

# 1. SOLID STATE

## Can you recall ?

- What are the three most common states of matter?
- How does solid state differ from the other two states ? (Answer with reference to volume, shape, effect of temperature and pressure on these and the motion of constituent particles and interparticle forces.)



**1.1 Introduction :** As studied earlier, the solid state of matter is characterised by strong interparticle forces of attraction. As a result most solids have definite shape and volume, which change only slightly with change in temperature and pressure. The smallest constituent particles of various solids are **atoms, ions or molecules**. All such smallest constituent particles of solids will be referred to as 'particles' in this chapter.

**1.2 Types of solids :** There are two types of solids, namely crystalline solids and amorphous solids.

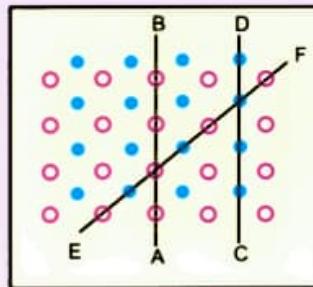
## Observe and discuss...



- Collect the following solids : granular sugar, common salt, blue vitriol.
- Observe a few granules of these solids under a magnifying lens or microscope.
- Discuss your observations with reference to the following points : (i) Shape of the granules, (ii) Smoothness of faces of the granules and (iii) Angles between various edges of the granules.
- All the above solids are crystalline solids. Name the properties of crystals that you observed in this activity.



## Try this...



● Particle 1 ○ Particle 2

Observe the above figure carefully. The two types of circles in this figure represent two types of constituent particles of a solid.

- Will you call the arrangement of particles in this solid regular or irregular ?
- Is the arrangement of constituent particles same or different in directions  $\vec{AB}$ ,  $\vec{CD}$ , and  $\vec{EF}$  ?

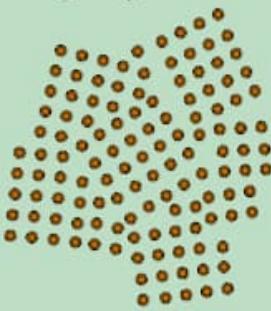
**1.2.1 Crystalline solids :** Study of many crystalline solids indicates that they possess the following characteristic properties.

- i. There is a **regularity** and **periodicity** in the arrangement of constituent particles in crystalline solids. The ordered arrangement of particles extends over a long range.
- ii. Crystalline solids have **sharp melting points**, that is, they melt at a definite temperature.
- iii. All crystalline substances except those having cubic structure are **anisotropic**. In other words their properties like refractive index, thermal and electrical conductivity, etc, are different in different directions.

Ice, salts such as NaCl, metals such as sodium, gold, copper and materials such as diamond, graphite, ceramics are examples of crystalline solids.

### Do you know ?

- A single crystal has ordered (regular and periodic) arrangement of constituent particles throughout its bulk.
- Majority of crystalline solids, including metals, are polycrystalline in nature. Single granule of a polycrystalline solid is made of many single crystals or crystallites packed together with different orientations.
- Single crystals are difficult to obtain. Diamond is an example of naturally formed single crystal.



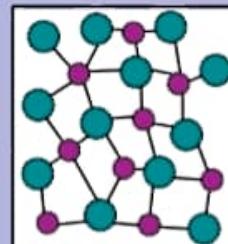
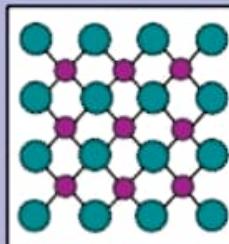
**1.2.2 Amorphous solids :** The particles of a liquid are in constant motion. The stop action photograph of a liquid describes the amorphous state. In fact, they are supercooled liquids. Amorphous solids have the following characteristics.

- i. The constituent particles in amorphous solids are **randomly arranged**. The particles do not have long range ordered structure, but they do have a short range order.
- ii. Amorphous solids do not have sharp melting points. They melt gradually over a **temperature interval**. On heating, amorphous solids gradually and continuously soften and start to flow.
- iii. These solids are **isotropic**. In other words, their properties such as refractive index, conductivity are all independent of direction of measurement. They exhibit the same magnitude for any property in every direction.

Glass, plastic, rubber, tar, and metallic glass (metal-metalloid alloy) are a few examples of amorphous solids.

### Use your brain power

Identify the arrangements A and B as crystalline or amorphous.



### 1.2.3 Isomorphism and polymorphism

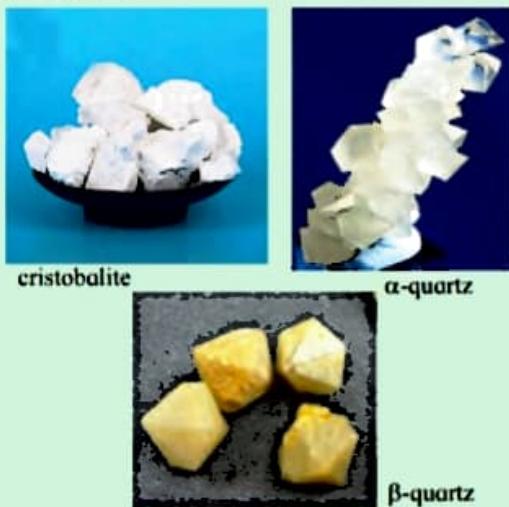
Similarity or dissimilarity in crystal structure of different solids is described as isomorphism and polymorphism.

**i. Isomorphism :** Two or more substances having the same crystal structure are said to be isomorphous. In these substances the chemical composition has the same atomic ratio. For example (i) NaF and MgO (ii) NaNO<sub>3</sub> and CaCO<sub>3</sub> are isomorphous pairs, and have the same atomic ratios, 1:1 and 1:1:3, respectively, of the constituent atoms.

**ii. Polymorphism :** A single substance that exists in two or more forms or crystalline structures is said to be polymorphous. Polymorphs of a substance are formed under different conditions. For example : Calcite and aragonite are two forms of calcium carbonate;  $\alpha$ -quartz,  $\beta$ -quartz and cristobalite are three of the several forms of silica. Polymorphism occurring in elements is called **allotropy**. For example: three polymorphic (allotropic) forms of carbon are diamond, graphite and fullerene.

### Do you know ?

Many crystalline forms of silica ( $\text{SiO}_2$ ) are found in nature. Three of them are  $\alpha$ -quartz,  $\beta$ -quartz and cristobalite.



### 1.3 Classification of crystalline solids :

Crystalline solids are further classified into four categories : ionic solids, covalent network solids, molecular solids and metallic solids.

#### 1.3.1 Ionic crystals :

Ionic crystals have the following characteristics :

- The constituent particles of ionic crystals are **charged ions**. The cations and anions may differ in size.
- Each ion of a given sign of charge is bonded to ions of opposite charge around it by coulomb force. In other words, the particles of ionic crystals are held by **electrostatic force of attraction** between oppositely charged ions.
- Ionic crystals are **hard and brittle**. They have **high melting points**.
- These are **nonconductors of electricity** in solid state. However, they are good conductors when melted or dissolved in water.

For example :  $\text{NaCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CaF}_2$ ,  $\text{KCl}$  are ionic crystals.

### 1.3.2 Covalent network crystals

Characteristics of covalent network crystals are as follows :

- The constituent particles in covalent network solids are **atoms**.
- The atoms in these crystals are linked by a continuous system of **covalent bonds**. The result is a rigid three dimensional network that forms a giant molecule. The entire crystal is a single molecule.
- As a result of rigid and strongly bonded structure, covalent network crystals are **very hard**. In fact they are the hardest and most **incompressible** of all the materials. These crystals have **high melting and boiling points**.
- The electrons are localised in covalent bonds and hence are not mobile. As a result, covalent solids are **poor conductors** of heat and electricity.

For example : diamond, quartz ( $\text{SiO}_2$ ), boron nitride, carborandum are covalent network solids.

### Do you know ?

Diamond is the hardest known material.

### Try this...

Graphite is a covalent solid yet soft and good conductor of electricity. Explain.

### Can you recall ?

- What are structures of diamond and graphite ?
- What are the types of covalent bonds those link carbon atoms in diamond and graphite ?
- Are all the valence electrons of carbon atoms in graphite localized to specific covalent bonds ?

### Remember...

Both ionic and covalent crystals are hard and have high melting and boiling points. We can use electrical properties to distinguish between them. Both are insulators at low temperature.



Ionic solids become good conductors only at high temperature, above their melting points.

The conductivity of covalent solids is in general low and increases with temperature. However, there is no abrupt rise in conductivity when substance is melted.

**1.3.3 Molecular crystals :** Substances such as  $\text{Cl}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$  on solidification give molecular crystals. Crystalline organic compounds are also molecular solids.

- The constituent particles of molecular solids are **molecules** (or unbonded single atoms) of the same substance.

### Can you recall ?

What is a hydrogen bond ?



- The bonds within the molecules are covalent. The molecules are held together by various intermolecular forces of **attraction**. (Refer to XI Std. Chemistry Textbook, Chapter 10). For example :

- Weak dipole-dipole interactions** in polar molecules such as solid  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ , which possess permanent dipole moment.
- Very weak dispersion or London forces** in nonpolar molecules such as solid  $\text{CH}_4$ ,  $\text{H}_2$ . These forces are also involved in monoatomic solids like argon, neon. (These substances are usually gases at room temperature.)

c. **Intermolecular hydrogen bonds** in solids such as  $\text{H}_2\text{O}$  (ice),  $\text{NH}_3$ ,  $\text{HF}$  and so forth.

- Because of weak intermolecular attractive forces, molecular solids are usually soft substances with **low melting points**.
- These solids are **poor electrical conductors** and are good insulators.

**1.3.4 Metallic crystals :** These are crystalline solids formed by atoms of the same metallic element, held together by a metallic bond.

**Metallic bond :** In a solid metal, the valence electrons are delocalised over the entire crystal leaving behind positively charged metal ions. Therefore, metallic crystals are often described as an array of positive ions immersed in a sea of mobile electrons. The attractive interactions between cations and mobile electrons constitute the metallic bonds. (For more details refer to section 1.9.2)

Metallic crystals have the following properties:

- Metals are **malleable**, that is, they can be hammered into thin sheets.
- Metals are **ductile**, that is, they can be drawn into wires.
- Metals have **good electrical and thermal conductivity**.

Examples : metals such as Na, K, Ca, Li, Fe, Au, Ag, Co, etc.

The properties of different types of crystalline solids are summarized in Table 1.1.

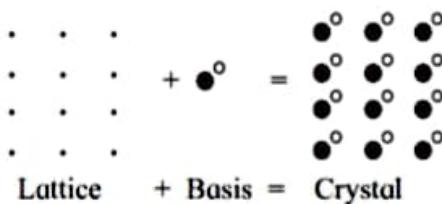
**1.4 Crystal structure :** The ordered three dimensional arrangement of particles in a crystal is described using two terms, namely, lattice and basis.

