each row is arranged on one another, we will have the arrangement of type AAA A...as shown in figure 1.8(a)

Fig 1.8(a) Square close packing

In this arrangement, other four spheres are arranged as neighbours around each sphere. Hence, the co-ordination number will be 4 in two dimensional arrangement. If we join the centres of the four spheres we will get a square. So this structure is called two dimensional **square close packing.**

(b) In the second method we will arrange the second row stack in slightly deviated method, so that the spheres of the second stack arrange on the depressions formed by the first stack. If we call, the first type of arrangement of stack as A then the arrangement of spheres in second stack will be a separate B type stack. Thus, if we arrange the stacks alternately then we have ABABAB....type structure. This type of structure is more rigid and more efficient packing possessing than square close packing. In this type of structure, 6 spheres are arranged around each sphere and so it is called two dimensional **hexagonal close packing** which is shown in figure 1.8 (b)
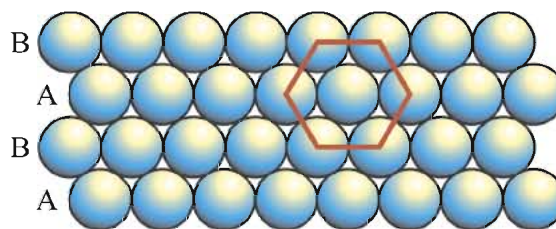
Fig 1.8(b) Hexagonal close packing of spheres in two dimensions

(3) Three dimensional close packing : All real structures or configurations we see are all three dimensional structures. Such a structure is like the arrangement of each stack in the structure. i.e. square close packing or hexagonal close packing. Now, we will study how close packing occurs in third dimension.

(i) Three dimensional close packing from two dimensional square close packing : If we arrange the stack as A and then put the second stack exactly on other sphere as on A, the spheres of first A stack and the spheres of second A stack will be exactly on the sphere of A. As shown in figure 1.9 they will remain completely and equally arranged horizontally as well as vertically.

Fig. 1.9 Simple cube lattice formed by AAA....arrangement

If we call the first stack as A, then, all the stacks will be of same type i.e. AAAA....type stack. The lattice structure obtained this way is called simple cubic lattice structure and only one primary cubic unit cell is there in the unit cell.

(ii) Formation of three dimensional close packing structure from two dimensional hexagonal packing structure : Three dimensional close packing can be formed by placing one layer on the other.

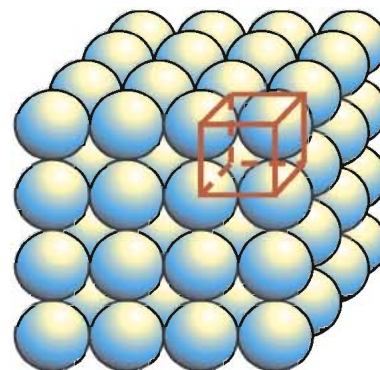**(a) Arranging second layer on first layer :** Suppose, we arrange the spheres of the second layer on the voids in the first layer A possessing two dimensional close packing, here the spheres are aligned differently and so we will call it layer B, which is shown in fig 1.10

(a) Observing from top	(b) Observing from side	(c) Geometrical shape of hole
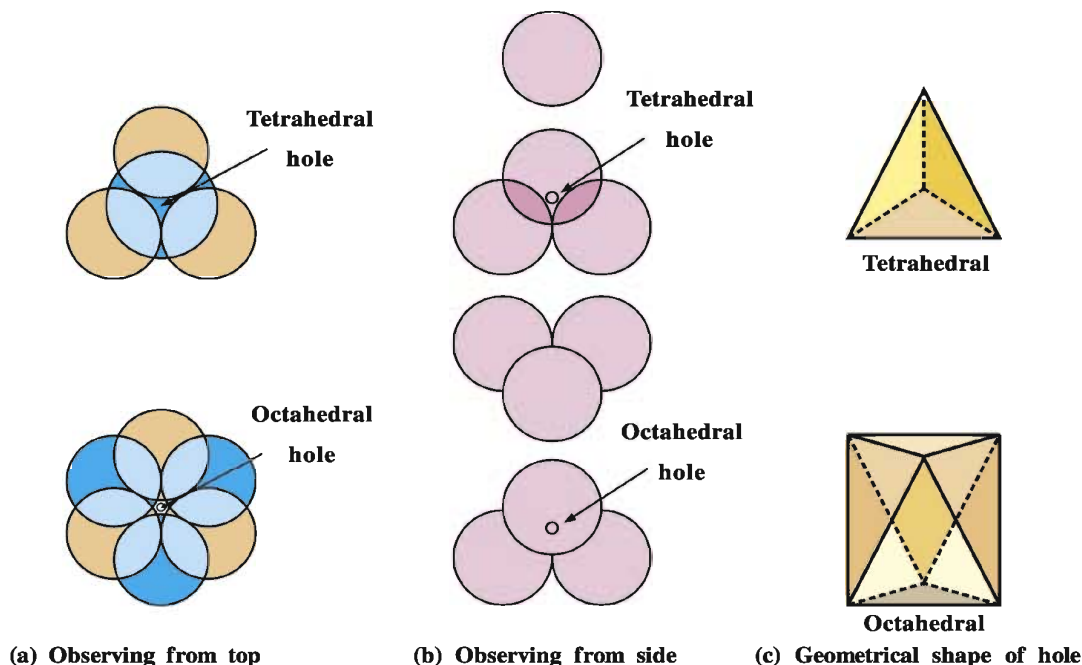
Fig 1.10 Tetrahedral and Octahedral Voids

It is clear from the figure that the triangular voids of the first layer are not completely covered by the spheres of second layer. Hence, different arrangements are possible. When the spheres of second layer are aligned on the voids of the first layer, or if it is reverse, then tetrahedral voids are formed. These voids are called **tetrahedral voids** because if the centres of the four spheres are joined, construction of tetrahedron takes place.

