Notes

6

THE SOLID STATE

You are aware that the matter exists in three different states viz., solid, liquid and gas. In these, the constituent particles (atoms, molecules or ions) are held together by different forces of attraction between them. However, the nature and magnitude of the forces varies. In the first two lessons of this module you have learnt about the gaseous and the liquid states of matter. In this lesson you would learn about solid state- a compact state of matter. The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them. Here, you would learn about structure, classification and properties of solids.

OBJECTIVES

After reading this lesson, you should be able to:

- explain the nature of solid state;
- explain the properties of solids in terms of packing of particles and intermolecular attractions;
- differentiate between crystalline and amorphous solids;
- explain the melting point of a solid;
- classify the crystalline solids according to the forces operating between the constituent particles;
- define the terms crystal lattice and unit cell;
- describe different types of two dimensional and three dimensional unit cells;
- explain different types of packing in the solids;
- define coordination number;

MODULE - 3

States of Matter

Notes

- calculate the number of particles in simple cubic, face-centrad cubic and body centered cubic unit cells;

- relate the density of a solid to the properties of its unit cell;

- calculate the packing efficiency of simple cubic body central cubic and CCP/HCP lattices;

- define radius ratio;

- correlate the radius ratio with the structure of solids;

- explain the structure of simple ionic compounds;

- explain Frenkel and Schottky defects;

- classify solids on the basis of their electrical and magnetic properties; and

- explain the effect of doping of semiconductors by electron deficit and electron rich impurities.

6.1 NATURE OF SOLID STATE

You have learnt in lesson 6 that according to *Kinetic Molecular Theory*, the gases consist of a large number of molecules, which are in constant random motion in all directions in the available space. These molecules have very weak or negligible forces of attraction between them. A sample of gas can be compressed, as there is a lot of free space between the molecules Fig. 6.1(a) In liquids Fig. 6.1(b) on the other hand the molecules are also in constant motion but this motion is relatively restricted. Since there is very little free space available between the molecules the liquids are relatively incompressible.

(a)   (b)   (c)
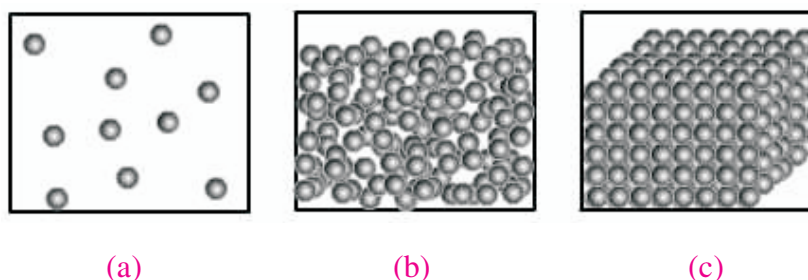
Fig. 6.1: *A pictorial representation of the three states of matter: (a) gas (b) liquid and (c) solid state.*

In solid state the constituent particles are arranged in a closely packed ordered arrangement Fig. 6.1 (c) with almost no free space. They can just vibrate about their fixed positions. These are in close contact and cannot move around like the molecules of a gas or a liquid. As a consequence, the solids are incompressible, rigid and have a definite shape. Like liquids, the volume of a solid is independent of the size or the shape of the container in which it is kept.

6.2 CLASSIFICATION OF SOLIDS

On the basis of nature of arrangements of the constituent particles the solids are classified into amorphous and crystalline solids.

6.2.1 Amorphous and Crystalline Solids

In **crystalline solids** the constituent particles are arranged in a regular and periodic pattern and give a well defined shape to it. The term 'crystal' comes from the Greek word, *krustallos* meaning ice. The regular pattern extends throughout the solid and such solids are said to have **long range order**. On the other hand, some solids have only a short range of order. This means that the particles are arranged regularly in only some regions of the solid and are relatively disordered in other regions. Such solids are called **amorphous solids**. In Greek, *a* means without and *morph* means form. Thus the word *amorphous* means without form. Sodium chloride and sucrose are common examples of crystalline solids while glass, fused silica, rubber and high molecular mass polymers are some examples of amorphous solids.

An important difference between the amorphous and crystalline solids is that while amorphous solids are **isotropic** in nature (i.e., these exhibit same value of some physical properties in all directions) the crystalline solids are **anisotropic** (i.e., the values of some physical properties are different in different directions). Refractive index and coefficient of thermal expansion are typical physical properties, which have different values when measured along different directions of a given crystal. Another difference between amorphous and crystalline solids is that while crystalline solids have a sharp or definite melting point, whereas the amorphous solids do not have definite melting point, these melt over a range of temperature.

The crystalline solids can be further classified on the basis of nature of interaction between the constituent particles as discussed below.

6.2.2 Classification of Crystalline Solids

In crystalline solids the constituent particles are arranged in an ordered arrangement and are held together by different types of attractive forces. These forces could be coulombic or electrostatic, covalent, metallic bonding or weak intermolecular in nature. The differences in the observed properties of the solids are due to the differences in the type of forces between the constituting particles. The types of forces binding the constituent particles can be used as a basis for classification of crystalline solids. On this basis, the crystalline solids can be classified into four different types- ionic, molecular, covalent and metallic solids. The characteristics and the properties of different types of solids are compiled in Table 6.1.

Notes

Table 6.1: Characteristics and properties of different types of solids.

Type of Solid	Constituent Particles	Nature of interaction between the particles	Appearance	Melting Point	Examples
Ionic	Ions	Coulombic	Hard and brittle	High	Sodium chloride, zinc sulphide, etc
Molecular Non polar Polar	Molecules	van der Waals Dipole-dipole	Soft brittle	low	Iodine, naphthalene water carbon dioxide.
Covalent	Atoms	Covalent bonding	Hard	Very high	Diamond, graphite, silica, etc.
Metallic	Atoms	Metallic bonding	Hard and malleable	Variable	Copper, silver, etc.

Sodium chloride is an example of an ionic solid because in this case the sodium ions and chloride ions are attracted to each other by electrostatic interactions. Iodine on the other hand is an example of a molecular solid because in this the molecules are held together by weak van der Waals forces. Diamond, with strong covalent bonds between the constituent carbon atoms is an example of covalent solids while in metals a large number of positive cores of the atoms are held together by a sea of electrons.

6.3 PROPERTIES OF CRYSTALLINE SOLIDS

You are familiar with the following properties of solids on the basis of handling solids in day to day work.

- Solids are rigid in nature and have well defined shapes

- Solids have a definite volume irrespective of the size and shape of the container in which they are placed

- Solids are almost incompressible.

You are familiar with a number of crystalline solids like sugar, rock salt, alum, gem stones, etc. You must have noticed that such solids have smooth surfaces. These are called 'faces' of the crystal. These faces are developed in the process of crystal formation by ordered arrangements of the constituent particles. It is generally observed that the faces of crystals are developed unequally. The internal angle between a pair of faces is called **interfacial angle** and is defined as the angle between the normals to the intersecting faces. An important characteristic of crystalline solids is that irrespective of the size and shape of the crystal of a given substance, the interfacial angle between a pair of faces is always the same.

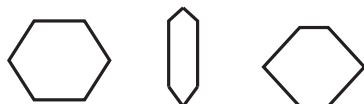This fact was stated by Steno as *the law of constancy of interfacial angles* (Fig. 6.2).

Fig. 6.2 *The constancy of interfacial angles*

6.3.1 Melting Point of a Solid

What is the effect of heat on a solid? You would have observed that when a solid is heated it becomes hot and eventually gets converted into a liquid. This process of conversion of a solid to a liquid on heating is called **melting.** You would also have observed that different solids need to be heated to different extents to convert them to liquids. The temperature at which a solid melts to give a liquid is called its **melting point.** Every solid is characterized by a definite melting point. This in fact is a test of the purity of the solid. The melting point of a solid gives us an idea about the nature of binding forces between constituent particles of the solid. Solids like sodium chloride (m.p = 1077 K) have very high melting points due to strong coulombic forces between the ions constituting it. On the other hand molecular solids like naphthalene (m.p. = 353 K) have low melting points.

The effect of heat on a solid can be understood in terms of energy and motion of the constituent particles. You are aware that in a solid the constituent particles just vibrate about their mean position. As the heat is supplied to the solid, the constituent particles gain energy and start vibrating more vigorously about their equilibrium positions. As more and more heat is supplied, the energy keeps on increasing and eventually it becomes greater than the binding forces between them. As a consequence the solid is converted into a liquid.