**1.4.1 Crystal, lattice and basis :** Lattice is a geometrical arrangement of points in a three dimensional periodic array. A crystal structure is obtained by attaching a constituent particle to each of the lattice points. Such constituent particles that are attached to the lattice points form the basis of the crystal lattice. Crystal

**Table 1.1 : Properties of four types of crystalline solids**

| Property \ Type                        | Ionic solids   | Covalent network solids   | Molecular solids                                   | Metallic solids  |
|--|--|---|--|--|
| 1. Particles of unit cell              | Cations and anions   | Covalently bonded atoms   | Monatomic or polyatomic molecules                  | Metallic ions in a sea of electrons                                      |
| 2. Interparticle forces                | Electrostatic  | Covalent bonds  | London, dipole-dipole forces and/or hydrogen bonds | Metallic bonds (attraction between cations and mobile valence electrons) |
| 3. Hardness                            | Hard and brittle   | Very hard   | Soft   | Variable from soft to very hard  |
| 4. Melting points                      | High<br>600°C to 3000°C  | High<br>1200°C to 4000°C  | Low<br>(-272°C to 400°C)                           | Wide range<br>(-39°C to 3400°C)  |
| 5. Thermal and electrical conductivity | Poor electrical conductors in solid state. Good conductors when melted or dissolved in water | Poor conductors<br>Exceptions :<br>i. Graphite : good conductor of electricity.<br>ii. Diamond : good conductor of heat | Poor conductor of heat and electricity             | Good conductor of heat and electricity                                   |
| 6. Examples                            | NaCl, CaF <sub>2</sub>   | diamond, silica   | ice, benzoic acid                                  | Na, Mg, Cu, Au   |

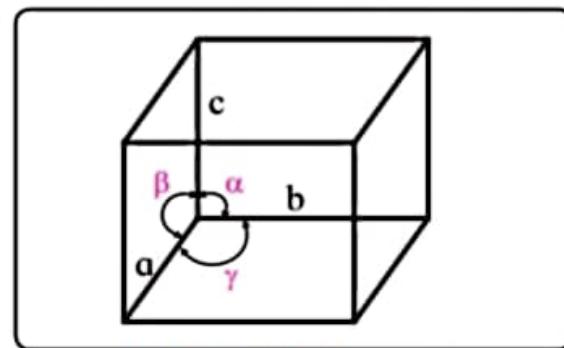
lattice is also called space lattice of crystal. Thus, crystal is the structure that results by attaching a basis to each of the lattice points. It is represented by the following equation.



**1.4.2 Unit Cell :** The space lattice of a crystal is built up of a three dimensional basic pattern. This basic pattern is repeated in three dimensions to generate the entire crystal. The smallest repeating structural unit of a crystalline solid is called unit cell.

When the unit cells are stacked together to generate the crystal, each unit cell shares its faces, edges and corners with neighbouring unit cells. It is important to understand that the geometric shape of a unit cell is same as that of the macroscopic crystal. For example, if the crystal has cubic shape the unit cell will also have its constituent particles arranged to form a tiny cube.

The dimensions of unit cell along the three axes are denoted by the symbols  $a$ ,  $b$  and  $c$ . The angles between these axes are represented by the symbols  $\alpha$ ,  $\beta$  and  $\gamma$  as shown in Fig 1.1.



**Fig. 1.1 : Unit cell parameters**

**1.4.3 Types of unit cell :** There are four types of unit cells.

**i. Primitive or simple unit cell :** In primitive unit cell, the constituent particles are present at its corners only.

**ii. Body-centred unit cell :** In this type of unit cell, one constituent particle is present at the centre of its body in addition to the corner particles.

**iii. Face-centred unit cell :** This unit cell consists of particles at the centre of each of the faces in addition to the corner particles.

**iv. Base-centred unit cell :** This unit cell consists of particles at the centre of any two of its opposite faces in addition to the corner particles.

**1.4.4 Crystal systems :** By mathematical analysis, it has been proved that only fourteen different kinds of space lattices are possible. In other words, there are only 14 ways in which similar points can be arranged in a three dimensional order. These 14 lattices, which describe the crystal structure, are called **Bravais lattices**.

Fourteen Bravais lattices are divided into seven crystal systems. The possible combinations of lattice point spacings ( $a$ ,  $b$  and  $c$ ) along three axes and the angles ( $\alpha$ ,  $\beta$  and  $\gamma$ ) between these axes give rise to seven crystal systems. In other words, seven crystal systems are associated with 14 Bravais lattices also called 14 unit cells.

The seven crystal systems are named as **cubic**, **tetragonal**, **orthorhombic**, **rhombohedral**, **monoclinic**, **triclinic** and **hexagonal system**. Cubic system will be discussed in the following section.

**1.5 Cubic system :** There are three kinds of unit cells in cubic system : primitive or simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) (Fig. 1.2).

**i. Simple cubic unit cell (sc)** has a particle at each of the eight corners of a cube.

**ii. Body-centred cubic unit cell (bcc)** has particles at its eight corners and an additional particle in the center of the cube.

**iii. Face-centred cubic unit cell (fcc)** has particle at the centre of each of six faces in addition to the particles at eight corners of the cube.

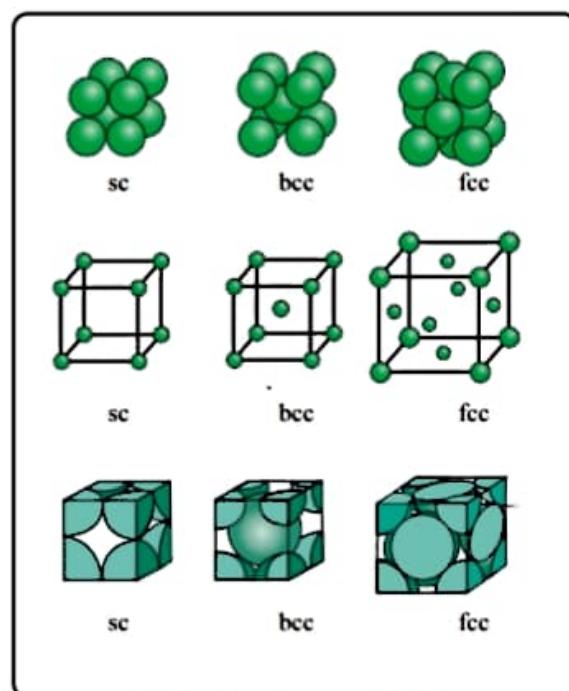


Fig. 1.2 : Cubic unit cell

### 1.5.1 Number of particles in cubic unit cells

**i. Primitive or simple cubic unit cell (sc) :** A simple cubic cell has particles at its eight corners. When these unit cells are stacked together, particle at each corner of a given unit cell is shared with seven other neighbouring cubes that come together at that corner. As a result the corner particle contributes its  $1/8^{\text{th}}$  part to the given unit cell. Thus, a simple cubic cell has  $1/8 \times 8 = 1$  particle per unit cell.

**ii. Body-centred cubic unit cell (bcc) :** A bcc unit cell has eight corner particles and an additional particle at the centre of the cube. One eighth of each particle from eight corners belongs to the given unit cell as mentioned in simple cubic unit cell.

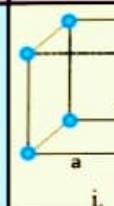
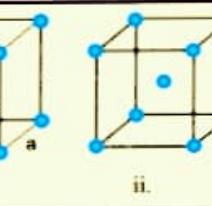
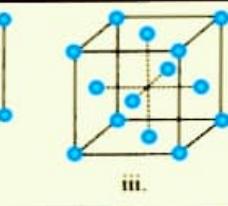
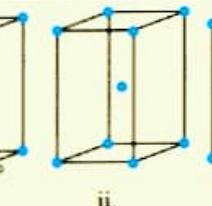
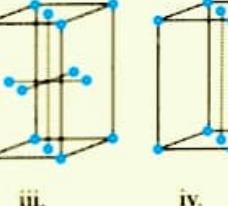
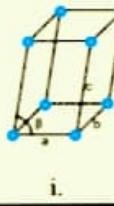
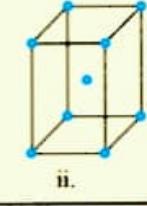
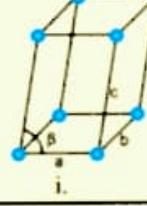
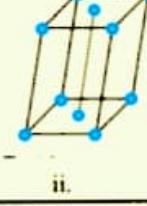
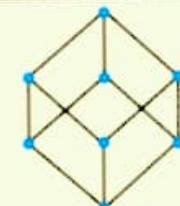
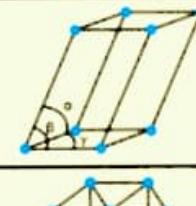
The particle at the centre of a given cube is not shared by any other cube. Hence, it belongs entirely to the given unit cell. Thus bcc unit cell has one particle from eight corners plus one particle in the centre of the cube, making total of **2 particles per bcc unit cell**.

**iii. Face-centred cubic unit cell (fcc) :** A fcc unit cell has particles at the eight corners plus particles at the centre of its six faces. As described in simple cubic unit cell, one particle

### Do you know ?

The names of fourteen Bravais lattices (unit cells) for each of the seven crystal system are shown below.



| Crystal system  | Bravais lattices  |  |                          |
|-----------------|---|--|--------------------------|
|                 | Name  | unit cell structure  |                          |
| 1. Cubic        | i. simple or primitive<br>ii. body-centred<br>iii. face-centred                     |      | i.<br>ii.<br>iii.        |
| 2. Orthorhombic | i. simple or primitive<br>ii. body-centred<br>iii. face-centred<br>iv. base-centred |     | i.<br>ii.<br>iii.<br>iv. |
| 3. Tetragonal   | i. simple or primitive<br>ii. body-centred  |    | i.<br>ii.                |
| 4. Monoclinic   | i. simple or primitive<br>ii. base centred  |     | i.<br>ii.                |
| 5. Rhombohedral | i. simple or primitive  |    |                          |
| 6. Triclinic    | i. simple or primitive  |    |                          |
| 7. Hexagonal    | i. simple or primitive  |    | c.                       |

from eight corners belongs to the given unit cell.

Each particle at the centre of the six faces is shared with one neighbouring cube. Thus,  $1/2$  of each face particle belongs to the given unit cell. From six faces,  $1/2 \times 6 = 3$  particles belong to the given unit cell.

Therefore, **fcc unit cell has one corner particle plus 3 face particles, total 4 particles per unit cell.**

#### Remember...

Each corner particle of a cube is shared by 8 cubes, each face particle is shared by 2 cubes and each edge particle is shared by 4 cubes.



