
UNIT 5 SOLID STATE

Structure

- 5.1 Introduction
 - Objectives
- 5.2 Definition of Terms Used in Crystal Systems
 - Lattice
 - Basis
 - Unit Cell
- 5.3 Bravais Lattices and Crystal Systems
 - Cubic System Geometry
 - Bravais Lattice
- 5.4 Crystal Planes and Miller Indices
- 5.5 X-rays and Crystal Structure
 - Principles of Diffraction
 - Bragg Law and Bragg Equation
- 5.6 Experimental Method for the Determination of Crystal Structure
 - Powder Method
 - Some Experimental Findings
- 5.7 Determination of Unit Cell
 - Number of Net Atoms in a Cubic Unit Cell
 - Density Calculation
 - Experimental Method
- 5.8 Nature of Bonds in Solids
- 5.9 Ionic, Covalent and Molecular Crystals
 - Ionic Crystals
 - Covalent Crystals
 - Molecular Crystals
- 5.10 Commonly Encountered Metallic Structures
- 5.11 Semiconductors
 - Intrinsic Semiconductors
 - Extrinsic Semiconductors
- 5.12 Summary
- 5.13 Terminal Questions
- 5.14 Answers

5.1 INTRODUCTION

In the earlier units, we had drawn a comparison amongst the three states of matter—solid, liquid and gas. These states of matter were described in terms of a few physical properties like “solids are denser than liquids and gases” or “it takes enormous pressure to compress a solid even by a fraction of its volume”, etc. However, instead of defining the states of matter in terms of the physical properties, it is much more useful to think in terms of the binding forces (ionic, covalent, van der Waals, etc.) involved in a particular state imparting different properties to solids, liquids and gases. Thus, solid state could be defined as a state of a substance in which the neighbouring particles (molecules, atoms or ions) are close enough for van der Waals forces to operate. As a consequence, the motion of the molecules is restricted with respect to its neighbours.

The solids can be of two types — **crystalline** and **amorphous**. Let us explain what a crystalline solid is. Those solids which are formed due to regular repetition of identical building blocks are called crystals. It is like having a collection of identical bricks which could be arranged in some regular fashion to construct a wall. On the other hand, there are solids which do not appear to have any regular internal arrangement in every part and thus do not show regular shape; these are called amorphous solids. Amorphous solid means a solid without regular form. Glass, polyethylene as in plastic bags, etc., are common examples of amorphous substances. Though the study of amorphous substances is also quite useful and interesting, we shall confine ourselves to the study of the crystalline solids in this unit.

Different crystalline structures are associated with different physical properties. Hence, we discuss crystal forms and crystal structure determination method in this unit. Further, the theories of metallic bonding and semiconductors are also explained with particular reference to electrical conduction. The information obtained from crystal structure studies could help us in understanding the physical and chemical properties of solids.

Objectives

After studying this unit, you should be able to:

- define lattice, basis, unit cell, primitive and nonprimitive cells,
- describe the seven crystal systems and the fourteen Bravais lattices,
- identify the face, corner, edge, face-centre and body-centre in a cube,
- state the crystal planes in terms of Miller indices,
- state Bragg law,
- describe the determination of crystal structure by X-ray diffraction method,
- determine the type of unit cell based on experimental and calculated values of density,
- explain the types of bonds in solids,
- discuss the structures of some ionic, covalent and metallic crystals, and,
- describe the types of semiconductors.

5.2 DEFINITION OF TERMS USED IN CRYSTAL SYSTEMS

Atom is used in general sense in this unit; it stands for an atom or an ion or a molecule.

We have already seen that a crystal is defined in terms of a regular and repetitive arrangement of particles (atoms/molecules/ions) in space. In order to understand crystals and their structures, we encounter a few new terms. These terms form a kind of crystallographic language. Let us now look at the definitions of some of these terms.

5.2.1 Lattice

A parallel net-like arrangement of points in space is known as lattice.

Lattice is defined as an arrangement of geometrical points in a definite pattern in space (Fig. 5.1a). It resembles a scaffold (a framework) erected for the construction of a building. Putting it in a simpler way, one can define a lattice as a regular periodic arrangement of points in space.

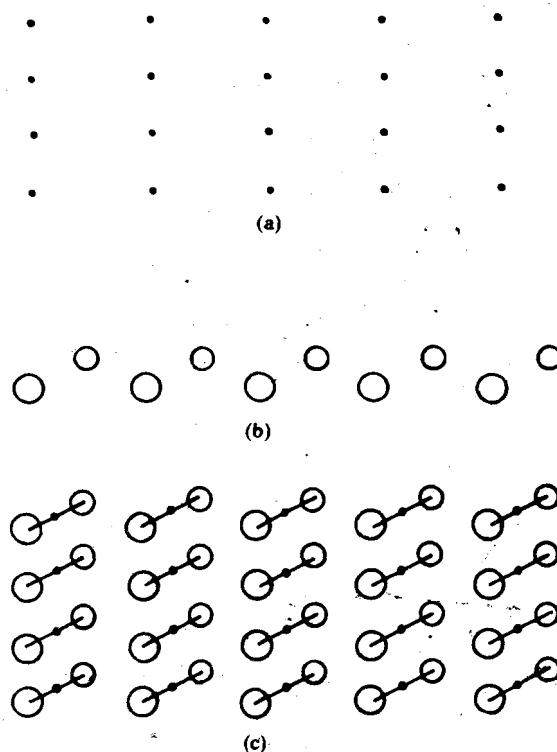


Fig. 5.1 : Representation of a) lattice in two dimensions, b) basis (with two atoms), c) crystal structure, showing the basis of two atoms in relation to lattice points.

5.2.2 Basis

Whenever there is a group of atoms around a lattice point, then the basis is defined.

When atoms are attached regularly to each lattice point, it forms a crystal. However, instead of an atom, we can have a group of atoms attached to each lattice point. The group is called a basis (Fig. 5.1b). The basis consists of the atoms, their spacings and internal bond angles. Every basis is identical in composition, arrangement and orientation. Fig. 5.1c shows the

crystal structure where you can recognise the basis and imagine the lattice. For a large number of crystals, the basis has only a small number of atoms but in a few instances, the basis exceeds 1000 atoms. For example, the basis in iodine crystal is I_2 molecule whereas in the ice crystal, H_2O molecule is the basis.

5.2.3 Unit Cell

The unit cell is the fundamental unit in a crystal. The repetitive arrangement of unit cells in three dimensions produces a crystal just as a wall is built from identical bricks. In other words, a unit cell is the smallest unit of a crystal which on translational displacement in three dimensions will produce the crystal. A unit cell chosen to represent the crystal may be quite different in size and shape from another unit cell which may represent the crystal equally well. The main point is that whatever the unit cell may be, it should be the simplest representation and, when repeated in three dimensions, it should produce the crystal.

Identical repetition of basis about each lattice point in three dimensions gives a crystal structure.

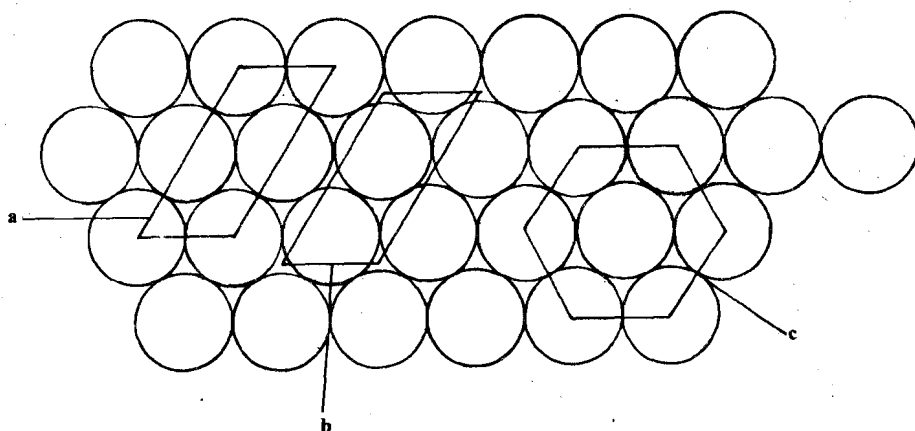


Fig. 5.2 : Choice of unit cell.

Fig. 5.2 shows four rows of spheres—representing atoms—in a closely packed structure in two dimensions. If we join the centres or any other points, say, gaps between the spheres, of different atoms in successive three rows, we get a cell of the type a, b or c. All the other rows of atoms are a repetition of the first three rows. It is immaterial whether the unit cell chosen is a, b or c, but it is the simplest representation which on repetition in two dimensions will produce the entire assembly as shown in Fig. 5.2. The situation in a crystal is somewhat similar to the above except that the unit cell and the resulting crystal are three dimensional. Thus, we can say that the simplest repeating unit in a crystal is called a unit cell.

