

# THE STRUCTURE OF SOLIDS

# 6

Solids, as is well known, are characterised by *incompressibility, rigidity and mechanical strength*. This indicates that the molecules, atoms or ions that make up a solid are *closely packed, i.e.,* they are held together by strong forces and cannot move at random. Thus, *in solids there is well-ordered arrangement of molecules, atoms or ions*. The properties of solids not only depend upon the number and kind of constituents but also on their arrangements.

Solids can be classified into the following two categories.

**1. Crystalline Solids.** *A substance whose constituents are arranged in an orderly manner in a definite geometric form is called a crystalline solid.* X-ray diffraction studies of these solids reveal that the regular arrangement of the constituents (molecules, atoms or ions) *extends over large distances in three-dimensional network of crystals.* In other words, the crystalline solids are said to exhibit *long range order*. Some common examples of crystalline solids are sodium chloride, sulphur, diamond, sugar, etc.

**2. Amorphous Solids.** *A substance whose constituents are not arranged in an orderly manner is called an amorphous solid.* These substances do possess properties such as incompressibility and rigidity to a certain extent but they do not have definite geometric forms. Some amorphous solids may have some orderly arrangement but *it does not extend to more than a few Angstrom units*. Thus, amorphous solids have only *short range order*. Some common examples of amorphous solids are glass, rubber, plastics, etc.

**Difference between Crystalline and Amorphous Solids.** Crystalline and amorphous solids differ from one another in the following respects.

**1. Characteristic Geometry.** A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in three-dimensional space. An amorphous solid, on the other hand, does not have any pattern or arrangement of its constituents and, therefore, does not have any definite geometric shape.

**2. Melting Points.** A crystalline substance has a *sharp melting point, i.e.,* it changes abruptly into liquid state at a fixed temperature. An amorphous substance, on the contrary, does not have a sharp melting point. For example, if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change into liquid state. Strictly speaking, *solid state refers only to crystalline state, i.e., only a crystalline material can be considered to be a true solid.*

**3. Isotropy and Anisotropy.** Amorphous solids differ from crystalline solids in another important respect. *The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index of an amorphous solid are the same in all directions.* Amorphous substances are, therefore, said to be **isotropic**. Liquids and gases are also isotropic.

Crystalline solids, on the other hand, are **anisotropic, i.e.,** *their physical properties are different in different directions.* For example, the velocity of light passing through a crystal varies with the direction

in which it is measured. Thus, a ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction**. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangement in such materials. This can be shown on reference to Fig. 1 in which a simple two-dimensional arrangement of only two different kinds of atoms is depicted. If the properties are measured along the direction indicated by the slanting line  $CD$ , they will be different from those measured in the direction indicated by the vertical line  $AB$ . The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case, each row is made up of one type of atoms only. In amorphous solids, atoms or molecules are arranged at random and in a disorderly manner and, therefore, all directions are identical and all properties are alike in all directions.

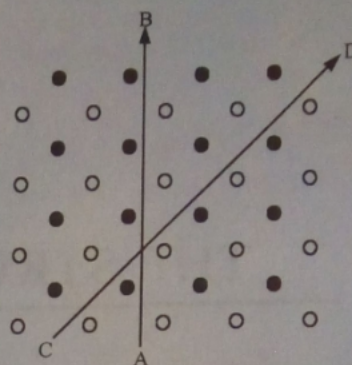


Fig. 1. Anisotropic behaviour of a crystal.

**Size and Shape of Crystals.** Several naturally occurring solids have definite crystalline shapes which can be recognised easily. There are many other solid materials which occur as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape. *Such solids in which the crystals are so small that they can be recognised only under a powerful microscope, are said to be microcrystalline.* The size of a crystal depends on the rate at which it is formed; the slower the rate, the bigger the crystal. This is because time is needed by the ions or atoms or molecules to get into their proper positions in the crystal structure. Thus, large transparent crystals of sodium chloride, silver chloride, lithium chloride, etc., can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the minerals formed by geological processes are often very large.

**Interfacial Angles.** Crystals are bound by plane faces. *The angle between any two faces is called an interfacial angle.* It is measured by an instrument called *goniometer*. It may be noted that the size of the faces or even shapes of the crystals of *one and the same substance* may vary widely with conditions of their formation. Although a crystal may have different shapes yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is also known as law of constancy of interfacial angles or law of crystallography. This is illustrated in Fig. 2. Although the external shapes are different yet the interfacial angle is the same.

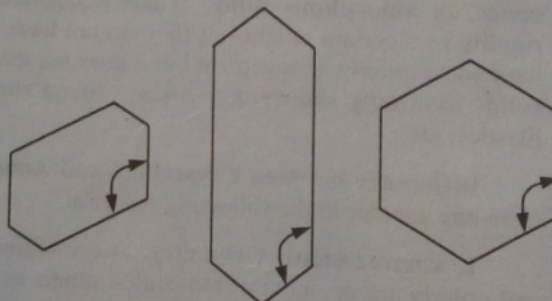


Fig. 2. Interfacial angles in a crystal.

### SYMMETRY IN CRYSTALS

Besides the interfacial angles, another characteristic property of crystals is their symmetry. The symmetry of a crystal may be understood in terms of symmetry operation and symmetry elements.

The **symmetry operation** is an operation performed around a line, plane or point on a body so that it yields the same or similar appearance of the body after the operation. To illustrate this, let us consider a symmetry operation such as rotation around an axis. Suppose we are looking at a cube. If we rotate the cube through  $90^\circ$  about an imaginary axis passing through the centres of the top and bottom faces (Fig. 3), the appearance after rotation is exactly similar to the appearance before rotation. The cube on further rotation presents similar appearance three times more in one complete rotation. Thus, a cube gives similar

appearance by rotation through  $90^\circ$  about an axis passing perpendicularly through the centre. In this example, the rotation about an axis is called *symmetry operation* and the axis of rotation about which the cube is rotated is called a *symmetry element*.

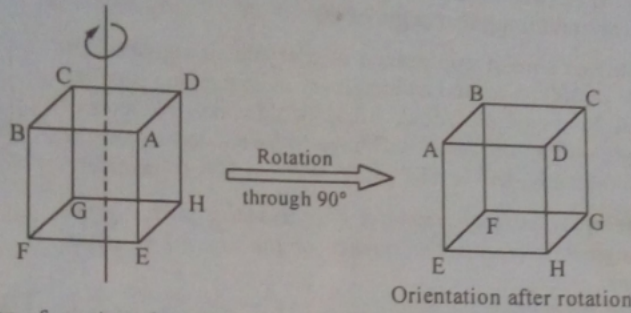


Fig. 3. Illustration of rotation of a cube around an axis. Rotation of a cube through  $90^\circ$  about an axis passing through the centres of the top and bottom faces yields exactly similar appearance.

There are various types of symmetry elements, only three of which will be described here. These are : (1) *Plane of symmetry* (2) *Axis of symmetry* and (3) *Centre of symmetry*.

**1. Plane of symmetry.** When an imaginary plane can divide a crystal into two parts such that one is the exact mirror-image of the other, the crystal is said to have a plane of symmetry.

**2. Axis of Symmetry.** An axis of symmetry is an imaginary line about which the crystal may be rotated such that it presents the same or similar appearance more than once during the complete rotation. For example, in the case of a cube (as discussed above), an axis passing perpendicularly through the centres is such that when the cube is rotated, it presents similar appearance in four rotations of  $90^\circ$  each and the same appearance after the fourth rotation. Such an axis is called a **four-fold** or a **tetrad axis** of symmetry (Fig. 3). In a cube, there are 3 four-fold axes of symmetry, as shown in Fig. 4.

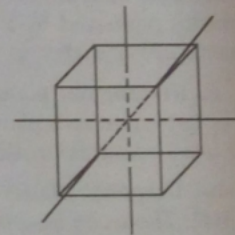


Fig. 4. Three four-fold axes in a cube.

If the same or similar appearance is repeated after an angle of  $120^\circ$ , the axis is called a **three-fold** or **triad axis of symmetry**. One of the three-fold axes in a cube is shown in Fig. 5(a). To illustrate the rotation more clearly, it is held as shown in Fig. 5(b) and rotated around the body diagonal. Since there are four body diagonals in a cube, it has 4 three-fold axes of symmetry.

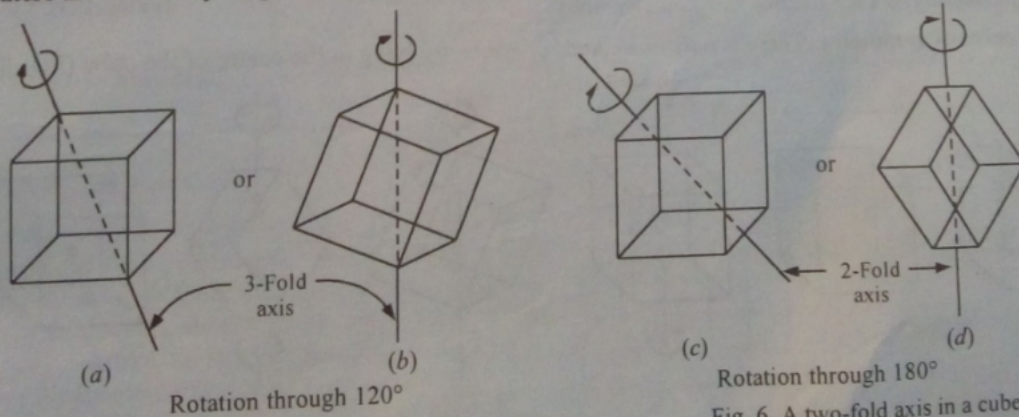


Fig. 5. A three-fold axis in a cube.

Fig. 6. A two-fold axis in a cube.

Similarly, if the same or similar geometry appears after an angle of  $180^\circ$ , the axis is called a **two-fold** or a **diad axis**. One of the two-fold axes in a cube is shown in Fig. 6(a). The rotation can be understood by holding the cube as shown in Fig. 6(b). There are, evidently, 2 two-fold axes in a cube.

Likewise, if the same or similar geometry appears after rotation through an angle of  $60^\circ$ , the axis is called a **six-fold** or **hexad axis**. A hexagonal crystal has one six-fold axis (Fig. 7). It is clear from the figure that similar appearance is repeated after rotating the crystal through an angle of  $60^\circ$ .