INTEXT QUESTIONS 6.1

a) Differentiate between solid, liquid and gaseous state.

b) How are solids classified on the basis of the intermolecular forces.

c) What is Steno's law of constancy of interfacial angles?

6.4 CRYSTAL LATTICE AND UNIT CELLS

You know, the crystalline solids have long-range order and the closely packed constituent particles are arranged in an ordered three dimensional pattern. The

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structure of the crystalline solids can be represented as an ordered three dimensional arrangement of points. Here each point represents the location of a constituent particle and is known as **lattice point** and such an arrangement is called a **crystal lattice** or **space lattice** or simply a **lattice.**

6.4.1 Two Dimensional Lattice and Unit Cells

To understand the meaning of the term *lattice*, let us first start with a two dimensional lattice. A two dimensional lattice has a set of points arranged in a regular pattern on a plane or a surface (in two dimensions). One such lattice is shown in Figure 6.4(a). The arrangement of lattice points is as shown in Fig. 6.4(a). When these lattice points are joined, the geometry of the lattice becomes clear (Fig. 6.4(b). The entire pattern can be generated by repeating a set of four points. On joining these points we get a **unit cell** of the lattice (shown in dark). The unit cell of a two dimensional lattice is a parallelogram which is defined in terms of two sides a and b and the angle between them γ. Only five types of unit cells are possible in two dimensional lattice. These are shown in Fig. 6.4(b).
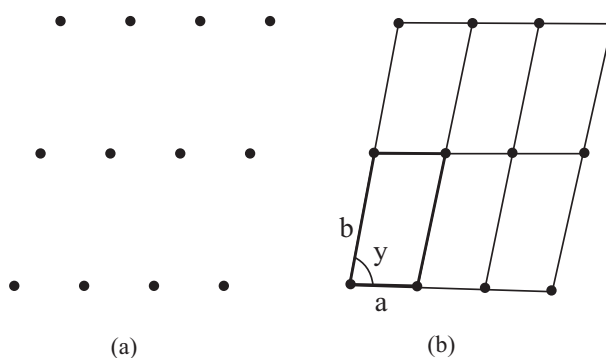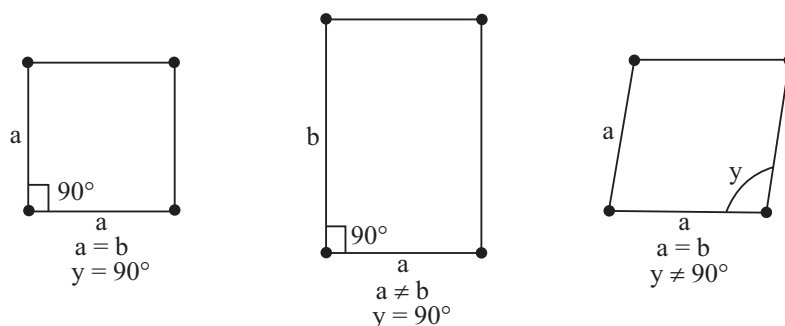

(a)   (b)

Fig. 6.3 (a) A two dimensional lattice (b) and its unit cell

$a = b$
$y = 90°$

$a \neq b$
$y = 90°$

$a = b$
$y \neq 90°$
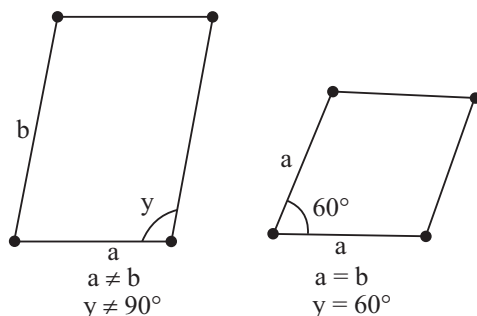
b

y

a

a ≠ b
y ≠ 90°

a

60°

a

a = b
y = 60°

Fig. 6.4: Five types of two dimensional unit cells

6.4.2 Three Dimensional Lattice and Unit Cells

In three dimensions, the crystal structure of a solid is represented as a three dimensional array of lattice points. Remember that the lattice points represent the positions of the constituent particles of the solid (Fig. 6.5(a)).
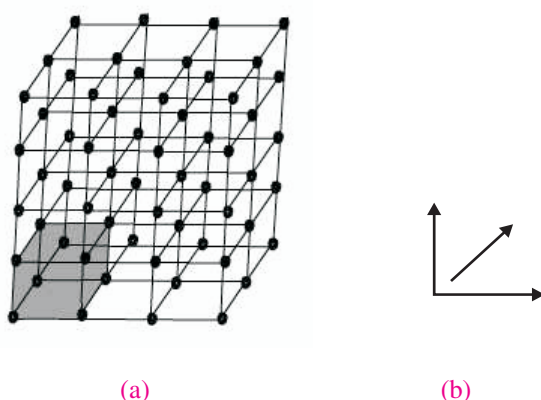

(a)   (b)

Fig. 6.5: *Schematic representation of a three dimensional crystal lattice.*

In a crystal lattice we can select a group of points which can be used to generate the whole lattice. Such a group is called **repeat unit** or the **unit cell** of the crystal lattice. The shaded region in the Fig. 6.5(a) represents a unit cell of the crystal lattice. The unit cell is characterized by three distances along the three edges of the lattice (a, b and c) and the angles between them (α, β and γ) as shown in the Fig. 6.5(b). We can generate the whole crystal lattice by repeating the unit cell in the three directions.

On the basis of the external appearance the known crystals can be classified into seven types. These are called **crystal systems**. In terms of the internal structure also the crystal lattices contain only seven types of unit cells. The seven crystal systems and the definition of their unit cells in terms of their unit distances and the angles are compiled in Table 6.2. The seven simple unit cells are given in Fig. 6.6.

Notes

Table 6.2: The seven crystal systems and their possible lattice types.

Systems	Axes	Angles	Possible lattice types
Cubic	$a = b = c$	$a = \beta = \gamma = 90°$	P, F, I
Tetragonal	$a = b \neq c$	$a = \beta = \gamma = 90°$	P, I
Orthorhombic	$a \neq b = c$	$a = \beta = \gamma = 90°$	P, F, I, C
Rhombohedral	$a = b = c$	$a = \beta = \gamma \neq 90°$	P
Hexagonal	$a = b \neq c$	$a = \beta = 90°; \gamma = 120°$	P
Monoclinic	$a \neq b = c$	$a = \gamma = 90°; \beta \neq 90°$	P, I
Triclinic	$a \neq b \neq c$	$a \neq \beta \neq \gamma \neq 90°$	P

* P= primitive, I= body centered, F= face centered and C= side centered

The unit cell shown in Fig. 6.5 and the ones given in Fig..6.5 have the lattice points at the corners only.
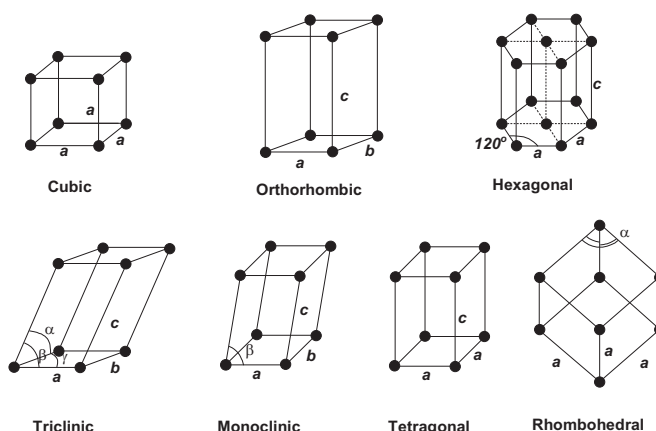

Fig. 6.6 : *The primitive unit cells; the relative dimensions of the three repeat distances (a, b and c) and the angles between them (a, β and γ) are given in Table 6.2.*

Such unit cells are called **primitive** (P) unit cells. Sometimes, the unit cell of a crystal contains lattice point(s) in addition to the ones at the corners. A unit cell containing a lattice point each at the centers of its faces in addition to the lattice points at the corners is called a **face centered** (F) unit cell. On the other hand a unit cell with lattice points at the center of the unit cell and at the corners is called a **body centered** unit cell (I). In some cases, in addition to the lattice points at the corners there are two lattice points located at the centers of any two opposite faces. These are called as **end centered** (C) unit cells. The possible lattice types in different crystal systems are also indicated in Table 6.2. The seven crystal systems when combined with these possibilities give rise to 14 lattice types. These are called **Bravais lattices**.

