Unit 1

The Solid State

The vast majority of solid substances like high temperature superconductors, biocompatible plastics, silicon chips, etc. are destined to play an ever expanding role in future development of science.

Objectives

After studying this Unit, you will be able to

- describe general characteristics of solid state;
- distinguish between amorphous and crystalline solids;
- classify crystalline solids on the basis of the nature of binding forces;
- define crystal lattice and unit cell;
- explain close packing of particles;
- describe different types of voids and close packed structures;
- calculate the packing efficiency of different types of cubic unit cells;
- correlate the density of a substance with its unit cell properties;
- describe the imperfections in solids and their effect on properties;
- correlate the electrical and magnetic properties of solids and their structure.

From our earlier studies, we know that liquids and gases are called *fluids* because of their ability to flow. The fluidity in both of these states is due to the fact that the molecules are free to move about. On the contrary, the constituent particles in solids have fixed positions and can only oscillate about their mean positions. This explains the rigidity in solids. These properties depend upon the nature of constituent particles and the binding forces operating between them. The correlation between structure and properties helps in the discovery of new solid materials with desired properties. For example, carbon nanotubes are new materials that have potential to provide material that are tougher than steel, lighter than aluminium and have more conductive property than copper. Such materials may play an expanding role in future development of science and society. Some other materials which are expected to play an important role in future are high temperature superconductors, magnetic materials, biodegradable polymers for packaging, biocompliant solids for surgical implants, etc. Thus, the study of this state becomes more important in the present scenario.

In this Unit, we shall discuss different possible arrangements of particles resulting in several types of structures and explore why different arrangements of structural units lend different properties to solids. We will also learn how these properties get modified due to the structural imperfections or by the presence of impurities in minute amounts.
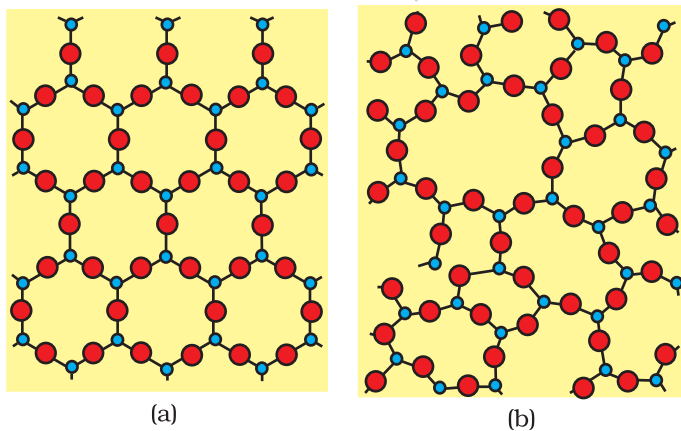
1.1 General Characteristics of Solid State

In Class XI you have learnt that matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure, which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. These are **intermolecular forces** which tend to keep the molecules (or atoms or ions) closer, and the thermal energy, which tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

(i) They have definite mass, volume and shape.

(ii) Intermolecular distances are short.

(iii) Intermolecular forces are strong.

(iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.

(v) They are incompressible and rigid.

1.2 Amorphous and Crystalline Solids

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. The arrangement of constituent particles (atoms, molecules or ions) in a crystal is ordered and repetitive in three dimensions. If we observe the pattern in one region of the crystal, we can predict accurately the position of particles in any other region of the crystal however far they may be from the place of observation. Thus, crystal has a long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. Glass, rubber and many plastics do not form crystals when their liquids solidify on cooling. These are called amorphous solids. The term amorphous comes from the Greek word *amorphos*, meaning no form.The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only *short range order*. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Regular patterns are scattered and in between the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

(a)   (b)

Fig. 1.1: *Two dimensional structure of (a) quartz and (b) quartz glass*

Crystalline solids have a sharp melting point. At a characteristic temperature they melt abruptly and become liquid. On the other hand, amorphous solids soften, melt and start flowing over a range of temperature and can be moulded and blown into various shapes. Amorphous solids have the same structural features as liquids and are conveniently regarded as extremely viscous liquids. They may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called *pseudo solids* or *super cooled liquids*.

Amorphous solids are *isotropic* in nature. Their properties such as mechanical strength, refractive index and electrical conductivity, etc., are same in all directions. It is because there is no *long range* order in them and arrangement of particles is not definite along all the directions. Hence, the overall arrangement becomes equivalent in all directions. Therefore, value of any physical property would be same along any direction.
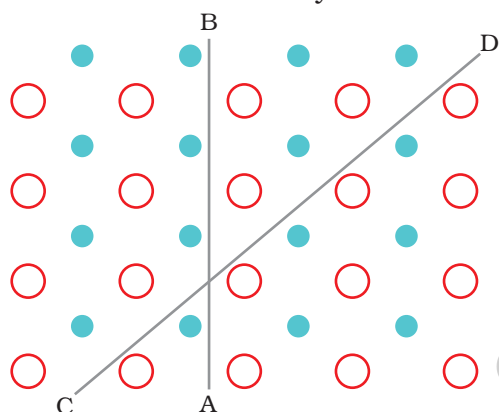
Fig. 1.2: *Anisotropy in crystals is due to different arrangement of particles along different directions.*

Crystalline solids are **anisotropic** in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. This figure shows a simple two-dimensional pattern of arrangement of two kinds of atoms. Mechanical property such as resistance to shearing stress might be quite different in two directions indicated in the figure. Deformation in CD direction displaces row which has two different types of atoms while in AB direction rows made of one type of atoms are displaced. The differences between the crystalline solids and amorphous solids are summarised in Table 1.1.

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic enthalpy of fusion	They do not have definite enthalpy of fusion

Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Besides crystalline and amorphous solids, there are some solids which apparently appear amorphous but have microcrystalline structures. These are called polycrystalline solids. Metals often occur in polycrystalline condition. Individual crystals are randomly oriented so a metallic sample may appear to be isotropic even though a single crystal is anisotropic.

Amorphous solids are useful materials. Glass, rubber and plastics find many applications in our daily lives. Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Intext Questions

1.1 Why are solids rigid?

1.2 Why do solids have a definite volume?

1.3 Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

1.4 Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

1.3 Classification of Crystalline Solids

In Section 1.2, we have learnt about amorphous substances and that they have only short range order. However, most of the solid substances are crystalline in nature. For example, all the metallic elements like iron, copper and silver; non-metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids.

Crystalline solids can be classified in various ways. The method depends on the purpose in hand. Here, we will classify crystalline solids on the basis of nature of intermolecular forces or bonds that hold the constituent particles together. These are — (i) Van der waals forces; (ii) Ionic bonds; (iii) Covalent bonds; and (iv) Metallic bonds. On this basis, crystalline solids are classified into four categories viz., molecular, ionic, metallic and covalent solids. Let us now learn about these categories.

1.3.1 Molecular Solids

Molecules are the constituent particles of molecular solids. These are further sub divided into the following categories:

(i) *Non polar Molecular Solids*: They comprise either atoms, for example, argon and helium or the molecules formed by non polar covalent

bonds, for example, H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) *Polar Molecular Solids*: The molecules of substances like HCl, SO_2, *etc.* are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room temperature and pressure. Solid SO_2 and solid NH_3 are some examples of such solids.