T = Tetrahderal void   O = Octahedral void
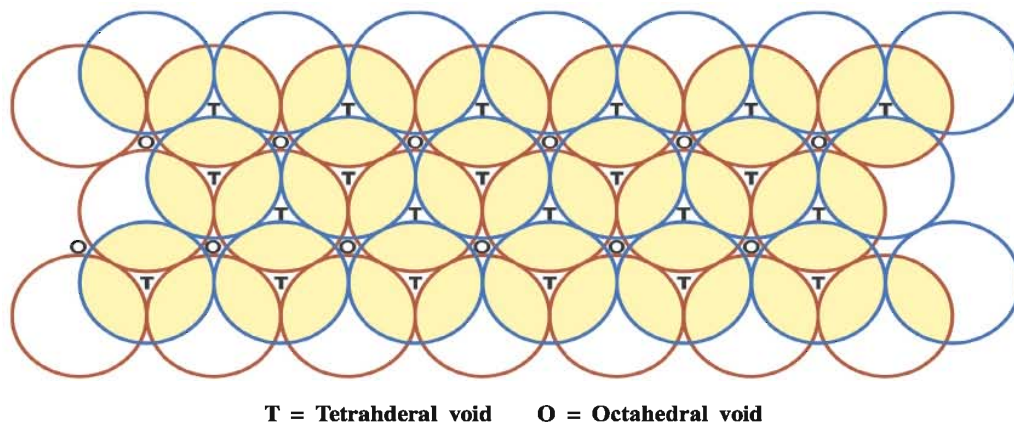
Fig 1.11 A stack of two layers of close packed spheres and voids generated in them

They are shown as T in the figure 1.11. In other places, the triangular voids of second layer are aligned as the triangular voids on the first layer their triangular shapes do not overlap. One of them indicates the triangular upper side and the second indicates towards lower side. Such voids are called octahedral voids. In figure 1.11 they are shown by symbol O. The number of these two types of void depends on the number of spheres of close packing.

Suppose,

The number of spheres of close packing is N.

The number of octahedral voids formed = N

The number of tetrahedral voids = 2N

Thus the number of tetrahedral voids is twice the number of octahedral voids.

(b) Alignment of third layer on the second layer : Now, suppose if we place third layer on the second layer, then there are two possibilities

(i) Covering tetrahedral voids : The tetrahedral voids of second layer will be covered by the spheres of third layer. In this situation the spheres of third layer will exactly be on the spheres of the first layer. Hence, there is repetition of the stacks formed alternately. It can be called ABAB....type stack and this structure is called hexagonal close packing (hcp) which is shown in fig 1.12

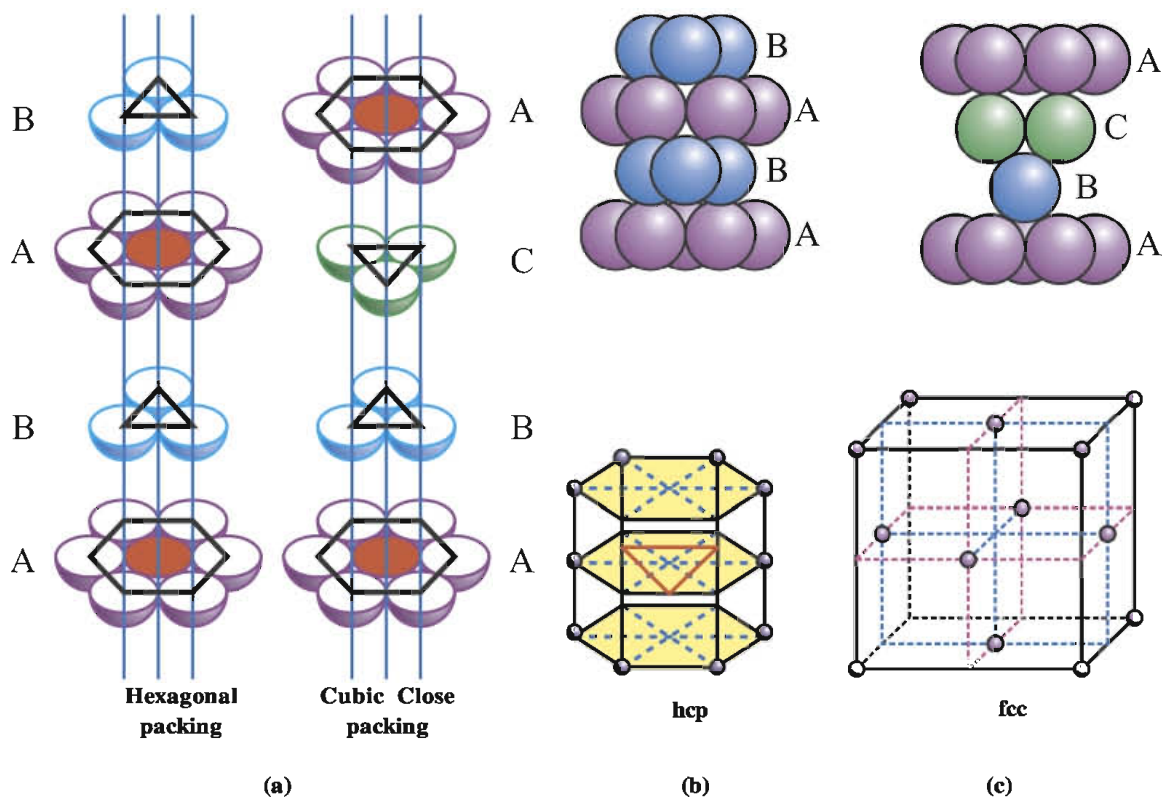This type of arrangement is observed in many metals like zinc, magnesium etc.

Fig 1.12 (a) Hexagonal cubic close packing exploded view showing stacking of layers of spheres
(b) four layers stacked in each case and (c) geometry of packing

(ii) Covering octahedral voids : In this type of structure, the third layer is placed on the second layer in such a way, that the spheres of the third layer cover the octahedral voids of second layer. By doing this type of arrangement, the spheres of the third layer do not align exactly with the spheres of first layer. This arrangement can be said to be of C-type. Now, when the fourth layer is arranged, the spheres of this layer are exactly in alignment with spheres of first layer which is shown in figures 1.13. Hence, this stack is of ABCABC.....type and this type is called **cubic close packing (ccp) or face centred cubic (fcc)** structure. Metals like copper and silver crystallise in this type of structure.

The close packing arrangement in these two types is of maximum efficiency and about 74% of space (volume) is occupied by their crystals. It is in contact with 12 spheres and so the co-ordination number is 12 in both the constructions.

Fig 1.13
(a) ABC ABC.... arrangement of layers when Octahedral void is covered
(b) cubic closed packing (ccp) or face centred cubic (fcc) structure.

1.6 Tetrahedral and Octahedral Voids

We have learnt about tetrahedral and octahedral voids during the study of close packing structure. Tetrahedral and octahderal voids are shown in figure 1.11. It is difficult to show three dimensional figures in books but if we study with the help of models, it will be more clear.