#### 1.5.2 Relationship between molar mass, density of the substance and unit cell edge length, is deduced in the following steps

- If edge length of cubic unit cell is  $a$ , the volume of unit cell is  $a^3$ .
- Suppose that mass of one particle is  $m$  and that there are  $n$  particles per unit cell.

$$\text{Mass of unit cell} = m \times n \quad \dots \quad (1.1)$$

- The density of unit cell ( $\rho$ ), which is same as density of the substance is given by

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{m \times n}{a^3} = \text{density of substance} \quad \dots \quad (1.2)$$

- Molar mass ( $M$ ) of the substance is given by

$$M = \text{mass of one particle} \times \text{number of particles per mole}$$

$$= m \times N_A \quad (N_A \text{ is Avogadro number})$$

$$\text{Therefore, } m = M/N_A \quad \dots \quad (1.3)$$

- Combining Eq. (1.1) and (1.3), gives

$$\rho = \frac{n M}{a^3 N_A} \quad \dots \quad (1.4)$$

By knowing any four parameters of Eq. (1.4), the fifth can be calculated

**Problem 1.1 :** When gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol.

**Solution :**

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

$$M = 197 \text{ g mol}^{-1}, n = 4 \text{ atoms for fcc, } N_A = 6.022 \times 10^{23} \text{ atoms mol}^{-1}, \\ a = 408 \text{ pm} = 408 \times 10^{-12} \text{ m} = 4.08 \times 10^{-8} \text{ cm}$$

Substitution of these quantities in the equation gives

$$\rho =$$

$$\frac{197 \text{ g mol}^{-1} \times 4 \text{ atom}}{(4.08 \times 10^{-8})^3 \text{ cm}^3 \times 6.022 \times 10^{23} \text{ atom mol}^{-1}}$$

$$= 19.27 \text{ g/cm}^3, 19.27 \times 10^3 \text{ kg/m}^3.$$

#### 1.6 Packing of particles in crystal lattice

Constituent particles of a crystalline solid are close packed. While describing the packing of particles in a crystal, the individual particles are treated as hard spheres. The closeness of particles maximize the interparticle attractions.

The number of neighbouring spheres that touch any given sphere is its coordination number. Magnitude of the coordination number is a measure of compactness of spheres in close-packed structures. The larger the coordination number, the closer are the spheres to each other.

**1.6.1 Close packed structures :** The three dimensional close packed structure can be understood conveniently by looking at the close packing in one and two dimensions.

**a. Close packing in one dimension :** A close packed one dimensional structure results by arranging the spheres to touch each other in a row (Fig. 1.3 (a)).

**b. Close packing in two dimensions :** A close packed two dimensional (planar) structure results by stacking the rows together such

that they are in contact with each other. There are two ways to obtain close packing in two dimensions.

i. **Square close packing** : One dimensional rows of close packed spheres are stacked over each other such that the spheres align vertically and horizontally (Fig. 1.3 (b)). If the first row is labelled as 'A' type, being exactly same as the first row, the second row is also labelled as 'A' type. Hence this arrangement is called A, A, A, A..... type two dimensional arrangement. In this arrangement, every sphere touches four neighbouring spheres. Hence, two dimensional coordination number, here, is 4. A square is obtained by joining the centres of these four closest neighbours (Fig. 1.3(b)). Therefore, this two dimensional close packing is called **square close packing in two dimension**.

ii. **Hexagonal close packing** : Close packed one dimensional row (Fig. 1.3 (a)) shows that there are depressions between the neighbouring spheres. If the second row is arranged in such a way that its spheres fit in the depressions of the first row, a staggered arrangement results. If the first row is called 'A' type row, the second row, being different, is called 'B' type. Placing the third row in staggered manner in contact with the second row gives rise to an arrangement in which the spheres in the third row are aligned with the spheres in the first row. Hence the third row is 'A' type. Similarly spheres in the fourth row will be aligned with the spheres in the second row and hence the fourth row would be 'B' type. The resulting two dimensional arrangement is 'ABAB...' type (Fig. 1.3 (c)). In this arrangement each sphere touches six closest neighbours. Thus, the two dimensional coordination number in this packing is 6. A regular hexagon is obtained by joining the centres of these six closest spheres (Fig. 1.3 (c)). Hence, this type of two dimensional close packing is called **hexagonal close packing in two dimensions**. Compared to the square close packing in two dimensions, the coordination number in hexagonal close packing in two dimensions is higher. Moreover

the free space in this arrangement is less than in square packing, making it more efficient packing than square packing. From Fig.1.3(c) it is evident that the free spaces (voids) are triangular in shape. These triangular voids are of two types. Apex of the triangular voids in alternate rows points upwards and downwards.

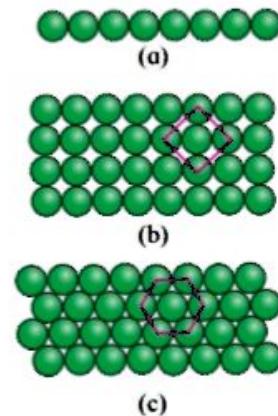
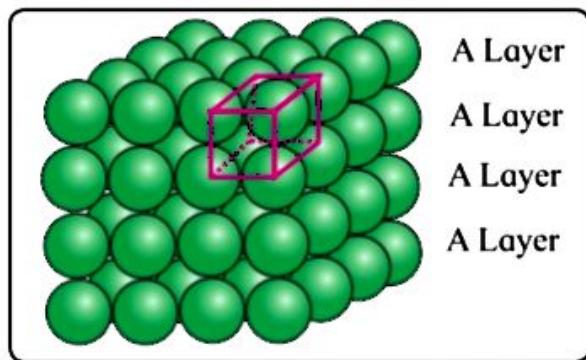


Fig. 1.3 : (a) Close packing in one dimension  
(b) square close packing  
(c) Hexagonal close packing in two dimension

c. **Close packing in three dimensions** : Stacking of two dimensional layers gives rise to three dimensional crystal structures. Two dimensional square close packed layers are found to stack only in one way to give simple cubic lattice. Two dimensional hexagonal close packed layers are found to stack in two distinct ways. Accordingly two crystal structures, namely, hexagonal close packed (hcp) structure and face centred cubic (fcc) structure are formed.

i. **Stacking of square close packed layers**: Stacking of square close packed layers generates a three dimensional simple cubic structure. Here, the second layer is placed over the first layer so as to have its spheres exactly above those of the first layer (Fig. 1.4). Subsequent square close packed layers are placed one above the other in the same manner. In this arrangement, spheres of all the layers are perfectly aligned horizontally as well as vertically. Hence, all the layers are alike, and are labelled as 'A' layers. This arrangement of layers is described as 'AAAA...' type. The

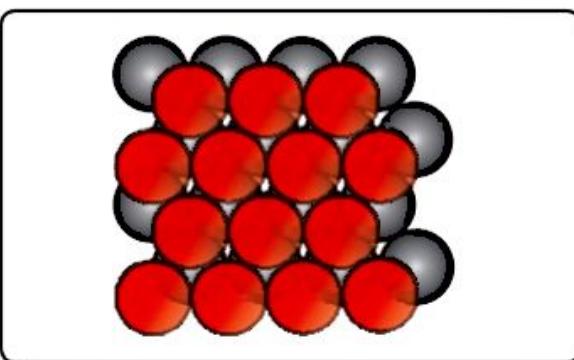
structure that results on stacking square close packed layers is **simple cubic**. Its unit cell is the **primitive cubic unit cell** (Fig. 1.4).



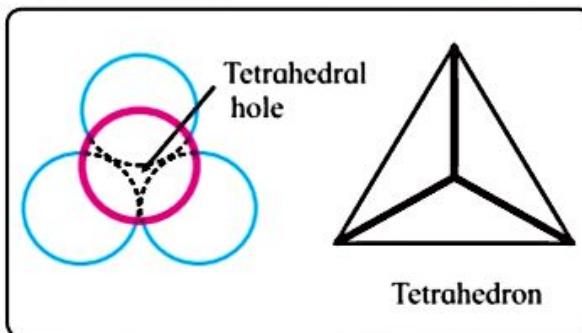
**Fig. 1.4 : Stacking of square closed packed layers**

It can be seen that in the simple cubic structure, each sphere touches six neighbouring spheres, four in its own layer, one in the layer above and one in the layer below. Hence, coordination number of each sphere is 6. Polonium is the only metal that crystallizes in simple cubic closed packed structure.

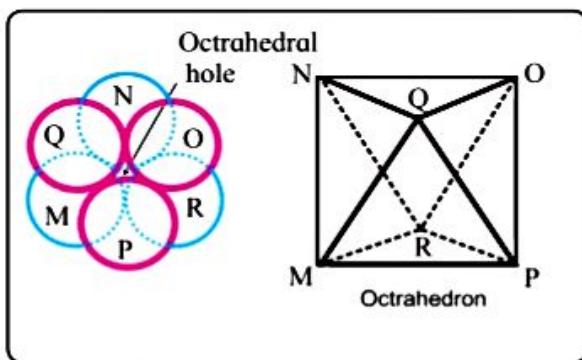
**ii. Stacking of two hexagonal close packed layers :** To generate a close packed three dimensional structure, hexagonal close packed layers are arranged in a particular manner. In doing so, spheres of the second layer are placed in the depression of the first layer (Fig. 1.5). If the first layer is labelled as 'A' layer, the second layer is labelled as 'B' layer because the two layers are aligned differently. It is evident from the Fig. 1.5 that all triangular voids of the first layers are not covered by the spheres of the second layer. The triangular voids that are covered by spheres of the second layer generate tetrahedral void (Fig. 1.6). A tetrahedral void is surrounded by four spheres. On joining the centres of these four spheres a tetrahedron is formed which encloses the tetrahedral voids (Fig. 1.6). The remaining triangular voids of the first layer have above them the triangular voids of the second layer. The overlapping triangular voids from the two layers together form an octahedral void which is surrounded by six spheres (Fig. 1.7).



**Fig. 1.5 : Two layers of closed packed spheres**



**Fig. 1.6 : Tetrahedral void**



**Fig. 1.7 : Octahedral void**

#### Remember...

It is important to note that the triangular shapes of depressions in A and B layer do not overlap. The apices of two triangular depressions in A and B layer point in opposite directions.

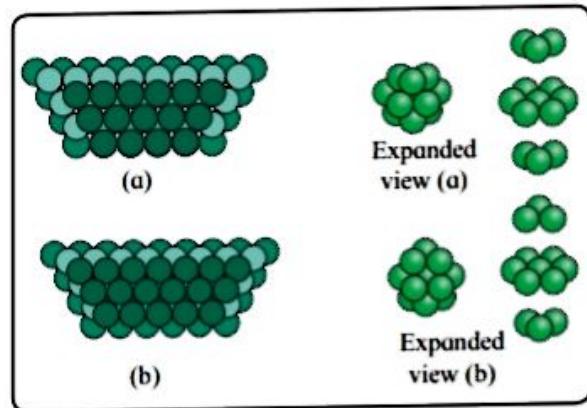


The depressions in which spheres of second layer rest are tetrahedral voids while the depressions in which no sphere rests are octahedral voids.

**iii. Placing third hexagonal close packed layer :** There are two ways of placing the third hexagonal close packed layer on the second.

One way of doing this is to align the spheres of the third layer with the spheres of the first layer. The resulting pattern of the layers will be 'ABAB....'. This arrangement results in **hexagonal close packed (hcp)** structure (Fig. 1.8(a)). Metals such as Mg, Zn, have hcp crystal structure.

The second way of placing the third hexagonal close packed layer on the second is to cover the octahedral voids by spheres of the third layer. In such placing, the spheres of the third layer do not align with the spheres of the second or the spheres of the first layer. The third layer is, therefore, called 'C' layer. The spheres of the fourth layer get aligned with the spheres of the first layer. Hence, the fourth layer is called 'A' layer. This pattern of stacking hexagonal close packed layers is called 'ABCABC....'. This arrangement results in **cubic close packed (ccp)** structure (Fig. 1.8(b)). This is same as fcc structure. Metals such as copper and Ag have ccp (or fcc) crystal structure.