6.5 NUMBER OF ATOMS IN CUBIC UNIT CELLS

Of the seven crystal systems, let us discuss unit cells belonging to the cubic crystal system in somewhat details. As you can see from Table 6.2 that in the cubic crystal system the three repeat distances are equal and all the three angles are right angles. The unit cells of three possible lattice types viz., primitive or simple cubic, body centered cubic and the face centered cubic, belonging to cubic crystal system are shown in Figure 6.7.

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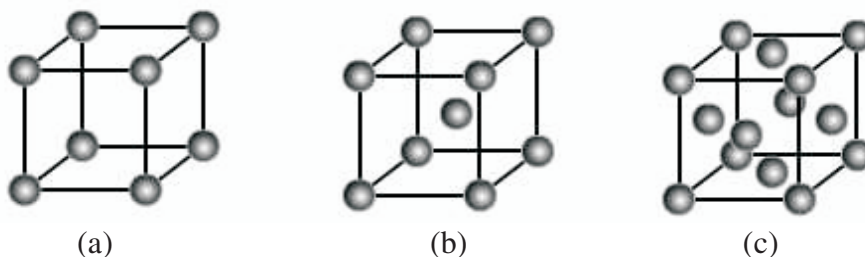
Fig. 6.7: *(a) primitive or simple (b) body centered and (c) face centered cubic unit cells.*

Number of atoms per unit cell

As you know that in unit cells the atoms can be on the corners, in the body center and on face centers. All the atoms do not belong to a single unit cell. These are shared amongst different unit cells. It is important to know the number of atoms per unit cell. Let us learn how to compute these for different cubic unit cells.

(a) Simple Cubic Unit Cell

The simple or primitive unit cell has the atoms at the corners of the cube (Fig. 6.7 (a)). A lattice point at the corner of the unit cell is shared by eight unit cells as you can see from the encircled atom in the Fig. 6.8. Therefore, the contribution of an atom at the corner to the unit cell will be 1/8. The number of atoms per unit cell can be calculated as follows:

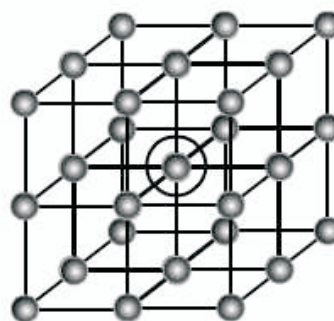**Fig. 6.8:** *A corner lattice point is shared by eight unit cells*

Number of corner atoms = 8

Contribution of each corner atom = $\dfrac{1}{8}$

The number of atoms in a simple cubic unit cell = $8 \times \dfrac{1}{8} = 1$

(b) Body Centered Cubic Unit Cell

A body centered cubic (*bcc*) unit cell has lattice points not only at the corners but

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also at the center of the cube(Fig. 6.7 (b)). The atom in the center of the cube belongs entirely to the unit cell, i.e., it is not shared by other unit cells. Each corner atom, on the other hand, as in the case of simple cubic unit cell, is shared by eight unit cells. Thus the number of atoms per unit cell can be calculated as

Number of corner atoms $= 8$

Contribution of each corner atom $= \dfrac{1}{8}$

$\therefore$ Contribution of all the corner atoms to the unit cell $= 8 \times \dfrac{1}{8} = 1$
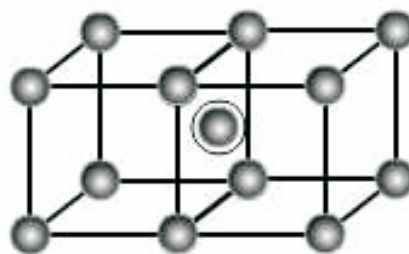
Number of atoms at the center of the cube $= 1$

Contribution to the unit cell $= 1$ (as it is not shared)

The number of atoms in a body centered cubic unit cell $= 1 + 1 = 2$

(c) Face Centered Cubic Unit Cell

A face centered cubic (fcc) unit cell has atoms not only at the corners but also at the center of each face. Thus it has eight lattice points at the corners and six at the face centers (Fig. 6.7 (c)). A face centered lattice point is shared by two unit cells, as shown in Fig. 6.9.

Fig. 6.9: *A face centered lattice point is shared by two unit cells*

Number of corner atoms $= 8$

Contribution of each corner atom $= \dfrac{1}{8}$

Contribution of all the corner atoms to the unit cell $= 8 \times \dfrac{1}{8} = 1$

Number of atoms at the face center $= 6$

Contribution of each atom at the face centre $= \dfrac{1}{2}$

Contribution of all the face centered atoms to the unit cell $= 6 \times \dfrac{1}{2} = 3$

The number of atoms points in a face centered cubic unit cell $= 1 + 3 = 4$

The number of atoms per unit cell in different types of cubic unit cells is given in Table 6.3.

Table. 6.3: Number of atoms per unit cell

S.No.	Type of unit cell	No. of atoms per unit cell
1.	Simple cubic	1
2.	Body centered cubic	2
3.	Face centered cubic	4

Notes

6.6 CALCULATION OF DENSITY OF UNIT CELL

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

(i) **Volume of Unit cell**

If the edge length of the cubic unit cell is 'a' its volume is a^3

(ii) **Mass of the Unit cell**

Let the molar mass of substance $= M$

$\therefore$ Mass of one atom or molecule $= \dfrac{M}{N_A}$

Where N_A = Avogadro's constant.

Let the number of atoms or molecules of the substance present per unit cell $= z$

(See table 6.3 for values of z for different type of cubic unit cells)

$\therefore$ Mass of unit cell $=$ (number of atoms/molecules present per unit cell)

$\times$ (mass of one atom/molecule)

$$= \frac{z \cdot M}{N_A}$$

(iii) **Density**

$$\text{Density} = \frac{\text{Mass of one unit cell}}{\text{Volume of one unit cell}}$$

$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Density of the unit of cell of a substance is the same as the density of the substance. In case of ionic substances, the formula unit is taken as one particle. (For example, formula unit of NaCl = $1Na^+ + 1Cl^-$ ions; of Na_2SO_4 = $2Na^+$ + $1SO_4^{2-}$ ions).

Notes

The above relation can be used to calculate z and hence the nature of cubic lattice if d and M are known or M if d and z are known

Example. The unit cell of a metallic element is face centred cubic and the side of the cube is 540.2 pm. Calculate the density of the metal in gcm^{-3} if its relative atomic mass is 202.4.

Solution

$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Given:

Side of the cube $= a = 540.2$ pm $= 540.2 \times 10^{-10}$ cm

Number of atoms per unit cell of a face-centred cubic unit cell $= z = 4$

Molar mass of the element, $M = 202.4$ g mol^{-1}

Putting these values in the above relation

$$d = \frac{4 \times 202.4 \text{ g mol}^{-1}}{(540.2 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{-23} \text{mol}^{-1})}$$

$$= 8.53 \text{ g cm}^{-3}$$

6.7 CLOSE PACKED STRUCTURES OF SOLIDS

In the process of the formation of a crystal the constituent particles get packed quite closely. The crystal structures of the solids can be described in terms of a close packing of identical spheres as shown in Fig. 6.10. These are held together by forces of attraction. Let us learn about the possible close packed structures of solids and their significance.

Fig. 6.10 : *Arrangement of identical spheres in one dimension*

A linear horizontal arrangement of identical spheres in one dimension forms a row (Fig. 6.10). A two dimensional close packed structure can be obtained by arranging a number of such rows to form a layer. This can be done in two possible ways. In one of these, we can place these rows in such a way that these are aligned as shown in (Fig. 6.11 (a)). In such an arrangement each sphere is in contact with four other spheres. This arrangement in two dimensions is called **square close packing.**

(a)   (b)
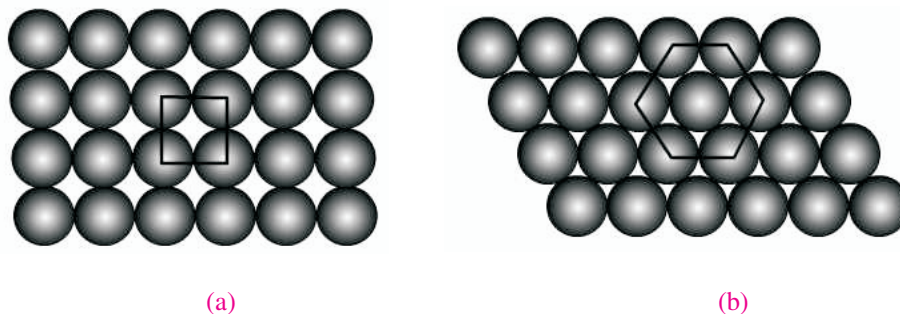
Fig. 6.11 : *(a) Square close packing and (b) hexagonal close packing of identical spheres in two dimensions*

In the other way we can place the spheres of the second row in the depressions of the first row and so on and so forth (Fig. 6.11(b)). You may notice that in such an arrangement each sphere is in contact with six other spheres. Such an arrangement in two dimensions is called hexagonal **close packing.** In such a packing, the spheres of the third row are aligned with the first row. You may also have noticed that in the hexagonal close packed the spheres are more efficiently packed. In Fig. 6.11 an equal number of identical spheres are arranged in two different types of packing.