It is true that the unit cell must have some regularity in structure. Does any type of regular shape constitute a unit cell? The answer is no. To understand this, let us consider the covering of a floor space by tiles without leaving a gap. Can we use any type of tiles—

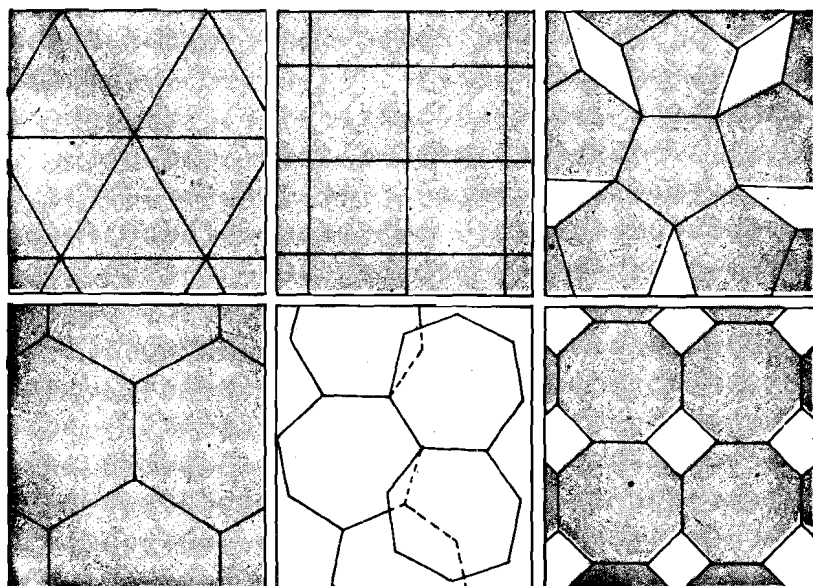


Fig. 5.3 : Of all the regular polygons, only triangles, squares and hexagons can fill a floor space without gap. Filled-in space is denoted by grey area.

triangular, square, pentagonal, hexagonal, heptagonal or octagonal? Against the answer is no. You can cover the floor space completely with triangular, square or hexagonal tiles but not with pentagonal, heptagonal or octagonal tiles (Fig. 5.3). Note the gaps in the interior floor space when pentagonal, heptagonal or octagonal tiles are used.

Just as tiles with specific shapes are useful in covering the floor space completely, unit cells with specific symmetry properties constitute the crystal lattice. The course on Spectroscopy deals with symmetry properties in detail.

SAQ 1

What is the essential characteristic of a unit cell?

.....

.....

.....

5.3 BRAVAIS LATTICES AND CRYSTAL SYSTEMS

A parallelepiped is a three dimensional model of a parallelogram.

The cell-edge lengths (a , b and c) are the repeat distances in a unit cell. Any point in a unit cell can be represented by coordinates which are fractions of a , b and c .

The basic shape of a unit cell is described by a parallelepiped. (Fig. 5.4a).

A unit cell has three coordinate axes, \mathbf{a} , \mathbf{b} and \mathbf{c} (note the bold letters). The cell-edge lengths in the three axes are a , b and c (note the italicised letters), respectively (Fig. 5.4b). The angles between \mathbf{a} and \mathbf{b} axes, \mathbf{b} and \mathbf{c} axes and \mathbf{c} and \mathbf{a} axes are γ , α and β , respectively. The quantities a , b and c are called lattice parameters or unit cell parameters.

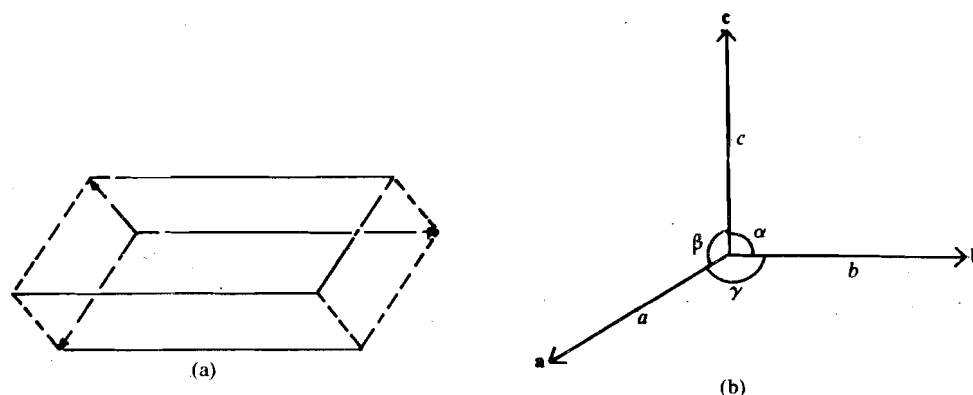


Fig. 5.4 : a) parallelepiped; b) three coordinate axes, cell-edge lengths and the angles between axes.

Based on the relationships among the axial angles and the edge-lengths, there are seven crystal systems as given in Table 5.1.

Table 5.1 : The Seven Crystal Systems

Systems	Axes	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CsCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ (rutile)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	CdSO ₄ , HgBr ₂
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO ₃ (calcite)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	SiO ₂
Monoöcnic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	KIO ₃ , NaHCO ₃
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	NaHSO ₄ , CuF ₂

5.3.1 Cubic System Geometry

Of the seven crystal systems, we are particularly interested in cubic system due to its simplicity and symmetry. A cube has the same value for all the three lattice parameters ($a = b = c$). We must understand the geometry of a cube. For this purpose, imagine that

you are sitting in a cubical room. Each wall (including floor and ceiling) of your room is called a face. A cubical room has six faces—four walls, the ceiling and the floor. You can consider the ceiling and the floor as horizontal walls!

Each point where three faces of a cube (or three walls in your room) meet is called a corner. A cube has eight corners and these are indicated by A to H in Fig. 5.5a.

Each face has four corners. By joining the corners of a face diagonally, two face diagonals are obtained. For example, in Fig. 5.5b, the lines AC and BD (obtained by joining A and C or B and D, respectively) are two of the twelve face diagonals in a cube. The centre point of a face where the two face diagonals meet is called a face-centre; one of the six face-centres is indicated by M in Fig. 5.5b.

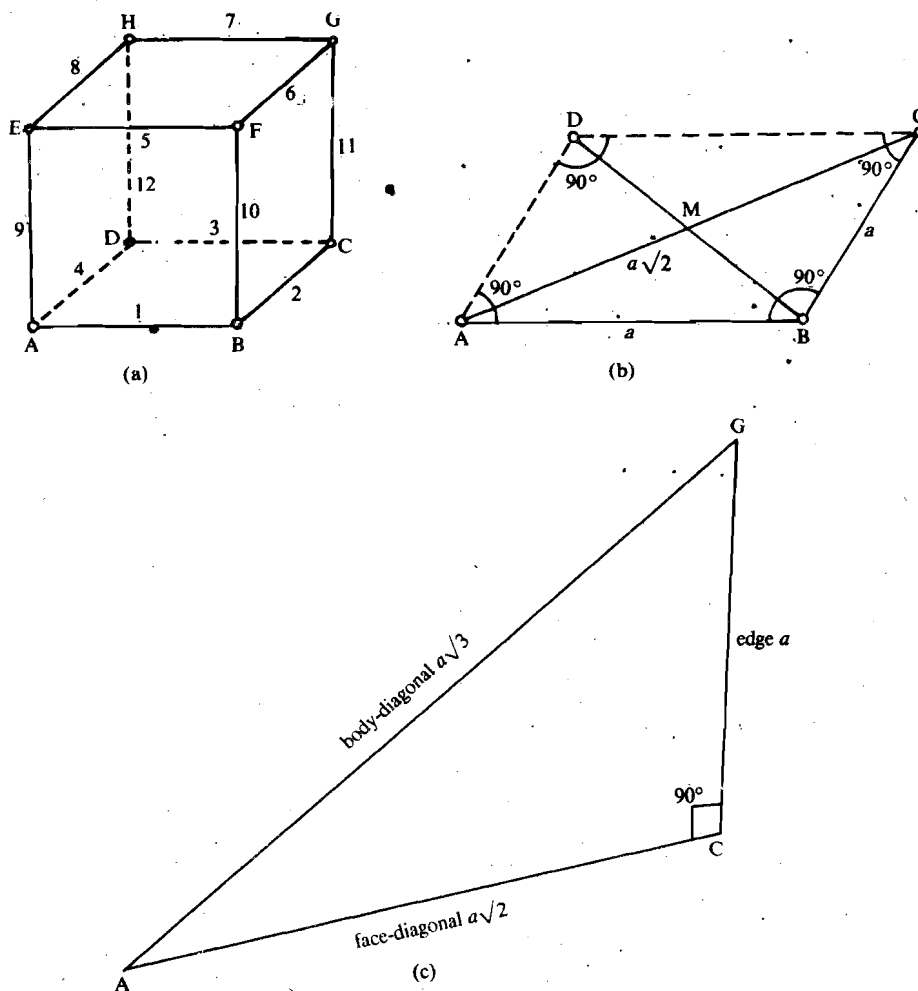


Fig. 5.5 : a) Eight corners in a cube indicated by letters A to H—each corner is marked by red dot; twelve edges indicated by number 1 to 12; b) bottom face ABCD of the cube shown; AC and BD are the face diagonals and M is face-centre; c) The right-angled $\triangle ACG$.