In general, if the same or similar appearance of a crystal is repeated on rotating it through an angle of  $360^\circ/n$  around an imaginary axis, the axis is called an **n-fold axis**. A crystal can have only the 2-fold, 3-fold, 4-fold and 6-fold axes of rotation. The angle through which the crystal will have to be rotated to get the same or similar appearance, evidently, will be  $180^\circ$ ,  $120^\circ$ ,  $90^\circ$  and  $60^\circ$ , respectively.

**3. Centre of Symmetry.** *Centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions.*

It may be pointed out that a crystal may have any number of planes or axes of symmetry but it has **only one centre of symmetry**.

**Elements of Symmetry of a Crystal.** As mentioned above, there are three different types of symmetry elements which are possible in a crystal. A crystal may have different numbers of each type of symmetry element. *The total number of planes, axes and centres of symmetries possessed by a crystal is termed as the elements of symmetry of the crystal.* To explain this term further, we may consider the elements of symmetry possessed by a **cubic crystal**, such as NaCl crystal. A cubic crystal possesses a **total of 23 elements of symmetry**, as will be clear from the discussion that follows. These elements of symmetry are :

**a. Rectangular planes of symmetry.** One rectangular plane of symmetry is shown in Fig. 8(a). There will be two more such planes, each of which will be at right angles to the plane shown in the figure. Thus, *there are 3 rectangular planes of symmetry in all.*

**b. Diagonal planes of symmetry.** One plane passing *diagonally* through the cube is shown in Fig. 8(b). *There can be a total of 6 such planes passing diagonally through the cube.*

**c. Axes of four-fold symmetry.** One of the four-fold axes is shown in Fig. 8(c). Evidently, *there can be a total of 3 such four-fold axes at right angles to one another.*

**d. Axes of three-fold symmetry.** One such axis passing through opposite corners is shown in Fig. 8(d). *There can be a total of 4 such three-fold axes.*

**e. Axes of two-fold symmetry.** One such axis emerging from opposite edges is shown in Fig. 8(e). There are, evidently, *6 such axes of two-fold symmetry.*

**f. Centre of symmetry.** There is *only one centre of symmetry* lying at the centre of the cube (Fig. 8f).

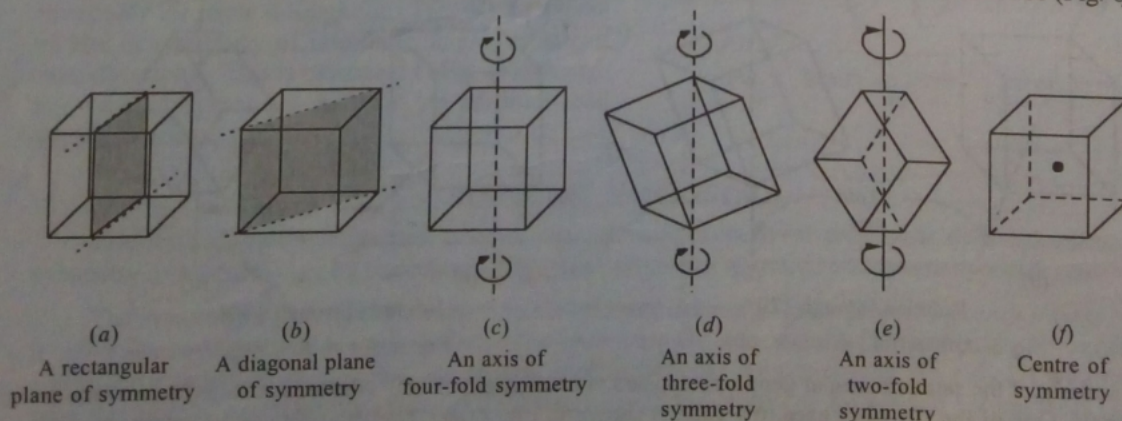


Fig. 8. Various elements of symmetry in a cubic crystal.

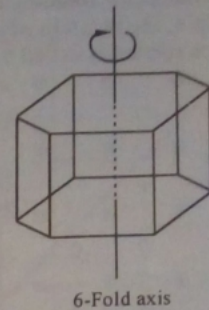


Fig. 7. A six-fold axis in a hexagonal crystal.

Thus, the numbers of symmetry elements of various types in a cubic crystal are :

$$\text{Planes of symmetry} = 3 + 6 = 9$$

$$\text{Axes of symmetry} = 3 + 4 + 6 = 13$$

$$\text{Center of symmetry} = 1$$

$$\text{Total number of symmetry elements} = 23$$

**Basic Crystal Systems.** It can be shown from geometrical considerations that, theoretically, there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems, however, have been grouped together so that we have only seven different categories, known as the seven basic crystal systems. These are *cubic*, *orthorhombic*, *tetragonal*, *monoclinic*, *triclinic*, *hexagonal* and *rhombohedral*.

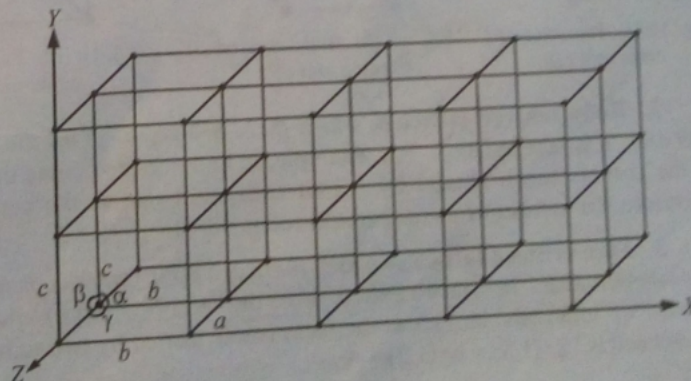
These systems together with the maximum number of planes of symmetry and axes of symmetry and their examples are given in Table 1.

TABLE I  
The Basic Crystal Systems and Their Maximum Symmetry Elements

System	Number of Maximum Axes and Planes of Symmetry	Examples
1. Cubic	Nine planes of symmetry Thirteen axes of symmetry	NaCl, KCl, CaF <sub>2</sub> , ZnS, Cu <sub>2</sub> O, Diamond, Alums, Pb, Ag, Au
2. Orthorhombic	Three planes of symmetry Three axes of symmetry	KNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub> , BaSO <sub>4</sub> , PbCO <sub>3</sub> , Mg <sub>2</sub> SiO <sub>4</sub> , Rhombic sulphur
3. Tetragonal	Five planes of symmetry Five axes of symmetry	SnO <sub>2</sub> , TiO <sub>2</sub> , ZrSiO <sub>4</sub> , KH <sub>2</sub> PO <sub>4</sub> , PbWO <sub>4</sub> , Sn
4. Monoclinic	One plane of symmetry One axis of symmetry	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O, Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O, CaSO <sub>4</sub> ·2H <sub>2</sub> O, Monoclinic sulphur
5. Triclinic	No plane of symmetry No axis of symmetry	CuSO <sub>4</sub> ·5H <sub>2</sub> O, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>3</sub> BO <sub>3</sub>
6. Hexagonal	Seven planes of symmetry Seven axes of symmetry	ZnO, CdS, HgS, Graphite, Ice, PbI <sub>2</sub> , Beryl, Mg, Zn, Cd
7. Rhombohedral	Seven planes of symmetry Seven axes of symmetry	NaNO <sub>3</sub> , ICl, Calcite, Magnesite, Quartz, As, Sb, Bi

### Space Lattice and Unit Cell

Crystals have definite orderly arrangements of their constituents (atoms, molecules or ions) in three dimensions. The positions of atoms, molecules or ions in a crystal, relative to one another in space, are designated usually by points. Such a representation is called *space lattice*. A space lattice is an array of points showing how atoms, molecules or ions are arranged at different sites in a



three-dimensional space. An example of an array of points in a three-dimensional space lattice is shown in Fig. 9. Each point represents an identical atom or group of atoms.

If we carefully look at a space lattice, it is observed that the entire lattice can be considered as a repetition of a small pattern (or motif). This smallest repeating pattern is called a *unit cell*. Thus, a *unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance*. The crystal may be considered to consist of infinite number of unit cells. Each unit cell in a three-dimensional space has, evidently, three vectors,  $a$ ,  $b$  and  $c$ , as shown in Fig. 9.

Note that these are the *points* and not the lines which constitute the space lattice. The lines joining the points are drawn simply for representing the three axes by means of which the relative positions of the points can be described. For example, in Fig. 9, three imaginary axes,  $OX$ ,  $OY$  and  $OZ$ , which are used to represent the unit cell, have been shown. In order to describe a unit cell, we should know : (i) the distances  $a$ ,  $b$  and  $c$  which give the lengths of the edges of the unit cell and (ii) the angles  $\alpha$ ,  $\beta$  and  $\gamma$  which give the angles between the three imaginary axes  $OX$ ,  $OY$  and  $OZ$ .

Knowing the unit cell dimensions, the **theoretical density** of a crystal can be calculated from the relation

$$\rho = n M_m / (N_A V) \quad \dots(1)$$

where  $n$  is the number of atoms in the unit cell,  $M_m$  is the molar mass,  $N_A$  is Avogadro's number and  $V$  is the volume of the unit cell.

### Bravais Lattices

Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven basic crystal systems put together is only 14, as given in Table 2 (column 2). These are known as **Bravais lattices**.

The crystals have four kinds of Bravais lattices depending upon the shapes of the unit cells. These are :

1. **Simple or primitive lattice** in which there are points at all the corners of the unit cell. It is labelled as P. A primitive cubic unit cell is shown in Fig. 10 (a). This unit cell consists of one atom at each of the eight corners. Since each atom at the corner is shared by 8 unit cells, therefore, only  $1/8$  th of the atom is within the unit cell. Thus, the number of atoms per unit cell in primitive lattice is  $8 \times (1/8) = 1$ .

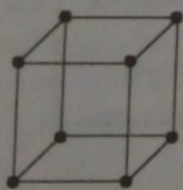


Fig. 10 (a). Primitive (P) cubic unit cell.

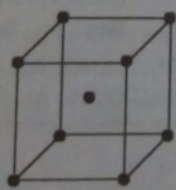


Fig. 10 (b). Body centred (I) cubic unit cell.

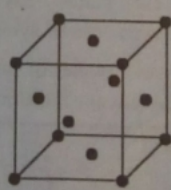


Fig. 10 (c). Face centred (F) cubic unit cell.