(iii) *Hydrogen Bonded Molecular Solids*: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

1.3.2 Ionic Solids

Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

1.3.3 Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

1.3.4 Covalent or Network Solids

A wide variety of crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal. They are also called **giant molecules**. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points and may even decompose before melting. They are insulators and do not conduct electricity. Diamond (Fig. 1.3) and silicon carbide are typical examples of such solids. Although Graphite (Fig. 1.4) also belongs to this class of crystals, but it is soft and is a conductor of electricity. Its exceptional properties are due to
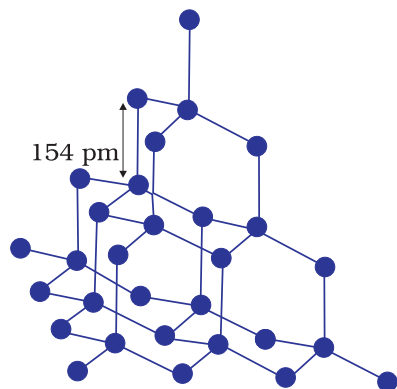
Fig. 1.3: Network structure of diamond
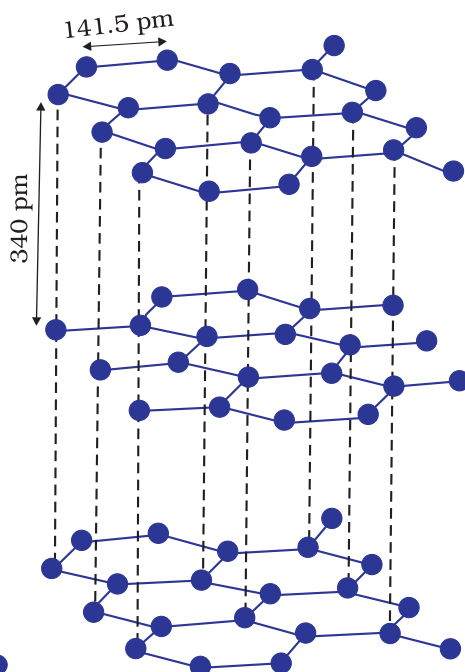
Fig. 1.4: Structure of graphite

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

The different properties of the four types of solids are listed in Table 1.2.

Table 1.2: Different Types of Solids

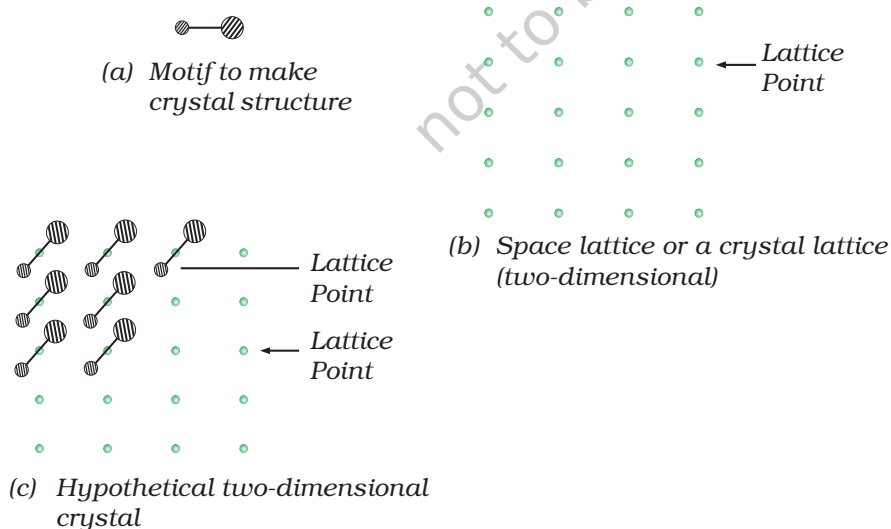| Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conduc- tivity	Melting Point
(1) Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl$_4$, H$_2$, I$_2$, CO$_2$	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO$_2$	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H$_2$O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF$_2$	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high

| (4) Covalent or network solids | Atoms | Covalent bonding | SiO_2 (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$ | Hard | Insulators | Very high |
| | | | | Soft | Conductor (exception) | |

1.4 Crystal Lattices and Unit Cells

You must have noticed that when tiles are placed to cover a floor, a repeated pattern is generated. If after setting tiles on floor we mark a point at same location in all the tiles (e.g. Centre of the tile) and see the marked positions only ignoring the tiles, we obtain a set of points. This set of points is the scaffolding on which pattern has been developed by placing tiles. This scaffolding is a space lattice on which two-dimensional pattern has been developed by placing structural units on its set of points (i.e. tile in this case). The structural unit is called basis or motif. When motifs are placed on points in space lattice, a pattern is generated. In crystal structure, motif is a molecule, atom or ion. A space lattice, also called a crystal lattice, is the pattern of points representing the locations of these motifs. In other words, space lattice is an abstract scaffolding for crystal structure. When we place motifs in an identical manner on points of space lattice,

(a) Motif to make crystal structure

(b) Space lattice or a crystal lattice (two-dimensional)

(c) Hypothetical two-dimensional crystal

Fig. 1.5: (a) Motif (b) Space lattice (two-dimensional (c) Hypothetical two-dimensional crystal structure

we get crystal structure. Fig. 1.5 shows a motif, a two-dimensional lattice and a hypothetical two-dimensional crystal structure obtained by placing motifs in the two-dimensional lattice.

Spacial arrangement of lattice points gives rise to different types of lattices. Fig 1.6 shows arrangement of points in two different lattices.
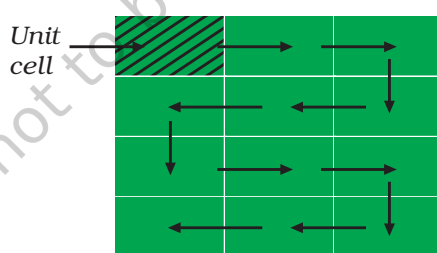

Lattice A   *Lattice B*

Fig. 1.6:   Arrangement of points in two different lattices

In the case of crystalline solids, space lattice is a three-dimensional array of points. The crystal structure is obtained by associating structurral motifs with lattice points. Each repeated basis or motif has same structure and same spacial orientation as other one in a crystal. The environment of each motif is same throughout the crystal except for on surface.

Following are the characteristics of a crystal lattice:

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

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

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

Fig. 1.7:   *Generating hypothetical two-dimensional crystal structure by shifting square in the direction of arrows.*

Unit cell

We need only a small part of the space lattice of a crystal to spacify crystal completely. This small part is called unit cell. One can choose unit cell in many ways. Normally that cell is chosen which has perpendicular sides of shortest length and one can construct entire crystal by translational displacement of the unit cell in three dimensions. Fig. 1.7 shows movement of unit cell of a two-dimensional lattice to construct the entire crystal structure. Also, unit cells have shapes such that these fill the whole lattice without leaving space between cells.

In two dimensions a parallelogram with side of length 'a' and 'b' and an angle *r* between these sides is chosen as unit cell. Possible unit cells in two dimensions are shown in Fig. 1.8.
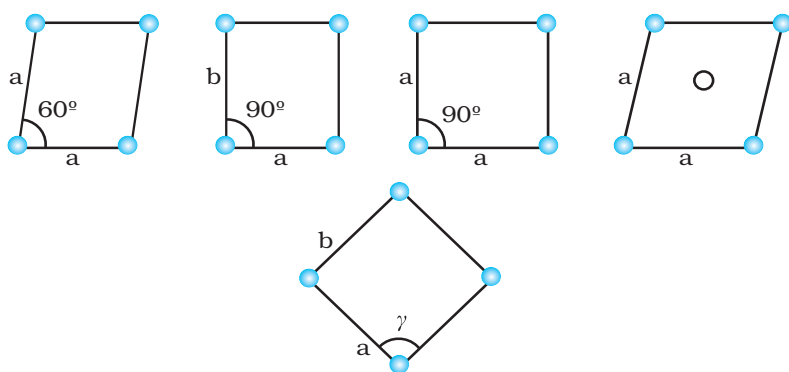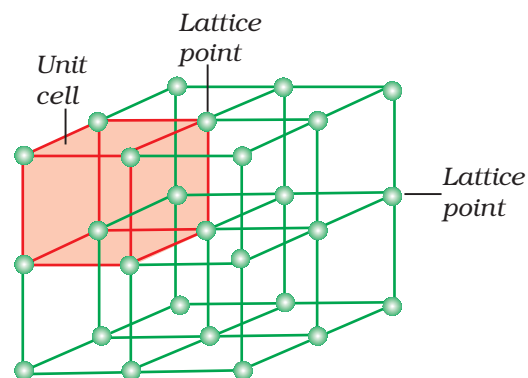
Fig. 1.9: *A portion of a three-dimensional cubic space of a crystal lattice and its unit cell.*

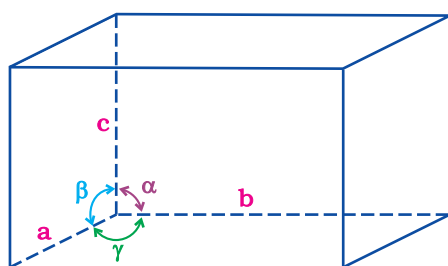Fig. 1.8: *Possible unit cells in two dimensions*

Fig. 1.10: *Illustration of parameters of a unit cell*

A portion of three-dimensional **crystal lattice** and its unit cell is shown in Fig. 1.9.