**Fig. 1.8 : Formation of hexagonal closed packed structures**

### 1.6.2 Coordination number in close packed structure

a. In the simple cubic (sc) crystal structure, that results from stacking of square close packed layers, each sphere is surrounded by 6 neighbouring spheres, 4 in its own layer,

1 above and 1 below. Hence coordination number of any sphere in sc is 6.

b. In both hcp and ccp/fcc structures that result from stacking of hexagonal close packed layers in two different ways, each sphere is surrounded by 12 neighbouring spheres, 6 in its own layer, 3 above and 3 below. Hence, the coordination number of any sphere in hcp or ccp/fcc structure is 12.

**1.6.3 Number of voids per atom in hcp and ccp :** The tetrahedral and octahedral voids occur in hcp and ccp/fcc structures. There are two tetrahedral voids associated with each atom. The number of octahedral voids is half that of tetrahedral voids. Thus, there is one octahedral void per atom.

#### Remember...



If  $N$  denotes number of particles, then number of tetrahedral voids is  $2N$  and that of octahedral voids is  $N$ .

**1.7 Packing efficiency :** Like coordination number, the magnitude of packing efficiency gives a measure of how tightly particles are packed together.

Packing efficiency is the fraction or a percentage of the total space occupied by the spheres (particles).

Packing efficiency =

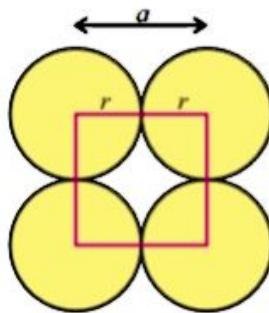
$$\frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100 \quad \dots \dots \dots (1.5)$$

**1.7.1 Packing efficiency of metal crystal in simple cubic lattice** is obtained by the following steps.

**Step 1 : Radius of sphere :** In simple cubic unit cell, particles (spheres) are at the corners and touch each other along the edge. A face of simple cubic unit cell is shown in Fig. 1.9. It is evident that

$$a = 2r \quad \text{or} \quad r = a/2 \quad \dots \dots \dots (1.6)$$

where  $r$  is the radius of atom and ' $a$ ' is the length of unit cell edge.



**Fig. 1.9 : Face of simple cubic unit cell**

**Step 2 : Volume of sphere :** Volume of a sphere =  $(4/3\pi)(r^3)$ . Substitution for  $r$  from Eq. (1.6) gives

Volume of one particle

$$= (4/3\pi)(a/2)^3 = \frac{\pi a^3}{6} \quad \dots \dots \dots (1.7)$$

**Step 3 : Total volume of particles :** Because simple cubic unit cell contains only one particle,

$$\text{volume occupied by particle in unit cell} = \frac{\pi a^3}{6}$$

**Step 4 : Packing efficiency**

Packing efficiency

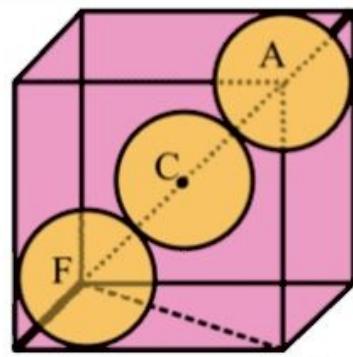
$$\begin{aligned} &= \frac{\text{volume occupied by particle in unit cell}}{\text{total volume of unit cell}} \times 100 \\ &= \frac{\pi a^3 / 6}{a^3} \times 100 = \frac{100\pi}{6} = \frac{100 \times 3.142}{6} = 52.36\% \end{aligned}$$

Thus, in simple cubic lattice, 52.36 % of total space is occupied by particles and 47.64% is empty space, that is, void volume.

### 1.7.2 Packing efficiency of metal crystal in body-centred cubic lattice

**Step 1 : Radius of sphere (particle) :**

In bcc unit cell, particles occupy the corners and in addition one particle is at the centre of the cube. Figure 1.10 shows that the particle at the centre of the cube touches two corner particles along the diagonal of the cube. To obtain radius of the particle (sphere) Pythagoras theorem is applied.



**Fig. 1.10 : bcc unit cell**

- For triangle FED,  $\angle FED = 90^\circ$ .  
 $\therefore FD^2 = FE^2 + ED^2 = a^2 + a^2 = 2a^2$  (because  $FE = ED = a$ )  $\dots \dots \dots (1.8)$
- For triangle AFD,  $\angle ADF = 90^\circ$   
 $\therefore AF^2 = AD^2 + FD^2 \quad \dots \dots \dots (1.9)$

Substitution of Eq. (1.8) into Eq. (1.9) yields

$$AF^2 = a^2 + 2a^2 = 3a^2 \text{ (because } AD = a)$$

$$\text{or } AF = \sqrt{3} a \quad \dots \dots \dots (1.10)$$

The Fig. 1.10 shows that  $AF = 4r$ .

Substitution for AF from equation (1.10) gives

$$\sqrt{3}a = 4r \text{ and hence, } r = \frac{\sqrt{3}}{4} a \quad \dots \dots \dots (1.11)$$

**Step 2 : Volume of sphere :** Volume of sphere particle =  $4/3 \pi r^3$ . Substitution for  $r$  from Eq. (1.11), gives

$$\text{volume of one particle} = \frac{4}{3} \pi (\sqrt{3}/4a)^3$$

$$= \frac{4}{3} \pi \times \frac{(\sqrt{3})^3}{64} a^3$$

$$= \frac{\sqrt{3} \pi a^3}{16}$$

**Step 3 : Total volume of particles :** Unit cell bcc contains 2 particles. Hence, volume occupied by particles in bcc unit cell

$$= 2 \times \frac{2\sqrt{3} \pi a^3}{16}$$

$$= \frac{\sqrt{3} \pi a^3}{8} \quad \dots \dots \dots (1.12)$$

#### Step 4 : Packing efficiency

Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\sqrt{3} \pi a^3}{8a^3} \times 100 = 68\%$$

Thus, 68% of the total volume in bcc unit lattice is occupied by atoms and 32% is empty space or void volume.

#### 1.7.3 Packing efficiency of metal crystal in face-centred cubic lattice (or ccp or hcp lattice)

**Step 1 : Radius of particle/sphere :** The corner particles are assumed to touch the particle at the centre of face ABCD as shown in Fig. 1.11.

The triangle ABC is right angled with  $\angle ABC = 90^\circ$ . According to Pythagoras theorem,

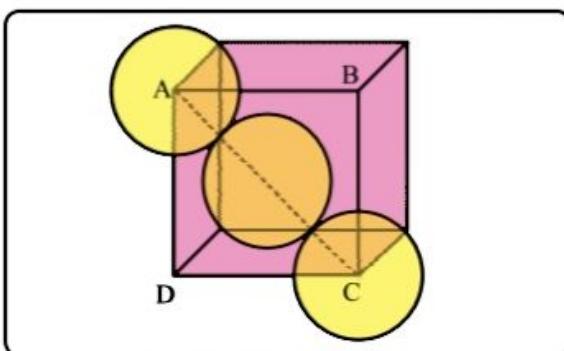
$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$


Fig. 1.11 : fcc unit cell

(because  $AB = BC = a$ )

$$\text{Hence, } AC = \sqrt{2} a \quad \dots \dots \dots (1.13)$$

Figure 1.11 shows that  $AC = 4r$ . Substitution for AC from Eq. (1.13) gives

$$\sqrt{2} a = 4r \text{ or } r = \frac{\sqrt{2}}{4} a = \frac{a}{2\sqrt{2}} \quad \dots \dots \dots (1.14)$$

**Step 2 : Volume of sphere :** Volume of one particle  $= \frac{4}{3} \pi r^3$ . Substitution for  $r$  from Eq. (1.14) gives

$$\text{Volume of one particle} = \frac{4}{3} \pi \left( \frac{a}{2\sqrt{2}} \right)^3$$

$$= \frac{4}{3} \pi a^3 \times \left( \frac{1}{2\sqrt{2}} \right)^3 \\ = \frac{\pi a^3}{12\sqrt{2}}$$

**Step 3 : Total volume of particles :** The unit cell of fcc lattice contains 4 particles. Hence, volume occupied by particles in fcc unit cell

$$= 4 \times \frac{\pi a^3}{12\sqrt{2}} = \frac{\pi a^3}{3\sqrt{2}}$$

#### Step 4 : Packing efficiency : Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

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

Thus in fcc/ccp/hcp crystal lattice, 74% of the total volume is occupied by particles and 26% is void volume or empty space.

Table 1.3 shows the expressions for various parameters of particles in terms of unit cell dimension for cubic systems.

#### Use your brain power



Which of the three lattices, sc, bcc and fcc has the most efficient packing of particles? Which one has the least efficient packing?

Table 1.3 : Edge length and particle parameters in cubic system

| Unit cell   | Relation between $a$ and $r$ | Volume of one particle          | Total volume occupied by particles in unit cell |
|-------------|------------------------------|---------------------------------|---|
| 1. sc       | $r = a/2 = 0.5000a$          | $\pi a^3/6 = 0.5237 a^3$        | $\pi a^3/6 = 0.5237 a^3$                        |
| 2. bcc      | $r = \sqrt{3}a/4 = 0.4330a$  | $\sqrt{3} \pi a^3/16 = 0.34a^3$ | $\sqrt{3} \pi a^3/8 = 0.68a^3$                  |
| 3. fcc/ ccp | $r = \sqrt{2}a/4 = 0.3535a$  | $\pi a^3/12\sqrt{2} = 0.185a^3$ | $\pi a^3/3\sqrt{2} = 0.74a^3$                   |

Table 1.4 shows the summary of coordination number of particles and packing efficiency in various cubic systems.

**Table 1.4 : Coordination number and packing efficiency in systems**

| Lattice        | Coordination number of atoms  | Packing efficiency |
|----------------|---|--------------------|
| 1. sc          | 6 : four in the same layer, one directly above and one directly below | 52.4 %             |
| 2. bcc         | 8 : four in the layer below and four in the layer above               | 68 %               |
| 3. fcc/ccp/hep | 12 : six in its own layer, three above and three below                | 74 %               |

#### 1.7.4 Number of particles and unit cells in $x$ g of metallic crystal :

The number of particles and the number of unit cells in given mass of a metal can be calculated from the known parameters of unit cell, namely, number of particles 'n' per unit cell and volume ' $a^3$ ' of unit cell. Density ( $\rho$ ) and molar mass (M) of a metal are related to each other through unit cell parameters as shown below :

$$\begin{aligned}\rho &= \frac{\text{mass}}{\text{volume}} \\ &= \frac{\text{number of particles in unit cell}}{\text{volume of unit cell}} \times \frac{M}{N_A} \\ \therefore \rho &= \frac{n}{a^3} \times \frac{M}{N_A} \\ \therefore M &= \rho \frac{a^3 N_A}{n}\end{aligned}$$

where 'n' is the number of particles in unit cell and ' $a^3$ ' is the volume of unit cell.