Let us think about formula of compound and the number of voids associated in it. As seen earlier, ccp or hcp structures are formed due to close packing and two types of voids are obtained. During formation of lattice, the number of tetrahedral voids are double the number of octahedral voids. In ionic compounds the size of anion is more than that in cation. Big anions take part in close pack structure, while cations arrange in the voids. If the ions are smaller in size than the void, they are arranged in tetrahedral void and if larger then they are arranged in octahedral voids. All the tetrahedral and octahedral voids are not occupied. Only a certain fraction of the total voids is occupied. This matter depends on the formula of the compound, which will be clear from the following examples.

Example 1 : A compound is formed of two elements A and B. The atoms of element B (anion) forms cubic close packing and atoms of element A occupies all the octahedral voids. What will be the formula of the compound ?

Solution : Element B forms cubic close packing and so the number of octahedral voids will be equal to number of atoms B. All the octahedral voids are occupied by all the atoms of A and so their number will be equal to number of B. Thus elements A and B will be in 1:1 proportion; so the formula of compound will be AB.

Example : 2 The atoms of element Y form hexagonal close packing and the atoms of element X occupies $\dfrac{2}{3}$ portion of the number of tetrahedral voids. Write the formula of the compound formed by X and Y.

Solution: The number of tetrahedral voids formed is double the number of atoms of element Y and only $\dfrac{2}{3}$ part is occupied by atoms of element Y. Hence, the ratio of atoms of X and Y will be $\dfrac{2 \times 2}{3}$: 1 or 4 : 3. Hence the formula of the compound will be X_4Y_3.
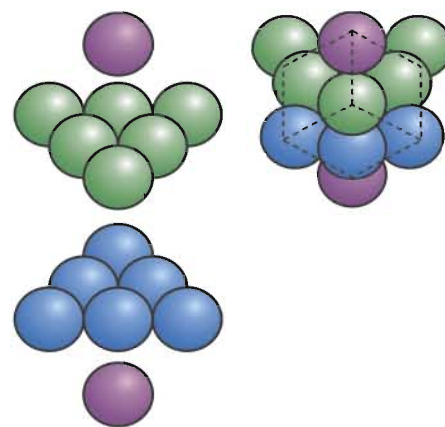
To locate the positions of tetrahedral and octahedral voids : We have studied that there are tetrahedral and octahedral voids in the close packing structures. We will locate the positions of voids in cubic close packing (ccp) and face centred close packing (fcp).

(a) To locate positions (sites) of tetrahedral voids : Let us take ccp or fcp and divide it in eight small cubes as shown in figure 1.14. Atoms are there on the alternate corners of each of these small solids. In each small cube, total four atoms are there. If we join them with each other, they form regular tetrahedron. Hence, there will be one void in each in the structure of each unit cell (ccp) in each of the small atoms. We know that there are four atoms in each ccp structrure. Hence, the number of voids is double the number of atoms.

(a) Eight tetrahedral voids per unit cell of ccp structure

(b) One tetrahedral void showing the gemetry
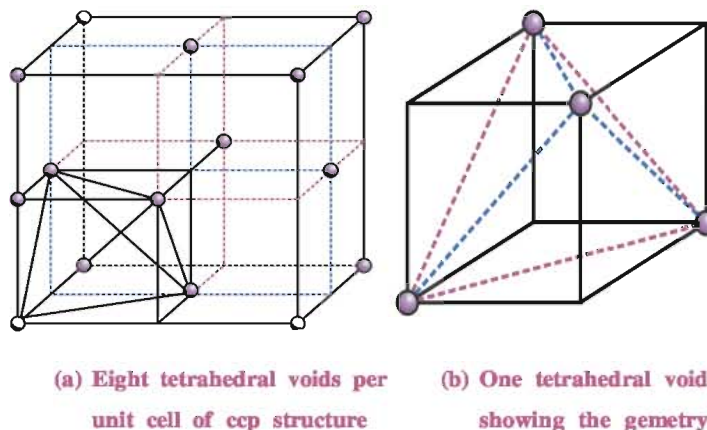
Fig. 1.14

(b) To locate positions (sites) of octahedral voids : Again we take the unit cell of cubic close packing (ccp) or face centred close packing (fcp). The body centre C of solid is not occupied but it is surrounded by atoms on six faces. If these face centres are joined octahedral structure will be formed. In this unit cell, there is one octahedral void on the centre of its each twelve edges. It is surrounded by six atoms, in which three to each unit cell are on corners and one in the centre of face and three on the one-two nearby unit cells. As the unit cell is shared by each edge of solid by four near by unit cells; accordingly octahedral void will get its location on its position.

(a) Body centred

(b) Void on centre of each edge
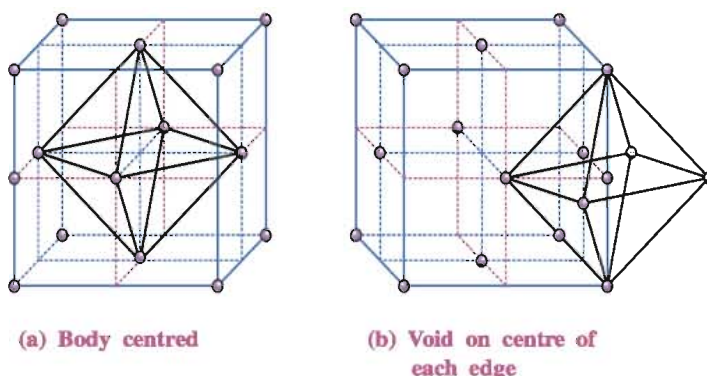
Fig. 1.15 Location of octahedral voids per unit cell of ccp or fcc structure (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown)

Each void has only $\frac{1}{4}$ of any one cell. Thus, in cubic close packing.

Octahedral void on the body centre of solid = 1

12 Octahedral voids arranged on each edge and four unit cells $= 12 \times \frac{1}{4} = 3$

Total number of octahderal voids = 1 + 3 = 4. As we know, that in cubic close packing structure each unit cell possesses four atoms. Hence the number of octahedral voids will be equal to that number.

1.7 Calculation of number of atoms in unit cell

Each corner of a unit cell in a crystal is associated jointly with eight unit cells. Hence, its each edge of the side is associated with four sides of the unit cell and each face with two unit cells. Hence, for the structure of the crystal if atoms, molecules or ions are associated with it, then their $\frac{1}{8}$ part is occupied by corners, $\frac{1}{4}$ part by edges of sides and $\frac{1}{2}$ part by faces. The particles on corner of unit cell and the particles combined jointly with many other cells. Hence, the calculation of number of atoms can be shown as below :

8 unit cells in simple cubic unit cell, and 8 atoms of corner are shared.