In the three-dimensional crystal structure, unit cell is characterised by:

 (i) its dimensions along the three edges *a*, *b* and *c*. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α (between *b* and *c*), β (between *a* and *c*) and γ (between *a* and *b*). Thus, a unit cell is characterised by six parameters *a*, *b*, *c*, α, β and γ.

These parameters of a typical unit cell are shown in Fig. 1.10.

1.4.1 Primitive and Centred Unit Cells

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

(a) Primitive Unit Cells

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

(b) Centred Unit Cells

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

  (i) *Body-Centred Unit Cells:* Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

 (ii) *Face-Centred Unit Cells:* Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) *End-Centred Unit Cells:* In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

Inspection of a wide variety of crystals leads to the conclusion that all can be regarded as conforming to one of the seven regular figures. These basic regular figures are called seven crystal systems. To which system a given crystal belongs to is determined by measuring the angles between its faces and deciding how many axis are needed to define the principal features of its shape. Fig. 1.11 shows seven crystal systems.
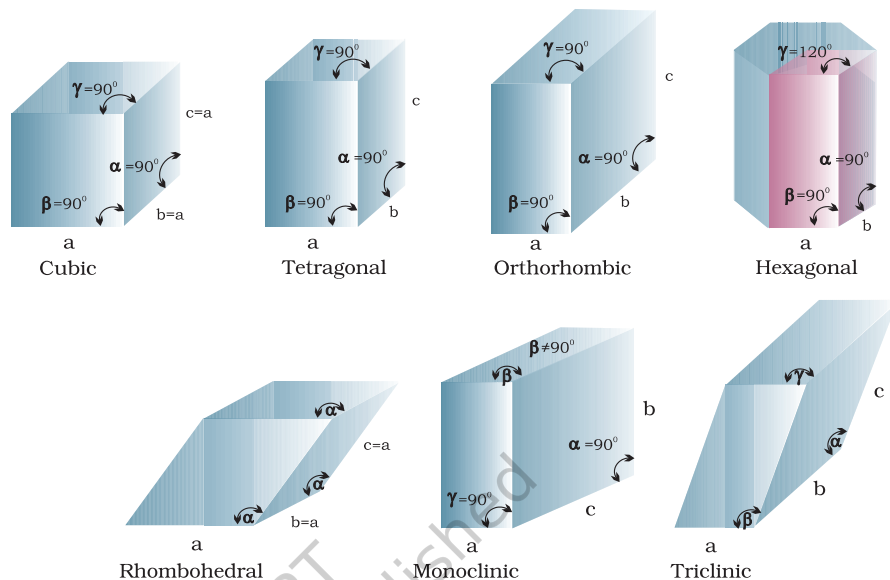

Fig. 1.11: *Seven crystal systems*

A French mathematician, Bravais, showed that there are only 14 possible three-dimensional lattices. These are called **Bravais lattices**. Unit cells of these lattices are shown in the following box. The characteristics of their primitive unit cells along with the centred unit cells that they can form have been listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells
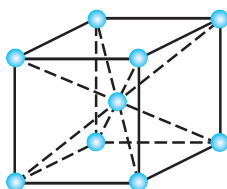
Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)

| Monoclinic | Primitive, End-centred | $a \neq b \neq c$ | $\alpha = \gamma = 90°$ $\beta \neq 90°$ | Monoclinic sulphur, $Na_2SO_4.10H_2O$ |
| Triclinic | Primitive | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90°$ | $K_2Cr_2O_7$, $CuSO_4. 5H_2O$, H_3BO_3 |

Unit Cells of 14 Types of Bravais Lattices
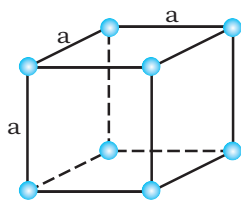
Primitive (or simple)   Body-centred   Face-centred
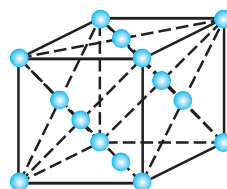
Unit cells of cubic lattices: all sides of same length, angles between faces all 90°
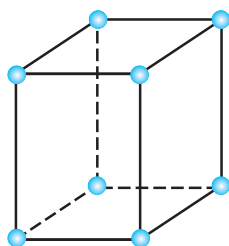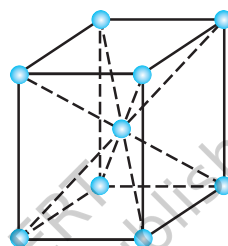
Primitive   Body-centred

Unit cells two tetragonal lattices: one side different in length to the other, two angles between faces all 90°
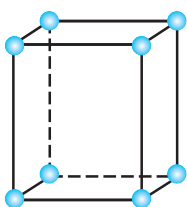
Primitive   End-centred   Body-centred   Face-centred

Unit cells of four orthorhombic lattices: unequal sides, angles between faces all 90°

More than 90°

Less than 90°
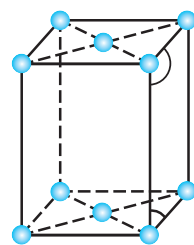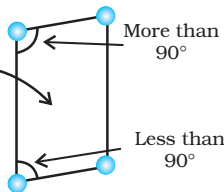
Primitive   End-centred

Unit cells of two monoclinic lattices: unequal sides, two faces have angles different to 90°

Unit cell of hexagonal lattice – one side different in length to the other two, the marked angles on two faces are 60°

Unit cell of rhombohedral lattice – all sides of equal length, angles on two faces are less than 90°

Unit cell of triclinic lattice – unequal sides a, b, c, A, B, C are unequal angles with none equal to 90°
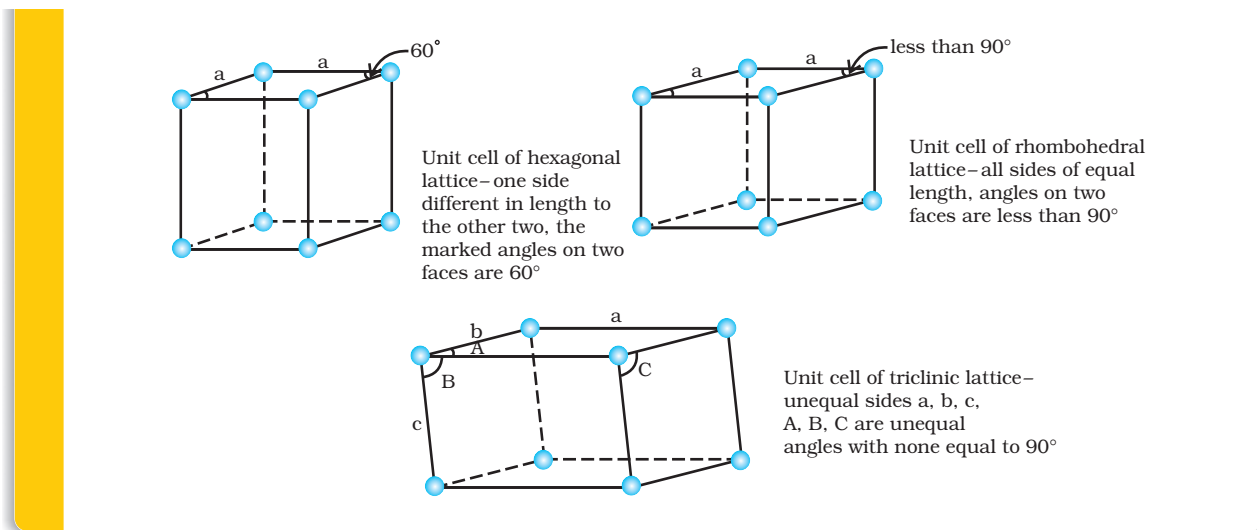
1.5 Number of Atoms in a Unit Cell

We know that any crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). Let us now work out what portion of each particle belongs to a particular unit cell.
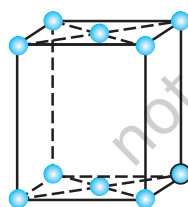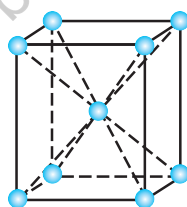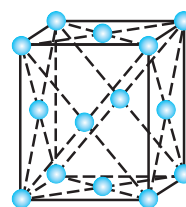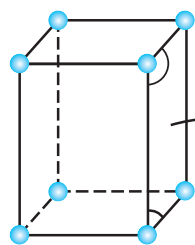
We shall consider three types of cubic unit cells and for simplicity assume that the constituent particle is an atom.