A three dimensional structure can be generated by placing such two dimensional layers on top of each other. Before we move on to the three dimensional packing let us look at the hexagonal close packed layer some what more closely (Fig. 6.12).

You may note from Fig. 6.12 that in a hexagonal close packed layer there are some unoccupied spaces or voids. These are triangular in shape and are called **trigonal voids**. You can further note that there are two types of triangular voids, one with the apex pointing upwards and the other with the apex pointing down-wards. Let us call these as X type and Y type voids respectively as marked in the Fig. 6.12.

IIIrd row

IInd row

Ist row
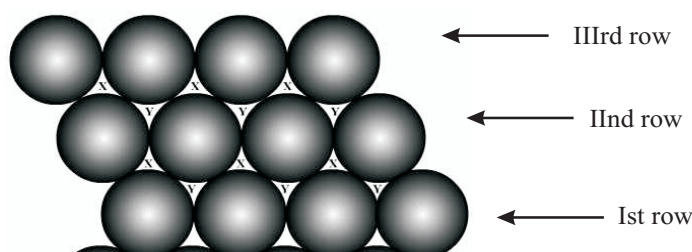
Fig. 6.12 : *A hexagonal Close Packed layer showing two types of triangular voids.*

Close Packed Structures in three dimensions

Let us take a hexagonal close packed layer and call it A layer and place another hexagonal close-packed layer (called the B layer) on it. There are two possibilities.

Notes

1. In one, we can place the second layer in such a way that the spheres of the second layer come exactly on top of the first layer.

2. In other, the spheres of the second layer are in such a way that these are on the depressions of the first layer. The first possibility is similar to square close packing discussed above and is accompanied by wastage of space. In the second possibility when we place the second layer into the voids of the first layer, the spheres of the second layer can occupy either the X or Y type trigonal voids but not both. You may verify this by using coins of same denomination. You would observe that when you place a coin on the trigonal void of a given type, the other type of void becomes unavailable for placing the next coin (Fig. 6.13).
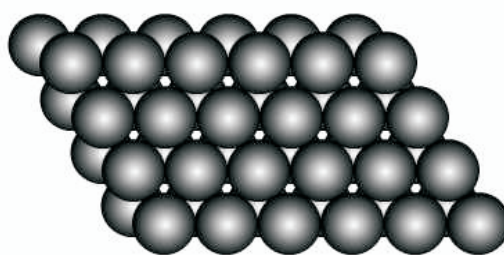
Fig. 6.13 : *Two layers of close packed spheres , the second layer occupies only one type (either X or Y) of triangular voids in the first layer.*

In this process, the sphere of second layer covers the trigonal voids of the first layer. It results into voids with four spheres around it, as shown in Fig. 6.14(a). Such a void is called a **tetrahedral void** since the four spheres surrounding it are arranged on the corners of a regular tetrahedron, Fig. 6.14(b). Similarly, the trigonal voids of the second layer will be placed over the spheres of the first layer and give rise to tetrahedral voids.

(a)   (b)
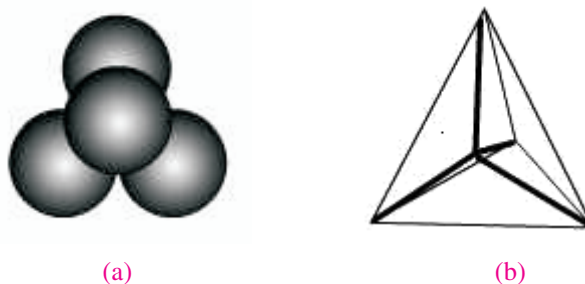
Fig. 6.14 : *A tetrahedral void*

In a yet another possibility, the trigonal voids of the first layer have another trigonal void of the opposite type (X type over Y and Y type over X type) from the second layer over it. This generates a void which is surrounded by six spheres, Fig..6.15 (a). Such a void is called an **octahedral void** because the six spheres

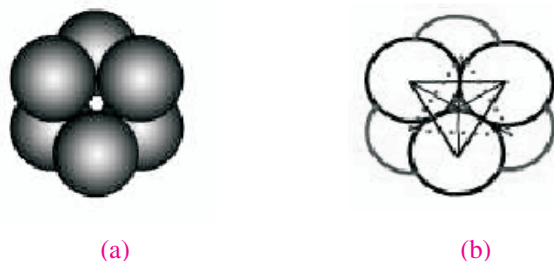surrounding the void lie at the corners of a regular octahedron, Fig..6.15 (b).

(a)   (b)

Fig. 6.15 :   *An octahedral void*

A closer look at the second layer reveals that it has a series of regularly placed tetrahedral and octahedral voids marked as 't' and 'o' respectively in Fig. 6.16.
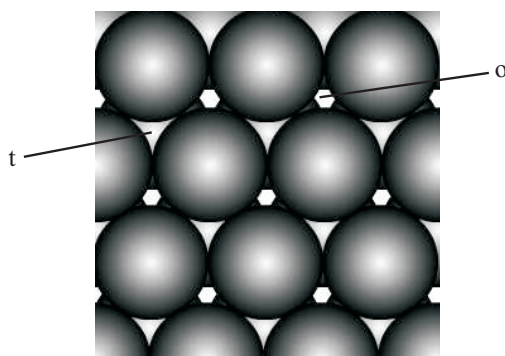

**Fig. 6.16 :** *The top view of the second layer showing the tetrahedral and octahedral voids.*

Now, when we place the third layer over the second layer, again there are two possibilities i.e., either the tetrahedral or the octahedral voids of the second layer are occupied. Let us take these two possibilities. If the tetrahedral voids of the second layer are occupied then the spheres in the third layer would be exactly on top (i.e., vertically aligned) of the first or A layer The next layer (4th layer) which is then placed would align with the B layer. In other words, every alternate layer will be vertically aligned. This is called AB AB …. pattern or AB AB …. repeat. On the other hand if the octahedral voids of the second layer are occupied, the third layer is different from both the first as well as the second layer. It is called the C layer. In this case the next layer, i.e., the fourth layer, howsoever it is placed will be aligned with the first layer. This is called ABC ABC …. pattern or ABC ABC.. …. repeat. In three dimensional set up the AB AB …. pattern or repeat is called **hexagonal closed packing** (hcp) (Fig. 6.10 (c) **)** while the ABC ABC …. pattern or repeat is called c**ubic closed packing** (ccp) (Fig. 6.17 (a)**)**.
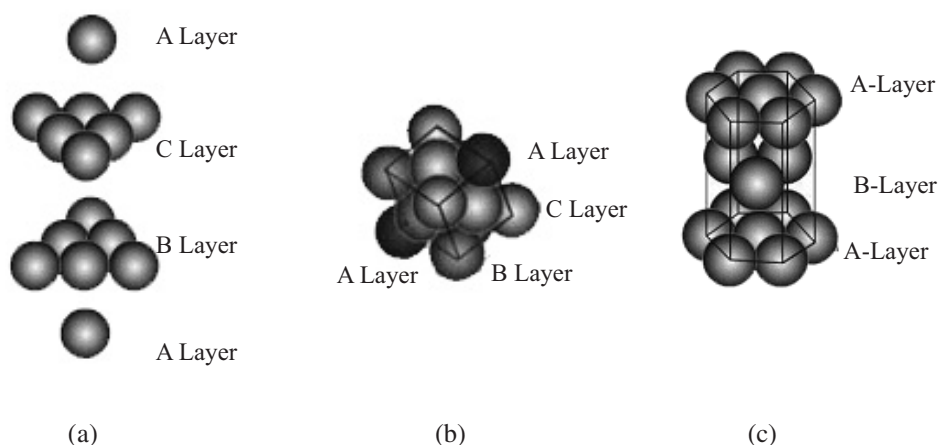
Fig. 6.17 : *(a) Cubic closed packing (ccp) as a result of ABC pattern of close packed spheres; (b) the layers in (a) tilted and brought closer to show fcc arrangement (c) hexagonal closed packing (hcp) as a result of ABAB pattern of close packed spheres.*

This process continues to generate the overall three dimensional packed structure. These three dimensional structures contain a large number of tetrahedral and octahedral voids. In general there is one octahedral and two tetrahedral voids per atom in the close packed structure. These voids are also called as **interstices.** As mentioned earlier, the identical spheres represent the positions of only one kind of atoms or ions in a crystal structure. Other kind of atoms or ions occupy these interstices or voids.