Hence,

8 corners $\times \frac{1}{8}$ atom per cell $= \frac{8}{8} = 1$ atom. Thus, there is only one atom in each unit cell in simple solid crystal.

In body centred cubic unit cell, 8 corners $\times \frac{1}{8}$ atom per unit cell $= \frac{8}{8} = 1$ and one atom in the body centre of each unit cell; So total number of atoms will be $1 + 1 = 2$. Thus there are two atoms in each unit cell of body centred cubic cell.

In face centred cubit unit cell 8 corners $\times \frac{1}{8}$ per unit cell $= \frac{8}{8} = 1$ and addition 6 face centred atom $\times \frac{1}{2}$ atom per unit $= 3$, so total number $= 1 + 3 = 4$ atoms.

Thus in face centred cubic unit cell there are 4 atoms per unit cell of crystal. The above calculations can be presented in the following table 1.4.

Table 1.4 Type of unit cell and Number of Atoms

Sr.	Type of unit cell	Number of atoms on the corner	Number of atoms in the face	Number of atoms in body center	Total atoms
1.	Simple cube	$8 \times \frac{1}{8} = 1$	0	0	1
2.	Body centred (bcc) cube	$8 \times \frac{1}{8} = 1$	0	1	2
3.	Face centred (fcc) cube	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

1.8 Point defects and their types

Before studying about the point defects let us think whether crystal is perfect or there are any imperfections. It is determined according to one estimate that in 1 mole constituent particles (6.022×10^{23} particles) there are 10^6 defects of constituent particles in the arrangement. This value

may be negligible in comparison to 6.022×10^{23} but its effect on properties, structure etc. of the crystal is definitely observed. These defects increase with increase in temperature. Thus, the crystal that appears to be ideal, has got imperfections in the arrangement of the particles and structure of the crystal. Suppose, we think the crystal to be the smallest form i.e. if we consider single crystal, even then there is probability of defects. To obtain single crystal is difficult but not impossible; but when a solid is prepared from such single crystals, there is increase in the number of defects in the solid. In the earlier standards, you have studied that the hot solution should be cooled slowly during crystallisation because there is possibility of defects to remain if it is cooled very fast. Eventhough you cool the solution slowly and obtain single crystal the defects remain.

It is suggested in the definition of third law of thermodynamics that the entropy of a completely pure crystalline substance is zero at absolute zero. You must have read somewhere in physics or chemistry that it is impossible to obtain absolute zero temperature. Hence, it can be said that even if we assume completely pure crystalline substance at absolute zero, there is probability of defects. With the increase in temperature, there is effect on the crystal and because of this there is displacement in position or randomness is created and the number of defects increases.

Thus, the defect can be defined as, the irregularity in the structure of crystal due to particles is the defect. There are two types of such defects. (1) Point defect and (2) Line defect. The point defect is due to the irregularity around the atoms or points in the ideal structure of crystalline substance, while line defects are due to the irregularity or deviation in the ideal arrangement of the entire rows of lattice points. Both these types of defects are called crystal defects.

The types of defects are two - (A) Stoichiometric and (B) Non-stoichiometric. In addition to these two types of point defects, there is third type of defect (C) Impurity defect. We shall now study them in detail.

(A) Stoichiometric defect : This is such a point defect that it does not disturb the stoichiometry of the solid. It is called an intrinsic or thermodynamic defect. It changes with temperature. This is also of two types (1) Vacancy defect and (ii) Interstitial defect.

(i) Vacancy defect : Some of the sites of the lattice are vacant i.e. there is vacancy instead of particle. Such a crystal is called a crystal having vacancy defect (Fig 1.16) Because of this, there is decrease in density of the substance because the number of atoms in unit cell decreases. If the substance is heated, such defects develop.

(ii) Interstitial defect : In some crystals when the particles like atom or molecule get arranged in the interstitial sites of the crystal it is called that the crystal posseses interstitial defect. This defect increases the density of the substance because the number of atoms for unit volume increases (fig 1.17).

Both the types of defects as shown above are exhibited by non ionic solids. Ionic compounds have always to maintain the electrical neutrality. This type of defect has two types (a) Schottky defect (b) Frenkel defect.
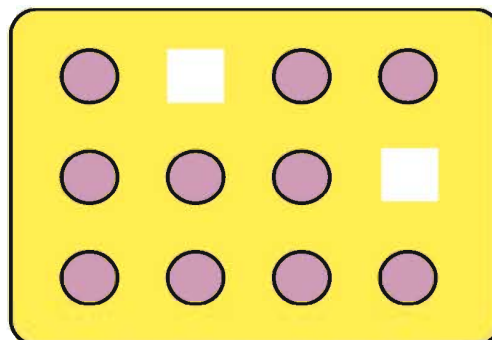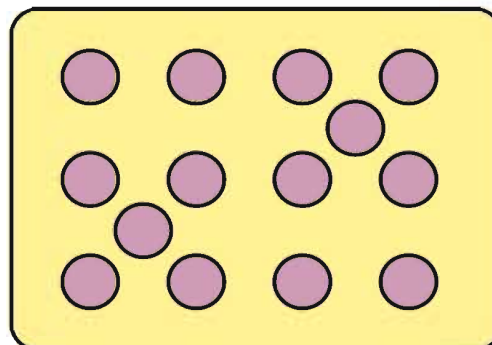

Fig. 1.16 Vacancy defect
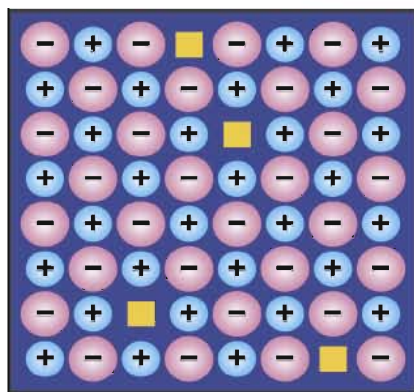

Fig. 1.17 Interstitial defect

Fig. 1.18 Schottky defect

(a) Schottky defect : This defect is originally the vacancy defect in the ionic solid. The number of cations and anions either not available or are not arranged in the crystal will be same, because the crystal even after the defects is electrially neutral. This is shown in figure 1.18.