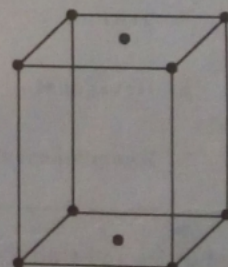


Fig. 10 (d). End centred (C) orthorhombic unit cell.

2. **Body centred lattice** in which there are points at all the corners as well as in the centre of the unit cell. It is labelled as I. For example, in body centred cubic unit cell (Fig. 10 b), there are eight atoms at the corners (each shared by 8 unit cells) and one at the centre (belonging to only one unit cell). Therefore, the number of atoms per unit cell is  $8 \times (1/8) + 1 = 2$ .

3. **Face centred lattice** in which there are points at the corners as well as at the centre of each face. It is labelled as F. In a face centred cubic unit cell (Fig. 10 c), there are eight atoms at the corners (each shared by 8 unit cells) and six at the faces (each shared by two unit cells). Therefore, the number of atoms per unit cell is  $8 \times (1/8) + 6 \times (1/2) = 4$ .

4. **End centered lattice** in which there are points at the corners and at the centres of two end faces. It is labelled as C. For example, in an end centred orthorhombic unit cell\* (Fig. 10 d), there are eight atoms at the corners and two at the end faces so that the number of atoms per unit cell is  $8 \times (1/8) + 2 \times (1/2) = 2$ .

The Bravais space lattices associated with various crystal systems are shown in Figs. 11 (a), (b), (c) and (d). The unit cell is described by the lengths  $a$ ,  $b$  and  $c$  of the three intersecting edges and the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the pairs of edges  $b, c$ ;  $a, c$  and  $a, b$ , respectively.

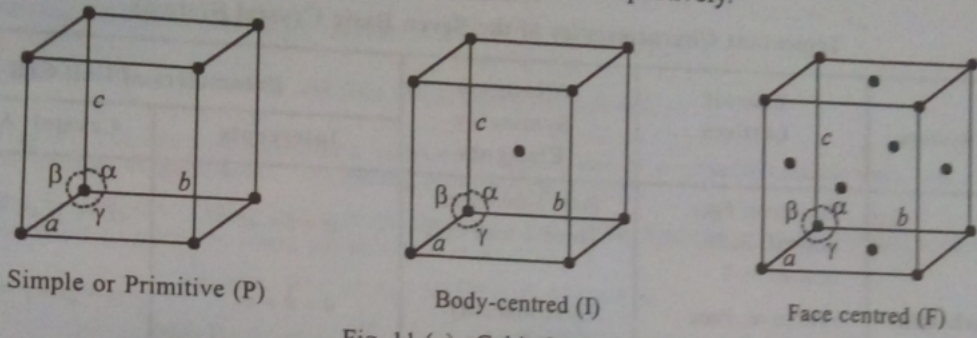


Fig. 11 (a). Cubic Space Lattices

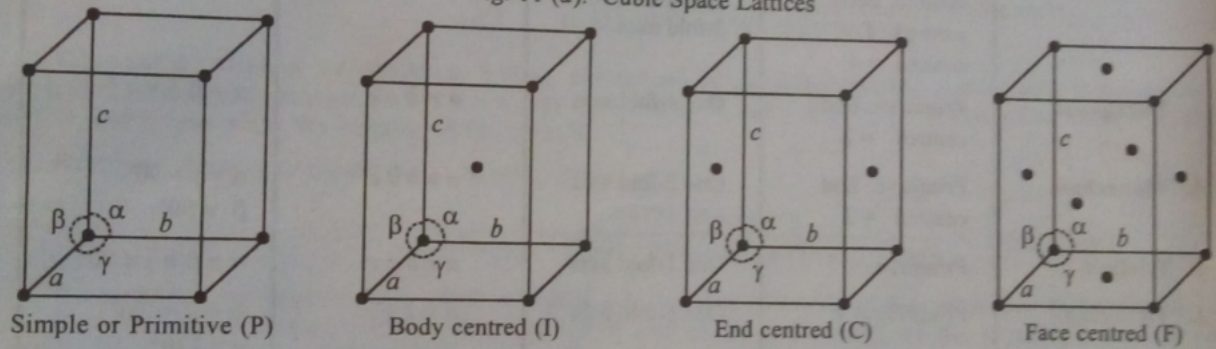


Fig. 11 (b). Orthorhombic Space Lattices.

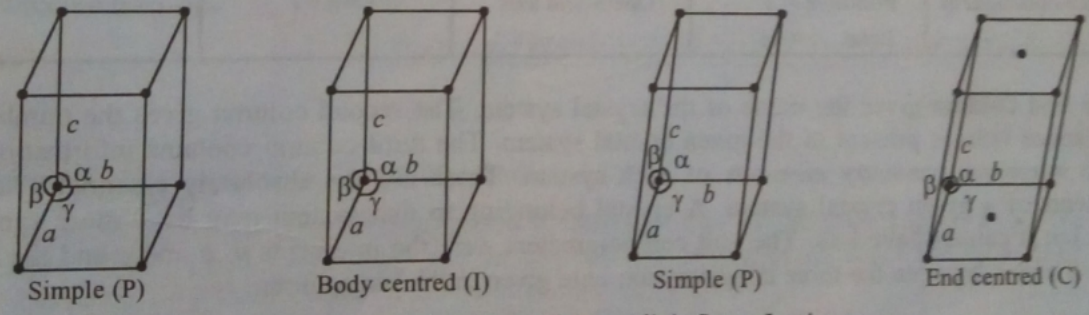


Fig. 11 (c). Tetragonal and Monoclinic Space Lattices

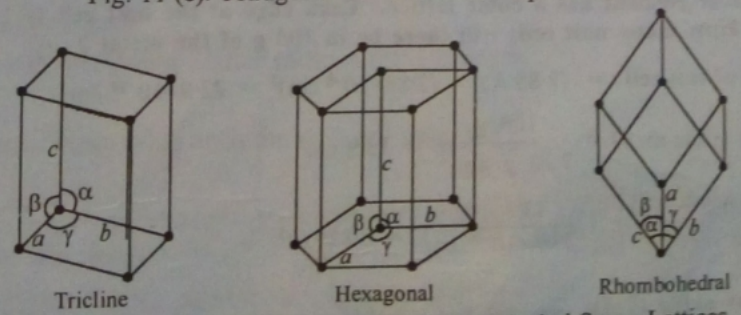


Fig. 11(d). Triclinic, Hexagonal and Rhombohedral Space Lattices.

The actual lattice in a crystal of a given kind consists of a repetition of a unit cell of that kind all over in three-dimensional space. As already mentioned, there can only be a maximum of 32 combinations of elements of symmetry (point groups).

Some detailed descriptions of the seven basic crystal systems and their Bravais lattices are given in Table 2.

TABLE 2  
Important Characteristics of the Seven Basic Crystal Systems

Crystal System	Bravais Lattices	Minimum Symmetry Elements	Parameters of Unit Cell	
			Intercepts	Crystal Angles
1. Cubic	Primitive, Face centred, Body centred = 3	Four 3-fold axes Three 4-fold axes	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2. Orthorhombic	Primitive, Face centred, Body centred, End centred = 4	Three mutually perpendicular 2-fold axes	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3. Tetragonal	Primitive, Body centred = 2	One 4-fold axis	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
4. Monoclinic	Primitive, End centred = 2	One 2-fold axis	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$
5. Triclinic	Primitive = 1	One 1-fold axis	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
6. Hexagonal	Primitive = 1	One 6-fold axis	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
7. Rhombohedral	Primitive = 1 Total = 14	One 3-fold axis	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

The first column gives the name of the crystal system. The second column gives the number and types of space lattices present in the given crystal system. The third column contains information with regard to *minimum symmetry elements* of each system. These are the absolutely essential symmetry requirements of a given crystal system. A crystal belonging to that system may have more symmetry elements but it cannot have less. The unit cell parameters, viz., the intercepts  $a$ ,  $b$  and  $c$  and the crystal angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the three imaginary axes are given in the last column.



The concept of Miller indices may be illustrated as follows :

Consider the shaded plane in Fig. 12. It is clear from the figure that the intercepts of the shaded plane along X, Y and Z axes are :

$a \quad b/2 \quad c/2$  and the fractional intercepts are  $a/a \quad b/2b \quad c/2c$  or  $1 \quad 1/2 \quad 1/2$

∴ Miller indices (reciprocals of the intercepts) are :

$1/1 \quad 2/1 \quad 2/1$  or  $1 \quad 2 \quad 2$

Let us now describe the planes in a cube. It should be remembered that if a plane is parallel to an axis, its intercept with that axis would be infinity. Thus, the Miller index for that plane will be zero ( $1/\infty = 0$ ). For example, consider the shaded plane in Fig. 13. It is clear from the figure that the fractional intercepts of the shaded plane are :

$\infty \quad 1 \quad \infty$

∴ Miller indices are

$1/\infty \quad 1/1 \quad 1/\infty$  or  $0 \quad 1 \quad 0$

Similarly, the Miller indices of some planes in cubic crystals, shown shaded in Fig. 14 are as given below.

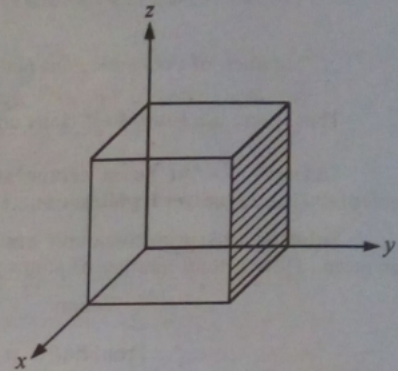


Fig. 13. A plane in a cube having Miller indices 010.

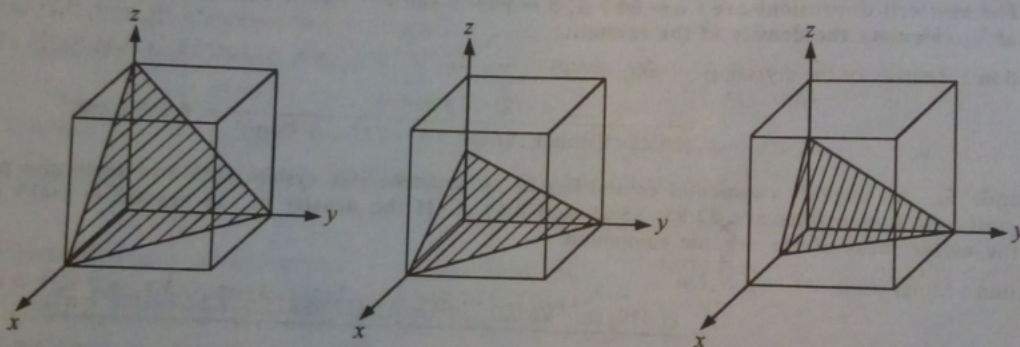


Fig. 14. Miller indices for some planes in cubic crystals.