1.5.1 Primitive Cubic Unit Cell

Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig. 1.12, four unit cells in the same layer and four unit cells of the upper (or lower) layer. Therefore, only $\frac{1}{8}$ th of an atom (or molecule or ion) actually belongs to a particular unit cell. In Fig. 1.13, a primitive cubic unit cell has been depicted in three different ways. Each small sphere in Fig. 1.13(a) represents only the centre of the particle occupying that position and not its actual size. Such structures are called *open structures*. The arrangement of particles is easier to follow in open structures. Fig. 1.13(b) depicts space-filling representation of the unit cell with actual particle size and Fig. 1.13 (c) shows the actual portions of different atoms present in a cubic unit cell.

Fig. 1.12: In a simple cubic unit cell, each corner atom is shared between 8 unit cells.

In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom.

(a)　　　　(b)　　　　(c)

Fig. 1.13: A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

1.5.2 Body-Centred Cubic Unit Cell

A body-centred cubic (*bcc*) unit cell has an atom at each of its corners and also one atom at its body centre. Fig. 1.14 depicts (a) open structure (b) space filling model and (c) the unit cell with portions of atoms actually belonging to it. It can be seen that the atom at the
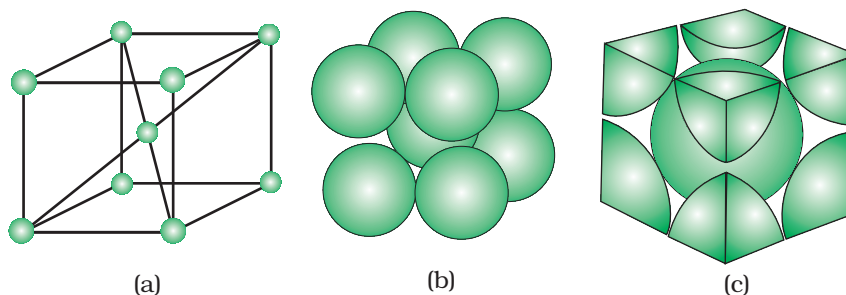
Fig. 1.14: A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

(i) 8 corners × $\frac{1}{8}$ per corner atom $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 1 body centre atom = 1 × 1 = 1 atom

∴ Total number of atoms per unit cell = 2 atoms

1.5.3 Face-Centred Cubic Unit Cell

A face-centred cubic (*fcc*) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.15 that each atom located at the face-centre is shared between two adjacent unit cells and only $\frac{1}{2}$ of each atom belongs to a unit cell. Fig. 1.16 depicts (a) open structure (b) space-filling model and (c) the unit cell with portions of atoms actually belonging to it. Thus, in a face-centred cubic (*fcc*) unit cell:

(i) 8 corners atoms × $\frac{1}{8}$ atom per unit cell $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 6 face-centred atoms × $\frac{1}{2}$ atom per unit cell = 6 × $\frac{1}{2}$ = 3 atoms

∴ Total number of atoms per unit cell = 4 atoms
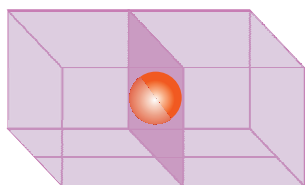
Fig. 1.15: An atom at face centre of unit cell is shared between 2 unit cells
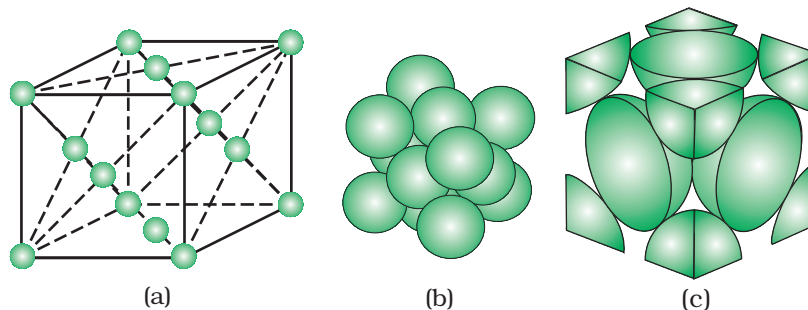
Fig 1.16: A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

Intext Questions

1.9 Give the significance of a 'lattice point'.

1.10 Name the parameters that characterise a unit cell.

1.11 Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells.

1.12 Explain how much portion of an atom located at (i) corner and (ii) body-centre of a cubic unit cell is part of its neighbouring unit cell.

1.6 Close Packed Structures

In solids, the constituent particles are close-packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres and build up the three-dimensional structure in three steps.

(a) Close Packing in One Dimension

There is only one way of arranging spheres in a one-dimensional close packed structure, that is to arrange them in a row and touching each other (Fig. 1.17).

Fig. 1.17: Close packing of spheres in one dimension

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its **coordination number**. Thus, in one dimensional close packed arrangement, the coordination number is 2.

(b) Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

(i) 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. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.18 (a).

(a)
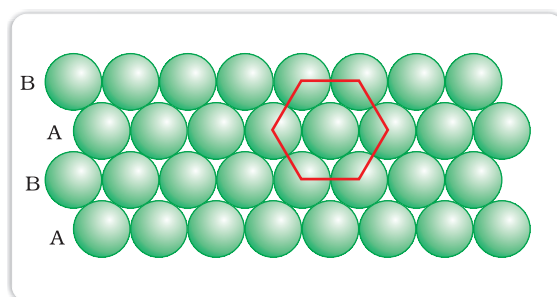
(b)

Fig. 1.18: (a) Square close packing (b) hexagonal close packing of spheres in two dimensions

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called **square close packing in two dimensions**.

(ii) 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 r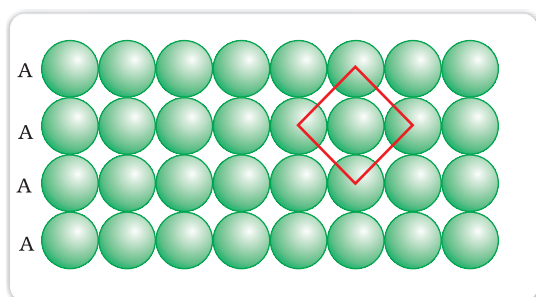ow. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type. In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon (Fig. 1.18 b) hence this packing is called **two dimensional hexagonal close-packing.** It can be seen in Figure 1.18 (b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

(c) Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. In the last Section, we discussed close packing in two dimensions which can be of two types; square close-packed and hexagonal close-packed. Let us see what types of three dimensional close packing can be obtained from these.

(i) *Three-dimensional close packing forms two-dimensional square close-packed layers:* While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in Fig. 1.19. Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (See Fig. 1.19).