In the close packed structures (*hcp* and *ccp*) discussed above, each sphere is in contact with six spheres in its own layer (as shown in Fig. 6.12) and is in contact with three spheres each of the layer immediately above and immediately below it. That is, each sphere is in contact with a total of twelve spheres. This number of nearest neighbor is called its **coordination number**. The particles occupying the interstices or the voids will have a coordination number depending on the nature of the void. For example an ion in a tetrahedral void will be in contact with four neighbors i.e., would have a coordination number of four. Similarly the atom or ion in an octahedral void would have a coordination number of six.

INTEXT QUESTIONS 6.2

(a) What is the difference between the square close packed and hexagonal close packed structures?

(b) Which of the above two, is more efficient way of packing?

(c) Clearly differentiate between, trigonal, tetrahedral and octahedral voids.

6.8 PACKING EFFICIENCY

In all closed packed structures there are always some *voids* or empty spaces. The percentage of the total space that is filled by the constituent particles is called the **packing efficiency.** It is calculated from the following relation:

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100\%$$

It depends upon the nature of crystal lattice. For the three types of cubic lattices, the calculations are given below:

(1) **Packing Efficiency of Simple Cubic Lattice**

In simple cubic lattice, the constituent particles occupy only the corner positions of the cubic unit cell. These particles touch one another *along the edge of the cube* as shown in the Figure 6.18. Let *a* be the edge length of the cube and *r* the radius of the particle then
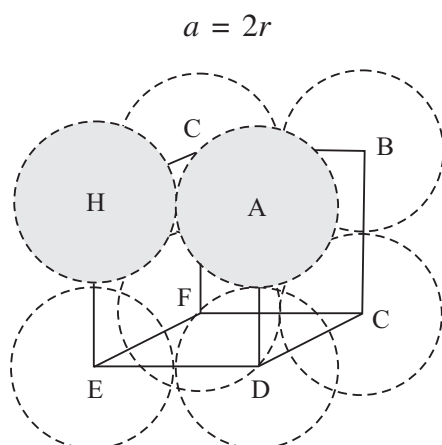
$$a = 2r$$

Fig. 6.18: Simple cubic unit cell

The volume of the cube = (edge length/side)^3 = a^3 = $(2r)^3$ = $8r^3$

No. of constituent particles present in each unit cell = 1

The volume of the filled space = volume of 1 particle = $\dfrac{4}{3}\pi r^3$

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100$$

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

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

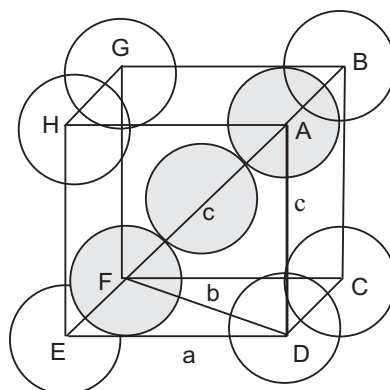(2) **Packing Efficiency of Body Centred Cubic Lattice**

Fig. 6.19. Body centred cubic until cell.

The body centred cubic unit cell has constitutent particles present at all its corners as well as at its body centre. The particle at the body-centre touches the particle at corner positions. Thus, the particles are in contact along the body-diagonal of the cube. Consider the body-diagonal AF along which the contact between the central particles with those at corners A and F has been shown in Fig. 6.19.

$\therefore$ Length of body-diagonal $AF = c = 4\ r$ (6.1)

(Whole of the central particle ($2r$) and one-half of each of the two corner particle ($r + r$) occupy the body-diagonal)

Length of the body-diagonal

In the triangle EFD on the face CDEF, $EF \perp ED$.

$\therefore$ $FD^2 = EF^2 + ED^2$

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

Where a is the edge-length or side of the cube.

In the triangle AFD, $AD \perp FD$

$\therefore$ $AF^2 = AD^2 + FD^2$

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

$\therefore$ $c = \sqrt{3}a$ (6.2)

But $c = 4r$

$\therefore \qquad a = \dfrac{4r}{\sqrt{3}}$ (6.3)

The number of constituent particles in a body-centred cubic unit cell = 2

$\therefore$ Volume of filled space $= 2 \times \dfrac{4}{3}\pi r^3$ (6.4)

Volume of the cubic unit cell $= a^3 = \left(\dfrac{4r}{\sqrt{3}}\right)^3$ (6.5)

Packing efficiency $= \dfrac{\text{filled space}}{\text{total space}} \times 100 = \dfrac{2 \times \dfrac{4}{3}\pi r^3}{\left(\dfrac{4r}{\sqrt{3}}\right)^3} \times 100$

$= \dfrac{\dfrac{8}{3}\pi r^3}{\dfrac{64}{3\sqrt{3}}r^3} \times 100 = \dfrac{\sqrt{3}\pi}{8} \times 100 = 68.0\%$

(3) **Packing Efficiency of *CCP* and *HCP* Lattices**

Cubic close packed or *face centred cubic (FCC)* and *hexagonal close packed* lattices have equal packing efficiency. Packing efficiency of face centred cubic (*FCC*) or cubic close packing (*CCP*) unit cell can be calculated with the help of Figure 6.20. Let the edge length or the side of the cubic unit cell be *a* and its face diagonal AC be *b*. In the triangle ABC, $AB \perp BC$, therefore,

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

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

or $\qquad b = \sqrt{2}a.$ (6.6)

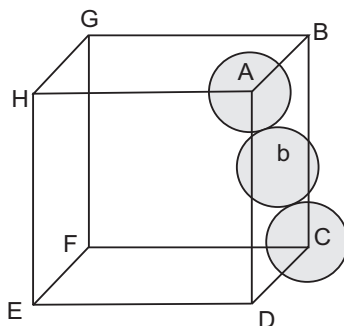**Fig. 6.20:** *Face centred cubic or cubic close packing unit cell*

Unit cell of *fcc* (or *ccp*) lattice has constituent particles at all the corners and at the centre of each face.

The particle of face-centre touches the particles occupying the corner positions of the same face.

$\therefore$ Length of the face diagonal AC $= b = 4r$ (6.7)

Where r is the radius of the constitutent particle (whole of central particle, $2r$, and one-half of each of the two corner particles, $r + r$)

From equations 1 and 2

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

or $$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$ (6.8)

The number of constituent particles in a face centred cubic unit cell = 4

$\therefore$ The Volume of filled space $= 4 \times \frac{4}{3}\pi r^3$

Volume of the cubic unit cell $= (\text{side})^3 = a^3 = (2\sqrt{2}r)^3$

Packing efficiency $= \dfrac{\text{filled space}}{\text{total space}} \times 100 = \dfrac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} \times 100$

$$= \frac{\frac{16}{3}\pi}{16\sqrt{2}} \times 100 = \frac{\pi}{3\sqrt{2}} = 74\%$$

Packing efficiencies of the three types of cubic lattices are summarized in the table 6.4.

Table 6.4: Packing efficiency of cubic unit cells

S.No.	Lattice	Packing Efficiency %
1.	Simple Cubic	52.4%
2.	Body Centred Cubic	68.0%
3.	Face Centred Cubic or Cubic close packing	74.0%

6.9 STRUCTURES OF IONIC SOLIDS

In case of ionic solids that consist of ions of different sizes, we need to specify the positions of both the cations as well as the anions in the crystal lattice. Therefore, structure adopted by an ionic solid depends on the relative sizes of the two ions. In fact it depends on the ratios of their radii (r+/r-) called **radius ratio**. Here r+ is the radius of the cation and r- is that of the anion. The radius ratios and the corresponding structures are compiled in Table 6.5.

Notes

Table 6.5 : The radius ratios (r + /r–) and the corresponding structures

| Radius ratio (r+/r–)	Coordination number	Structure adopted
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 0.91	8	Body centered cubic
>=1.00	12	Cubic Close Packed structure

The common ionic compounds have the general formulae as MX, MX_2, and MX_3, where M represents the metal ion and X denotes the anion. We would discuss the structures of some ionic compounds of MX and MX_2 types.