Fractional intercepts	1	1	1	Fractional intercepts	1	1	1/2	Fractional intercepts	1/3	1	2/3
Miller indices	1/1	1/1	1/1	Miller indices	1/1	1/1	2/1	Miller Indices	3/1	1/1	3/2
	1	1	1		1	1	2		6	2	3

Example 6. Calculate the Miller indices of crystal planes which cut through the crystal axes at (i)  $(2a, 3b, c)$  (ii)  $(a, b, c)$  (iii)  $(6a, 3b, 3c)$

Solution : Following the procedure given above, we prepare the table as follows :

(i)	$a$	$b$	$c$	
	2	3	1	Fractional Intercepts
	1/2	1/3	1	Reciprocals
	3	2	6	Clear fractions

Hence, the Miller Indices are (326).

(ii)	$a$	$b$	$c$	
	1	1	1	Fractional Intercepts
	1	1	1	Reciprocals
	1	1	1	Clear fractions

Hence, the Miller indices are (111).

### Designation of Planes in Crystals : Miller Indices

A number of methods have been suggested to represent the various planes in crystals. The method proposed by W.H. Miller is commonly used. In this method, the planes are described by a set of integers ( $h$ ,  $k$  and  $l$ ) known as **Miller indices**. *The Miller indices of a plane of a crystal are the reciprocals of the fractional intercepts of that plane on the various axes.*

The procedure for determining Miller indices for a plane is as follows :

1. Prepare a three-column table with the unit cell axes at the tops of the columns.
2. Enter in each column the intercept (expressed as a multiple of  $a$ ,  $b$  or  $c$ ) of the plane with these axes.

Divide these intercepts by the corresponding lengths  $a$ ,  $b$ ,  $c$  of axis of unit cell to obtain fractional intercepts on the axis.

3. Invert all numbers.
4. Clear fractions to obtain  $h$ ,  $k$  and  $l$ .

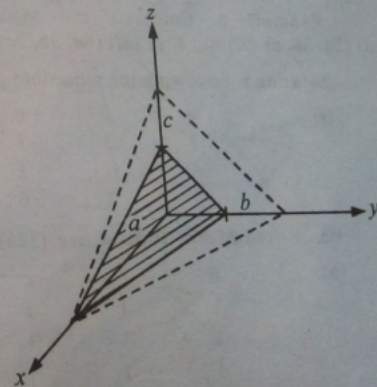


Fig. 12. A plane having Miller indices 122.

## CRYSTALS OF THE TYPE AX

**Structure of Sodium Chloride (NaCl).** The unit cell of sodium chloride crystal is shown in Fig. 34. In this structure, the sodium ions are represented by hollow circles and chloride ions by solid circles.

The salient features of this structure are as follows :

1. The chloride ions are arranged in *cubic close packing (ccp)* arrangement. In this arrangement, there are  $\text{Cl}^-$  ions at the corners of the cube as well as at the centre of each face (*face centred cubic arrangement*).

2. The sodium ions occupy all the *octahedral sites*.

3. There is only one octahedral site per atom in a close packed lattice. Therefore, there will be one  $\text{Na}^+$  ion for every  $\text{Cl}^-$  ion. This corresponds to 1 : 1 stoichiometry of sodium chloride crystal. This stoichiometry can also be understood by counting the number of  $\text{Na}^+$  and  $\text{Cl}^-$  ions which contribute to the unit cell, as discussed below.

It is clear from Fig. 34 that there are eight  $\text{Cl}^-$  ions at the corners and six at the faces of the unit cell. We can easily understand from the figure that each ion at the corner is shared between eight unit cells and its contribution per unit cell is  $1/8$ . Similarly, each ion on a face is shared by two unit cells so that its contribution per unit cell is  $1/2$ . Therefore, the number of  $\text{Cl}^-$  ions for the unit cell is equal to  $8 \times (1/8) + 6 \times (1/2) = 4$ . The number of sodium ions can also be calculated in a similar way. There are twelve  $\text{Na}^+$  ions on the edges and one inside the cell. It can be easily seen that each ion on the edge is shared by four unit cells and its contribution per unit cell is  $1/4$ , while the ion at

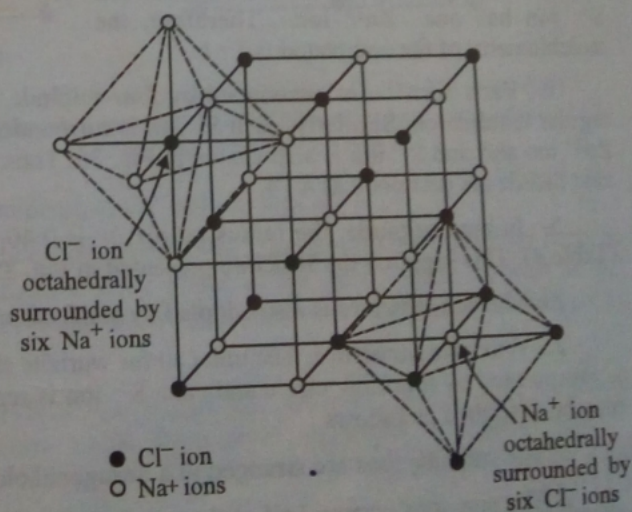


Fig. 34. Unit cell representation of NaCl structure, Hollow circles represent  $\text{Na}^+$  ions and solid circles represent  $\text{Cl}^-$  ions.

the body centre contributes only to one unit cell. Therefore, the number of  $\text{Na}^+$  ions for the unit cell is equal to  $12 \times (1/4) + 1 = 4$ . Thus, the stoichiometry is 1 : 1.

4. In this structure, each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions which are disposed towards the corners of a regular octahedron. This has also been shown in the figure. Similarly, each  $\text{Cl}^-$  ion is surrounded by six  $\text{Na}^+$  ions. Thus, the coordination number of  $\text{Na}^+$  ion as well as that of  $\text{Cl}^-$  ion is 6.

5. We have seen that for cations to fit into octahedral sites, the radius ratio  $r_+/r_-$  should be equal to 0.414 (Table 4). The radius of  $\text{Na}^+$  ion is 0.95 Å and that of  $\text{Cl}^-$  ion is 1.81 Å so that  $r_{\text{Na}^+}/r_{\text{Cl}^-}$  is 0.524. Therefore, to accommodate somewhat larger sized  $\text{Na}^+$  ions,  $\text{Cl}^-$  ions move apart slightly. In other words, the *ccp* arrangement of  $\text{Cl}^-$  ions is slightly opened up. This type of structure is adopted by most of the alkali metal halides, the alkaline earth metal oxides and  $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ , etc.

**Structure of Zinc Sulphide ( $\text{ZnS}$ ).** It has two types of structures known as

1. Zinc blende Structure

**1. Zinc Blende Structure.** The unit cell of zinc blende structure is shown in Fig. 35. In this structure, the zinc ions are represented by hollow circles and the sulphide ions are represented by solid circles. The salient features of this structure are as follows :

1. The sulphide ions are arranged in *ccp* arrangement, *i.e.*, at the corners of the cube and at the centre of each face.

2. The zinc ions occupy half of the tetrahedral sites.

3. Since there are two tetrahedral sites per atom in a close packed lattice, this means that there are two tetrahedral sites per  $\text{S}^{2-}$  ion. In this arrangement, only half of the tetrahedral sites are occupied by  $\text{Zn}^{2+}$  ions so that each  $\text{S}^{2-}$  ion has one  $\text{Zn}^{2+}$  ion. Therefore, the stoichiometry of the compound is 1 : 1.

4. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, each  $\text{S}^{2-}$  ion is surrounded by four  $\text{Zn}^{2+}$  ions. The arrangement around one  $\text{Zn}^{2+}$  ion and one  $\text{S}^{2-}$  ion is also shown in Fig. 35. Thus, the coordination numbers of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  ions in zinc blende are described as 4 : 4.

5. In zinc sulphide, the radius ratio  $r_+/r_-$  is 0.40. This suggests that the coordination number is 4 (Table 4). This supports the structure presented in Fig. 35.

Zinc blende structure is also adopted by some other compounds such as  $\text{ZnO}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ , etc.

**2. Wurtzite Structure.** The unit cell for wurtzite structure is shown in Fig. 36 in which each  $\text{Zn}^{2+}$  ion is represented by a hollow circle and each  $\text{S}^{2-}$  ion is represented by a solid circle. The wurtzite structure may be described as follows :

1. The sulphide ions are arranged in a hexagonal close packed (*hcp*) arrangement.

2. The zinc ions occupy half of the tetrahedral sites.

3. There are two tetrahedral sites for each  $\text{S}^{2-}$  ion in the lattice. Since only half of them are occupied by  $\text{Zn}^{2+}$  ions, the stoichiometry of the compound is 1 : 1.

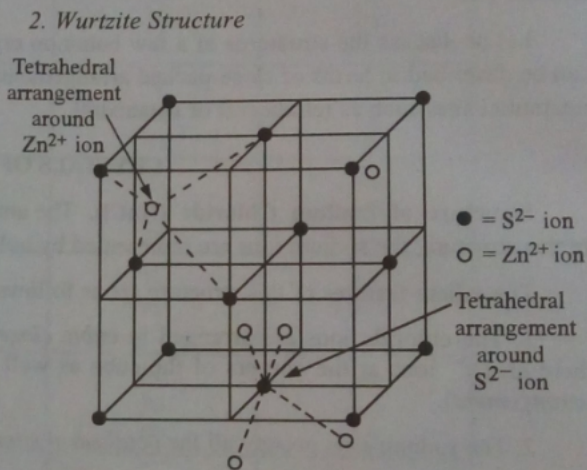


Fig. 35. Unit cell representation of zinc blende structure. Hollow circles represent  $\text{Zn}^{2+}$  ions and solid circles represent  $\text{S}^{2-}$  ions.