(ii) *Three dimensional close packing from two dimensional hexagonal close packed layers:* Three dimensional close packed structure can be generated by placing layers one over the other.
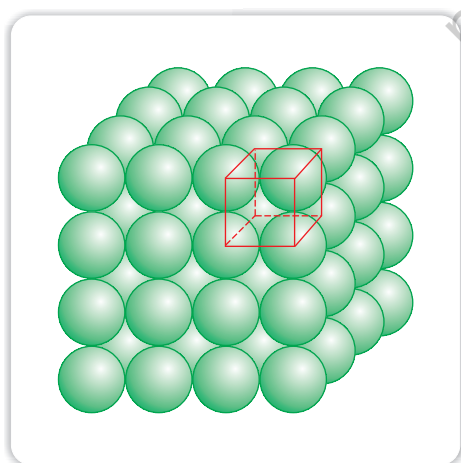
Fig. 1.19: *Simple cubic lattice formed by A A A .... arrangement*

(a) Placing second layer over the first layer

Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from Fig. 1.20 that all the triangular voids of the first layer are not covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is
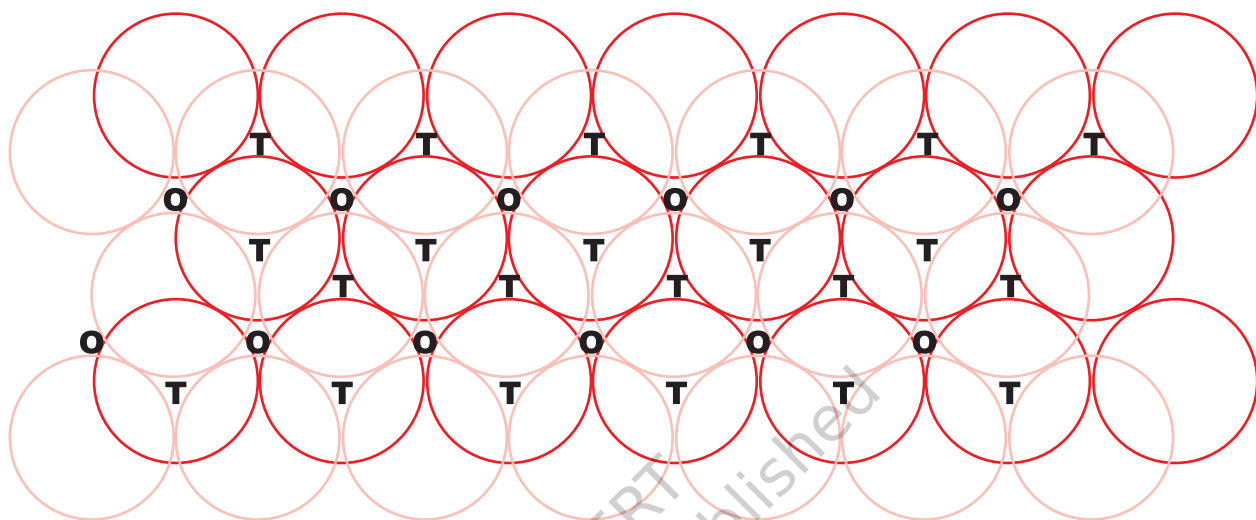
Fig. 1.20: *A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void*

formed. These voids are called **tetrahedral voids** because a *tetrahedron* is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig. 1.20. One such void has been shown separately in Fig. 1.21.
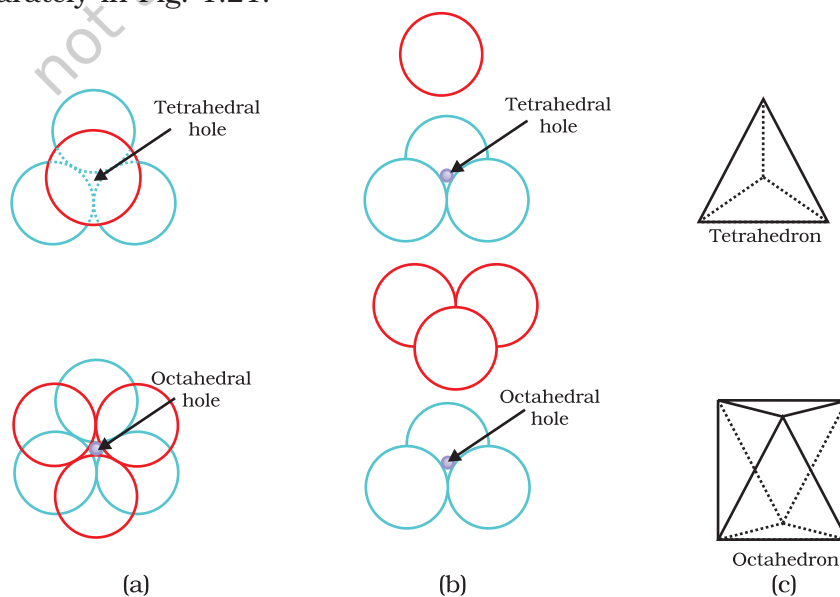
Fig 1.21
Tetrahedral and octahedral voids
(a) top view
(b) exploded side view and
(c) geometrical shape of the void.

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 1.20. Such voids are surrounded by six spheres and are called **octahedral voids.** One such void has been shown separately in Fig. 1.21. The number of these two types of voids depend upon the number of close packed spheres.

Let the number of close packed spheres be *N*, then:

The number of octahedral voids generated = *N*

The number of tetrahedral voids generated = *2N*

(b) Placing third layer over the second layer

When third layer is placed over the second, there are two possibilities.

(i) *Covering Tetrahedral Voids*: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB .... pattern. This structure is called hexagonal close packed (*hcp*) structure (Fig. 1.22). This sort of arrangement of atoms is found in many metals like magnesium and zinc.
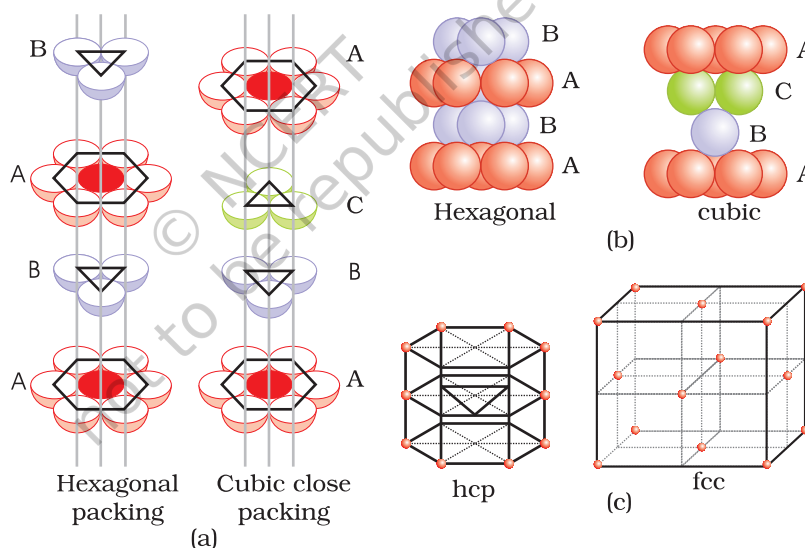
Fig. 1.22
(a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing.

Fig. 1.23
(a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.
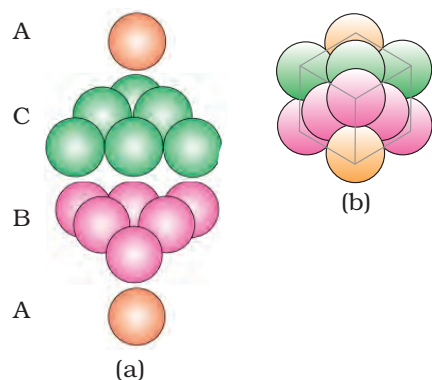
(ii) *Covering Octahedral Voids*: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called 'C' type. Only when fourth layer is placed, its spheres are aligned with

those of the first layer as shown in Figs. 1.22 and 1.23. This pattern of layers is often written as ABCABC .... This structure is called cubic close packed (*ccp*) or face-centred cubic (*fcc*) structure. Metals such as copper and silver crystallise in this structure.

Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

1.6.1 Formula of a Compound and Number of Voids Filled

Earlier in the section, we have learnt that when particles are close-packed resulting in either *ccp* or *hcp* structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids. All octahedral or tetrahedral voids are not occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

Example 1.1

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution

The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

Example 1.2

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?

Solution

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is 2 × (2/3):1 or 4:3 and the formula of the compound is A_4B_3.

Locating Tetrahedral and Octahedral 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.

(a) Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice [Fig. 1(a)]. The unit cell is divided into eight small cubes.