By joining any two corners which are not in the same face, a body diagonal is obtained. There are, four body diagonals in a cube—AG, BH, FD and EC in Fig. 5.5a. All the body diagonals meet at the body-centre. The definitions of face, corner, edge, face-centre and body-centre apply to other crystal systems also.

5.3.2 Bravais Lattice

Some crystal systems, may have one or more types of lattices depending on the number of lattice points. If there are lattice points only at the eight corners of a unit cell, it is called a simple or primitive (*P*) cell. A cell which has lattice points at the eight corners and the six face centres is called a face-centred (*F*) cell. A cell that has eight lattice points at the corners and two more at the centres of a pair of any two opposite faces is called an end-centred (*C*) cell. If a cell has eight lattice points at the corners and one at the body centre, it is called a body-centred (*I*) cell. The unit cells of the type *F*, *C* and *I* are called nonprimitive cells. Based on the presence of lattice points in the seven crystal systems, there are fourteen Bravais lattices; these are given in Fig. 5.6.

For a cubic crystal, the cell-edge lengths are the same along the three axes and are represented as a .

$$\text{In } \triangle ABC, \angle ABC = 90^\circ$$

$$\begin{aligned} \text{Length of face diagonal, AC} \\ &= \sqrt{AB^2 + BC^2} \\ &= a\sqrt{2} \end{aligned}$$

$$\text{In } \triangle ACG, \angle ACG = 90^\circ.$$

(See Fig. 5.5c)

$$\begin{aligned} \text{Length of the body diagonal, AG} \\ &= \sqrt{AC^2 + CG^2} \\ &= \sqrt{2a^2 + a^2} \\ &= a\sqrt{3} \end{aligned}$$

A non-Bravais lattice structure is composed of two or more sublattices.

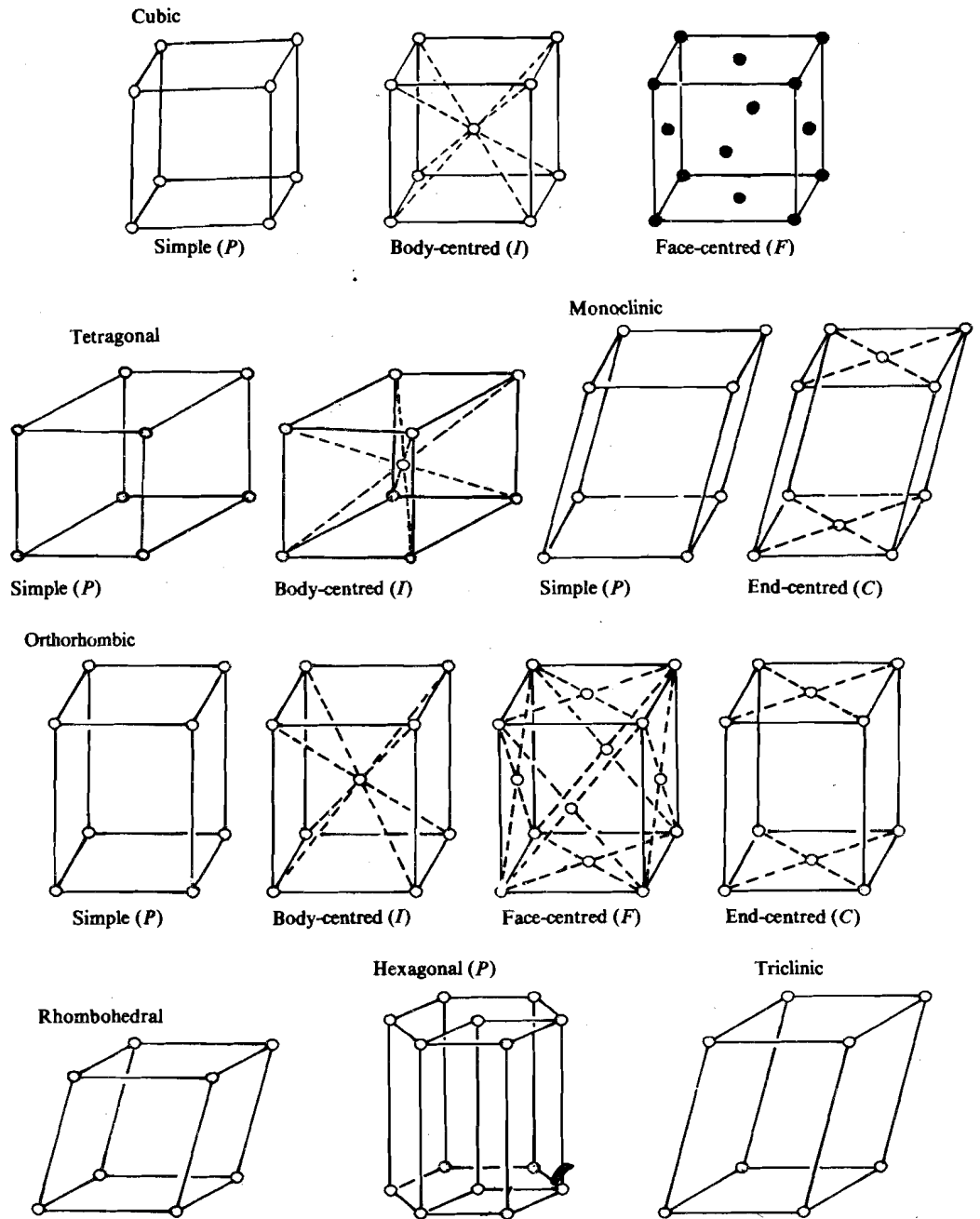


Fig. 5.6 : Fourteen Bravais Lattices.

Of these Bravais lattices, we shall consider simple cubic (*sc*), body-centred cubic (*bcc*) and face-centred cubic (*fcc*) lattices only. In the next section, let us see how to represent the crystal planes.

SAQ 2

Describe the following : simple cubic, body-centred cubic and face-centred cubic crystals.

.....

.....

5.4 CRYSTAL PLANES AND MILLER INDICES

Crystal planes are represented by certain numbers known as Miller indices. These indices are determined in the following way :

- i) Find the intercepts of a crystal plane on the axes, *a*, *b* and *c* in terms of cell-edge lengths *a*, *b* and *c*. Suppose that a crystal plane makes intercepts $3a$, $2b$, $2c$ as shown in Fig. 5.7.

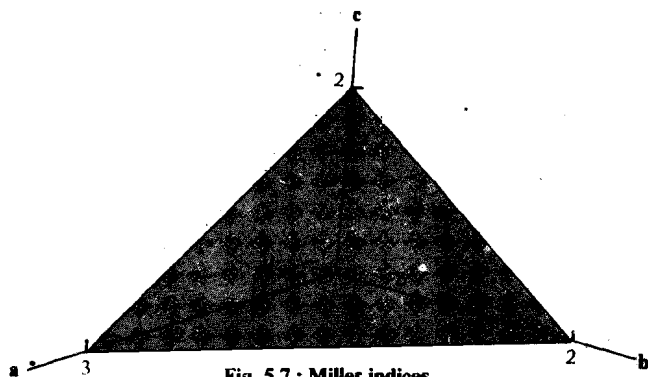


Fig. 5.7 : Miller indices.

- ii) Divide the intercepts by the respective cell-edge lengths (a , b and c). For the crystal plane in Fig. 5.7, this step gives $\frac{3a}{a}$, $\frac{2b}{b}$, $\frac{2c}{c}$, i.e., 3, 2, 2 as the answer.
- iii) Take the reciprocal of the above numbers. Corresponding to Fig. 5.7, this step gives $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$ as the answer.
- iv) Finally reduce the above fractions to the smallest integers having the same ratio. Write these numbers enclosed in parentheses without comma signs; these are the Miller indices of the given crystal plane. For the illustration in Fig. 5.7, the Miller indices are (233); this is to be pronounced as two three three plane.

Miller indices are generally represented as (hkl) . You will notice that the Miller indices are defined in such a way that all equivalent and parallel planes are represented by the same set of Miller indices. Thus, planes whose intercepts are $3a$, $2b$, $2c$ or a , $\frac{2b}{3}$, $\frac{2c}{3}$ or $9a$, $6b$, $6c$, etc. are all represented by a set of Miller indices (233).