6.9.1 Structures of the Ionic Compounds of MX Type

For the MX type of ionic compounds three types of structures are commonly observed. These are sodium chloride, zinc sulphide and caesium chloride structures. Let us discuss these in some details.

(a) Caesium Chloride Structure

In CsCl the cation and the anions are of comparable sizes (the radius ratio = 0.93) and has a bcc structure in which each ion is surrounded by 8 ions of opposite type. The Cs^+ ions is in the body center position and eight Cl^- ions are located at the corners (Fig. 6.21) of the cube. Thus it has a coordination number of 8.

Caesium Ion

Chloride Ions
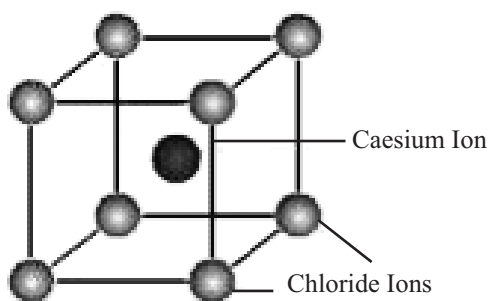
Fig. 6.21: *Caesium chloride structure*

(b) Sodium Chloride Structure

In case of NaCl the anion (Cl^-) is much larger than the cation (Na^+). It has a radius ratio of 0.52. According to Table 3.3 it should have an octahedral arrangement. In sodium chloride the(Cl^-) form a *ccp* (or *fcc*) structure and the sodium ion occupy the octahedral voids. You may visualise the structure having

chloride ions at the corners and the face centers and the sodium ions at the edge centers and in the middle of the cube (Fig. 6.22).
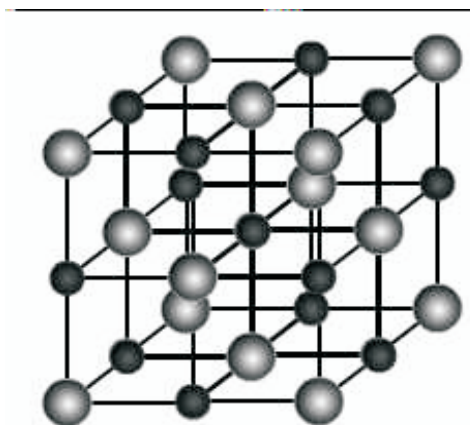

Fig. 6.22 : *Sodium chloride structure.*

(c) Zinc Sulphide Structure

In case of zinc sulphide the radius ratio is just = 0.40. According to Table 3.3 it should have an tetrahedral arrangement. In Zinc sulphide structure, the sulphide ions are arranged in a ccp structure. The zinc ions are located at the corners of a tetrahedron, which lies inside the cube as shown in the Fig. 6.23. These occupy alternate tetrahedral voids.

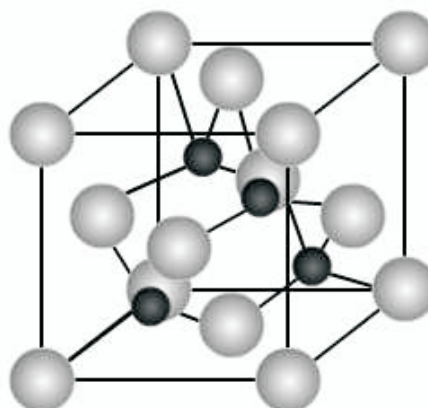**Fig. 6.23 :** *Zinc Sulphide structure.*
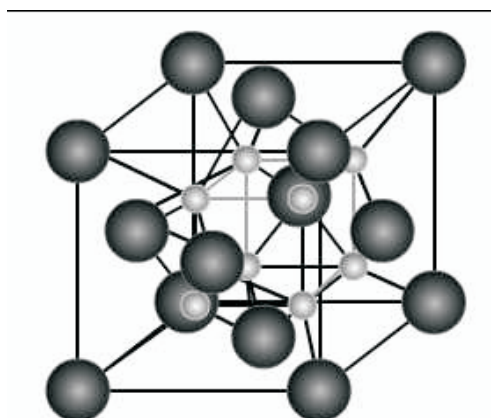
6.9.2 Structure of Ionic Compounds of MX$_2$ type

(a) Calcium fluoride or fluorite structure

In this structure the Ca^{2+} ions form a *fcc* arrangement and the fluoride ions are located in the tetrahedral voids (Fig. 6.24).

Fig. 6.24 : *Calcium fluoride or Fluorite structure; calcium ions occupy the corners of the cube and face centers The F⁻ ions are on the corners of the smaller cube which dipict the positions of tetrahedral void.*

(b) Antifluorite Structure

Some of the ionic compounds like Na_2O have antifluorite structure. In this structure the positions of cations and the anions in fluorite structures are interchanged. That is why it is called antifluorite structure. In Na_2O the oxide ions form the ccp and the sodium ions occupy the tetrahedral voids (Fig. 6.25).
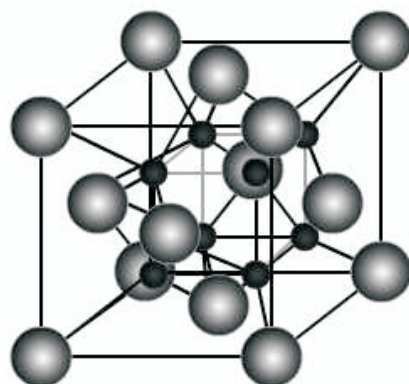
Fig. 6.25: *Antifluorite structure adopted by Na_2O; The oxide ions occupy the corners of the cube and face centers and the Na^+ ions (shown in black) are on the corners of the smaller cube.*

6.10 DEFECTS IN IONIC CRYSTALS

You have learnt that in a crystalline solid the constituent particles are arranged in a ordered three dimensional network. However, in actual crystals such a perfect order is not there. Every crystal has some deviations from the perfect order. These deviations are called imperfections or defects. These defects can be broadly grouped into two types. These are **stoichiometric** and

non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material. Here, we would deal only with stoichiometric defects. In such compounds the number of positive and negative ions are in stoichiometric proportions. There are two kinds of stoichiometric defects, these are

● Schottky defects

● Frenkel defects

(a) Schottky defects : This type of defect are due to the absence of some positive and negative ions from their positions. These unoccupied lattice sites are called holes. Such defects are found in ionic compounds in which the positive and negative ions are of similar size e.g., NaCl and CsCl. The number of missing positive and negative ions is equal. The presence of Schottky defects decreases the density of the crystal [Fig. 6.26(a)].

(b) Frenkel defects : This type of defect arise when some ions move from their lattice positions and occupy interstitial sites. The interstitial sites refer to the positions in between the ions. When the ion leaves its lattice site a hole is created there. ZnS and AgBr are examples of ionic compounds showing Frenkel defects. In these ionic compounds the positive and negative ions are of quite different sizes. Generally the positive ions leave their lattice positions, as these are smaller and can accommodate themselves in the interstitial sites. The Frenkel defects do not change the density of the solids [Fig. 6.26(b)].
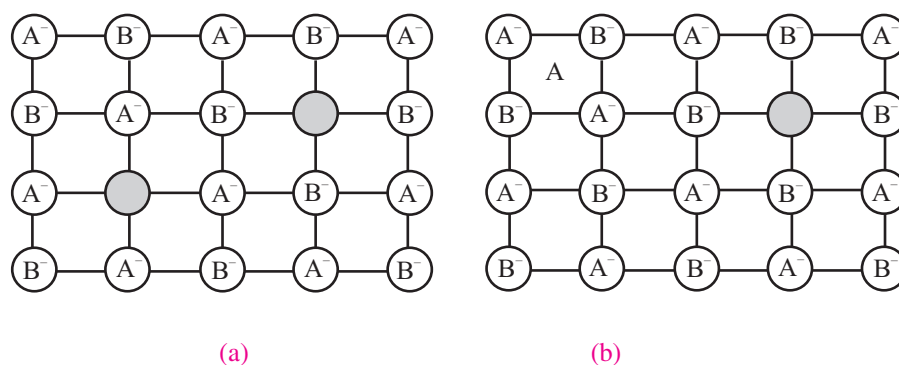
Fig. 6.26: *Stoichiometric defects a) Schottky and b) Frenkel defects*

These defects cause the crystal to conduct electricity to some extent. The conduction is due to the movement of ions into the holes. When an ion moves into a hole it creates a new hole, which in turn is occupied by another ion, and the process continues.