Schottky defect produces decrease in density of substance as it is in vacancy defect. The number of this defect is very significant. As mentioned earlier, there are approximately 10^6 Schottky defects per mole of NaCl crystal at room temperature. There are approximately 10^{22} ions in $1 cm^3$ volume. Hence, there is one Schottky defect per 10^{16} ions approximately. The cations and anions in ionic solids whose sizes are same or whose co-ordination numbers are high, show Schottky defect. e.g. NaCl, KCl, AgBr. It is necessary to note that AgBr shows both the types of defects- Schottky and Frenkel defects.
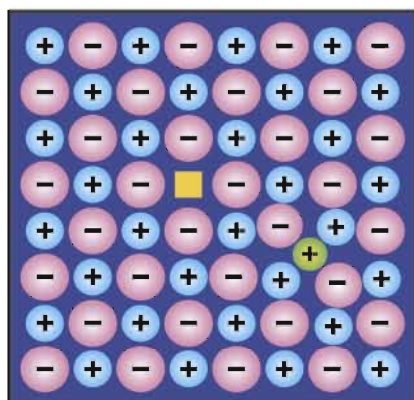

Fig. 1.19 Frenkel defect

(b) Frenkel defect : This defect is also shown by ionic solids. Generally the smaller ion (cation) displaces from its general (original) site and arranges in the interstitial site in the middle. Hence it creates vacancy defect and produces interstitial defect at its original sites. Frenkel defect is also called dislocation defect. There is change in the place of particle. There is no increase or decrease of them and so density of the solid does not change. Frenkel defect is observed in such ionic solid substances in which there is large difference between the ionic sizes of cations and anions. e.g. ZnS, AgCl, AgBr, AgI. The reason for this is that the ions Zn^{2+} and Ag^+ are of smaller size. This defect is seen in solid substances whose co-ordination numbers are low.

(B) Non-stoichiometric defect : In the defects that we have studied, there was no disturbance in the stoichiometry of elements but many inorganic solids are known which possess non-stoichiometry. The constituent elements in that are in non-stoichiometric ratio. The reason for this is the defect in the crystal structure. There are two types of this defect :
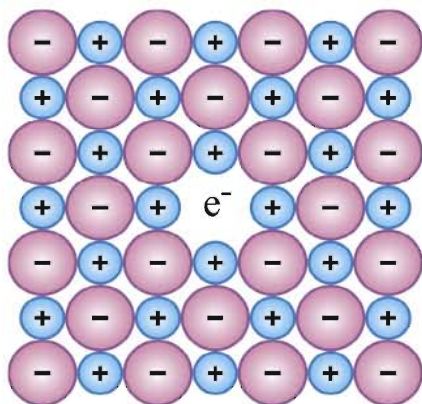

Fig. 1.20 F-centre in crystal

(i) Metal excess defect : Metal excess defect due to the vacancy by anion : Alkali halides like NaCl and KCl show this type of defect. Suppose sodium chloride is heated in presence of vapour of sodium, sodium deposits on the surface of the crystal. Hence, Cl^- ions diffuse in the layer of the crystal and combines with sodium atom and forms NaCl. It is due to the loss of electron in formation of Na^+ from Na atom. The electrons released diffuse in the crystal and reach the site of the anion. Because of this, there is increase of sodium in the crystal. The anionic sites occupied by unpaired electrons are called F–centres. (where F– is for the German word Farbenzenter indicating the coloured centres). Hence, the crystal of NaCl possesses yellow colour. When the visible light falls on the crystal of NaCl, the energy is absorbed and electron

is excited. As a result the yellow colour appears. Similarly, excess of lithium in lithium chloride crystal shows light pink colour and excess of potassium in KCl shows the violet colour due to excitation.

Excess metal defect due to presence of extra cations on the interstitial sites : Zinc oxide is a white coloured substance at room temperature. It becomes yellow when heated because it loses oxygen.

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
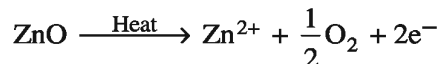
Now, Zn^{2+} increases in the crystal and so its formula will be $Zn_{1+x}O$. This extra Zn^{2+} ion will be arranged in interstital site and electron will be arranged in the neighbouring interstitial site.

(ii) Metal deficiency defect : It is very difficult to prepare so many solid substances according to their stoichiometry and they possess less number of metal atoms than the calculated ones according to stoichiometry. The well known example in this is of FeO which is mostly in the form showing stoichiometry $Fe_{0.95}O$. In fact, it is in the range of $Fe_{0.93}O$ and $Fe_{0.96}O$. In the crystal FeO, some of Fe^{2+} ions are found missing and the decrease in positive charge is satisfied by Fe^{3+} ions.

(iii) Displacement defect : Some times the atoms in the lattice of the crystal are exchanged mutually from their sites to the sites of the other lattice of the crystal and produce displacement. In such cases displacement defect is observed and displacement randomness is produced. This type of defect is observed in the alloys of copper and silver.

(C) Impurity defect : Suppose we add little amount of $SrCl_2$ to molten NaCl, and then crystallise, then in the crystal some sites of Na^+ are occupied by Sr^{2+} (Fig.1.21) each Sr^{2+} ion displaces two Na^+ ion. It occupies one site and second site remains vacant. Thus the number of cationic vacancy is same as the number of Sr^{2+} ions. The other examples is the solid solution of $CdCl_2$ and AgCl.
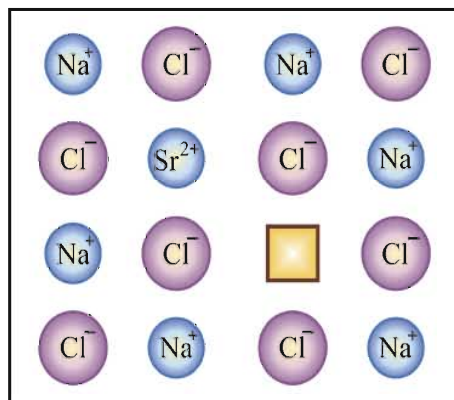

Fig. 1.21 Entry of Na^+ from NaCl by Sr^{2+} in vacancy defect

Band theory in Metals : It is accepted in the band theory that there are two bands in a metal or substance. One valence band in which the valence electrons of the substance are included. The second band over this band is called conduction band. For the electrical conductance of a substance, there must be electrons in the conduction band. The space between these two bands is called **energy gap.** The distance of this energy gap is more important for the electrons of valence band to go to conduction band. As the energy gap is less in metals, the electrons can easily go to conduction band from valence band. Hence, the conduction of electricity in metals is very easy and so they are called good conductors. In some substances, the distance of energy gap is more and so in normal conditions the electrons from valence band are not able to go to conduction band and so conduction of electricity does not occur. Hence, they are called non-conductors. Non-metals are mostly non-conductors. The situation in between these two is that of semiconductors. There are four electrons in the valence band of semimetal like silicon. They are not free. Hence, silicon under normal conditions, does not conduct electricity and is a non-conductor but if the temperature is increased or special types of radiations are impinged on it, the electrons of the valence band go to conduction band and conduction of electricity takes place. The vacant places created in the valence band are occupied by other electrons of the substance. These electrons go in less

proportion and so under definite conditions they become electrical conductor and so they are called semiconductors. Thus, conductor; non-conductor and semiconductor can be explained on the basis of band theory and distance between conductance band and valence band-energy gap.