- **Number of particles in 'x' g metal :**

$\because$  Molar mass,  $M$ , contains  $N_A$  particles

$$\therefore x \text{ g of metal contains } \frac{x N_A}{M} \text{ particles.}$$

substitution of  $M$  gives

$$\begin{aligned}\text{Number of particles in 'x' g} &= \frac{x N_A}{\rho a^3 N_A / n} \\ &= \frac{x n}{\rho a^3}\end{aligned}$$

- **Number of unit cells in 'x' g metal :**

$\because$  'n' particles correspond to 1 unit cell

$$\therefore \frac{x n}{\rho a^3} \text{ particles correspond to } \frac{x n}{\rho a^3} \times \frac{1}{n} \text{ unit cells.}$$

$$\therefore \text{Number of unit cells in 'x' g metal} = \frac{x}{\rho a^3}$$

- **Number of unit cells in volume 'V' of metal** =  $\frac{V}{a^3}$

**Problem 1.2** A compound made of elements C and D crystallizes in fcc structure. Atoms of C are present at the corners of the cube. Atoms of D are at the centres of faces of the cube. What is the formula of the compound?

**Solution:**

i. C atoms are present at the 8 corners. The contribution of each corner atom to the unit cell is  $1/8$  atom. Hence, the number of C atom that belongs to the unit cell =  $8 \times (1/8) = 1$

ii. D atoms are present at the centres of six faces of unit cell. Each face-centre atom is shared between two cubes. Hence, contribution of each face centre atom to the unit cell is  $1/2$  atom.

The number of D atoms that belong to unit cell =  $1/2 \times 6 = 3$

There are one C atom and three D atoms in the unit cell.

$\therefore$  Formula of compound =  $CD_3$

**Problem 1.3 :** The unit cell of metallic silver is fcc. If radius of Ag atom is 144.4 pm, calculate (a) edge length of unit cell (b) volume of Ag atom, (c) the percent of the volume of a unit cell, that is occupied by Ag atoms, (d) the percent of empty space.

**Solution:**

$$(a) \text{For fcc unit cell, } r = 0.3535 \text{ } \alpha$$

$$r = 144.4 \text{ pm} = 144.4 \times 10^{-12} \text{ m}$$

$$= 144.4 \times 10^{-10} \text{ cm}$$

$$\alpha = \frac{r}{0.3535} = \frac{144.4 \times 10^{-10} \text{ cm}}{0.3535}$$

$$= 4.085 \times 10^{-8} \text{ cm}$$

$$(b) \text{Volume of Ag atom} = \frac{4}{3} \pi r^3$$

$$= \frac{4}{3} \times 3.142 \times (144.4 \times 10^{-10} \text{ cm})^3$$

$$= 1.261 \times 10^{-23} \text{ cm}^3$$

(c) In fcc unit cell, there are 4 Ag atoms

Volume occupied by 4 Ag atoms

$$= 4 \times 1.26 \times 10^{-23} \text{ cm}^3$$

$$= 5.044 \times 10^{-23} \text{ cm}^3$$

Total volume of unit cell =  $\alpha^3$

$$= (4.085 \times 10^{-8} \text{ cm})^3$$

$$= 6.817 \times 10^{-23} \text{ cm}^3$$

Percent of volume occupied by Ag atoms

$$= \frac{\text{volume occupied by atoms in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{5.044 \times 10^{-23} \text{ cm}^3}{6.817 \times 10^{-23} \text{ cm}^3} = 74\%$$

(d) Percent empty space =  $100 - 74 = 26\%$

**Problem 1.4 :** A compound is formed by two elements A and B. The atoms of element B forms ccp structure. The atoms of A occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

**Solution :** The atoms of element B form ccp structure. The number of tetrahedral voids generated is twice the number of B atoms.

Thus, number of tetrahedral voids =  $2B$

The atoms A occupy  $(1/3)$  of these tetrahedral voids.

Hence, number of A atoms =  $2B \times 1/3$

Ratio of A and B atoms =  $2/3 B : 1B$

$$= 2/3 : 1 = 2 : 3$$

Formula of compound =  $A_2B_3$

**Problem 1.5 :** Niobium forms bcc structure. The density of niobium is  $8.55 \text{ g/cm}^3$  and length of unit cell edge is 330.6 pm. How many atoms and unit cells are present in 0.5 g of niobium?

**Solution:**

$$\text{i. Number of atoms in } x \text{ g niobium} = \frac{x n}{\rho \alpha^3}$$

$x = 0.5 \text{ g}, n = 2$  (for bcc structure),

$$\rho = 8.55 \text{ g/cm}^3,$$

$$\alpha = 330.6 \text{ pm} = 3.306 \times 10^{-8} \text{ cm.}$$

Number of atoms in 0.5 g of niobium

$$= \frac{0.5 \text{ g} \times 2}{8.55 \text{ g cm}^{-3} \times (3.306 \times 10^{-8} \text{ cm})^3}$$

$$= 3.25 \times 10^{21}$$

$$\text{ii. Number of unit cells in } x \text{ g} = \frac{x}{\rho \alpha^3}$$

Number of unit cells in 0.5 g of niobium

$$= \frac{0.5 \text{ g} \times 2}{8.55 \text{ g cm}^{-3} \times (3.306 \times 10^{-8} \text{ cm})^3}$$

$$= 1.62 \times 10^{21}$$

**Problem 1.6 :** A compound forms hcp structure. What is the number of (a) octahedral voids (b) tetrahedral voids (c) total voids formed in 0.4 mol of it.

**Solution :**

$$\begin{aligned}\text{Number of atoms in } 0.4 \text{ mol} &= 0.4 \times N_A \\ &= 0.4 \times 6.022 \times 10^{23} = 2.4098 \times 10^{23}\end{aligned}$$

(a) Number of octahedral voids = number of atoms =  $2.4098 \times 10^{23}$

(b) Number of tetrahedral voids

$$\begin{aligned}&= 2 \times \text{number of atoms} \\ &= 2 \times 2.4098 \times 10^{23} \\ &\approx 4.818 \times 10^{23}\end{aligned}$$

(c) Total number of voids

$$\begin{aligned}&= 2.409 \times 10^{23} + 4.818 \times 10^{23} \\ &\approx 7.227 \times 10^{23}\end{aligned}$$

**1.8 Crystal defects or imperfections :** The real, naturally occurring crystalline substances do not have perfect crystal structures. They have some disorders or irregularities in the stacking of atoms. Such irregularities in the arrangement of constituent particles of a solid crystal are called defects or imperfections.

Defects are created during the process of crystallization. The imperfections are more if the crystallization occurs at a faster rate. It means that the defects can be minimized by carrying out crystallization at a slower rate.

In fact ideal crystals with no imperfections are possible only at the absolute zero of temperature. Above this temperature no crystalline materials are 100 % pure. They contain defects.

Whatever be the nature of a crystal defect, electrical neutrality of the solid is maintained.

It is important to note that sometimes defects are to be intentionally created for manipulating the desired properties in crystalline solids.

There are three types of defects: point defects, line defects and plain defects. Only point defects will be discussed in this chapter.

**1.8.1 Point defects :** These defects are irregularities produced in the arrangement of basis at lattice points in crystalline solids.

There are three major classes of point defects: stoichiometric point defects, impurity defects and nonstoichiometric point defects.

**a. Stoichiometric point defects :** Chemical formula of a compound shows fixed ratio of number of atoms or number of cations and anions. This fixed ratio is the stoichiometry of the compound.

In stoichiometric defect, the stoichiometry remains unchanged. In other words, the ratio of number of atoms or number of cations and anions of compound remains the same as represented by its chemical formula.

There are four types of stoichiometric point defects: vacancy defect, self interstitial defect, Schottky defect and Frenkel defect.

**i. Vacancy defect :** During crystallization of a solid, a particle is missing from its regular site in the crystal lattice. The missing particle creates a vacancy in the lattice structure. Thus, some of the lattice sites are vacant because of missing particles as shown in Fig. 1.12. The crystal is, then, said to have a vacancy defect. The vacancy defect can also be developed when the substance is heated.

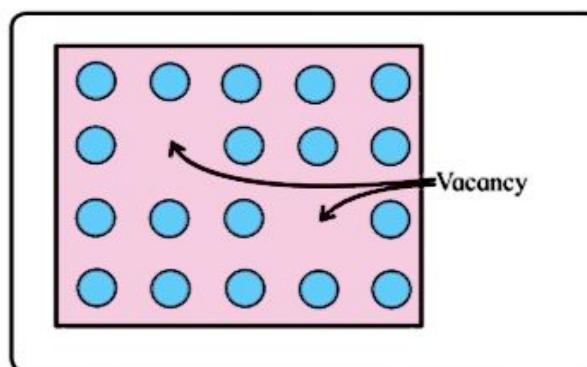


Fig. 1.12 : Vacancy defect

Due to the absence of particles, the mass of the substance decreases. However, the volume remains unchanged. As a result the density of the substance decreases.

### ii. Self interstitial defect in elemental solid

Interstitial sites in a crystal are the spaces or voids in between the particles at lattice points. When some particles of a crystalline elemental solid occupy interstitial sites in the crystal structure, it is called self interstitial defect.

This defect occurs in the following two ways :

**Firstly**, an extra particle occupies an empty interstitial space in the crystal structure as shown in Fig. 1.13. This extra particle is same as those already present at the lattice points.

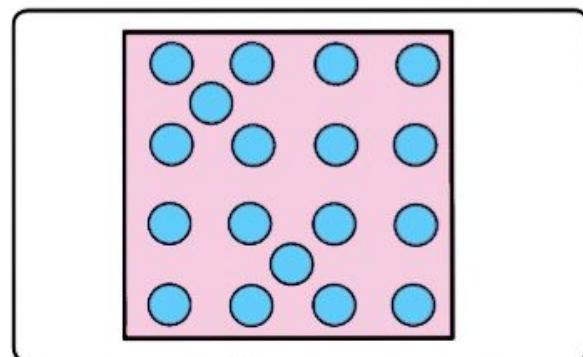


Fig. 1.13 : Self interstitial defect

The extra particles increase the total mass of substance without increasing volume. Hence its density increases.

**Secondly**, in an elemental solid a particle gets shifted from its original lattice point and occupies an interstitial space in the crystal as shown in the Fig. 1.14.

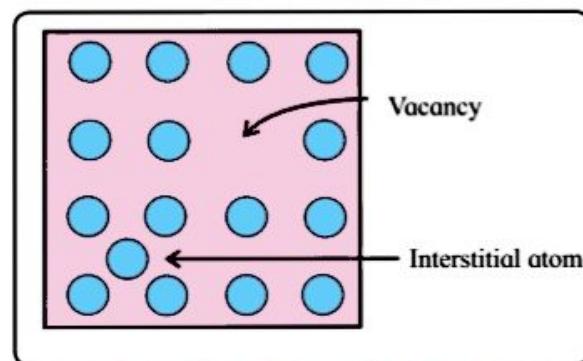


Fig. 1.14 : Self interstitial defect

It is interesting to note that in this second case, because of the displacement of a particle a vacancy defect is created at its original regular lattice site. At the same time interstitial defect results at its new position. We can, therefore, say that in this defect there is a combination of vacancy defect and self interstitial defect.

This defect preserves the density of the substance because there is neither loss nor gain in mass of a substance.

**iii. Schottky defect :** In an ionic solid, equal number of cations and anions are missing from their regular positions in the crystal lattice creating vacancies as shown in Fig. 1.15. It means that a vacancy created by a loss of cation is always accompanied by a vacancy formed by a loss of anion.