If a face is parallel to an axis, theoretically the corresponding intercept is equal to ∞ . To illustrate this, let us draw a crystal plane of a cubic cell which makes intercepts a , ∞ , ∞ . That is, the plane is parallel to b and c axes. Applying the above steps in order, we get the

Miller indices for this plane as (100). Remember $\frac{1}{\infty}$ is equal to zero. The origin (O) and

the axes directions are shown in Fig. 5.8a. The (100) plane is indicated in Fig. 5.8b.

Similarly, corresponding to the planes with intercepts a , a , ∞ and a , a , a , the Miller indices are (110) and (111), respectively; these are shown in Figs. 5.8 c and d, respectively.

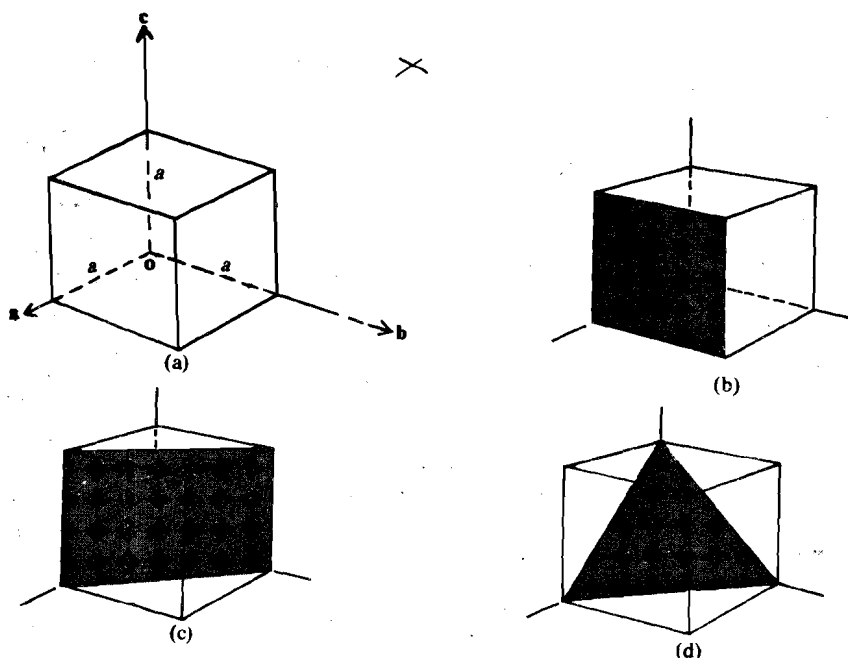


Fig. 5.8 : a) The origin, O, the axes and the cell-edge length a in a cubic cell; b) (100) plane; c) (110) plane; d) (111) plane.

We can calculate the distance between the adjacent planes labelled by the same Miller indices (hkl), but no generalised formula can be written. The actual formula in a particular case would depend upon the crystal structure. For example, the distance d_{hkl} between the (hkl) planes of a cubic lattice is given by,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \dots (5.1)$$

where a is the cell-edge length of the cell and (hkl) are the Miller indices. Thus, in sodium chloride crystal, the cell-edge length is 5.63×10^{-10} m. The distance between (111) planes is given by Eq. 5.1,

$$d_{111} = \frac{5.63 \times 10^{-10} \text{ m}}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{5.63 \times 10^{-10} \text{ m}}{\sqrt{3}} = 3.25 \times 10^{-10} \text{ m}$$

Eq. 5.1 could be used only for cubic crystals. For an orthorhombic cell, the equation for d_{hkl} turns out to be,

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \quad \dots (5.2)$$

Using Eq. 5.2, work out the following SAQ.

SAQ 3

An orthorhombic crystal has the following parameters:

$$a = 8.2 \times 10^{-10} \text{ m}; b = 9.4 \times 10^{-10} \text{ m}; c = 7.5 \times 10^{-10} \text{ m}.$$

What is the distance between (123) planes?

.....

.....

.....

5.5 X-RAYS AND CRYSTAL STRUCTURE

Crystal structures are usually determined with the help of X-rays. In addition to X-rays, other forms of radiations having similar properties—like a beam of neutrons or electrons—could also be used. However, our discussion will be limited to the use of X-rays only. We know that X-rays are electromagnetic radiations of wavelengths much shorter than either visible or ultraviolet light. In 1911, Ewall showed that whenever the wavelength of radiation is of the same order of magnitude as the size of the particle in a material, the radiation would be diffracted by the particle. In 1912, Laue suggested that since the order of the magnitude of the wavelength of X-rays and the crystal lattice distances are the same, we should expect diffraction of X-rays by crystals. This was soon confirmed experimentally by Friedrich and Knipping. Let us explain the principle of diffraction, in general, and the diffraction of X-rays by crystals, in particular.

5.5.1 Principles of Diffraction

Diffraction pattern arises due to interference of waves. When the waves are in phase, the intensity is increased, (this is known as constructive interference; Fig. 5.9a); when they are out of phase (known as destructive interference), the intensity is decreased (Fig. 5.9b). If there are two waves starting from a common source, their **phase difference** will be directly proportional to their path difference.

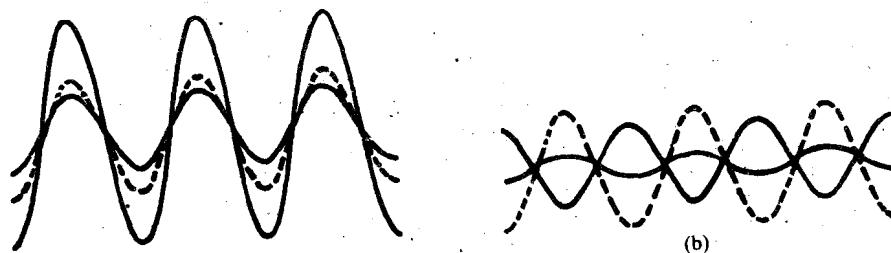


Fig. 5.9 : Two waves (shown by dotted and solid lines) giving rise to a resultant (shown by red colour) : a) constructive interference (in-phase wave—greater amplitude); b) destructive interference (out-of-phase wave—smaller amplitude).

The amplitude is directly related to the intensity of the beam.

The bending of light round the edges of an obstacle is called diffraction. Consider a beam of light passing through two slits (S_1 and S_2), cut near to each other on a screen and falling on a second screen placed beyond the slits (Fig. 5.10). A series of dark and bright bands are observed on the screen, which are due to the constructive and destructive interference of the two beams passing through the two slits. When their amplitudes are in-phase, the intensity is enhanced and when their amplitudes are out-of-phase, the intensity is decreased. Whether the beams are in-phase or out-of-phase will depend on the path difference between the two rays.

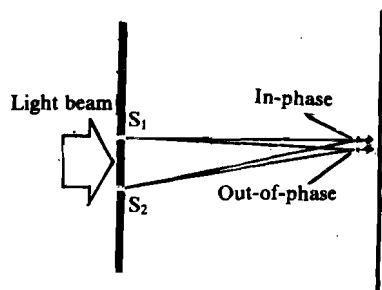


Fig. 5.10 : In-phase and out-of-phase waves.

5.5.2 Bragg Law and Bragg Equation

If the path difference between the two rays is an integral multiple ($n = 1, 2, 3, \dots$) of the wavelength of X-rays, then the two rays will be in-phase and the diffraction pattern will be bright (i.e., with enhanced intensity). This is called **Bragg law**. Stated mathematically, for a bright diffraction pattern,

$$\text{path difference} = n \lambda \quad \dots (5.3)$$

Bragg derived an equation (Eq. 5.9) for X-ray diffraction of crystals. This equation is named after him. Some of the assumptions made by Bragg in deriving Eq. 5.9 are given below :

- The incident waves are reflected by parallel planes of atoms in a crystal such that the angle of incidence is equal to the angle of reflection. This is called specular (mirror-like) reflection.
- Each plane reflects only a fraction of incident radiation.
- When the reflections from parallel planes interfere constructively, the diffraction pattern arises.
- The wavelength of the X-rays is not changed on reflection; i.e., X-rays undergo elastic scattering on the lattice planes. Using geometric considerations, Bragg equation can be derived easily.

Two parallel beams PA and QC are incident at an angle θ on the parallel planes EF and GH (Fig. 5.11). The perpendicular distance (AC) between the two planes is d . The beams are reflected along AR and CS at an angle θ . The path difference between the two sets of incident and reflected beams (PAR and QCS) is the extra distance travelled by QCS as compared to PAR. To calculate the path difference, draw $AB \perp QC$ and $AD \perp CS$.