1.9 Electrical and Magnetic effects of defects-Band theory in metals

A great range is observed in electrical conductances of solid substances. The solid substances are showing electrical conductivities from about 10^{-20} to 10^7 Ohm^{-1} m^{-1}. Hence, the solid substances can be divided into three sections on the basis of their electrical conductivities. (1) Electrical conductors (2) Electrical non-conductors (c) Semi- conductors.

(1) **Electrical conductors :** The substances whose electrical conductivities are in the range of 10^4 to 10^7 Ohm^{-1} m^{-1} are conductors or good conductors. Generally metals are included in such solid substances.

(2) **Electrical non-conductors :** The solid substances, whose electrical conductances are very less i.e. 10^{-20} to 10^{-10} Ohm^{-1} m^{-1} are called electrical non-conductors(insulators).

(3) **Electrical semiconductors :** The solid substances whose electrical conductances are in the range 10^{-6} to 10^4 Ohm^{-1} m^{-1} are called electrical semiconductors.

Conduction of Electricity in Metals : The conduction of electricity in conductors is either by electrons or through ions. Metals conduct electricity by electrons while electrolytes conduct electricity through ions. Metals conduct electricity in solid or molten states and their conductance depend on the number of electrons in the valence shells available in their atom. The atomic orbitals which form molecular orbital are very near to each other that a band is formed. It overlaps with this half filled band or the valence band which is just above the conductance band. When electric current is passed the electrons conduct it easily and the metal shows electrical conductance.
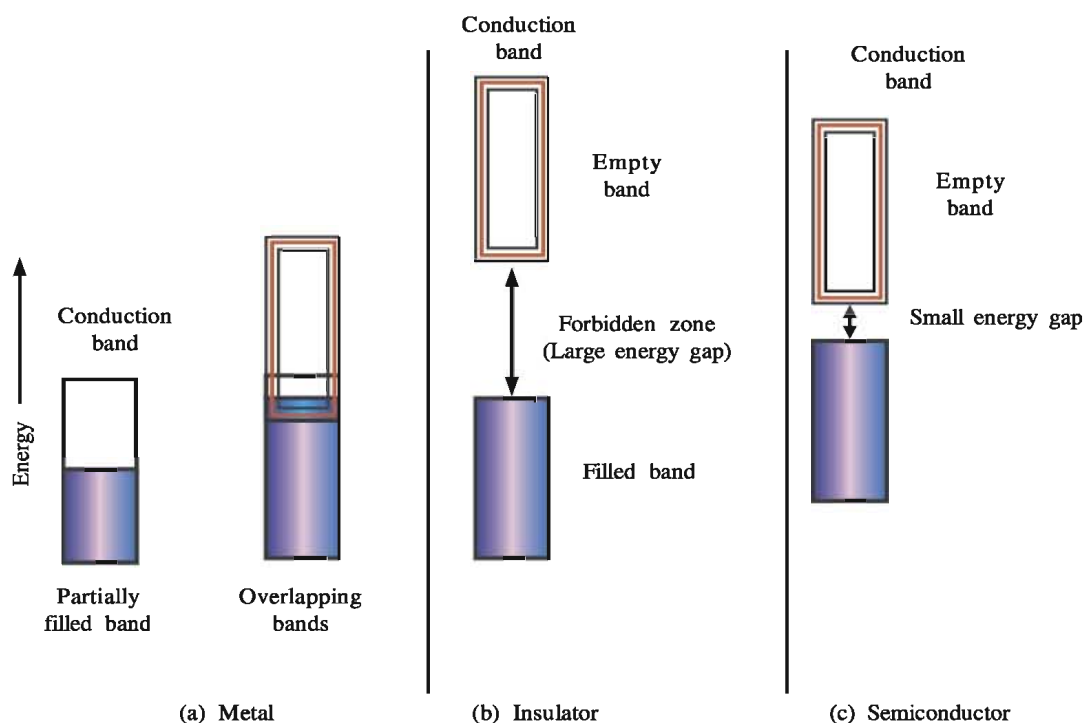
Fig 1.22 Distinction in (a) Metals (b) Insulators and (c) Semiconductors

If the vacant space (gap) is more between the filled valence band and the upper unfilled band (conductance band) the electrons cannot jump into conductance band and so the substance conducts very less amount of electricity or it does not conduct and so it acts as a non-conductor.

Electrical conductance in Semiconductors : In the case of semiconductors, the distance between valence band and conduction band is less (Fig.1.22). Hence, some of the electrons can go from valence band to conductance band, and so it will conduct less amount of electricity. The electrical conductivity of semiconductor increases with increase in temperature because, the energy obtained by increase in temperature can make the electrons jump from valence band to conduction band. Hence, the conduction of electricity becomes easy and more. Thus, semiconductor may appear as non conductor at normal temperature but with increase in temperature it appears to be a good conductor. Elements like silicon and germanium show this type of behaviour and so they are called intrinsic semiconductors. The electrical conductance of such semiconductors is so low that its practical use cannot be made, but if any suitable substance in some suitable proportion is added to it as an impurity, its conductance can be increased. This process is called **'doping'.** This doping can be carried out by adding electron rich and electron deficient elements (in comparison to the intrinsic semiconductors-silicon and germanium). These impurities can be known as electron defects in them.

We will take two general examples. Suppose a semiconductor like silicon or germanium (in which there are four electrons in valence shell) is dopped with electron rich element e.g. P or As (in which five electrons are there in valence shell) then, we obtain semiconductor with one excess electron. As electron is more and it possesses negative charge, so the doped semiconductor obtained is called **semiconductor of negative type** or **n-type.**

Similary, if elements like B, Al or Ga (which have three electrons in their valence shell) are doped with the silicon or germanium, there will be deficiency of electron. Such doped semiconductors are called **positive type semiconductor** or **p-type semiconductors.** You must have studied in detail about semiconductors in physics.

n and p-type semiconductors are used in preparation of many electronic parts or components. Diode is the combination on n-type and p-type semidoncutors which is used as rectifiers. It is used in transistors. By combination of semiconductors of the type pnp or npn can be prepared having different properties. With the help of the photodiode, light energy can be converted to electricity. Semiconductors like gallium arsenide (Ga As) have created a revolution by things having such semiconductors because of their very fast response.