Each small cube has atoms at alternate corners [Fig. 1(a)]. 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.

(a)   (b)
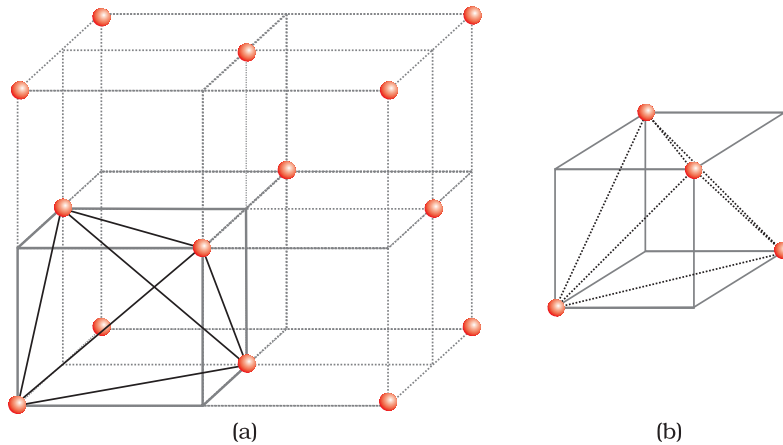
Fig. 1: *(a) Eight tetrahedral voids per unit cell of ccp structure*
(b) one tetrahedral void showing the geometry.

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(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(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 $\frac{1}{4}^{th}$ of each void belongs to a particular unit cell.

(a)   (b)
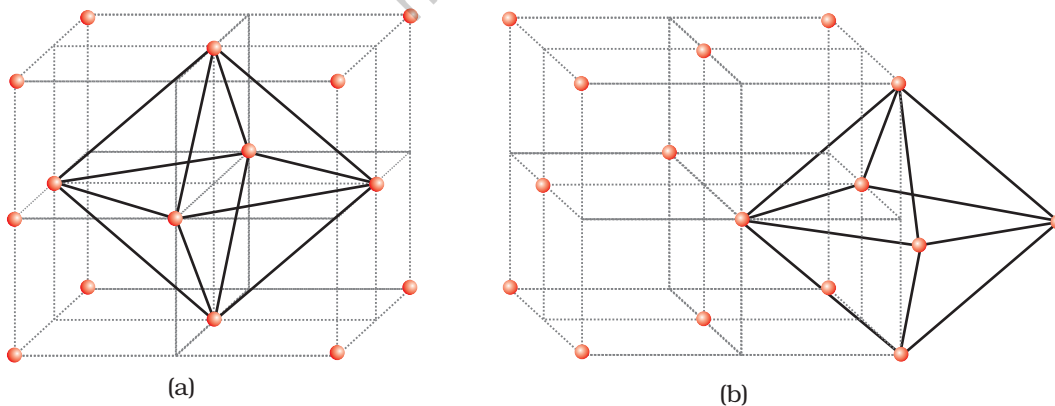
Fig. 2: *Location of octahedral voids per unit cell of ccp or fcc lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).*

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

∴ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in *hcp* and *ccp* Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.24 let the unit cell edge length be 'a' and face diagonal AC = b.

In Δ ABC

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

$= a^2 + a^2 = 2a^2$ or

$b = \sqrt{2}a$

If *r* is the radius of the sphere, we find

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

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

(we can also write, $r = \dfrac{a}{2\sqrt{2}}$)
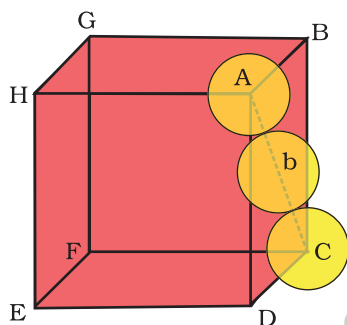
Fig. 1.24: *Cubic close packing other sides are not provided with spheres for sake of clarity.*

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $\left(2\sqrt{2}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

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

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

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.25, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

In Δ EFD,

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

$b = \sqrt{2}a$

Now in Δ AFD

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

$c = \sqrt{3}a$

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

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

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

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

Fig. 1.25: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\dfrac{4}{3}\right)\pi r^3$.

Volume of the cube, a^3 will be equal to $\left(\dfrac{4}{\sqrt{3}}r\right)^3$ or $a^3 = \left(\dfrac{4}{\sqrt{3}}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

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

$$= \frac{(8/3)\pi r^3 \times 100}{64/\left(3\sqrt{3}\right)r^3}\% = 68\%$$

1.7.3 Packing Efficiency in Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge (Fig. 1.26).
Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$a = 2r$

The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

Since a simple cubic unit cell contains only 1 atom

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

Fig. 1.26
Simple cubic unit cell. The spheres are in contact with each other along the edge of the cube.
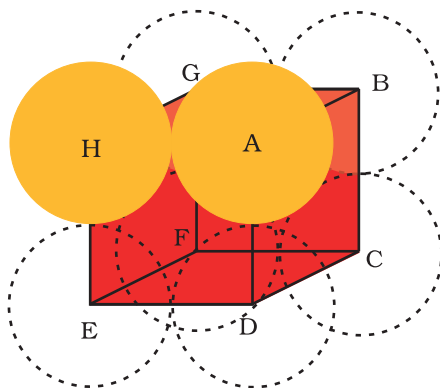
∴ Packing efficiency

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

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

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

Thus, we may conclude that *ccp* and *hcp* structures have maximum packing efficiency.

1.8 Calculations Involving Unit Cell Dimensions

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate method of determination of **Avogadro constant**. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is *a*, *d* the density of the solid substance and *M* the molar mass. In case of cubic crystal:

Volume of a unit cell = a^3

Mass of the unit cell

= number of atoms in unit cell × mass of each atom = $z \times m$

(Here *z* is the number of atoms present in one unit cell and *m* is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \text{ (M is molar mass)}$$

Therefore, density of the unit cell

$$= \frac{mass\,of\,unit\,cell}{volume\,of\,unit\,cell}$$

$$= \frac{z.m}{a^3} = \frac{z.M}{a^3.N_A} \quad or \quad d = \frac{zM}{a^3 N_A}$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (*d*, *z*, *M*, *a* and N_A), if any four are known, we can determine the fifth.

Example 1.3 An element has a body-centred cubic *(bcc)* structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm³. How many atoms are present in 208 g of the element?

Solution Volume of the unit cell = (288 pm)³

= (288×10⁻¹² m)³ = (288×10⁻¹⁰ cm)³

= 2.39×10⁻²³ cm³

Volume of 208 g of the element

$$= \frac{mass}{density} = \frac{208 g}{7.2\, g\, cm^{-3}} = 28.88\, cm^3$$

Number of unit cells in this volume

$$= \frac{28.88 cm^3}{2.39 \times 10^{-23} cm^3 / unit\ cell} = 12.08 \times 10^{23}\ \text{unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell) × 12.08 × 10²³ unit cells

$$= 24.16 \times 10^{23}\ \text{atoms}$$

X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10⁻⁸ cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm³, calculate the atomic mass of copper.

In case of *fcc* lattice, number of atoms per unit cell, z = 4 atoms

Therefore, $M = \dfrac{dN_A a^3}{z}$

$$= \frac{8.92\, g\, cm^{-3} \times 6.022 \times 10^{23}\, atoms\, mol^{-1} \times (3.608 \times 10^{-8} cm)^3}{4\, atoms}$$

= 63.1 g/mol

Atomic mass of copper = 63.1u

Silver forms *ccp* lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

Since the lattice is *ccp*, the number of silver atoms per unit cell = z = 4

Molar mass of silver = 107.9 g mol⁻¹ = 107.9×10⁻³ kg mol⁻¹

Edge length of unit cell = a = 408.6 pm = 408.6×10⁻¹² m

Density, $d = \dfrac{z.M}{a^3 .N_A}$

$$= \frac{4 \times (107.9 \times 10^{-3} kg\, mol^{-1})}{(408.6 \times 10^{-12} m)^3 (6.022 \times 10^{23} mol^{-1})} = 10.5 \times 10^3\ \text{kg m}^{-3}$$

= 10.5 g cm⁻³

Intext Questions

1.13 What is the two dimensional coordination number of a molecule in *square close*-packed layer?

1.14 A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

1.9 Imperfections in Solids

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, *point defects* and *line defects*. **Point defects** are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the *line defects* are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called *crystal defects*. We shall confine our discussion to point defects only.