4. Each  $S^{2-}$  ion is surrounded by four  $Zn^{2+}$  ions which are disposed towards the corners of a regular tetrahedron. Similarly, each  $Zn^{2+}$  ion is surrounded by four  $S^{2-}$  ions. The arrangement around one  $Zn^{2+}$  ion and one  $S^{2-}$  ion is shown in Fig. 36. Therefore, the coordination numbers of  $Zn^{2+}$  and  $S^{2-}$  ions in wurtzite structure are 4 : 4.

5. The radius ratio  $r_+/r_-$  in this structure is 0.40 which also suggests that the coordination number is 4 (Table 4) and that the crystal has a tetrahedral structure. Thus, the radius ratio rule supports the above structure. The compounds such as  $AgI$ ,  $ZnO$ ,  $NH_4F$  and  $AlN$  have wurtzite structure.

It will be noted that the basic difference between zinc blende and wurtzite structure is that whereas in the former case the sulphide ions are arranged in *ccp* type of packing, in the latter case they are arranged in *hcp* type of packing.

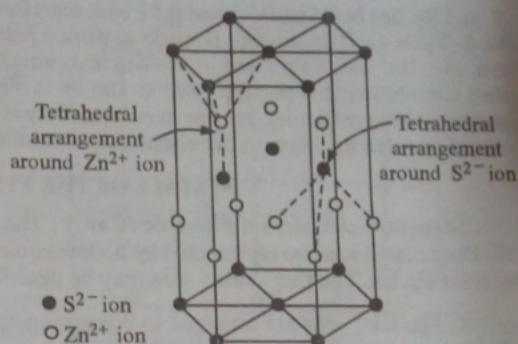


Fig. 36. Unit cell representation of wurtzite structure.  $S^{2-}$  ions (solid circles) adopt *hcp* arrangement and  $Zn^{2+}$  ions (hollow circles) occupy half of the tetrahedral sites.

**Structure of Cesium Chloride ( $CsCl$ ).** The unit cell of  $CsCl$  is shown in Fig. 37. In this structure, cesium ions are represented by hollow circles whereas chloride ions are represented by solid circles. The structure of  $CsCl$  may be described as follows :

1. The  $Cl^-$  ions form the simple cubic arrangement and the  $Cs^+$  ions occupy the cubic interstitial sites. In other words, the  $Cl^-$  ions may be regarded as lying at the corners of a cube and cesium ions are present at the body centre of each cube.

2. Each  $Cs^+$  ion is surrounded by eight  $Cl^-$  ions which are disposed towards the corners of a cube. This is clear from Fig. 37(a). When the unit cell is extended as shown in Fig. 37 (b), it becomes clear that each  $Cl^-$  ion is also surrounded by eight  $Cs^+$  ions. Thus, both types of ions are in equivalent positions. Therefore, the coordination numbers of  $Cs^+$  and  $Cl^-$  ions are 8 : 8.

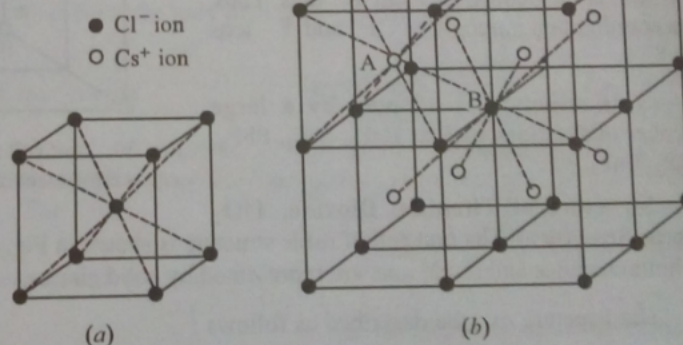


Fig. 37. (a) Unit cell representation of  $CsCl$ . The  $Cl^-$  ions adopt simple cubic arrangement and  $Cs^+$  ions occupy cubic sites. (b) The extended unit cell.

The above structure may be described as body centred cubic. But, this would be a misnomer because the body centred cubic structure is one which has the same atoms at the body centre as well as the corners. But in  $CsCl$ , the atoms at the corners are different from the atoms at the centre. This type of structure is adopted by  $CsBr$ ,  $CsI$ ,  $TlCl$ ,  $TlBr$ , etc.

Since coordination numbers of ions in  $CsCl$  (8 : 8) are higher than those in  $NaCl$  (6 : 6), we might expect that cesium chloride lattice would be more stable since each ion would have more ions of opposite charge as its neighbours. This is actually the case. The cesium chloride lattice is 1 per cent more stable than the sodium chloride lattice.

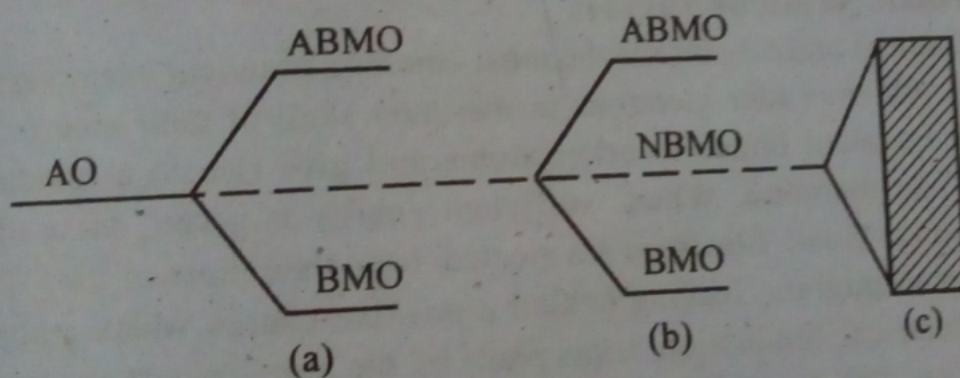
Here question arises that if  $CsCl$  lattice is more stable then why do the halides of  $Li$ ,  $Na$ ,  $K$  and  $Rb$  not have this lattice ? The answer lies in the radius ratio effect. The radius ratio in the halides of  $Li$ ,  $Na$ ,

## Metallic bond Band theory :

This theory was introduced by Hund and Muliken. This is also known as the Molecular Orbital Theory (MOT).

A metal piece contains about  $10^{20}$  atoms. A large number of molecular orbitals (MO's) are formed from a large number of atomic orbitals (AO's)

Let us consider two atoms forming a molecule. In the formation of this molecule the two AO's of equal energy combine to give two MO's one bonding and one antibonding. For 'n' atoms where 'n' is large, we may have 'n' distinct energy levels. In the metallic crystal 'n' is about  $10^{23}$ . So many orbitals form a band of energy levels. This band appears to be continuous. So it is called a 'quasi continuum'. Note that there are 'n' energy levels and 'n' electrons. So the band is only half filled. The formation of MO's for two atoms (fig. a), three atoms (fig. b) and 'n' atoms (fig. c) are shown below:



BMO = Bonding molecular orbital  
 ABMO = Antibonding molecular orbital  
 NBMO = Non bonding molecular orbital

Band model can readily explain the metallic properties. When a metal is connected to a source of current the electrons acquire energy and start moving because there are several empty antibonding orbitals. Thus if a positive electrode is placed at one end of the metal and a negative electrode is at the other then electrons will move towards the anode. Thus it conducts electric current.

Similarly conduction of heat can also be explained. If one end of a piece of metal is heated, electrons at that end gain energy and move to unoccupied MO where they can travel rapidly to any other part of the metal which in turn becomes hot.

Thus we see that electrons in the lower energy MO's are not localised. These delocalised electrons absorb and re-emit light. So the metal surface becomes shiny and lustrous.

Since the bonding electrons are not localised, there are no rigid bonds between the various atoms present in a metallic crystal. So the lattice can be easily deformed. This explains the malleability and ductility of metals.

## **Semiconductors**

Semiconductors are solids that are insulators at absolute zero but which conduct electricity by the passage of electrons at normal temperatures. Eg., : Silicon, germanium.

Semiconductors are of two types :

- i. Intrinsic semiconductors,
- ii. Extrinsic semiconductors (n-type and p-type)

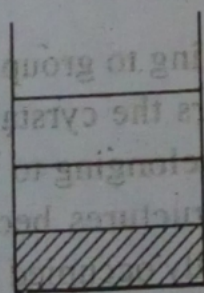
### **1. Intrinsic semiconductors**

Germanium and silicon are the most common practical examples. The atoms of both have four electrons in the outer shell of their atoms. They form four covalent bonds to other atoms and give rise to a tetrahedral structure like diamond. When sufficient energy is given, some of the covalent bonds break. Electrons are ejected from their normal sites. These electrons then migrate, leaving behind a positive charge where a bond is missing. Electrical conduction takes place by the migration of electrons in one direction. The positive holes migrate in other direction. This is called intrinsic conduction.

Intrinsic semiconductors generally consist of covalent crystals. They may be elements or compounds. Unlike normal metallic conductors the conduction of a semiconductor increases with a rise in temperature and the presence of impurities. So they do not conduct current at low temperatures. This is because a rise in temperature will create more carriers as more bonds are broken by thermal energy. Semiconductors have an energy band structure in which the filled valence band is separated from the

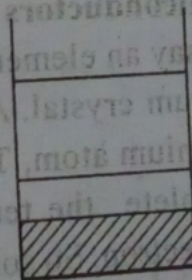
empty conduction band. (Insulators are also having a similar structure) The space between the filled valency band and the empty conduction band is known as the forbidden energy band. This forbidden energy band is in semiconductors is much narrower than in the case of an insulator. At low temperatures, the thermal energy of the electrons in the valence band is much too low. So these electrons do not cross the forbidden energy band. So they will exhibit very low conductivity at this temperature.

When the temperature is raised, the thermal energy of the electrons increase. Some valency electrons overcome the relatively narrow forbidden band and reach the conduction band. Thus when an electric field is applied, these few electrons are free to flow through the crystal. Thus they exhibit a limited electrical conductance at the higher temperature. Further increase in temperature will increase the number of electrons in the conduction band and result in increased electrical conduction. At the same time, the unfilled levels in the valence band will also increase conduction of the crystal by the movement of electrons into the now vacant energy levels in the valence band. Thus this type of conduction is due to the movement of the vacancies, or, 'holes' under the influence of the electric field. Semiconductors which consist of atoms of a single type (E.g. Silicon and germanium) and which depend for their semiconductivity on the electrons, which are thermally excited across the forbidden band are known as intrinsic conductors.



(i)

Insulator



(ii)

Semiconductor

a = Filled valance band; b = Forbidden band;  
c = Conduction band;

- i. Insulator in which the forbidden band is wide.
- ii. Semiconductors in which the forbidden band is narrow.