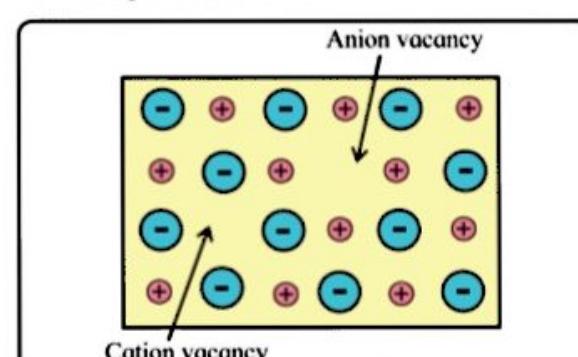


Fig. 1.15 : Schottky defect

Thus, there exist two holes per ion pair lost, one created by missing cation and the other by a missing anion. Such a paired cation-anion vacancy defect is a Schottky defect.

### Conditions for the formation of Schottky defect

i. Schottky defect is found in ionic compounds with the following characteristics :

- High degree of ionic character.
- High coordination number of anion
- Small difference between size of cation and anion. The ratio  $r_{\text{cation}}/r_{\text{anion}}$  is not far below unity.

### Consequences of Schottky defect

- As the number of ions decreases, mass decreases. However, volume remains unchanged. Hence, the density of a substance decreases.
- The number of missing cations and anions is equal, the electrical neutrality of the compound is preserved.

This defect is found in ionic crystals such as NaCl, AgBr and KCl.

**iv. Frenkel defect :** Frenkel defect arises when an ion of an ionic compound is missing from its regular lattice site and occupies interstitial position between lattice points as shown in Fig. 1.16.

The cations are usually smaller than anions. It is, therefore, more common to find the cations occupying interstitial sites. It is easier for the smaller cations to accommodate the interstitial spaces.

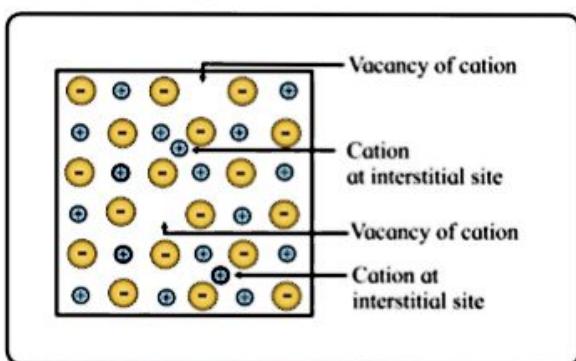


Fig. 1.16 : Frenkel defect

#### Do you know ?

Frenkel defect is not found in pure alkali metal halides because cations of alkali metals due to large size cannot occupy interstitial space.

It is important to note that the smaller cation is displaced from its normal site to an interstitial space. It, therefore, creates a vacancy defect at its original position and interstitial defect at its new location in the same crystal. Frenkel defect can be regarded as the combination of vacancy defect and interstitial defect.

### Conditions for the formation of Frenkel defect

- Frenkel defect occurs in ionic compounds with large difference between sizes of cation and anion.
- The ions of ionic compounds must be having low coordination number.

### Consequences of Frenkel defect

- As no ions are missing from the crystal lattice as a whole, the density of solid and its chemical properties remain unchanged.
- The crystal as a whole remains electrically neutral because the equal numbers of cations and anions are present.

This defect is found in ionic crystals like ZnS, AgCl, AgBr, AgI, CaF<sub>2</sub>.

**b. Impurity defect :** Impurity defect arises when foreign atoms, that is, atoms different from the host atoms, are present in the crystal lattice. There are two kinds of impurity defects : Substitutional and interstitial impurity defects.

**i. Substitutional impurity defect :** In this defect, the foreign atoms are found at the lattice sites in place of host atoms. The regular atoms are displaced from their lattice sites by impurity atoms.

#### For example :

- Solid solutions of metals (alloys) :** Brass is an alloy of Cu and Zn. In brass, host Cu atoms are replaced by impurity of Zn atoms. The Zn atoms occupy regular sites of Cu atoms as shown in Fig. 1.17.

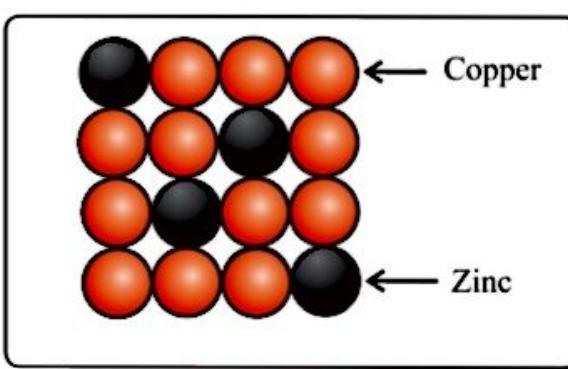
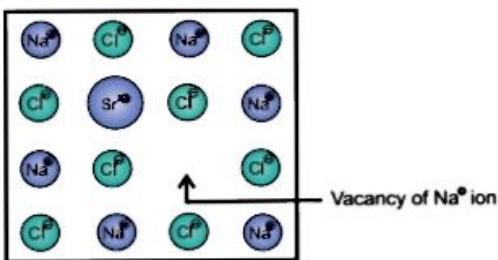


Fig. 1.17 : Brass

- Vacancy through aliovalent impurity :**

Vacancies are created by the addition of impurities of aliovalent ions (that is, ions with oxidation state (o.s.) different from that of host ions) to an ionic solid.

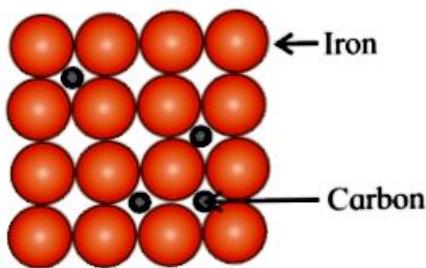


**Fig. 1.18 : Vacancy through aliovalent ion**

Suppose that a small amount of  $\text{SrCl}_2$  impurity is added to  $\text{NaCl}$  during its crystallization. The added  $\text{Sr}^{2+}$  ions (O.S. + 2) occupy some of the regular sites of  $\text{Na}^+$  host ions (O.S.+1).

In order to maintain electrical neutrality, every  $\text{Sr}^{2+}$  ion removes two  $\text{Na}^+$  ions. One of the vacant lattice sites created by removal of two  $\text{Na}^+$  ions is occupied by one  $\text{Sr}^{2+}$  ion. The other site of  $\text{Na}^+$  ion remains vacant as shown in Fig. 1.18.

**ii. Interstitial impurity defect :** In this defect, the impurity atoms occupy interstitial spaces of lattice structure. For example in steel, Fe atoms occupy normal lattice sites. The carbon atoms are present at interstitial spaces, as shown in Fig. 1.19.



**Fig. 1.19 : Stainless steel**

- c. Nonstoichiometric defects :**

Nonstoichiometric defect arises when the ratio of number of atoms of one kind to that of other kind or the ratio of number of cations to anions becomes different from that indicated by its chemical formula. In short, stoichiometry of the compound is changed.

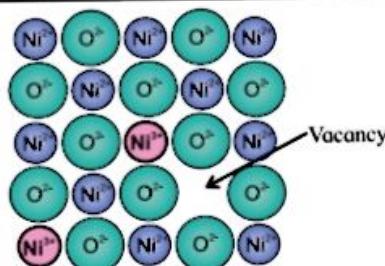
It is important to note that the change in stoichiometry does not cause any change in the crystal structure.

There are two types of nonstoichiometric defects

**i. Metal deficiency defect :** This defect is possible only in compounds of metals that show variable oxidation states.

In some crystals, positive metal ions are missing from their original lattice sites. The extra negative charge is balanced by the presence of cation of the same metal with higher oxidation state than that of missing cation.

For example, in the compound  $\text{NiO}$  one  $\text{Ni}^{2+}$  ion is missing creating a vacnacy at its lattice site. The deficiency of two positive charges is made up by the presence of two  $\text{Ni}^{3+}$  ions at the other lattice sites of  $\text{Ni}^{2+}$  ions as shown in Fig. 1.20. The composition of  $\text{NiO}$  then becomes  $\text{Ni}_{0.97}\text{O}_{1.0}$ .

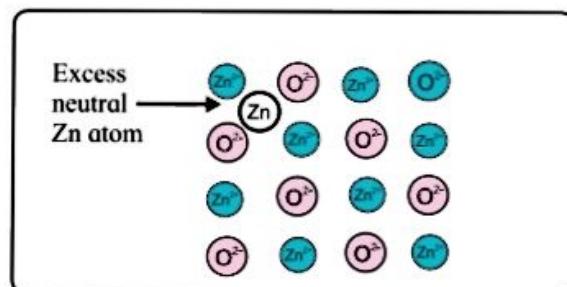


**Fig. 1.20 : Nonstoichiometric  $\text{Ni}_{0.97}\text{O}_{1.0}$**

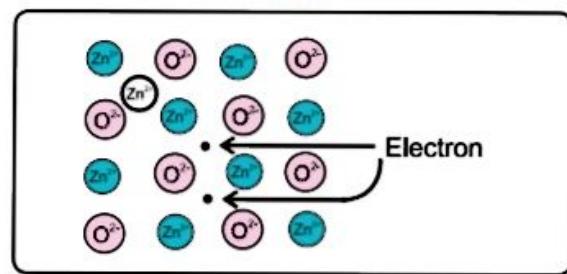
**ii. Metal excess defect :** There are two types of metal excess defects.

- A neutral atom or an extra positive ion occupies interstitial position :**  $\text{ZnO}$  presents two ways of metal excess defect. In the first case in  $\text{ZnO}$  lattice one neutral

Zn atom is present in the interstitial space as shown in Fig. 1.21(a)

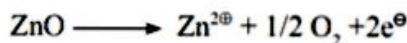


**Fig. 1.21 (a) : Neutral Zn atom at interstitial site**



**Fig. 1.21 (b) : Zn<sup>2+</sup> ions and electrons at interstitial sites**

In the second case, when ZnO is heated it decomposes as :



The excess Zn<sup>2+</sup> ions are trapped in interstitial site in the lattice. The electrons also diffuse in the crystal to occupy interstitial sites as shown in Fig. 1.21(b).

In both the cases, nonstoichiometric formula of ZnO is Zn<sub>1-x</sub>O<sub>1.0</sub>

#### Can you think ?

When ZnO is heated it turns yellow and returns back to original white colour on cooling. What could be the reason ?



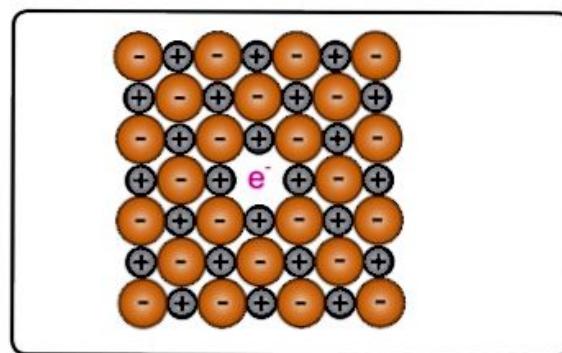
#### • By anion vacancies (Colour or F-centres)

This type of defect imparts colour to the colourless crystal. For example, when NaCl crystal is heated in the atmosphere of sodium vapour, sodium atoms are deposited on the crystal surface.