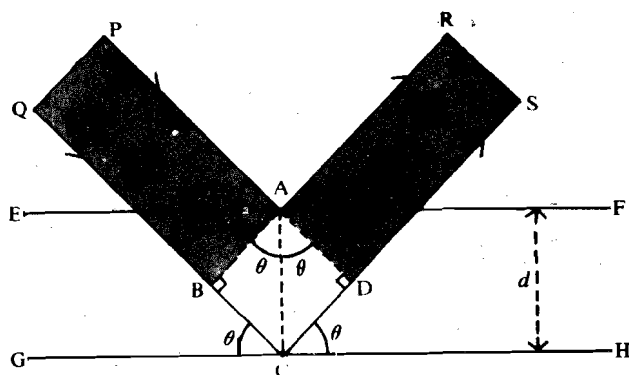


Fig. 5.11 : The incident and the reflected beams and the two parallel lattice planes.

The bright and dark spots which appear on a photographic film are called diffraction pattern; it should not be confused with diffraction phenomenon which is just the bending of light around the edges of an obstacle.

$$\begin{aligned}
 \text{Path difference} &= (QC + CS) - (PA + AR) \\
 &= (QB + BC) + (CD + DS) - (PA + AR) \\
 &= BC + CD \quad \dots (5.4) \\
 &[\because QB = PA \text{ and } DS = AR, \text{ being opposite sides of the rectangles shown} \\
 &\text{by the shaded portions in Fig. 5.11].}
 \end{aligned}$$

$$\text{Since } AC \perp GH, \angle ACG = 90^\circ = \angle ACB + \angle BCG = \angle ACB + \theta$$

$$[\because \angle QCG \text{ and } \angle BCG \text{ are same as } \theta]$$

$$\angle ACB = 90^\circ - \theta \quad \dots (5.5)$$

$$\text{In the right-angled } \triangle ABC, \angle BAC + \angle ACB + \angle CBA = 180^\circ$$

$$\text{Using Eq. 5.5, } \angle BAC + (90^\circ - \theta) + 90^\circ = 180^\circ$$

$$\angle BAC = 180^\circ - (180^\circ - \theta) = \theta$$

$$\text{Also, } \frac{BC}{AC} = \sin \theta \text{ or } BC = AC \sin \theta$$

$$\text{Since, } AC = d, BC = d \sin \theta \quad \dots (5.6)$$

$$\text{Similarly, we can prove that } CD = d \sin \theta \quad \dots (5.7)$$

Using Eqs. 5.4, 5.6 and 5.7,

$$\text{path difference} = 2d \sin \theta \quad \dots (5.8)$$

Again substituting in Eq. 5.3, we get,

$$n\lambda = 2d \sin \theta \quad \dots (5.9)$$

Bragg equation assumes that incident X-rays are reflected specularly (mirrorlike) such that the angle of incidence is equal to the angle of reflection. This assumption is convincing only because it explains the experimental results.

Eq. 5.9 is known as Bragg equation. It is useful in crystal structure determination. In this equation, λ is the wavelength of X-rays used, d is the distance or the spacing between the planes. The value of n gives the order of reflection.

If $n = 1$, it is first-order reflection.

If $n = 2$, it is second-order reflection and so on.

After reading the above section you should be able to solve the following SAQ.

SAQ 4

If the separation between the lattice layers in a crystal is 404 pm and the wavelength of X-rays used is 154 pm, what would be the angle of incidence at which reflection would occur? Assume $n = 1$.

.....

.....

.....

.....

15.6 EXPERIMENTAL METHODS FOR THE DETERMINATION OF CRYSTAL STRUCTURE

In any method of crystal structure determination, we must find out θ as well as the intensity of the diffracted beam. There are basically three methods—Laue, powder and the rotating crystal—which are used for the determination of the above quantities. In this section we shall discuss the outline of powder method only.

5.6.1 Powder Method

In this method, we use a powdered sample containing microcrystals which are randomly oriented. There are enough of microcrystals which will have the proper orientation for diffraction. The diffraction beam corresponding to each scattering fans out in the form of a cone, the axis of which lies along the incident beam as shown in Fig. 5.12. This gives rise to bright rings on a circular photographic film and is known as powder pattern. The X-ray

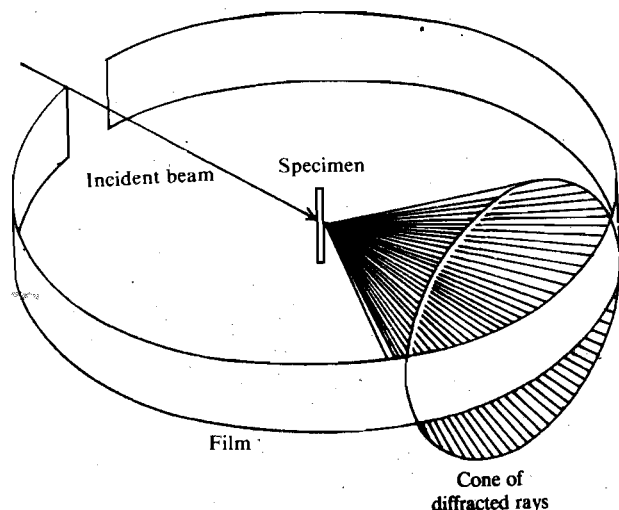


Fig. 5.12 : Powder method.

powder pattern for sodium chloride is shown in Fig. 5.13. Using powder method, the interplanar spacing can be found out since both λ and θ are known.

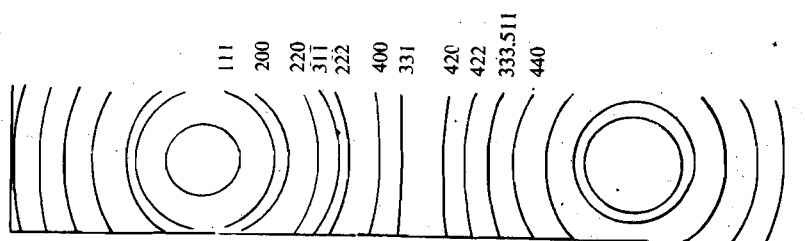


Fig. 5.13 : X-ray powder pattern for sodium chloride.

5.6.2 Some Experimental Findings

Some noteworthy features in crystal structure determination by X-ray diffraction are given below:

- It appears that a set of planes is reflecting the X-ray beam.
- The reflection takes place only for certain values of θ ; these values of θ must satisfy Bragg equation (Eq. 5.9).
- It is a common practice to set $n = 1$ in Eq. 5.9, unless specified otherwise. Higher order reflections ($n > 1$) are weak.

The X-ray diffraction method leads us to the value of cell-edge length which can be used to determine the density of the crystal.

5.7 DETERMINATION OF UNIT CELL

The comparison between the experimental and the theoretical values of density could help us in determining the cubic cell type. First let us calculate the number of atoms belonging to a unit cell in each type of cubic cell.

5.7.1 Number of Net Atoms in a Cubic Unit Cell

An atom at the body-centre of a unit cell belongs to that cell only (Fig. 5.14a). An atom on the face-centre of a unit cell is shared by two unit cells (Fig. 5.14b) and thus, only half of such an atom belongs to one unit cell. An atom at the edge-centre of a unit cell is shared by four unit cells (Fig. 5.14c); one-fourth of an atom in the edge-centre belongs to one unit cell. But an atom at the corner of a unit cell will be shared by eight unit cells as shown in Fig. 5.14d. Hence, we can say that one eighth of an atom in a corner belongs to a particular unit-cell. Using this background, let us calculate the number of net atoms present per unit cell for a simple cubic, face-centered cubic or body-centred cubic structure.

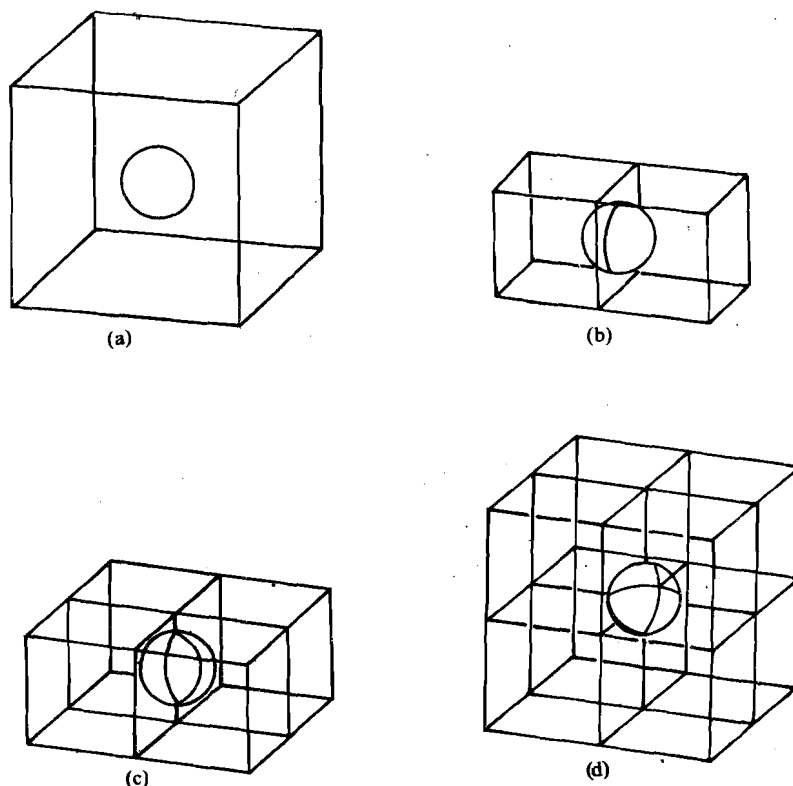


Fig. 5.14 : a) An atom at the body-centre of a unit cell; b) An atom at the face-centre shared by two unit cells; c) An atom at the edge-centre shared by four unit cells; d) An atom in the corner shared by eight unit cells.