It is interesting to know that transition metals show notable differences in electrical conductances, Oxides like TiO, CrO_2, ReO_3 behave like metals. ReO_3 possesses conductance and appearance like metallic copper. Other oxides like VO, VO_2, VO_3 and TiO_2 show metallic properties or nonconductors which depends on temperature.

Magnetic properties : We know that electron possesses electric charge and it also moves. Hence, it possessess magnetic property. Electron is present in each substance and shows magnetic properties associated to some extent with them. In each atom, electron behaves like a very small magnet. Its magnetic moment can be produced from its two types of motion, one is the motion around the nucleus and the second on its own axis. Thus electron being a particle possessing electric charge and having this type of motion, it can be considered as a loop of current which possesses magnetic moment. Thus, permanent rotation and orbital magnetic moment are associated with each electron. The magnitude of magnetic moment is very small. Its measurement is done in Bohr magneton units. Its value is 9.27×10^{-24} Am^2.

Thus, substances can be divided into five types on the basis of their magnetic properties : (1) Paramagnetic (2) Diamagnetic (3) Ferromagnetic (4) Antiferromagnetic and (5) Ferrimagnetic. We shall study all these five types.

(1) Paramagnetism : The paramagnetism is due to unpaired electrons. Paramagnetic substances are weakly attracted in presence of magnetic field. In absence of magnetic field their magnetism is removed. The paramagnetism is due to one or more unpaired electrons, because they are attracted by magnetic field. Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2 etc. are the examples of such paramagnetic substances.

(2) Diamagnetism : Diamagnetism substances are weakly repelled by magnetic field. NaCl, H_2O, C_6H_6, N_2 etc. are the examples of such substances. They are weakly attracted or repelled of magnetic field and are in opposite directions. The substances in which all the electrons are paired or there is no unpaired electrons, show the diamagnetic property. The pair formed by the spin of electrons in corresponding opposite directions cancel the magnetic moment and so they lose the property of magnetism.

(3) Ferromagnetism : Substances like iron, cobalt, nickel, gadolinium, CrO_2 etc. possess very strong attraction in presence of magnetic field. Such substances are called ferromagnetic substances. In addition to strong attraction, these substances become permanently magnetic. In solid state, metal ions of ferromagnetic substances are arranged as Domains in a small area, collectively in a group. Each of such domains acts as a small magnet. In the nonmagnetic piece of ferromagnetic substance these domains are arranged randomly and their magnetic moments are cancelled. When substance is placed in the magnetic field, all the domains are oriented in the direction of magnetic field. Fig 1.23(a) and so strong magnetic effect is produced.

If magnetic field is removed, the alignment in the domain is maintained and hence ferromagnetic substances become permanent magnets.

(4) Antiferromagnetism : Substances like MnO show antiferromagnetism. The formation of their domains is similar to the ferromagnetic substances but the domains are oriented opposite to each other and so cancel the magnetic moment of each other. Fig 1.23 (b).

(5) Ferrimagnetism : When the magnetic moments of domains in substances are arranged parallel or antiparallel to each other but are in unequal number, the substance is called ferrimagnetic substance. Fig 1.23 (c).

They are more weakly attracted in comparison to ferro-magnetic substance. Substances like magnetite (Fe_3O_4), Ferrites ($MgFe_2O_4$) and $ZnFe_2O_4$ show ferrimagnetism. Such substances when heated lose ferrimagnetism and become paramagnetic.
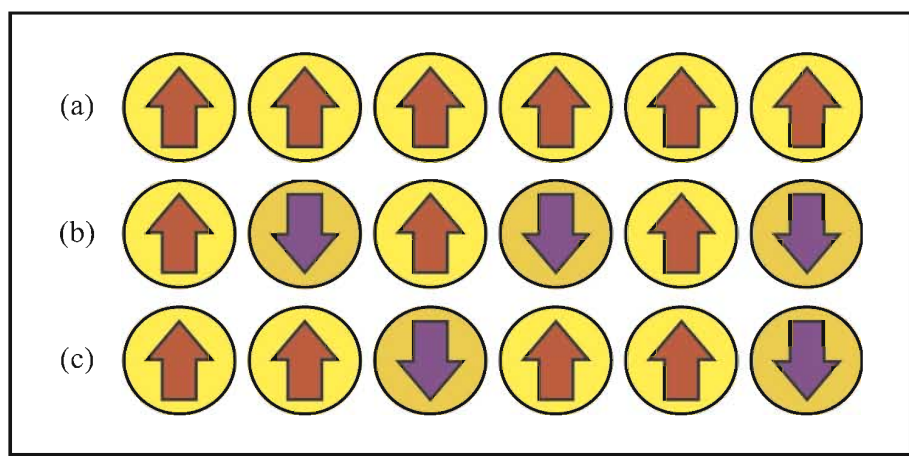

Fig. 1.23 Schematic alignment of magnetic moments in
(a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic

SUMMARY

There are three main states of matter-solid, liquid and gas. In addition to these, other two states are plasma and Bose-Einstein condensate. We have studied the solid state of matter. Solid substance has definite mass, volume and shape because the positions (sites) of their component particles are definite. They are arranged near to each other and there are strong interattraction forces. There are two main types of solids-crystalline and amorphous. In crystalline substance structure, arrangement definite melting etc. are systematic and so more information about it is given in this unit. The arrangement, of constituent particles in amorphous substances are systematic upto a small distance so they have no definite shape, and definite melting points. They can be known as supercooled liquids, while in crystalline solids, there are definite melting points, systematic arrangement, characteristic shape, etc. There is strong interaction between its component particles, they possess specific properties. The solid substances can be divided into different sections on the basis of their structure and attraction forces etc. viz. Molecular ionic, metallic, covalent etc. They all show notable differences in their properties.