Cl<sup>⊖</sup> ions diffuse to the crystal surface creating vacancies at their regular sites. These Cl<sup>⊖</sup> ions combine with Na atoms on the surface to form NaCl, by releasing electron from sodium atom.



The electrons released diffuse into the crystal and occupy vacant sites of anions as shown in Fig. 1.22. The anion vacant sites occupied by electrons are F-centres or colour-centres.



**Fig. 1.22 : An F-centre in a crystal**

**NaCl shows yellow colour due to the formation of F-centre.** The crystal of NaCl has excess Na. The nonstoichiometric formula of NaCl is the Na<sub>1+x</sub>Cl<sub>1.0</sub>

#### 1.9 Electrical properties of solids

##### Can you recall ?

- What is electrical conductivity ?
- What is meant by the terms 'insulator' and 'semiconductor' ?



Solids show very wide range of electrical conductivity. Accordingly solids are classified into the following three categories : conductors, insulators and semiconductors.

**i. Conductors :** Solids having electrical conductivities in the range 10<sup>4</sup> to 10<sup>7</sup> Ohm<sup>-1</sup>m<sup>-1</sup> are called conductors. Metals and electrolytes (ionic solids) are examples of electrical conductors. Metals conduct electricity by movement of electrons while electrolytes conduct electricity by movement of ions. In

this section we will study some aspects of electronic conduction of electricity.

**ii. Insulators :** Solids having low electrical conductivities in the range  $10^{-20}$  to  $10^{-10} \text{ Ohm}^{-1}\text{m}^{-1}$  are called insulators. Most nonmetals and molecular solids belong to this category.

**iii. Semiconductors :** Solids having electrical conductivities in the range  $10^{-6}$  to  $10^4 \text{ Ohm}^{-1}\text{m}^{-1}$  are semiconductors. This range is intermediate between conductors and insulators. Metalloids like silicon, germanium belong to this category.

**1.9.1 Band theory :** Electrical conductivities of solid metals, nonmetals and metalloids are explained in terms of band theory. A band is made of closely spaced electronic energy levels. Band formation can be correlated to formation of molecular orbitals (MOs) by interaction of atomic orbitals. (Refer to Std. XI Chemistry Textbook, chapter 5).

#### Can you recall ?

- How many molecular orbitals are formed by interaction of two atomic orbitals ?
- What is metallic bond ?



According to MO theory interaction of atomic orbitals of combining atoms results in formation of equal number of MOs which spread over the entire molecule. Similar to this, interaction of energy levels of electrons in the closely spaced constituent atoms in solids result in formation of bands. Band theory considers formation of two types of bands, namely, conduction band and valence band. Another important concept of band theory is the band gap.

**i. Conduction band :** The highest energy band containing electrons is the conduction band. It is formed by interaction of the outermost energy levels of closely spaced atoms in solids. Conduction band may be partially occupied or vacant. Electrons in conduction band are mobile and delocalized over the entire solid.

They conduct electricity when electrical potential is applied.

**ii. Valence band :** The band having lower energy than conduction band is the valence band.

The electrons in valence band are not free to move because they are tightly bound to the respective nuclei.

**iii. Band gap :** The energy difference between valence band and conduction band is called band gap. Size of the band gap decides whether electrons from valence band can be promoted to vacant conduction band or not when band gap is too large to promote electrons from valence band to vacant conduction band by thermal energy, it is called **forbidden zone**. When band gap is small, electrons from higher energy levels in valence band can be promoted to conduction band by absorption of energy (such as thermal, electromagnetic).

#### Do you know ?

The band gap energy values of a few solids are as shown here.

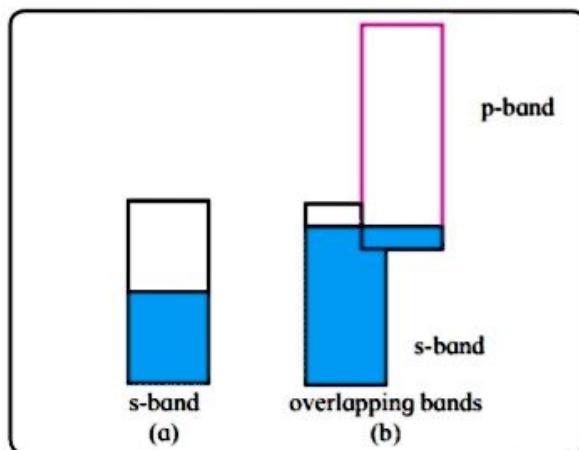


| Solid     | $E_{\text{gap}}$ eV |
|-----------|---------------------|
| Diamond   | 5.47                |
| Sodium    | 0                   |
| Silicon   | 1.12                |
| Germanium | 0.67                |

The electrical properties of metallic conductors, insulators and semiconductors are explained in terms of band theory as follows :

**1.9.2 Metals :** Metals are good conductors of electricity. The outermost electrons of all the atoms in the metallic crystal occupy conduction band. The number of electrons in conduction band of metals is large. Hence metals are good conductors of electricity. The conduction bands in metals can be further labelled as 's' band (Fig. 1.23 (a)), overlapping s and p bands (Fig. 1.23(b)) and so on. This

depends on the atomic orbitals involved in band formation. Band formation in metallic conductors, thus, results in delocalization of the outermost electrons of all the metal atoms leaving behind metal ions. This is described as 'cations of metal are immersed in the sea of electrons'.



**Fig. 1.23: Metallic conductor**

The cations of metal atoms occupying lattice sites vibrate about their mean positions. At higher temperatures, metal cations undergo increased vibrational motion about their lattice sites. The flow of electrons is interrupted by increased vibrational motion. As a result conductivity of metals decreases with increase in temperature. (Refer to Std. XI Physics chapter 11).

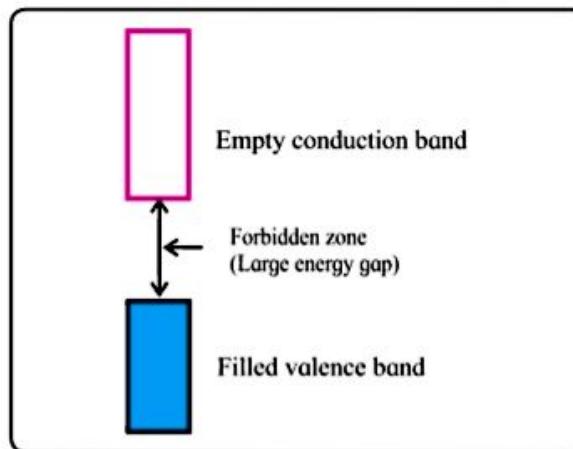
#### Do you know ?

- **Metallic sodium** is an example of conductor where the conduction band is partially filled and there is no band gap. Electronic configuration of Na is [Ar]3s<sup>1</sup>. Interaction of the partially filled 3s AOs of all the Na atoms gives rise to same number of MOs. All these closely spaced MOs together form a continuous band of energies which is called 3s band. Lower half of 3s band corresponds of BMOs and is filled while the upper half of 3s band corresponds to AMOs and is empty. There is no gap

between these two halves. The 3s band in sodium is the conduction band which contains same number of electrons as the sodium atoms. This is responsible for the high conductivity of metallic sodium.

- **Metallic magnesium** is an example of conductor with overlapping bands. Electronic configuration of Mg is [Ar]3s<sup>2</sup>3p<sup>0</sup>. Interaction of completely filled 3s AOs of all the Mg atoms gives rise to the same number of MOs all of which are filled. These together form the 3s band which is a completely filled band. Interaction of vacant 3p AOs of all the Mg atoms gives rise to the same number of vacant MOs together called 3p band. This is the vacant band. The filled 3s band and vacant 3p band overlap each other. As a result, higher energy electrons move from 3s band to 3p band.

**1.9.3 Insulators :** In insulators the valence band is completely filled with electrons and the conduction band is empty.



**Fig. 1.24: Insulators**

The valence band and conduction band in insulators are separated by a large energy gap called forbidden zone as shown in Fig. 1.24. Here, thermal energy is insufficient to promote electrons from valence band to conduction band.

As a result the conduction band remains vacant. The material is, therefore, an insulator.

**1.9.4 Semiconductors :** Electrical conductivity of a semiconductor material is intermediate between that of metals and insulators. The metalloids Si and Ge are semiconductors.

Like insulators, the valence band in semiconductor is completely filled with electrons and conduction band is empty. However, the energy gap between the two bands is smaller than that in an insulator. (Fig. 1.25)

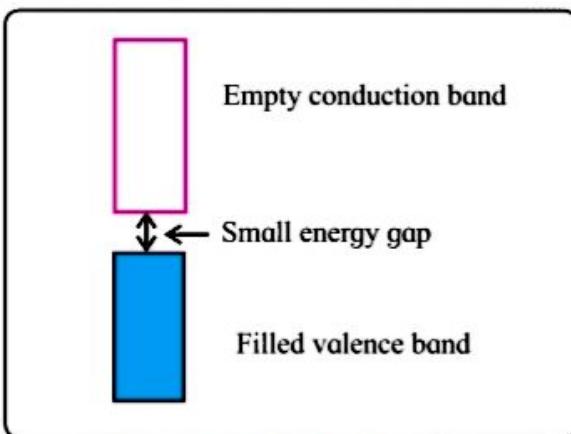


Fig. 1.25 : Semiconductors

At a temperature above absolute zero a few electrons in the valence band have enough thermal energy to jump through the small band gap and occupy higher energy conduction band. The conduction band, thus, becomes partially filled and the valence band becomes partially empty.

The electrons in conduction band are free to move. When electric potential is applied to a semiconductor, it conducts a small amount of electricity.

Such a pure semiconductor material which has a very low but finite electrical conductivity is called **intrinsic semiconductor**.

The electrical conductivity of a semiconductor increases with increasing temperature. This is because, the number of electrons with sufficient energy so as to get promoted to the conduction band increases as temperature rises. Thus, at higher temperatures, there are more mobile electrons in the conduction band and more vacancies in

the valence band than at lower temperature. In fact semiconductors are insulators at low temperatures and conductors at high temperatures.

#### Remember...

Electrical conductivity of metals decreases and that of semiconductor increases with increasing temperature.



#### 1.9.5 Extrinsic semiconductors and doping :

The conductivity of a semiconductor can be increased by doping. The process of addition of minute quantity of impurities to a semiconductor to increase its conductivity is called **doping**. The added impurity is called **dopant**.

A doped semiconductor, having higher conductivity than pure intrinsic semiconductor, is an **extrinsic semiconductor**.

There are two types of extrinsic semiconductors, namely, **n-type** and **p-type** semiconductors.

i. **n-type semiconductor** : n-type semiconductor contains increased number of electrons in the conduction bond.

An n-type semiconductor is obtained by adding group 15 element to intrinsic semiconductor which belongs to group 14.

#### Can you tell ?

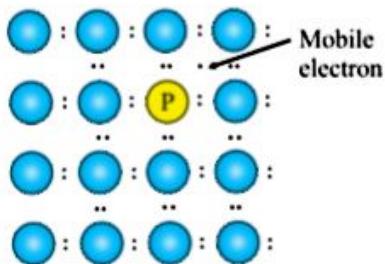


Let a small quantity of phosphorus be doped into pure silicon.