## 2. Extrinsic semiconductors

### i. n-type semiconductors

Germanium and silicon belong to group IV of the periodic table. These elements, in pure state, have very low electrical conductivity. However on adding even traces of an element belonging to group III or V, the electrical conductivity is greatly enhanced.

Usually the impurity atoms are introduced by adding a known amount of impurity to the melt of the pure metal and then the crystal is allowed to grow. Alternately the impurity can be diffused into the pure semiconductor crystal.

Let us say an element like arsenic belonging to group V is added to, say germanium crystal. An arsenic atom enters the crystal lattice and replaces a germanium atom. Four of the electrons in arsenic form covalent bonds with the surrounding germanium atoms. The fifth electron of arsenic remains free. Thus, one extra electron, over and above the number required for forming four covalent bonds, gets introduced into the crystal. This extra electron helps in the conduction of electricity. That is, it behaves like a conduction electron as in metal. The germanium containing traces of arsenic is called the 'arsenic doped' germanium. It exhibits fairly high electrical conductivity. This type of conduction current is called n-type semiconduction. This is a type of extrinsic conduction. It is much greater than the intrinsic conduction discussed above.

### ii. p-type semiconductors

Now, let us say an element like indium belonging to group III is added to, say, germanium crystal. An indium atom enters the crystal lattice and replaces a germanium atom. The three electrons belonging to indium are not able to complete the tetrahedral covalent structures because of the shortage of one electron. So some of the sites normally occupied by electrons will be left empty.

This give rise to electron vacancies. These electron-vacant sites are called 'positive holes' because the net charge at these sites is positive. When an electric field is applied adjacent electrons move into the positive holes. This movement creates positive holes elsewhere. The migration of positive holes thus continues and current is carried across the crystal. Thus doping of germanium with traces of indium increases the electrical conductivity of germanium crystal. In this type of conduction current is

carried by positive holes. So this is called p-type semi conduction.

Both n - type and p - type semiconductors are electrically neutral. This is because each atom of the added impurity is neutral in itself containing equal number of protons and electrons.

The conductivity of semiconductors increases with a rise in temperature. In this they differ from metals in which conductivity decreases with a rise in temperature.

This is due to the fact that the 'extra electron' or the 'positive hole', is bound weakly to the crystal lattice. So when heat energy is supplied they are freed from the crystal lattice and thus conduct the current more freely. The combination of n-and p-types of conduction is known as 'n-p junction'. These are used in the manufacture of transistors.

## X-RAY DIFFRACTION BY CRYSTALS

### Principle :

X-rays are electromagnetic radiations with wave lengths of about 0 - 1 nm or  $\text{Å}$ . X rays can be prepared by producing cathode rays in highly evacuated discharge tube and allowing them to fall on a metal target called an anticathode.

Laue suggested that the distance between the lattice planes in the crystals are in the order of a few angstroms. Therefore he suggested that the crystal should act as a diffraction grating for the X-rays since the wave length of X-rays are also in the order of  $1 \text{ Å}$ . Bragg suggested that crystal's can act as reflection grating also. He developed a simple equation to determine the structure of a crystal using the X-rays. This equation is known as the Bragg's equation or Bragg's law.

### Derivation of Bragg's Equation :

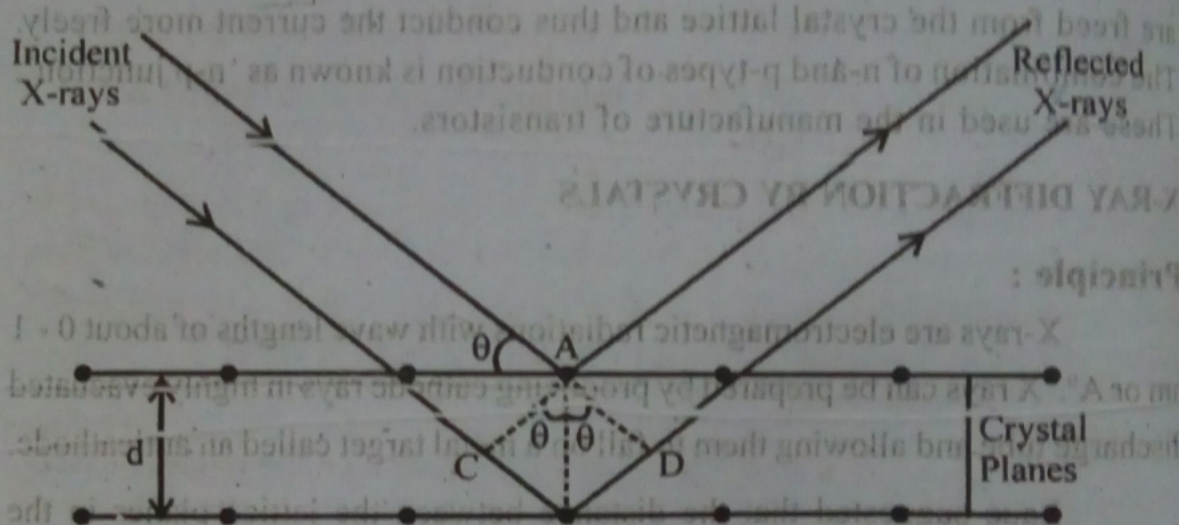
$$\text{Equation : } n\lambda = 2d \sin \theta$$

### Explanation of the terms :

$n$  = order of reflection ;  $\lambda$  = wavelength of the X-ray used ;  $d$  = Inter planar distance;  $\theta$  = glancing angle of the incident X-ray.

### Derivation :

The figure shows a beam of X-rays falling on the crystal surface. Two successive atomic planes of the crystal are shown separated by a distance 'd'. Let the X-rays of wavelength  $\lambda$  strike the first plane at an angle  $\theta$ . Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane if the extra distance travelled by them (CB + BD) is equal to integral number, n, of wavelengths. That is



Reflection of X - rays from two different planes of a crystal.

$$n\lambda = CB + BD \quad (1)$$

Geometry shows that

$$CB = BD = AB \sin \theta$$

From (1) and (2) it follows that

$$n\lambda = 2AB \sin \theta$$

or

$$n\lambda = 2d \sin \theta$$

This is known as the **Bragg equation**. The reflection corresponding to  $n = 1$  (for given series of planes) is called the **first order reflection** corresponding to  $n = 2$  is the **second order reflection** and so on.

Bragg equation is used chiefly for determination of the spacing between the crystal planes 'd'. For X-rays of specific wave length  $\lambda$ , the angle  $\theta$  can be measured with the help of Bragg X-ray spectrometer. The interplanar distance 'd' can then be calculated with the help of Bragg equation.

Uses :

- i. We know from Bragg's equation  $n\lambda = 2d \sin \theta$ . By knowing  $\lambda$  and  $\theta$  we can find the ratio  $d/\lambda$ . From this we can calculate d if  $\lambda$  is known and vice versa
- ii. From Bragg's law we can determine the crystal structure of NaCl, KCl and CsCl.
- iii. We can determine the Avogadro's number using Bragg's law

### 1. Laue's Method :

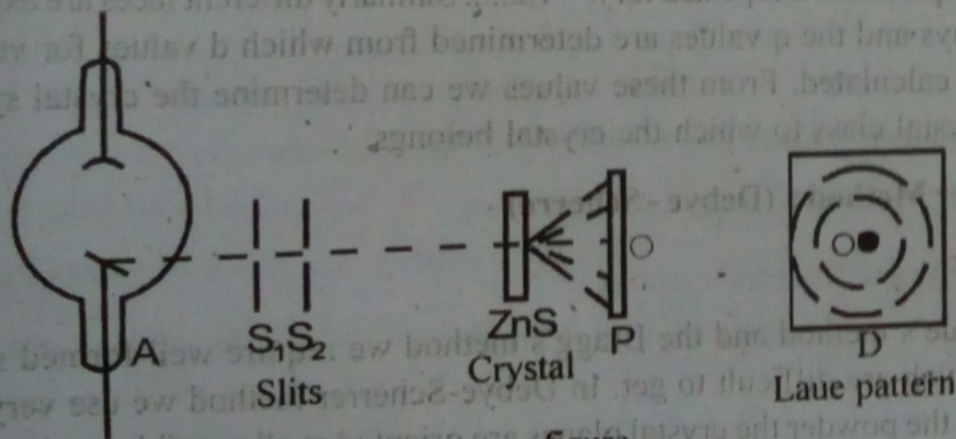
Principle : We know from Bragg's equation

$$n\lambda = 2d \sin \theta$$

In this method, the angle of incidence ( $\theta$ ) is fixed and X-rays with the whole range of wave lengths are used. A certain set of planes which fulfil the condition given by Bragg's Law gives a spot. The various sets of planes present in the crystal give several such spots. We get the Laue pattern of spots.

Procedure :

The apparatus is shown in figure. X-ray from the X-ray tube, 'A' are passed through slits  $S_1, S_2$  and converted into a beam. It is allowed to fall on ZnS crystal.



figure

The various atoms in various planes of the crystal satisfying the Bragg's Law scatter or deflect some of the X-rays from the original path. These X-rays are photographed at P and developed. We get the Laue pattern 'D'. From a study of the Laue patterns the crystal structure is determined.

## 2. Bragg's Method:

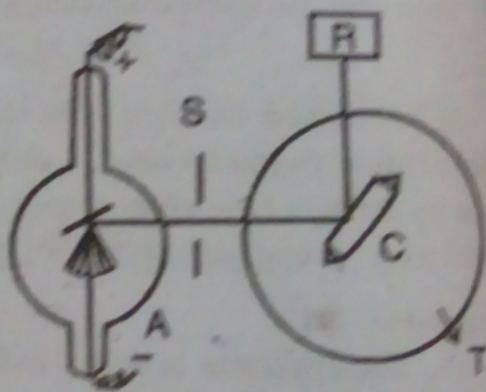
### Principle :

In the Bragg's method ' $\lambda$ ' the wavelength of the X-ray is fixed and  $\theta$  is varied by rotating the crystal about its axis. The angles for which reflections are maximum give the ' $\theta$ ' values which are substituted in the equation.

$$n\lambda = 2d \sin \theta$$

The lowest angle at which the maximum reflection occurs corresponds to  $n = 1$ . This is called the first order reflection. The next higher angle at which the maximum reflection occurs corresponds to  $n = 2$ . Similarly, we can explain other orders of reflections also. This is called the second order reflection and so on. The process is carried out for each plane of the crystal.