The constituent particles are systematically arranged. On its basis the structure of crystal forms. The smallest particle of a crystal is called unit cell and in the crystal, these unit cells are arranged in three dimensional directions. Such an arrangement is called lattice structure. Different types of lattice structures is called Bravias lattice. Unit cell is of primitive type in which the particles are on the corners or in the centre. Face-centred, body centred and end-centred are the crystals of this type. Primitive cells are of seven types. Lattice having high efficiency because of close packing of particles, lattice is formed, in which hexagonal close packing (hcp), cubic close packing (ccp), face centred close packing (fcp) are important. Their packing efficiencies are different. It is about 54 % in ccp, about 68 % in bcp and about 74 % in fcp. Because of the arrangement of different types of crystal structure there are holes or spaces called voids. They are of two types-tetrahedral and octahedral. The number of tetrahedral voids is double the number of octahedral voids.

Crystals are not so perfect as they appear. There are imperfections in them which we call defects. These types of defects may be of different types viz. non-stoichiometric, stoichiometric, impurity, point defects etc. From these, Schottky and Frenkel defects are observed in ionic crystals. Because of the decrease in number of constituent paritcles in Schottky defect, there is decrease in density in Frenkel defects because the constituent particles are arranged in interstitial sites. Crystal like AgBr shows both types of the defects. By making use of such defects, some elements or constituents can be added in their places and crystals which are very useful can be obtained. It is called doping. By use of elements like aluminium or boron, pnp type semiconductor and by addition of elements like arsenic and gallium npn type semiconductors can be prepared. They can be used in transistors etc.

The crystals show different magnetic properties on the basis of the electrons present in them and their arrangement, viz. paramagnetic- in which there is effect of magnetic field and is due to unpaired electrons. In diamagnetic substances, no effect is observed of magnetic field. It indicates paired electronic configuration. In addition, metals like iron, cobalt, nickel show specific type of magnetic effect. It is called ferromagnetism. If permanent arrangement takes place due to the effect of magnetic field, ferromagnetism is observed and if no effect is observed it is antiferromagnetism.

Conductors can be divided into three types-good conductors which allow the electric current to pass through them; which do not allow electric current to pass through them called non conductors and those which conduct electricity when heated or by impingment of radiation of some special type are called semiconductors.

The conduction of electricity in substances can be explained on the basis of band theory. It can be explained on the basis of two bands- one conduction band and second valence band. Conduction band is at higher energy level than valence band. Hence the space between the two is known as energy gap. If electron can easily go from valence band to conduction band, it becomes good conductor. If electron can be sent by giving some energy (by increase in temperature), it is called semiconductor and if it is not possible to send the electrons, it is called non-conductor. In other words, it can be said that larger space difference between the two bands, more difficult it will be to send electrons from valence band to conduction band and more the nonconductor. Thus, the study of metals, ionic solids, molecular solids, covalent solids etc. and their uses from these studies, structure of crystal etc. is called 'solid state chemistry'.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

    (1) What type of solid is sodium chloride ?

        (A) Ionic   (B) Molecular   (C) Covalent   (D) Metallic

    (2) The melting points of ionic solids are

        (A) Very high   (B) Normal   (C) Very low   (D) Abnormal

    (3) What type of solid is quartz ?

        (A) Ionic   (B) Molecular   (C) Covalent   (D) Metallic

    (4) What type of crystal structure is of silver metal ?

        (A) fcc   (B) Simple cube   (C) bcc   (D) Metallic

    (5) What is the percentage packing efficiency of simple cube ?

        (A) 53.26   (B) 68.0   (C) 74.0   (D) 52.36

    (6) How many times is the number of octahedral voids as compared to tetrahedral voids ?

        (A) 4   (B) 8   (C) 2   (D) 0.5

    (7) What is the number of atoms in the unit cell of body centred cube ?

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

    (8) What is the number of atoms in face centred cube ?

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

    (9) In which of the following compounds Schottky defect is present ?

        (A) NaCl   (B) ZnS   (C) SiO_2 (D) $SrCl_2$

    (10) In which of the following compounds Frenkel defect is present ?

        (A) NaCl   (B) ZnS   (C) KBr   (D) $SrCl_2$

(11) Which of the following compounds shows metal deficiency defect ?

(A) $Fe_{0.95}O$ (B) $Fe_2O_{3.6}$ (C) Fe_3O_4 (D) $FeS_{1.6}$

(12) Which of the following elements is a semiconductor ?

(A) Na   (B) Al   (C) Fe   (D) Ge

(13) Which type of semiconductor is obtained by doping Si with B ?

(A) n-type   (B) p-type   (C) pnp-type   (D) npn-type

(14) With which element, the conductivity of ReO_3 is matching ?

(A) Copper   (B) Zinc   (C) Iron   (D) Aluminium

(15) Which of the following will be paramagnetic ?

(A) O_2^{2-} (B) Cr^{3+} (C) Na^+ (D) Cu^+

(16) Which theory is useful in explaining electrical conductivity in conductors and semiconductors ?

(A) Pauli's principle   (B) Avogadro's theory

(C) Band theory   (D) Hybridisation theory

2. Write the answers of the following in short :

(1) Write types of solids on the basis of binding forces.

(2) Give examples of crystalline and amorphous solids.

(3) Write the definition of unit cell.

(4) Mention the types of packing in solids.

(5) What is meant by tetrahedral and octahderal voids ?

(6) Mention the number of atoms in the unit cell of different types of solids.

(7) Write one example, of each of conductor, semiconductor and non-conductor.

(8) What is band theory explaining conductivity ?

(9) Write four types of magnetic properties.

(10) What is meant by defect ? Mention the types of defects in solid.

3. Write answers of the following questions :

(1) Explain giving examples, ionic and molecular solids.

(2) Explain network solid compounds with example.

(3) Write three differences of amorphous and crystalline solid substances.

(4) Explain the types of different solids and write their characteristics.

(5) Calculate number of atoms in body centred and face centred cubic soilds.

(6) Calculate the volume occupied by atoms in simple cube.

(7) Explain the tetrahedral and octahderal voids by drawing diagram.

(8)   Describe the band theory explaining conductivity in semiconductor.

(9)   Explain ferromagnetism and antiferromagnetism

(10) What is meant by doping ? Explain giving example.

4. Write the answers of the following in detail :

(1)   Explain two dimensional and three dimensional close packing.

(2)   Mention characteristics of face centred and body centred cubes.

(3)   Calculate the volume occupied by atoms in body centred cube.

(4)   Write types of defects and describe Schottky and Frenkel defects.

(5)   Write in detail about metal deficiency and non-stoichiometric defects.

(6)   Explain band theory about conductivity in solid substances.

(7)   Explain in detail, ferromagnetism, ferrimagnetism and antiferromagnetism.

(8)   Write a detailed note on energy gap, conduction band and valence band.

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