The number of net atoms per unit cell are one, two and four in simple cubic, *bcc* and *fcc* structures.

- In a simple cubic cell, there are atoms only at the eight corners; and hence, a simple cubic structure has only one net atom ($8 \times \frac{1}{8} = 1$) per unit cell.
- On the other hand, in a *bcc* structure, there are atoms in the eight corners and the centre of the cell; hence, there are two net atoms [$(8 \times \frac{1}{8}) + 1 = 2$] per unit cell of a *bcc* structure.
- Finally, for a *fcc* structure, there are atoms in the eight corners and six face centres. That is, a *fcc* structure has four net atoms [$(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 1 + 3 = 4$] per unit cell.

The density of a crystal depends on the number of atoms, their mass and the volume of the unit cell. Let us now see the calculation of the densities of these three types of unit cells.

5.7.2 Density Calculation

$$\text{It is known that density} = \frac{\text{Mass}}{\text{Volume}} \quad \dots (5.10)$$

In this unit, the cell-edge lengths and the distance between the planes are given in m or pm units; but it is

usual to state such data in Å unit also.
 $1 \text{ Å} = 10^{-10} \text{ m}$.

X-ray measurements give us the cell-edge length. If the cell-edge length is a m, (i.e., a metre) then the volume of the unit cell = $a^3 \text{ m}^3$... (5.11)

The mass of an atom of the substance is obtained by dividing the mass of one mole atoms [i.e., atomic mass (w) in kg mol^{-1}] by Avogadro constant (N_A , which is equal to $6.022 \times 10^{23} \text{ mol}^{-1}$).

$$\text{Mass of one atom} = \frac{w \text{ kg mol}^{-1}}{N_A \text{ mol}^{-1}} = \frac{w}{N_A} \text{ kg} \quad \dots (5.12)$$

A simple cubic structure has only one atom per unit cell; hence, mass of unit cell of a simple cubic crystal is given by Eq. 5.12. Substituting the proper values from Eqs 5.11 and 5.12 in Eq. 5.10, we get,

$$\left. \begin{array}{l} \text{the density} \\ \text{of a simple} \\ \text{cubic cell} \end{array} \right\} = \frac{w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.13)$$

Since, simple cubic, *bcc* and *fcc* unit cells have one, two and four atoms per unit cell, the densities of *bcc* and *fcc* are given by :

$$\text{Density of a } bcc \text{ cell} = \frac{2w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.14)$$

$$\text{Density of a } fcc \text{ cell} = \frac{4w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.15)$$

$$\text{In general, the density of a cubic unit cell } (\rho) = \frac{n w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.16)$$

where n is the number of net atoms per unit cell.

Rearranging Eq. 5.16, we get,

$$n = \frac{\rho N_A a^3}{w} \quad \dots (5.17)$$

5.7.3 Experimental Method

The cell-edge length (a) and the density (ρ) of a crystal are experimentally determined. These values are substituted in Eq. 5.17 and n is calculated. Depending on whether $n = 1$ or 2 or 4, the unit cell is simple cubic or *bcc* or *fcc*. Let us work out an example.

Nickel metal packs in a cubic unit cell with a cell-edge length (a) of 3.524×10^{-10} m. The density (ρ) of nickel is 8.90×10^3 kg m⁻³. Let us find out the unit cell type for nickel. Since atomic mass of nickel is 58.7, $w = 0.0587$ kg mol⁻¹.

First we have to calculate n using Eq. 5.17

$$\begin{aligned} n &= \frac{\rho N_A a^3}{w} \\ &= \frac{8.90 \times 10^3 \text{ kg m}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times (3.524 \times 10^{-10} \text{ m})^3}{0.0587 \text{ kg mol}^{-1}} \\ &= 4 \text{ (rounded to the nearest whole number).} \end{aligned}$$

Since there are four atoms per unit cell, nickel has a *fcc* lattice.

In the following section, we shall study the nature of bonds responsible for holding the solid together. Before that attempt the following SAQ.

SAQ 5

Tungsten forms *bcc* crystals. Its cell-edge length is 3.16×10^{-10} m. Find the density of tungsten:

.....

.....

.....

.....

5.8 NATURE OF BONDS IN SOLIDS

There are basically two theories or models to explain the nature of bonds in solids. One is known as bond model and the other as band model. These two names may sound new; however, they are the same two approaches that we have already studied (in Units 4 and 5 of **Atoms and Molecules** course) in connection with the formation of a molecule by the combination of two or more atoms. Thus the bond model is the same as the valence bond approach. Here we consider a crystal as a three dimensional arrangement of atoms and each of these atoms has valence electrons which can form normal chemical bonds with neighbouring atoms. These bonds may be ionic, covalent or van der Waals in character. In the other approach, which is called the band model, we follow the molecular orbital treatment. All the nuclei with their core electrons are considered as a fixed periodic array

over which the valence electrons are spread out. It is like pouring of electron cement over a fixed arrangement of nuclear bricks. We have already read about ionic bond, covalent bond, hydrogen bond, etc., in Unit 3 of **Atoms and Molecules** course. We shall now study metallic bonding in terms of the above two models.

Metallic Bonding

According to the bond theory, the metallic solids can be considered as having simple covalent bonds between adjacent atoms. However, in these cases, the number of electron pairs available for bond formation is less than the number of orbitals available. Hence, when such substances are placed under an applied electric field, the electrons from the filled orbitals can easily flow into the vacant orbitals, thus making them highly conducting.

In the band theory of metals, a crystalline metallic solid is considered as a single giant molecule. Linear combination of atomic orbitals on all the atoms is taken to give molecular orbitals of the solid just as in the case of simple diatomic molecule. It is also assumed that there is negligible overlap of inner shell atomic orbitals and the energies of these remain practically the same as atomic orbitals on isolated atoms. However, the outer orbitals do combine to give molecular orbitals of bonding and antibonding character. Suppose that a crystal of sodium contains N atoms, where N is of the order of 10^{23} . Neglecting the inner orbitals, there are N number of $3s$ orbitals on all the atoms in the crystal which can combine to give N molecular orbitals or delocalised crystal orbitals. Since each molecular orbital can hold 2 electrons, the total number of electrons which these orbitals can hold is $2N$. The actual number of electrons is however only N , since each atom is contributing only one $3s$ electron. Hence, only half of the molecular orbitals will be occupied by the electrons and half will remain vacant. Further, since there are N molecular orbitals and the total energy difference between the highest and the lowest orbital is very small, the energy separation between the adjacent molecular orbitals would be very small. For all practical purposes we can consider these molecular orbitals as forming a continuous band of energy rather than separate energy levels. Thus we have a situation where a band of vacant energy levels lie very near to a band of occupied energy levels. Therefore, the electrons present in the occupied lower energy levels can easily move out to vacant band. This is the reason given for metals being good conductors of electricity. In the next section, we shall study the structures of ionic, covalent and molecular crystals.

5.9 IONIC, COVALENT AND MOLECULAR CRYSTALS

In this section we shall consider the structures of some crystals, which have either ionic or covalent bonds; examples are also given for crystals having covalent bonding with van der Waals attraction or hydrogen bonding.

5.9.1 Ionic Crystals

As examples for ionic crystals, we shall consider caesium chloride and sodium chloride which have *bcc* and *fcc* structures, respectively.

bcc Structure

The structure of a *bcc* crystal can be defined in terms of unit cell-edge length and two unique positions in the cell. Consider a crystal like CsCl which has *bcc* structure and has two different ions in lattice positions. Suppose the centre of a cube is occupied by Cs^+ ion; then, this is one of the unique positions of the crystal. It is unique because there is no other point within the cell which is one cell-edge length away and which can be occupied by another Cs^+ ion. Now if one of the corners of the cube is occupied by a chloride ion, then all the eight corners of the cube must be occupied by chloride ions. This is so because each of the corners is one unit cell-edge length away from its nearest neighbours and if one corner is occupied by Cl^- ion, its immediate neighbours which are unit cell-edge length away must also be occupied by chloride ions. We can say that any one corner position is unique in the sense that once you associate an atom with this position, then all the other corners automatically get associated with the similar atoms. Thus, once these two positions are defined, the whole crystal gets defined (Fig. 5.15).