**Procedure :** X-rays are generated in the X-rays tube 'A'. They are passed through a focussing slit 'S'. A narrow beam is got. It is allowed to strike a single crystal 'C' mounted on a turn table, 'T'. A particular face is exposed to the X-ray. The crystal is rotated gradually and the glancing angle  $\theta$  at which the reflections are maximum is determined using a recording device 'R'.

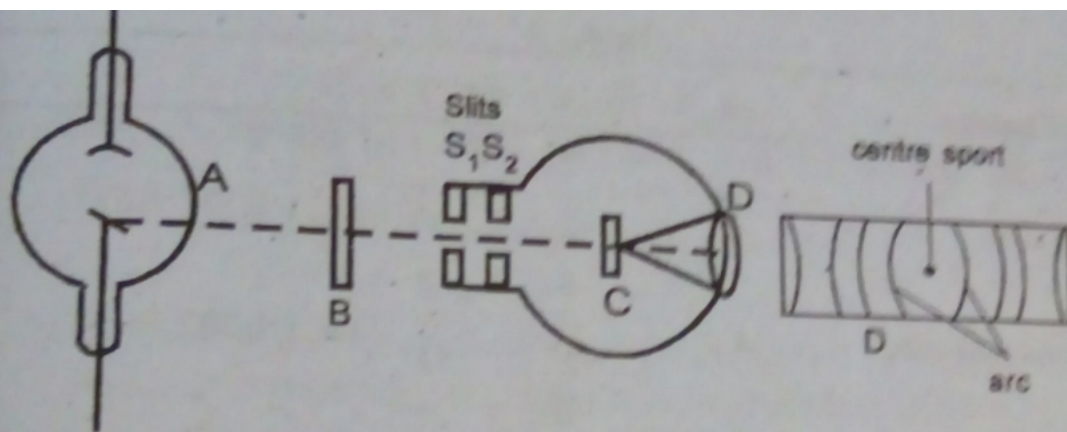


The experiment is repeated for  $n = 1, 2, \dots$ . Similarly different faces are exposed to the X-rays and the  $\theta$  values are determined from which  $d$  values for various planes are calculated. From these values we can determine the crystal system and the crystal class to which the crystal belongs.

## 3. Powder Method : (Debye - Scherrer)

### Principle :

In Laue's method and the Bragg's method we require well-formed single crystals which are difficult to get. In Debye-Scherrer method we use very fine powder. In the powder the crystal planes are oriented at all possible angles to the beam of X-rays i.e., some particles will have their (100) planes properly oriented to the X-rays; some will have (110) planes and some others will have (111) planes correctly oriented for reflection.



### Procedure:

X-rays are generated in the X-ray tube 'A'. (figure 18). They are passed through a focussing slit  $S_1$  and  $S_2$  and 'B'. A narrow beam is got. It is allowed to strike the powdered crystals in a glass capillary 'C'. The diffracted X - rays strike a photographic film strip 'D' which is placed in the form of a circular arc. We get a bright spot at the centre and arcs appear on either side of the bright spot. Each pair of arc is equi-distant from the centre. They correspond to a particular order of diffraction for a set of planes.  $\theta$  can be calculated from

$$2\theta = \frac{S}{r}$$

Where  $S$  = the distance of an arc from the central spot and  
 $r$  = distance from the powder to the film.

$\theta$  will be in radians. To convert into degree the  $\theta$  is multiplied by  $180/\pi$ . From  $\theta$  we can calculate 'd'. From 'd' the ratios of  $d_{100}$ ;  $d_{110}$ ;  $d_{111}$  are calculated. From these values we can determine the crystal system and the crystal class to which the, crystal belongs.

## DEFECT STRUCTURES IN CRYSTALS

The structures of ionic solids described in the preceding pages relate only to *ideal crystals*. An **ideal crystal** is the one which has the same unit cell and contains the same lattice points throughout the crystal.

At absolute zero, all ionic crystals show well-ordered arrangements of ions and there are no defects. With rise in temperature, however, there is a chance that one or more of the lattice sites may remain unoccupied by the ions. This constitutes a defect. The number  $n$  of such defects per  $\text{cm}^3$ , at a given temperature  $T$  on the absolute scale, is given by the equation

$$n = Ne^{-w/2RT} \quad \dots(11)$$

where  $N$  is the total number of sites per  $\text{cm}^3$  of the crystal and  $w$  is the work (energy) required to produce a defect ;  $R$  is the gas constant.

Defects in crystals may be discussed under two heads :

- A. Defects in Stoichiometric Crystals
- B. Defects in Non-Stoichiometric Crystals.

### A. Defects in Stoichiometric Crystals

**Stoichiometric crystals** are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae. For simplicity, we can consider the crystals of the type  $AB$  having equal number of  $A^+$  and  $B^-$  ions. In these crystals, two types of defects are generally observed. These are called (1) Schottky defect and (2) Frenkel defect.

**1. Schottky Defect.** This defect arises if *some of the lattice points are unoccupied*. The points which are unoccupied are called *lattice vacancies* or '*holes*'. The existence of two holes, one due to a missing positive ion and the other due to a missing negative ion in a crystal lattice, is illustrated in Fig. 45. It may be noted that the crystal, as a whole, remains neutral because the number of missing positive and negative ions is the same.

Schottky defect appears generally in ionic compounds having a high coordination number and in which the radius ratio,  $r_+/r_-$ , is not far below unity, *i.e.*, in which the positive and negative ions do not differ very much in size. Sodium chloride and cesium chloride

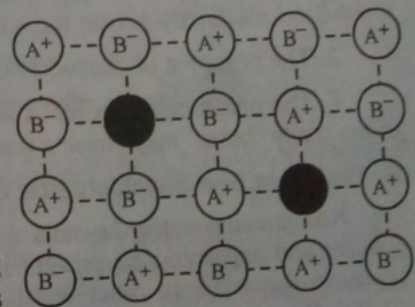


Fig. 45. The Schottky defect in crystals.

which have coordination numbers of 6 and 8, respectively, furnish good examples of ionic crystals in which Schottky defect appears.

**2. Frenkel Defect.** This defect arises when an ion occupies an interstitial position between the lattice points. This is shown in Fig. 46. It is seen that one of the positive ions occupies a position in the interstitial space rather than at its own appropriate site in the lattice. A 'hole' is thus created in the lattice as shown. It may be noted again that the crystal remains neutral since the number of positive ions is the same as that of the negative ions. Positive ions being smaller are more likely to occupy interstitial positions than the negative ions.

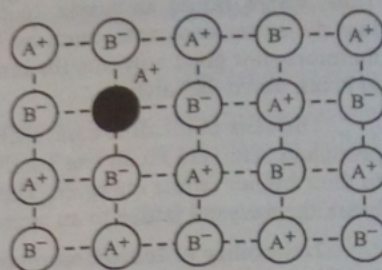


Fig. 46. The Frenkel defect in crystals.

Frenkel defect appears generally in compounds in which the negative ions are much larger than the positive ions, *i.e.*, the radius ratio,  $r_+/r_-$ , is low. The coordination number in such compounds is also low (Table 4). Hence, fewer attractive forces between oppositely charged ions have to be broken in causing movement of a positive ion from its appropriate site to the interstitial position.

In silver bromide, AgBr, some of the Ag<sup>+</sup> ions are generally missing from their regular positions and occupy positions in between the other ions in the lattice. The presence of Ag<sup>+</sup> ions in the interstitial spaces of the silver bromide crystal is responsible for the formation of a photographic image on exposure of silver bromide crystals (*i.e.*, photographic plate) to light. Zinc sulphide is another substance in which Frenkel defect appears. Zn<sup>2+</sup> ions are entrapped in the interstitial spaces leaving 'holes' in the lattice.

Lattice vacancies ('holes') occur in almost all types of ionic crystals. However, Schottky defect appears more often than Frenkel defect. The reason is that the *energy needed to form a Schottky defect is much less than that needed to form a Frenkel defect*. In sodium chloride, the energy required to form a Schottky defect is about 170 kJ per mole. The lattice energy of sodium chloride is -758.7 kJ per mole so that the energy required to break the NaCl lattice is 758.7 kJ per mole. It is, therefore, far easier to produce a Schottky defect than to break the lattice. The number of Schottky defects increases exponentially with rise in temperature. Thus, as revealed by X-ray diffraction of sodium chloride, while at room temperature this substance has one Schottky defect for 10<sup>15</sup> lattice sites, the number of defects for the same number of lattice sites rises to such a high value as 10<sup>6</sup> at 500°C and 10<sup>11</sup> at 800°C.

**Consequences of Schottky and Frenkel Defects.** Schottky and Frenkel defects in crystals lead to some interesting consequences.

1. The closeness of similar charges brought about by the Frenkel defect (Fig. 46) tends to increase the dielectric constant of the crystals.

2. A consequence of both types of defects is that the crystal is able to conduct electricity to a small extent by an ionic mechanism. It happens like this. As an electric field is applied, a nearby ion moves from its lattice site to occupy a 'hole'. This results in creating a new 'hole' and another nearby ion moves into it, and so on. This process continues and a 'hole', thereby, migrates from one end to the other end. Thus, it conducts electricity across the whole of the crystal.

3. The presence of 'holes' lowers the density of the crystal, as expected.

4. The presence of 'holes' also lowers the lattice energy or the stability of the crystal. The presence of too many 'holes' may cause a partial collapse of the lattice.

## B. Defects in Non-Stoichiometric Crystals

Non-stoichiometric crystals do not obey strictly the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. In other words, there is excess of either positive charge or negative charge in the crystal. However, the crystal as a whole is neutral. If positive charge is in excess, it is balanced by the presence of *extra electrons*. If negative charge is in excess, it is balanced by the presence of *extra positive ions*. The crystal structure, therefore, becomes irregular and this implies the presence of defects. Such



defects are called **non-stoichiometric defects**. These defects may exist in a crystal in addition to Schottky and Frenkel defects already discussed.

Non-stoichiometric defects, evidently, are of two types depending upon whether *positive ions are in excess or negative ions are in excess*. These are known as **metal excess defects** and **metal deficiency defects**, respectively.

**Metal Excess Defects.** In these defects, positive ions are in excess. These defects may arise in *two ways*.

1. A negative ion may be missing from its lattice site leaving a 'hole' which is occupied by an extra electron to maintain the electrical balance, as shown in Fig. 47. There is, evidently, an excess of positive (metal) ions, although the crystal, as a whole, is neutral.