1.9.1 Types of Point Defects

Point defects can be classified into three types : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

(a) Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called *intrinsic* or **thermodynamic defects.** Basically these are of two types, vacancy defects and interstitial defects.

(i) *Vacancy Defect*: When some of the lattice sites are vacant, the crystal is said to have **vacancy defect** (Fig. 1.27). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

(ii) *Interstitial Defect*: When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have **interstitial defect** (Fig. 1.28). This defect increases the density of the substance.

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

Fig. 1.27: Vacancy defects

(iii) *Frenkel Defect*: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 1.29). It creates a *vacancy defect* at its original site and an **interstitial defect** at its new location.
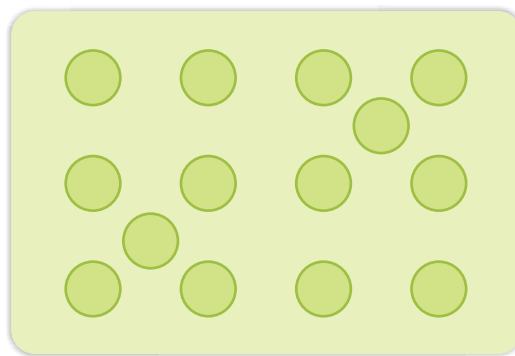
Fig. 1.28: Interstitial defects

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

(iv) *Schottky Defect*: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig. 1.30).
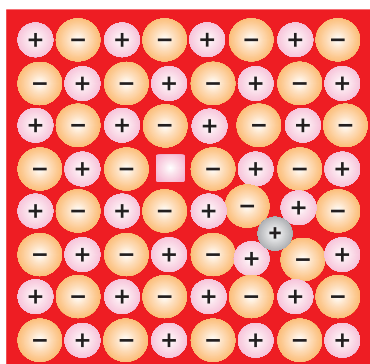
Fig. 1.29: Frenkel defects
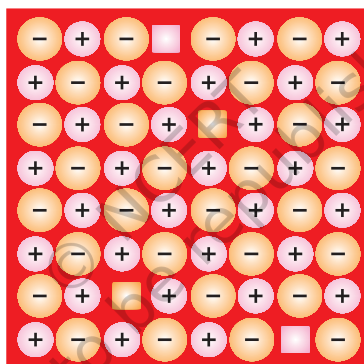
Fig. 1.30: Schottky defects

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

(b) **Impurity Defects**

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig.1.31). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.
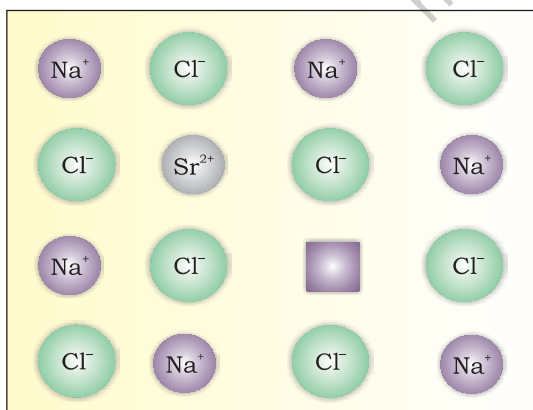
Fig. 1.31: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect

- *Metal excess defect due to anionic vacancies*: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.32). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).
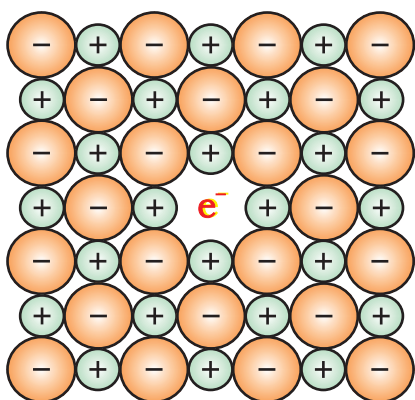
Fig. 1.32: An F-centre in a crystal

- *Metal excess defect due to the presence of extra cations at interstitial sites*: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

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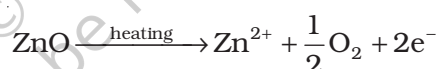
Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) Metal Deficiency Defect

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

1.10 Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^7 ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(i) *Conductors*: The solids with conductivities ranging between 10^4 to 10^7 ohm^{-1}m^{-1} are called conductors. Metals have conductivities in the order of 10^7 ohm^{-1}m^{-1} are good conductors.

(ii) *Insulators* : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.

(iii) *Semiconductors* : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm^{-1}m^{-1}.

1.10.1 Conduction of Electricity in Metals

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band.** If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity (Fig. 1.33 a).

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator (Fig. 1.33 b).

1.10.2 Conduction of Electricity in Semi-conductors

In case of semiconductors, the gap between the valence band and conduction band is small (Fig. 1.33 c). Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors.**

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called
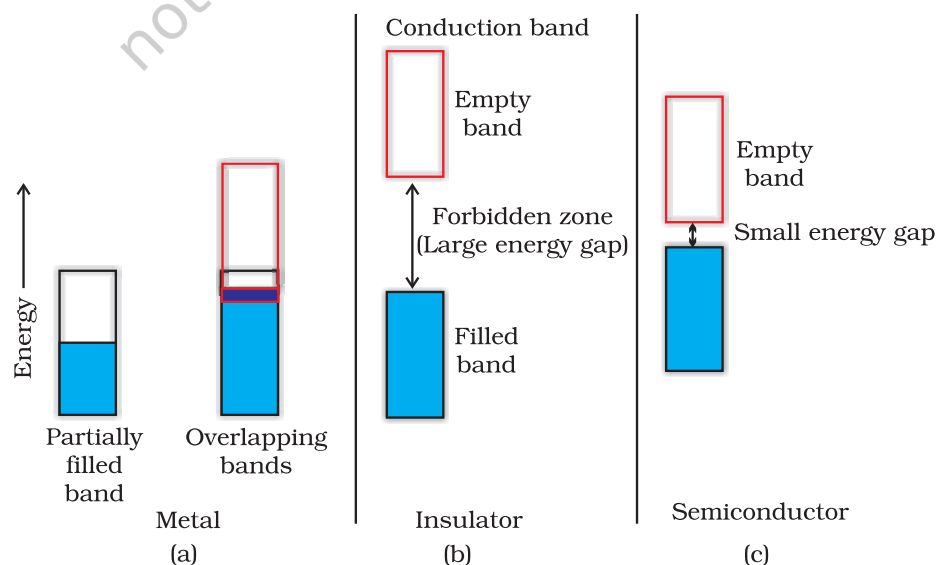
Fig. 1.33 Distinction among (a) metals (b) insulators and (c) semiconductors. In each case, an unshaded area represents a conduction band.

Conduction band

Empty band

Forbidden zone (Large energy gap)

Filled band

Empty band

Small energy gap

Energy →

Partially filled band

Overlapping bands

Metal
(a)

Insulator
(b)

Semiconductor
(c)

doping. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electronic defects* in them.

(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours (Fig. 1.34 a). When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal (Fig. 1.34 b). Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the *negatively* charged electron, hence silicon doped with electron-rich impurity is called *n*-type semiconductor.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called *electron hole* or **electron vacancy** (Fig. 1.34 c). An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an **electron hole** at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called *p-type* semiconductors.