INTEXT QUESTIONS 6.3

(a) What do you understand by crystal lattice?

b) What is a unit cell ?

c) How many atoms are there in a fcc unit cell?

Notes

6.11 ELECTRICAL PROPERTIES

Conductance of electricity is an important property of a substance. Solids show a very wide range of conductivities from a high of 10^7 to a low of 10^{-20} s m^{-1}, thus spanning 27 orders of magnitude. Based upon their ability to conduct electricity, solids may be classified into three categories; conductors, insulators and semiconductors.

6.11.1 Conductors' Insulators and Semiconductors

(i) Conductors

These are the solids with conductivities ranging from 10^4 to 10^7 S m^{-1}. Metals conduct electricity through movement of their electrons and are called *electronic conductors*. Ionic solids conduct electricity when in molten state or dissolved in water, through movement of their ions. They are called *electrolytic conductors*.

(ii) Insulators

These are the solids with extremely low conductivities ranging from 10^{-20} to 10^{-10} S m^{-1}. Insulators are used to provide protective covering on conductors.

(iii) Semiconductors

These are the solids with intermediate conductivities ranging from 10^{-6} to 10^4 S m^{-1}. Although semiconductors have low conductivities, they find vide applications in solid state devices like diodes and transistors. Their conductivities can be modified by introduction of a suitable impurity.

6.11.2 Conduction of Electricity in Metals

Metals conduct electricity through movement of their electrons. In unit 5 you have learnt that when two atoms come closer, their atomic orbitals overlap and they form an equal number of molecular orbitals. One-half of these have lower energy while the other half have higher energy than the energy of the atomic orbitals. As the number of molecular orbitals increases, the energy-separation between them decreases.

In a piece of metal, the number of metal atoms is very large and so is the number of their valence orbitals. This results in formation of an equally large number of molecular orbitals which are so close to one-another that they form a continuous *band*. The band in which the valence electrons are present is called **valence band**. Electrons present in this band are strongly bound to the nucleus and cannot conduct electricity. The band formed by vacant molecular orbitals of higher energy is called **conduction band.** When electrons reach conduction band from valence band on excitation, they become loosely bound to the nucleus and can conduct electricity by moving under the influence of an electric field. Such electrons are also called *free electrons.* Conductivity of a solid depends upon how easy or difficult it is for the valence electrons to jump to the conduction band. See figure 6.27.
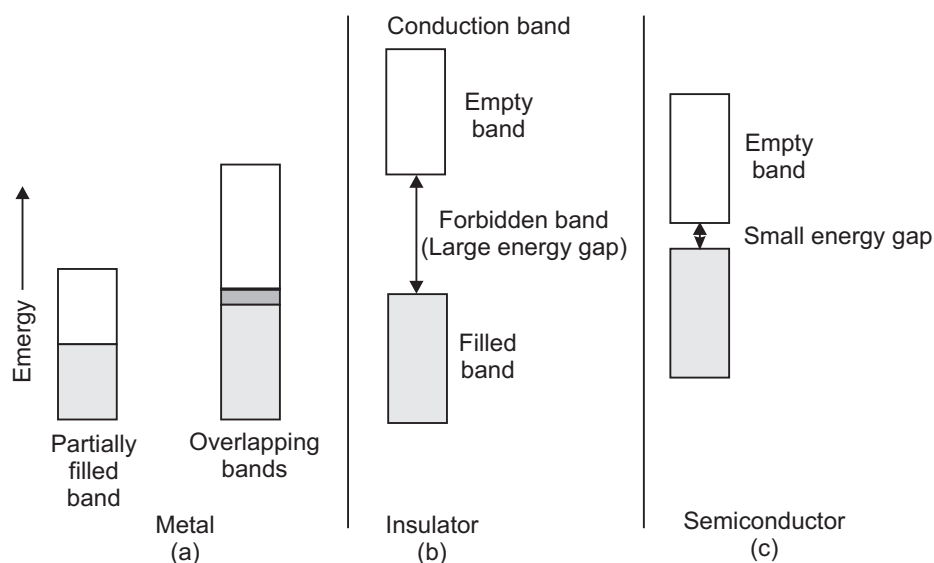
**Fig. 6.27:** Valence and conduction bands in (a) metals, (b) insulators and (c) semi conductors.

(i) **In conductors** either the valence band is only partially filled or it overlaps a vacant conduction band of slightly higher energy. In both the cases its electrons can easily flow under the influence of electric field and the solid behaves as a conductor (Fig. 6.27(a))

(ii) In **insulators** the gap between the valence band and conduction band is large. Due to this the valence electrons *cannot* jump to the conduction band and conduct electricity (Fig. 6.27(b))

(iii) **In semiconductors** the gap between the valence band and nearest conduction band is small (Fig. 6.27(c)). On applying the electric field, some electrons can jump to the conduction band and provide low conductivity. On increasing the temperature more electrons can jump to the conduction band and the conductivity increases. Silicon and germanium show this type of behaviour. They are called **intrinsic semiconductors.**

6.11.3 Doping of Semiconductors

Conductivities of silicon and germanium are too low to be put to any practical use. Their conductivities can be improved by introduction of controlled quantities of impurities which are either electron-rich or electron-deficit with respect to these elements. This process is known as **doping**.

(a) Doping with electron–rich impurities

Silicon and germanium both belong to group 14 of the periodic table and have 4 valence electrons each. In their crystal lattice each silicon (or germanium) atom forms four covalent bonds with its neighbours (Fig. 6.23(a)) when it is doped with a group 15 element like As or P, whose each atom carries 5 valence electrons which is one more than Si. After sharing its four electrons with four neighbouring Si atoms, it has 9 electrons in its valence shell (Fig. 6.28(b)) which is highly unstable electronic configuration. The ninth electron being highly unstable roams freely in the whole of the crystal lattice randomly. In the presence of an electric field this electron (*mobile electron*) moves from negative to positive terminal and increases the conductivity of Si (or Ge). Since the increased conductivity of Si (or Ge) is due to **negatively charged** mobile electrons, the Si doped with electron rich impurity becomes a *n*-type semiconductor.
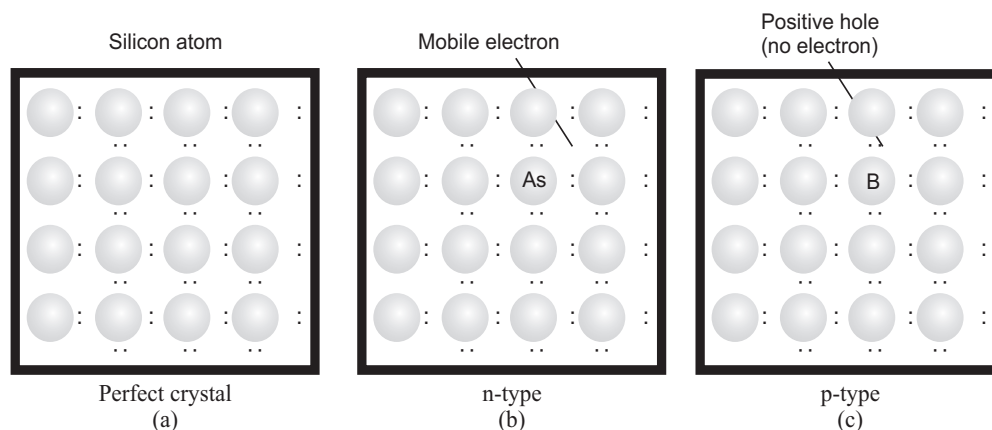
Fig. 6.28: Creation of *n*-type and *p*-type semiconductors

(b) Doping with electron-deficit impurities. When Si (or Ge) is doped with a group 13 element like B or Al containing 3 valence electrons (1 electron less than Si/Ge), this results in creation of one-electron vacancy in the structure which is called an **electron hole** (Fig. 6.28(c)). An electron from its neightbouring atom can come and occupy it, leaving a hole at its original position. Electrons can randomly occupy holes and the hole would appear to move randomly. On applying an electric field, the electrons move from negative to positive terminal and the *hole* would appear move in the opposite direction, i.e., from positive to negative terminal and would behave as if it is *positively charged*. Such semiconductors are called *p*-type semiconductors. The movement of electrons and the hole increases the conductivity of Si. Semiconductors like Si, doped

with electron-deficit or electron-rich impurities are called **extrinsic semiconductors.**

Applications of *n*-type and *p*-type semiconductors

Due to their special properties, *n*-and *p*-type semiconductors find several applications.