This defect is somewhat similar to Schottky defect but differs in having only one 'hole' and not a pair as in the latter case. This type of defect is not very common. It has been observed in those crystals which are likely to form Schottky defect. For example, when sodium chloride is treated with sodium vapour, a *yellow* non-stoichiometric form of sodium chloride is obtained in which there is excess of sodium ions. Similarly, if potassium chloride is exposed to potassium vapour, a *lilac* coloured non-stoichiometric form of potassium chloride is obtained in which there is excess of potassium ions. In each case, the extra positive charge due to extra metal ion is balanced by the presence of a free electron in the lattice.

2. An extra positive ion occupies an interstitial position in the lattice and to maintain electrical neutrality, an electron also finds a place in the interstitial space, as shown in Fig. 48.

This type of metal excess defect is somewhat similar to Frenkel defect but differs in having no 'holes' and in having interstitial electrons. This kind of defect is more common than the first kind of metal excess defect. It is formed in crystals which are likely to develop Frenkel defect. Zinc oxide crystal is a good example.

**Consequences of Metal Excess Defects.** 1. The crystals associated with metal excess defects of the first kind or second kind, *contain free electrons* (Figs. 47 and 48). Since these electrons can migrate in an electric field, *such crystals can conduct electricity*. However, since the number of defects and, therefore, the number of electrons is very small, these crystals can conduct only small amounts of current, very much smaller than the current conducted by metals, fused salts or salts dissolved in water. These materials are, therefore, termed as **semiconductors**. Since current, howsoever small, is carried by electrons in *normal way*, these substances are called **n-type semiconductors**.

2. The crystals with metal excess defects are generally coloured. This, again, is due to the presence of free electrons. These electrons get excited easily to higher energy levels by absorption of certain wave lengths from the visible white light and, therefore, the compounds appear coloured. Thus, non-stoichiometric sodium chloride is *yellow*, non-stoichiometric potassium chloride is *lilac* in colour. Zinc oxide which is white in cold, *appears yellow when hot*.

**Metal Deficiency Defects.** There are *two possible ways* in which metal deficiency defects can occur.

1. In the first way, one of the positive ions may be missing from its lattice site. The extra negative charge may be balanced by some nearby metal ion by acquiring an additional positive charge. This is represented in Fig. 49. The metal, obviously, must be in a position to exhibit variable valency. This

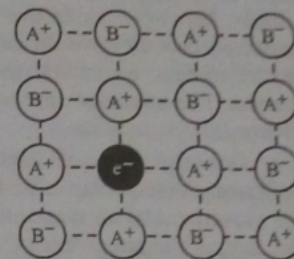


Fig. 47. Metal excess defect caused by a missing negative ion.

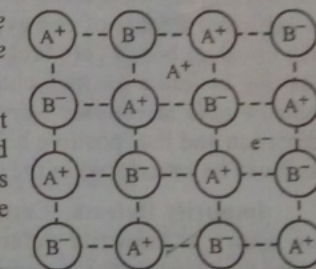


Fig. 48. Metal excess defect due to extra positive ion.

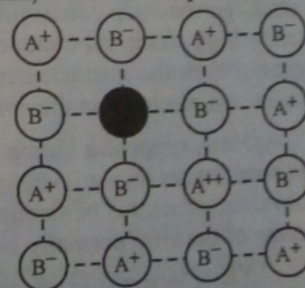


Fig. 49. Metal deficiency defect due to a missing positive ion.

type of defect, therefore, is generally found amongst the compounds of transition metals. Crystals of ferrous oxide, FeO, ferrous sulphide, FeS and nickel oxide, NiO, show this type of defect.

2. In the second way, an extra negative ion may occupy an interstitial position. The extra negative charge is balanced again by means of an extra charge on one of the adjacent metal ions, as shown in Fig. 50. The metal in this case also, should be capable of exhibiting variable valency, i.e., it should be one of the transition metals. However, since the negative ions are usually very large, it is not expected that they would be able to fit into the interstitial positions. As a matter of fact, no crystal showing this type of metal deficiency defect is known. The structure represented in Fig. 50, therefore, remains merely a theoretical possibility.

**Consequences of Metal Deficiency Defects.** Crystals with metal deficiency defects can also be semiconductors. This property arises from the movement of an electron from one ion to another. In this way, the ion, say,  $A^+$ , changes into  $A^{++}$ . Thus, the movement of an electron from  $A^+$  ion is an apparent movement of  $A^{++}$  ion. This is called movement of positive 'hole' and the substances permitting this type of movement are known as *p-type semiconductors*.

**Thermal Defects. Intrinsic Conduction.** Atoms of both germanium and silicon have four electrons in the outer shell. Each atom, therefore, is covalently bonded with four neighbouring atoms through  $sp^3$  hybrid bonds, giving rise to a highly stable tetrahedral structure as in diamond. There are no free or conducting electrons as we have in metals. The electrical conductance, therefore, is very low. Now, suppose a sufficient amount of energy, say, in the form of heat, is supplied to the crystal as a result of which one of the covalent bonds gets broken and the electrons are released. The electrons, thus released, can migrate leaving behind a positive charge, i.e., a 'positive hole', at the site of the missing bond. The crystal will now be able to conduct electricity because, when electric field is applied, the electrons migrate in one direction and the 'positive holes' in the other. This type of conduction is known as **intrinsic conduction** as it can be introduced in the crystal without adding an external substance.

**Impurity Defects.** Certain defects in crystals arise from the presence of chemical impurities. These are known as **impurity defects**. One important application of these defects lies in the use of externally added metal impurities to germanium and silicon crystals to make them act as **semiconductors**. Germanium and silicon belong to Group 14 of the periodic table. These elements, in pure state, have very low electrical conductivity. However, on adding even traces of an element belonging to Group 13 or 15, the electrical conductivity is greatly enhanced. This may be explained as follows :

Suppose, in the first instance, a Group 15 element, like arsenic, is added to a germanium crystal. As a germanium atom is substituted by an atom of arsenic, four of the electrons in arsenic form covalent bonds with the surrounding germanium atoms but the *fifth electron remains free*. In this way, an extra electron, over and above the number required for forming four covalent bonds, gets introduced into the crystal. This extra electron can serve to conduct electricity, i.e., it behaves like a conductor-electron as in metals. Thus, germanium containing traces of arsenic (known as **arsenic-doped germanium**) begins to exhibit fairly high electrical conductivity. This type of conduction is known as **extrinsic conduction**. It is much greater than the intrinsic conduction discussed above. Since, in this type of conduction, current is carried by excess electrons in the *normal way*, it is called **n-type semiconduction**.

Now, suppose a Group 13 element, like indium, having only three electrons in the outer shell, is added in small traces to, say, pure germanium. The atoms of indium, evidently, are not able to complete tetrahedral covalent structures of Group 14 elements because they are one electron short of the requirement. Hence, some of the sites normally occupied by electrons will be left empty. This gives rise to *electron-vacancies*.

The electron-vacant sites are known as 'positive holes' because the net charge at these sites is positive. When electric field is applied, adjacent electrons move into the positive holes and in this way other electron-vacancies (or positive holes) are formed. The migration of positive holes thus continues and current is carried thereby throughout the crystal.

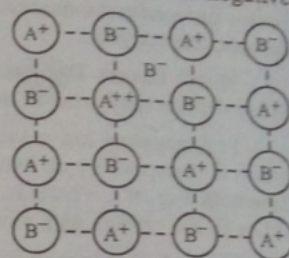


Fig. 49. Metal deficiency defect due to a negative ion.

Thus, doping of germanium with traces of indium increases the electrical conductivity of germanium crystal. Since the current, in the present case, is carried by *positive holes*, this type of conduction is called ***p-type semiconductor***.

It is clear from the above discussion that while doping germanium (or silicon) with arsenic (an element of Group 15) gives rise to *n-type* of semi-conduction, that with indium (an element of Group 13) gives rise to *p-type* of semiconductor. It may be noted that *n-type* as well as *p-type* of semiconductors are electrically neutral because each atom of impurity added is neutral in itself containing, as it does, equal number of protons and electrons. There is, no doubt, a surplus or shortage of one valency electron depending on whether an element of Group 15 or Group 13 is added, but the overall number of electrons remains equal to the number of positive nuclear charges.

**Effect of temperature on the conductivity of semiconductors.** *The conductivity of semiconductors, unlike that of metals, increases with rise in temperature.* This is due to the fact that extra electron or positive hole, as the case may be, is bound, though weakly, with the crystal and, therefore, some energy in the form of heat is needed to free it from the crystal lattice for the conduction of electricity.

**Applications of Semiconductors.** The combination of *n* and *p*-type semiconductors (known as ***n-p junctions***), finds interesting applications in the **fabrication of transistors**. This device can conduct electric current more easily in one particular direction than in the reverse direction and, therefore, can be used as a **rectifier** for changing alternating current into direct current. The device is schematically represented in Fig. 51. The material on the left side of each junction is *n*-type conductor obtained by doping germanium with, say, arsenic. The minus signs represent extra electrons. The material on the right side of the junction is *p*-type conductor obtained by doping germanium with, say, indium. The positive signs represent 'positive holes' arising from the deficiency of electrons at the indium impurity centres. When an external voltage is applied in such a way as to cause motion of electrons (*n*-current) from left to right and motion of positive holes (*p*-current) from right to left (Fig. 51a), current is readily conducted. If direction of voltage is reversed so that there is separation of electrons and positive holes as shown in Fig. 51(b), there is cancellation of *n* and *p*-currents and hence the conduction stops. Thus, the *n-p* junction permits the current from an outside source to flow *in one direction only*.

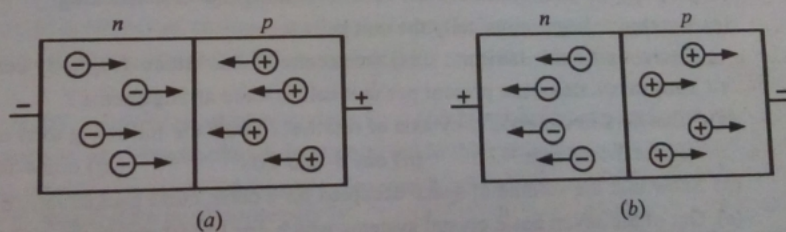


Fig. 51. Semiconductors acting as rectifier.