Unit cell-edge length must connect equivalent points. If there is an atom at the corner of a unit-cell, similar atoms must be present at all the corners. If there is an atom at a face-centre, the opposite face-centre also must have the similar atom.

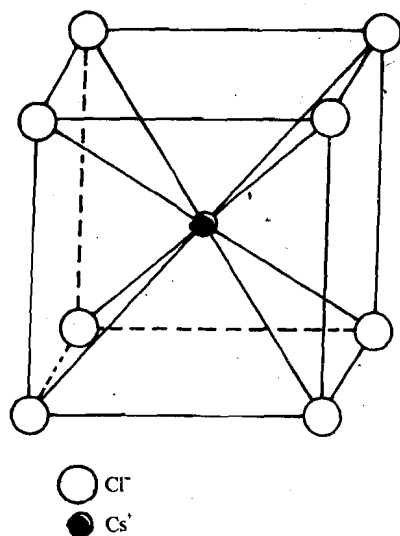


Fig. 5.15 : CsCl structure

Since CsCl crystal has one Cs^+ ion at the centre and eight Cl^- ions at the corners, it has one Cs^+ ion and one Cl^- ion ($8 \times \frac{1}{8} = 1$) belonging to one unit cell as per discussion in

Subsec. 5.7.1. That is, each CsCl unit cell has one formula unit.

fcc Structure

In a *fcc* structure, there are four unique positions; once these positions are defined, the rest of the crystal gets completely described. These are the centres of three adjacent faces and one corner. Once one corner is occupied by an atom, all other corners will have similar atoms. Further, if one atom occupies the centre of one face, the centre of the opposite face would also be occupied by similar atom. Thus, by describing the atoms which occupy the centres of adjacent three faces, we know the atoms occupying the centres of all the six faces. Similarly, all the eight corners are described, once we know the atom occupying one of the corner positions. Thus, the whole crystal is described. Sodium chloride is one such example. It can be considered to be composed of two interpenetrating *fcc* lattices, one made up of sodium ions and the other made up of chloride ions (Fig. 5.16).

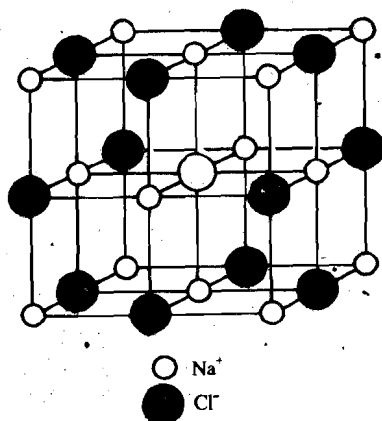


Fig. 5.16 : Structure of sodium chloride.

The sodium ion lattice is shifted in all the three dimensions by half cell-edge length from the chloride ion lattice. A unit cell of NaCl contains four formula units.

5.9.2 Covalent Crystals

In covalent crystals, definite covalent bonds join all the atoms in the crystal. The structure of a covalent crystal is related to the number of valence electrons, the nature of orbitals involved in bond formation and their orientation. One of the most commonly cited

A unit cell of sodium chloride can be considered to be made up of

- one *fcc* unit cell of sodium ions and
- one *fcc* unit cell of chloride ions.

Since each such *fcc* unit cell has four atoms (or ions), sodium chloride crystal has four NaCl formula units per unit cell.

examples is that of diamond (Fig. 5.17). Each carbon atom in diamond is tetrahedrally bonded to four neighbouring carbon atoms. This is so since each carbon has four sp^3 hybridised orbitals pointing towards the corners of a regular tetrahedron. These orbitals overlap with the similar set of orbitals on the neighbouring atoms. Crystals thus formed are hard and unreactive.

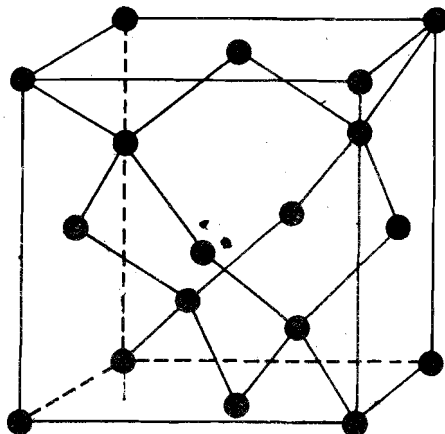


Fig. 5.17 : Structure of diamond.

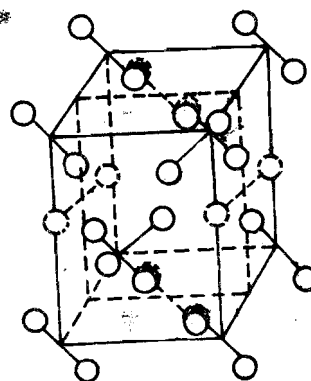


Fig. 5.18 : Structure of iodine crystal—the basis is I_2 molecule.

Let us now see another type of covalent crystals known as molecular crystals.

5.9.3 Molecular Crystals

In molecular crystals, the molecules are held together due to van der Waals interaction. These crystals acquire the structure which has the minimum energy maintaining the original shape of the discrete molecules. Iodine (Fig. 5.18) and carbon dioxide crystals are examples of this type.

There is a class of crystals which have hydrogen bonding between the molecules. An example of this type is ice. In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms, two being linked through covalent bonds in the same molecule and the other two through hydrogen bonds to different water molecules. In the next section, we shall illustrate the four main types of crystal structures in metals.

SAQ 6

The density of potassium bromide is $2.826 \times 10^3 \text{ kg m}^{-3}$. Its cell edge-length is $6.54 \times 10^{-10} \text{ m}$. It has a cubic structure. Find out whether it has CsCl or NaCl type of structure.

.....

.....

.....

.....

5.10 COMMONLY ENCOUNTERED METALLIC STRUCTURES

Most of the metals crystallise in one of the four basic structures—simple cubic, body-centred cubic (*bcc*), hexagonal closest packed (*hcp*) and face-centred cubic (or cubic closest packed—*ccp*). Simple cubic structure is not very common except perhaps for polonium metal which packs in this structure. Alkali metals, Ba, V, Cr, Mo, etc., crystallise in *bcc* structure. The number of nearest neighbours (coordination number) is 8 in *bcc* arrangement.

Each atom in *hcp* and *ccp* arrangements touches three atoms in the plane above, three in the plane below and six in the same plane. Thus, in both the cases, the coordination number is

In *hcp* and *ccp* structures, each layer of atoms is closely packed as the name suggests.

The unit cell with *ccp* arrangement is called *fcc* unit cell.

12. Further, in *ccp* and *hcp* structures, 74% of the total space is filled with atoms. The difference between the *hcp* and *ccp* structures (Figs. 5.19 a and b) is in the arrangement of the third layer of atoms with respect to the first layer. Metals like Be, Mg, Co, Zn pack in the *hcp* structure, whereas those like Ag, Au, Cu, Ni crystallise in *ccp* arrangement.

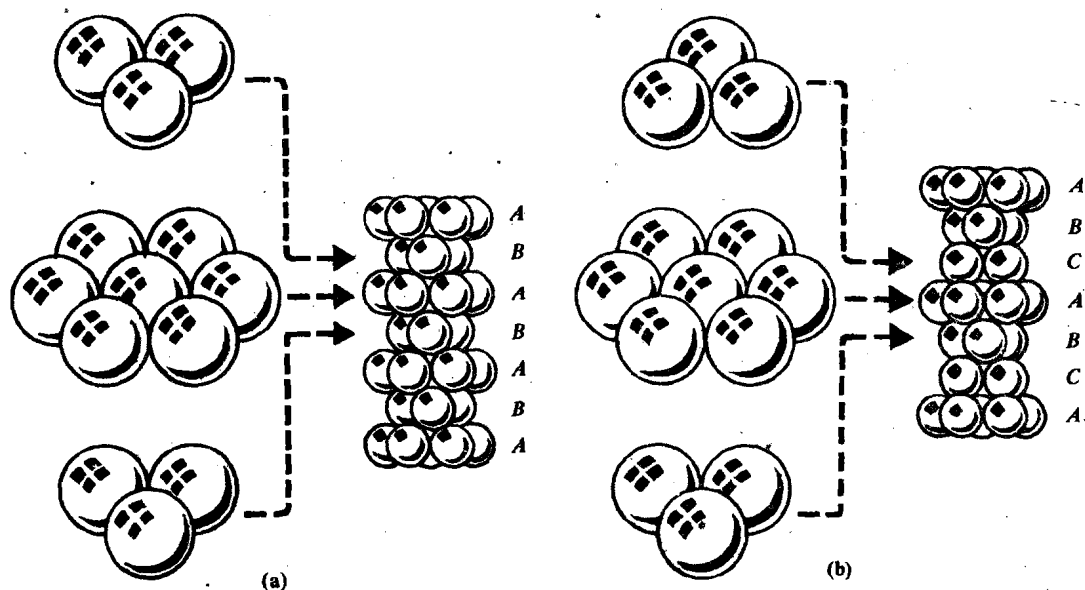


Fig. 5.19 : a) *hcp* arrangement—the atoms in the third layer are straight above those in the first layer—called ABAB arrangement; b) *ccp* arrangement—the atoms in the third layer arranged differently from those in the first—called ABCABC arrangement.