- Will the resulting material contain the same number of total number of electrons as the original pure silicon ?
- Will the material be electrically neutral or charged ?

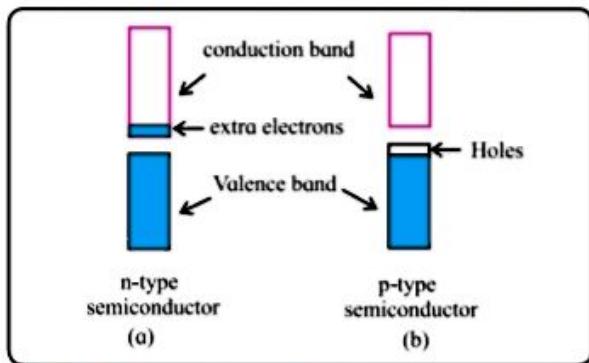
Consider, for example, doping of Si with phosphorus. Si has a crystal structure in which each Si atom is linked tetrahedrally to four other Si atoms. When small quantity of

phosphorous is added to pure Si, the P atoms occupy some vacant sites in the lattice in place of Si atoms, as shown in Fig. 1.26. The overall crystal structure of Si remains unchanged.



**Fig. 1.26 : P atom occupying regular site of Si atom**

Four of the five valence electrons of P are utilized in bonding the closest to four Si atoms. Thus, P has one extra electron than needed for bonding. Therefore, Si doped with P has more number of electrons in the conduction band than those in the conduction band in pure Si as shown in Fig. 1.27. It is thus transparent that the conductivity of Si doped with P is higher than that of pure Si. The electrons in conduction band move under the influence of an applied potential and conduct electricity.



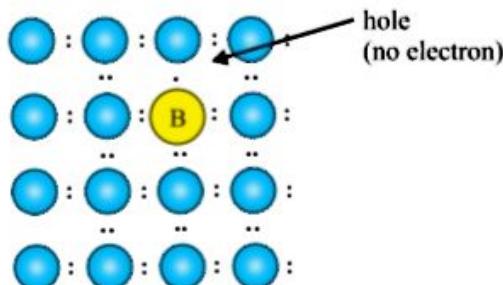
**Fig. 1.27 : n-type and p-type semiconductor**

Because the charge carriers are the increased number of electrons, Si or Ge doped with group 15 elements such as P, As, Sb or Bi is an n-type semiconductor.

**ii. p-type semiconductor :** A p-type semiconductor is produced by doping a pure semiconductor material (Si or Ge) with an impurity of group 13 elements. These elements

contain less number of valence electrons than that of the pure semiconductor.

Consider, for example, pure Si doped with boron. The B atoms occupy normal positions of some of the Si atoms in the lattice as shown in Fig. 1.28. Boron atom has only three valence electrons. It does not have enough electrons to form bonds with its four Si neighbours.



**Fig. 1.28 : B atom occupying regular site of Si atom**

B atom forms bonds with three Si atoms only. The missing fourth electron creates an electron vacancy. It is called a hole.

Fig. 1.28 shows the holes in the valence band of p-type semiconductor.

A hole has a tendency to accept electron from its close vicinity. Thus, a hole behaves as if it has a positive charge. The electrons in partially filled valence band move under the influence of an applied potential. The holes move in the opposite direction.

#### Remember...

- Whether intrinsic or extrinsic semiconductor, the material is electrically neutral.
- An n-type semiconductor such as Si doped with P has more electrons than those needed for bonding and thus has electrons in the partially filled conduction band.
- A p-type semiconductor such as Si doped with B has the less electrons than needed for bonding and thus has vacancies (holes) in the valence band.



Because the charge carriers are holes which behave like positive charge, the Si or Ge doped with group 13 elements like B, Ga or In, is a p-type semiconductor.

**1.10 Magnetic properties of solids :** Magnetic properties of solids can be understood easily in terms of classical picture of electron. The electrons spin about their own axis. The spinning electrons act like tiny magnets because their spinning action generates induced magnetic field.

If an orbital contains one electron, the unbalanced spin exhibits magnetism. However, when electrons are paired their spin is balanced and no magnetic property is observed. On the basis of magnetic properties solids are classified into three major classes : diamagnetic, paramagnetic and ferromagnetic.

**i. Diamagnetic solids :** The substances with all electrons paired, are weakly repelled by magnetic fields. These substances are said to be diamagnetic.

Pairing of electrons balances the spins and hence, cancels their magnetic moments.

N<sub>2</sub>, F<sub>2</sub>, NaCl, H<sub>2</sub>O and benzene are some examples of diamagnetic substances.

**ii. Paramagnetic solids :** The substances with unpaired electrons are weakly attracted by magnetic field. These substances are called paramagnetic substances.

The spinning of unpaired electron gives rise to a magnetic moment. The substance is attracted by magnetic field because of magnetic moment. It is important to understand that these substances exhibit magnetism in presence of external magnetic field only. They lose magnetism when the external magnetic field is removed.

Oxygen, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> are some examples of paramagnetic substances.

**iii. Ferromagnetism :** The substances containing large number of unpaired electrons are attracted strongly by magnetic field. These substances are said to be ferromagnetic.

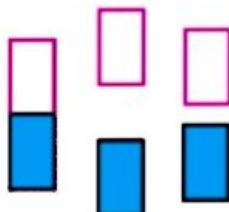
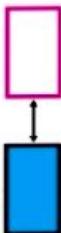
These substances can be permanently magnetised. They retain magnetism even after the removal of external magnetic field.

Some example of ferromagnetic substances are Fe, Co, Ni, Gd, CrO<sub>2</sub>.

### Exercises

#### 1. Choose the most correct answer.

- i. Molecular solids are
  - a. crystalline solids
  - b. amorphous solids
  - c. ionic solids
  - d. metallic solids
- ii. Which of the following is n-type semiconductor?
  - a. Pure Si
  - b. Si doped with As
  - c. Si doped with Ga
  - d. Ge doped with In
- iii. In Frenkel defect
  - a. electrical neutrality of the substance is changed.
  - b. density of the substance is changed.
  - c. both cation and anion are missing
  - d. overall electrical neutrality is preserved.
- iv. In crystal lattice formed by bcc unit cell the void volume is
  - a. 68 %
  - b. 74 %
  - c. 32 %
  - d. 26 %

- v. The coordination number of atoms in bcc crystal lattice is  
 a. 2      b. 4  
 c. 6      d. 8
- vi. Which of the following is not correct?  
 a. Four spheres are involved in the formation of tetrahedral void.  
 b. The centres of spheres in octahedral voids are at the apices of a regular tetrahedron.  
 c. If the number of atoms is N the number of octahedral voids is  $2N$ .  
 d. If the number of atoms is  $N/2$ , the number of tetrahedral voids is N.
- vii. A compound forms hcp structure. Number of octahedral and tetrahedral voids in 0.5 mole of substance is respectively  
 a.  $3.011 \times 10^{23}, 6.022 \times 10^{23}$   
 b.  $6.022 \times 10^{23}, 3.011 \times 10^{23}$   
 c.  $4.011 \times 10^{23}, 2.011 \times 10^{23}$   
 d.  $6.011 \times 10^{23}, 12.022 \times 10^{23}$
- viii. Pb has fcc structure with edge length of unit cell 495 pm. Radius of Pb atom is  
 a. 205 pm      b. 185 pm  
 c. 260 pm      d. 175 pm
- 2. Answer the following in one or two sentences**
- What are the types of particles in each of the four main classes of crystalline solids?
  - Which of the three types of packing used by metals makes the most efficient use of space and which makes the least efficient use?
  - The following pictures show population of bands for materials having different electrical properties. Classify them as insulator, semiconductor or a metal.
- 
- iv. What is the unit cell?  
 v. How does electrical conductivity of a semiconductor change with temperature? Why?  
 vi. The picture represents bands of MOs for Si. Label valence band, conduction band and band gap.
- 
- vii. A solid is hard, brittle and electrically nonconductor. Its melt conducts electricity. What type of solid is it?  
 viii. Mention two properties that are common to both hcp and ccp lattices.  
 ix. Sketch a tetrahedral void.  
 x. What are ferromagnetic substances?
- 3. Answer the following in brief.**
- What are valence band and conduction band?
  - Distinguish between ionic solids and molecular solids.
  - Calculate the number of atoms in fcc unit cell.
  - How are the spheres arranged in first layer of simple cubic close-packed structures? How are the successive

- layers of spheres placed above this layer?
- v. Calculate the packing efficiency of metal crystal that has simple cubic structure.
- vi. What are paramagnetic substances? Give examples.
- vii. What are the consequences of Schottky defect?
- viii. Cesium chloride crystallizes in cubic unit cell with  $\text{Cl}^-$  ions at the corners and a  $\text{Cs}^+$  ion in the centre of the cube. How many  $\text{CsCl}$  molecules are there in the unit cell?
- ix. Cu crystallizes in fcc unit cell with edge length of 495 pm. What is the radius of Cu atom?
- x. Obtain the relationship between density of a substance and the edge length of unit cell.
4. The density of iridium is  $22.4 \text{ g/cm}^3$ . The unit cell of iridium is fcc. Calculate the radius of iridium atom. Molar mass of iridium is  $192.2 \text{ g/mol}$ . ( $136 \text{ pm}$ )
5. Aluminium crystallizes in cubic close packed structure with unit cell edge length of  $353.6 \text{ pm}$ . What is the radius of Al atom? How many unit cells are there in  $1.00 \text{ cm}^3$  of Al? ( $125 \text{ pm}, 2.26 \times 10^{22}$ )
6. In an ionic crystalline solid atoms of element Y form hcp lattice. The atoms of element X occupy one third of tetrahedral voids. What is the formula of the compound? ( $\text{X}_2\text{Y}_3$ )
7. How are tetrahedral and octahedral voids formed?
8. Third layer of spheres is added to second layer so as to form hcp or ccp structure. What is the difference between the addition of third layer to form these hexagonal close-packed structures?
9. An element with molar mass  $27 \text{ g/mol}$  forms cubic unit cell with edge length of  $405 \text{ pm}$ . If density of the element is  $2.7 \text{ g/cm}^3$ . What is the nature of cubic unit cell? (fcc or ccp)
10. An element has a bcc structure with unit cell edge length of  $288 \text{ pm}$ . How many unit cells and number of atoms are present in  $200 \text{ g}$  of the element? ( $1.16 \times 10^{24}, 2.32 \times 10^{24}$ )
11. Distinguish with the help of diagrams metal conductors, insulators and semiconductors from each other.
12. What are n-type semiconductors? Why is the conductivity of doped n-type semiconductor higher than that of pure semiconductor? Explain with diagram.
13. Explain with diagram, Frenkel defect. What are the conditions for its formation? What is its effect on density and electrical neutrality of the crystal?
14. What is an impurity defect? What are its types? Explain the formation of vacancies through aliovalent impurity with example.

### Activity :



- With the help of plastic balls, prepare models of
  1. tetrahedral and octahedral voids.
  2. simple cubic, bcc and fcc unit cells.
  3. ccp and hcp lattices.
- Draw structures of network of carbon atoms in diamond and graphite. Discuss with reference to the following points :
  1. Are the outermost electrons of carbons in diamond localized or delocalized ?
  2. Is the energy gap between BMOs and AMOs in diamond expected to be large or small ?