(i) *Diodes:* Diode is a combination of a *n*-type and a *p*-type semiconductor. Diodes are used as rectifier to convert an AC signal to a DC signal.

(ii) *Transistors.* Transistors are made by combination of 3 layers of semiconductors. Transistor of *n-p-n* type is made by sandwiching a layer of *p*-type semiconductor between two layers of *n*-type semiconductors and *of p-n-p* type by sandwiching a layer of *n*-type semiconductors between two layers of *p*-type semiconductor. Transistors are used as detectors and amplifiers of radio or audio frequency signals. They are used in circuits of solid state devices.

(iii) *Solar cells*. Solar cells are photo diodes which have a special property of emitting electrons when sunlight falls on them. They are used to convert solar energy into electricity.

6.12 MAGNETIC PROPERTIES

All substances are affected (attracted or repelled) by a magnetic field. Magnetic properties present in any substance are due to the electrons present in it. Each electron in an atom behaves like a tiny magnet. Electrons are negatively charged particles. When an electron *revolves* around nucleus and *spins* about its own axis, two types of magnetic moments are created – *orbital magnetic moment* due to its revolution around the nucleus and *spin magnetic moment* due to its spin. Overall magnetic properties of a substance depend upon the orientation of these tiny magnets.

On the basis of magnetic properties, all substances can be classified into five categories:

(i) paramagnetic, (ii) diamagnetic, (iii) ferromagnetic, (iv) antiferromagnetic and (v) ferrimagnetic
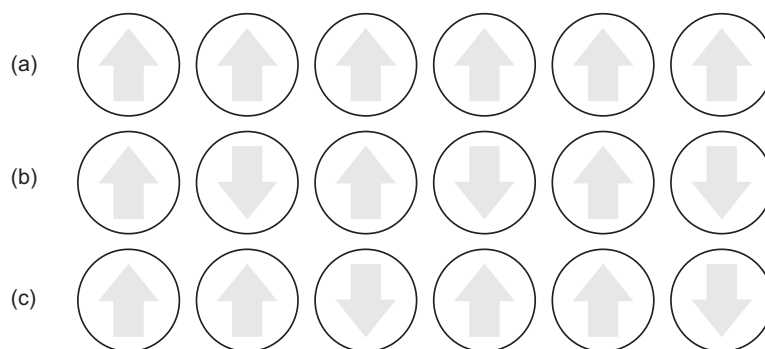
6.12.1 Paramagnetic Substances

On placing these substances in a magnetic field, these are weakly attracted by it. O_2, Cu^{2+}, Fe^{3+} and Cr^{3t} are some examples of paramagnetic substances Paramagnetism is due to the presence of one or more unpaired electrons in an atom, molecule or ion.

6.12.2 Diamagnetic Substances

When placed in a magnetic field, diamagnetic substances are weakly repelled by it. H_2O, NaCl and C_6H_6 are some examples of such substances. Diamagnetism is shown by substances in which all the electrons are paired.

6.12.3 Ferromagnetic Substances

When placed in a magnetic field, ferromagnetic substances are strongly attracted by it. Fe, Ni, Co, Gd, MnAs, $CrBr_3$ and CrO_2 are such substances. These substances can be permanently magnetized. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. In each domain, the individual magnetic moments of the metal ions are directed in the same direction and they add up. As a result, each domain acts as a tiny magnet. Ordinarily, these domains are randomly oriented which cancels out their magnetic moment. When

Notes

(a)

(b)

(c)

Fig. 6.29 Arrangement of magnetic moments of domains in (a) ferromagnetic, (b) anti ferromagnetic and (c) ferrimagnetic substances

placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. This adds up their magnetic moments and makes them strong magnets (Fig. 6.29(a)). They lose their ferromagnetism on being given mechanical jerks or on heating above a certain temperature, called *Curie temperature* they become paramagnetic.

6.12.4 Antiferromagnetic Substances

Some substance that have domains in them like ferromagnetic substances but their domains are oppositely oriented and cancel out the magnetic moments of each other (Fig. 6.29 (b)) are caled antiferro magnetic substances. FeO, $MnCl_2$, MnO, Mn_2O_3 and MnO_2 are examples of antiferromagnetic substances. They also become paramagnetic on heating above a certain temperature.

6.12.5 Ferrimagnetic Substances.

Some substances like Fe_3O_4 (magnetite) and ferrites (MFe_2O_4 where M is a bivalent cation like Cu^{2+}, Zn^{2+}) show an intermediate behavior between that

of ferromagnetic and antiferromagnetic substances. These substances are quite strongly attracted by magnetic field as compared to paramagnetic substances but weakly as compared to ferromagnetic substances. Their domains are aligned in parallel and antiparallel directions in unequal numbers (Fig. 6.29(c)). They also become paramagnetic on heating above a certain temperature.

WHAT YOU HAVE LEARNT

- In solid state the constituent particles are arranged in a closely packed ordered arrangement with almost no free space. These are held together by strong forces of attraction and vibrate about their fixed positions. Solids are incompressible and rigid and have definite shapes.

- Solids are classified into amorphous and crystalline solids. The crystalline solids have long range order while amorphous solids have only short range order.

- The crystalline solids can be classified into four different types- ionic, molecular, covalent and metallic solids on the basis of nature of forces of attraction between the constituent particles.

- The temperature at which a solid melts to give a liquid is called its melting point.

- The three dimensional internal structure of a crystalline solid can be represented in terms of a crystal lattice in which the location of each constituent particle is indicated by a point.

- The whole crystal lattice can be generated by moving the unit cell in the three directions.

- The crystal structures of the solids can be described in terms of a close-packing of identical spheres.

- In three dimensions there are two ways of packing identical spheres. These are hexagonal closed packing (hcp) and cubic closed packing (ccp). The hcp arrangement is obtained by ABAB repeat of the two dimensional layers whereas the ccp arrangement is obtained by ABCABC repeat.

- On the basis of the external appearance the known crystals can be classified into seven types called crystal systems.

- The unit cells of cubic crystal system has three possible lattice types. These are simple cubic, body centered cubic and the face centered cubic.

- The atoms at the corner of a cubic unit cell is shared by eight unit cells while a face centered atom is shared by two unit cells. The atom at the body center, on the other hand is exclusive to the unit cell as it is not shared.

Notes

- The number of atoms per unit cell for the simple cubic, bcc and fcc unit cells are 1,2 and 4 respectively.

- The structure adopted by an ionic solid depends on the ratios of their radii (r+/r-), called radius ratio.

- The structures of some simple ionic solids can be described in terms of ccp of one type of ions and the other ions occupying the voids.

- Actual crystals have some kind of imperfections in their internal structure. These are called defects.

- There are two types of defects called stoichiometric and non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material.

- There are two kinds of stoichiometric defects, these are called Schottky defects and Frenkel defects.

- Solid can be classified as conductors, insulators and semiconductors on the basis of their electrical conductivities.

- Electrical properties of solids can be explained with the help of band theory.

- On the basis of their interaction with external magnetic field, solids can be classified as paramagnetic, diamagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic substances.

TERMINAL EXERCISES

1. Outline the differences between a crystalline and an amorphous solid.

2. How can you classify solids on the basis of the nature of the forces between the constituent particles?

3. What do you understand by the melting point of a solid ? What information does it provide about the nature of interaction between the constituent particles of the solids?

4. What do you understand by coordination number? What would be the coordination number of an ion occupying an octahedral void.?

5. Explain the following with the help of suitable examples.

   (a) Schottky defect

   (b) Frenkel defect

6. Explain why a particular solid behaves as conductor or semiconductor or insulator on the basis of band theory.

7. What are (i) paramagnetic (ii) diamagnetic and (iii) ferromagnetic substances?

Notes

ANSWERS TO INTEXT QUESTIONS

6.1

1. Solids have definite shape and definite volume.

Liquids have indefinite shape but define volume.

Gases have indefinite shape and indefinite volume.

2. Coulombic forces, dipole-dipole attractions, covalent bonding and metallic bonding.

3. Irrespective of the size and shape of the crystal of a substance, the interfacial angle between a pair of faces is always the same

6.2

1. Refer to section 6.7.

2. Hexagonal close packed.

3. Refer to sections 6.7.

6.3

1. Ordered three dimensional arrangement of points representing the location of constituent particles.

2. A select group of points which can be used generate the whole lattice. Unit cell is characterised by three edges of the lattice and angles between them.

3. Four.