5.11 SEMICONDUCTORS

Semiconductors are solids which are insulators under normal conditions but become conductors when heated or doped with impurities. The electrical conductivity of a semiconductor increases with temperature. The semiconductors can be broadly classified into two types. Let us consider them one by one.

The addition of impurities to a semiconductor is called doping.

5.11.1 Intrinsic Semiconductors

Intrinsic semiconductors are pure substances which conduct electricity when heated. In an intrinsic semiconductor, the energy gap between the highest filled band and the next empty one is very small. Pure germanium, pure grey tin, etc., are intrinsic semiconductors. At absolute zero, they are insulators. But increase in temperature promotes some electrons from filled to next higher band across the gap; so they become conductors. The number of excited electrons increases as the temperature increases; so their conductivity increases with increase in temperature.

5.11.2 Extrinsic Semiconductors

Semiconductors with impurities are called extrinsic semiconductors. They can further be classified into *n*-type and *p*-type semiconductors.

n-type Semiconductors

When a semiconductor is doped with an impurity having more valence electrons than those in the semiconductor, a *n*-type semiconductor is produced. Such an impurity can donate electron(s) to the valence band of the semiconductor, and is called a donor. Phosphorus, arsenic or antimony (each having five valence electrons) are examples of donor impurities added to germanium or silicon (each semiconductor having four valence electrons). The addition of donor impurity to the semiconductor provides additional energy levels and if they are rightly related to the bands of the semiconductor, conductivity may result. That is, if the impurity contains a full energy level just below that of an empty band in the semiconductor, the electrons from the impurity go to empty band in the semiconductor; hence, it becomes negatively charged (*n*-type). Upto certain temperature, the conductivity of a *n*-type semiconductor increases with increase in temperature.

p-type Semiconductors

When the impurity used for doping has less valence electrons than the semiconductor, the impurity can accept electron(s) from the valence band of the semiconductor. Such an impurity is called acceptor. The addition of boron, aluminium, gallium or indium (each having three valence electrons) to silicon or germanium (each semiconductor having four valence electrons) is an example of this type. The essential feature is that the impurity must contain an empty energy level just above a full band in the semiconductor; the electrons from the full band in the semiconductor will pass to the empty level of the impurity. Passage of electrons from the semiconductor to impurity makes the former positively charged (*p*-type). The effect of temperature on the conductivity of a *p*-type semiconductor is similar to that of *n*-type semiconductor.

The combination of *p*-type and *n*-type semiconductor is called *p-n* junction. The *p-n* junctions are used as rectifiers, solar cells, light emitting diodes and other electronic devices.

SAQ 7

Differentiate between intrinsic and extrinsic semiconductors.

5.12 SUMMARY

In this unit, we have briefly described those solid substances which can be classified as crystals. We have also given a hint at the potential usefulness of crystal studies. We summarise below what we have studied so far :

- The terms—lattice, basis and unit cell—were explained.
- Seven crystal systems and fourteen Bravais lattices were discussed.
- Diffraction method and its utility in crystal structure determination were emphasised; an experimental technique was then discussed.
- The nature of bonding in crystals with special reference to metallic bonding was discussed briefly.
- Types of semiconductors were stated and defined.

5.13 TERMINAL QUESTIONS

- 1) Show that for a simple cubic cell, the ratio of the volume occupied to the volume of the unit cell is 0.52.
(Hint : Assume (i) atoms are spherical and (ii) they touch along the cell-edge, i.e.,
 $\text{radius} = \frac{a}{2}$).
- 2) In the following cases, mark '✓' for correct statement and '×' for wrong statement :
 - i) The Miller indices of a crystal plane which makes intercepts $2a$, $3b$, $2c$ are (232).
 - ii) The basis in ice crystal is H_2O molecule.
 - iii) A cube has twelve edges.
 - iv) The unit cell of caesium chloride crystal contains two formula units of CsCl .
- 3) What are the separations of the planes with Miller indices (111), (211) and (100) in a cubic crystal having cell-edge length of 432 pm?
- 4) How many net atoms are there in a *fcc* and *bcc* unit cell? Arrive at the conclusion by geometrical arguments.
- 5) Identify the type of attractive forces (or bonding) mainly responsible for crystal bonding in the following cases:
 - i) diamond
 - ii) potassium bromide
 - iii) aluminium
 - iv) helium

- 6) Sodium crystallises in a *bcc* lattice with a cell-edge length of 4.23×10^{-10} m. Calculate the density of sodium metal.
- 7) The density and cell-edge length of sodium chloride are $2.163 \times 10^3 \text{ kg m}^{-3}$ and 5.63×10^{-10} m, respectively. Using these data, arrive at the number of formula units per unit cell of sodium chloride crystal.

5.14 ANSWERS

Self Assessment Questions

- 1) A unit cell is the smallest unit chosen which repeats itself in three dimensions.
- 2) Simple cubic — lattice points at the eight corners only;
bcc — lattice points at the eight corners and the body-centre;
fcc — lattice points at the eight corners and the six face-centres.
- 3) $d_{123} = 2.132 \times 10^{-10}$ m.
- 4) Using Eq. 5.9,
 $\sin \theta = 0.191$
 $\therefore \theta = \sin^{-1} 0.191$
 $= 11^\circ$
- 5) Using Eq. 5.14, density of tungsten = $1.936 \times 10^4 \text{ kg m}^{-3}$
- 6) Let us find out the number of formula units of KBr present in a unit cell using Eq. 5.17.
 w = Molar mass of KBr = $0.119 \text{ kg mol}^{-1}$.

$$n = \frac{\rho a^3 N_A}{w}$$

$$= \frac{2.826 \times 10^3 \text{ kg m}^{-3} \times (6.54 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.119 \text{ kg mol}^{-1}}$$

$$= 4$$
 Since it has four formula units per unit cell, it has NaCl structure and not CsCl structure.
- 7) The conductivity of an intrinsic semiconductor is due to the existence of a vacant conduction band separated by a small energy gap from the filled valence band. An extrinsic semiconductor owes its electrical conductivity largely to the presence of an impurity with appropriate energy levels.

Terminal Questions

- 1) Since the spheres touch along the edge, the cell-edge length (a) is twice the radius of a sphere (r), i.e., $r = \frac{a}{2}$.
 The volume of a sphere = $\frac{4\pi r^3}{3} = \frac{\pi a^3}{6}$
 A simple cubic lattice has one net sphere only per unit cell (Subsec. 5.7.1). Hence,
 volume occupied in a unit cell = $\frac{\pi a^3}{6}$
 But the volume of the unit cell = a^3
 \therefore Fraction of the volume filled = $\frac{\text{Volume occupied}}{\text{unit cell volume}}$

$$= \frac{\pi a^3}{6 \times a^3} = 0.52$$
- 2) (i) \times (ii) \checkmark (iii) \checkmark (iv) \times .
- 3) 2.49×10^{-10} m; 1.76×10^{-10} m and 4.32×10^{-10} m.
- 4) A *fcc* unit cell has four net atoms while a *bcc* unit cell has two net atoms (see subsec. 5.7.1).

- 5) i) Covalent bonding
 ii) Electrostatic forces (ionic bonding)
 iii) Metallic bonding
 iv) van der waals interaction.
- 6) $1.01 \times 10^3 \text{ kg m}^{-3}$.
- 7) Substituting the density (ρ), cell-edge length (a) and molar mass (w) of sodium chloride in Eq. 5.17, we get,

$$n = \frac{2.163 \times 10^3 \text{ kg m}^{-3} \times (5.63 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.05845 \text{ kg mol}^{-1}}$$

$$= 4.$$

Further Reading

- 1) *Principles of Physical Chemistry*, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.
- 2) *Physical Chemistry*, Gilbert W. Castellan, Narosa Publishing House, Addison—Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.
- 3) *Physical Chemistry*, P.C. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.
- 4) *Physical-Chemistry through Problems*, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.
- 5) *Physical Chemistry—Principles and Problems*, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi, 1990.