Silicon atom   Mobile electron   Positive hole (no electron)

Perfect crystal   n-type   p-type

(a)   (b)   (c)
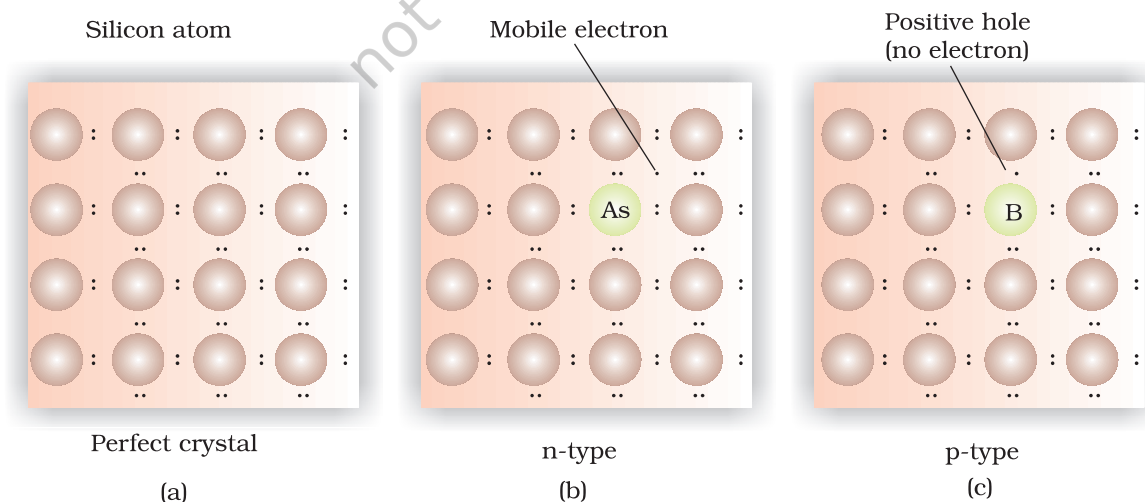
Fig. 1.34: *Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements.*

Applications of n-type and p-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. *Diode* is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier. Transistors 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.

Germanium 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 15 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.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

1.11 Magnetic Properties

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis (Fig. 1.35). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called **Bohr magneton**, μ_B. It is equal to 9.27×10^{-24}A m².
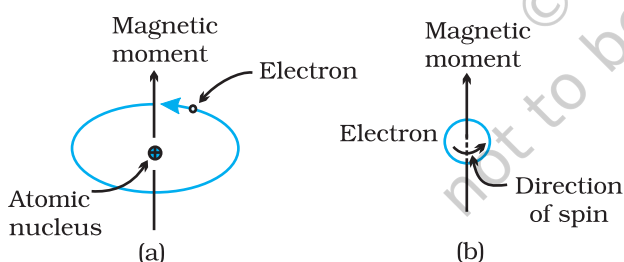
Fig.1.35: *Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.*

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) *Paramagnetism*: Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

(ii) *Diamagnetism*: Diamagnetic substances are weakly repelled by a magnetic field. H_2O, NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) *Ferromagnetism*: A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field (Fig. 1.36 a) and a strong magnetic effect is produced. This ordering of domains persist even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) *Antiferromagnetism*: Substances like MnO showing anti-ferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment (Fig. 1.36 b).

(v) *Ferrimagnetism*: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers (Fig. 1.36c). They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.
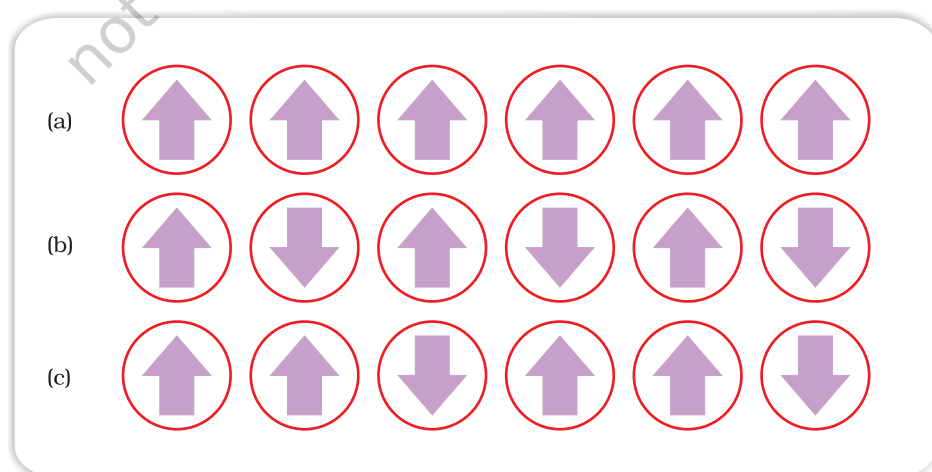
Fig 1.36: Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.

1.18 What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

1.19 What type of stoichiometric defect is shown by:
(i) ZnS (ii) AgBr

1.20 Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

1.21 Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

1.22 A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

1.23 What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Summary

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them. In **amorphous** solids, the arrangement of constituent particles has only **short range order** and consequently they behave like **super cooled liquids**, do not have sharp melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have sharp melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of **crystalline** solids depend upon the nature of interactions between their constituent particles. On this basis, they can be divided into four categories, namely: **molecular**, **ionic**, **metallic** and **covalent** solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each **lattice point** gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called **Bravais lattices**. Each lattice can be generated by repeating its small characteristic portion called **unit cell**. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either **primitive** which have particles only at their corner positions or **centred**. The centred unit cells have additional particles at their body centre (**body-centred**), at the centre of each face (**face-centred**) or at the centre of two opposite faces (**end-centred**). There are seven types of **primitive unit** cells. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen **Bravais lattices**.

Close-packing of particles result in two highly efficient lattices, **hexagonal close-packed** (**hcp**) and **cubic close-packed** (**ccp**). The latter is also called face-centred cubic (**fcc**) lattice. In both of these packings 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less

efficient packing of particles. While in **body-centred cubic lattice** (**bcc**) 68% space is filled, in simple cubic lattice only 52.4 % space is filled.

Solids are not perfect in structure. There are different types of **imperfections** or **defects** in them. Point defects and line defects are common types of defects. Point defects are of three types - **stoichiometric defects**, **impurity defects** and **non-stoichiometric defects**. **Vacancy defects** and **interstitial defects** are the two basic types of stoichiometric point defects. In ionic solids, these defects are present as **Frenkel** and **Schottky defects**. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of **metal excess type** and **metal deficient type.** Sometimes calculated amounts of impurities are introduced by **doping in semiconductors** that change their electrical properties. Such materials are widely used in electronics industry. Solids show many types of magnetic properties like **paramagnetism**, **diamagnetism**, **ferromagnetism**, **antiferromagnetism** and **ferrimagnetism**. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures.

Exercises

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

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

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

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

1.4   (i) What is meant by the term 'coordination number'?
     (ii) What is the coordination number of atoms:
          (a) in a cubic close-packed structure?
          (b) in a body-centred cubic structure?

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

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

1.7 How will you distinguish between the following pairs of terms:
   (i) Hexagonal close-packing and cubic close-packing?
   (ii) Crystal lattice and unit cell?
   (iii) Tetrahedral void and octahedral void?

1.8 How many lattice points are there in one unit cell of each of the following lattice?
   (i) Face-centred cubic
   (ii) Face-centred tetragonal
   (iii) Body-centred

1.9 Explain
   (i) The basis of similarities and differences between metallic and ionic crystals.
   (ii) Ionic solids are hard and brittle.

1.10 Calculate the efficiency of packing in case of a metal crystal for
   (i) simple cubic
   (ii) body-centred cubic
   (iii) face-centred cubic (with the assumptions that atoms are touching each other).

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

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

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

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

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

1.16 Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

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

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

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

1.20 Classify each of the following as being either a p-type or a n-type semiconductor:
   (i) Ge doped with In   (ii) Si doped with B.

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

1.22 In terms of band theory, what is the difference
   (i) between a conductor and an insulator
   (ii) between a conductor and a semiconductor?

1.23 Explain the following terms with suitable examples:
   (i) Schottky defect (ii) Frenkel defect (iii) Interstitials and (iv) F-centres.

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

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

1.26 Explain the following with suitable examples:
   (i) Ferromagnetism
   (ii) Paramagnetism
   (iii) Ferrimagnetism
   (iv) Antiferromagnetism
   (v) 12-16 and 13-15 group compounds.

Answers to Some Intext Questions

1.13 4

1.14 Total number of voids = 9.033×10^{23}

Number of tetrahedral voids = 6.022×10^{23}

1.15 M_2N_3

1.17 ccp