8

SOLID STATE

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

Objectives

After reading this lesson, you should be able to:

- explain the nature of solid state;

- explain the properties of solids in terms of packing of particles and intermolecular attractions;

- explain the melting point of a solid;

- differentiate between crystalline and amorphous solids;

- classify the crystalline solids according to the forces operating between the constituent particles;

- explain different types of packing in the solids;

- define coordination number;

- define unit cell;

- explain different types of unit cells;

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

- define radius ratio;

- *correlate the radius ratio with the structure of solids;*

- *explain the structure of simple ionic compounds and*

- *explain Frenkel and Schottky defects.*

8.1 Nature of Solid State

You have learnt in lesson 6 that according to *Kinetic Molecular Theory*, the gases consist of a large number of molecules, which are in constant random motion in all directions in the available space. These molecules have very weak or negligible forces of attraction between them. A sample of gas can be compressed, as there is a lot of free space between the molecules Fig. 8.1(a) In liquids Fig. 8.1(b) on the other hand the molecules are also in constant motion but this motion is relatively restricted. Since there is very little free space available between the molecules the liquids are relatively incompressible.
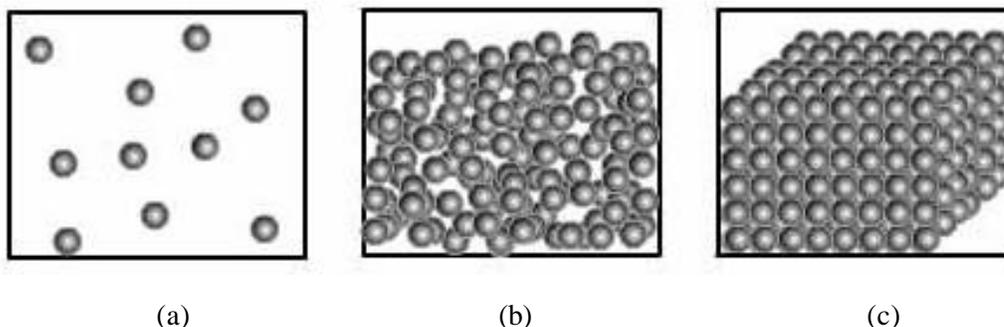

(a)	(b)	(c)

Fig: 8.1: *A pictorial representation of the three states of matter: (a) gas (b) liquid and (c) solid state.*

In solid state the constituent particles are arranged in a closely packed ordered arrangement Fig 8.1 (c) with almost no free space. They can just vibrate about their fixed positions. These are in close contact and cannot move around like the molecules of a gas or a liquid. As a consequence, the solids are incompressible, rigid and have a definite shape. Like liquids, the volume of a solid is independent of the size or the shape of the container in which it is kept.

8.2 Classification of Solids

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

8.2.1 Amorphous and Crystalline Solids

In **crystalline solids** the constituent particles are arranged in a regular and periodic pattern and give a well defined shape to it. The term 'crystal' comes from the Greek word, *krustallos* meaning ice. The regular pattern extends throughout the solid and such solids are said to have **long range order**. On the other hand, some solids have only a short range of order. This means that the particles are arranged regularly in only some regions of the solid and are relatively disordered in other regions. Such solids are called

amorphous solids. In Greek, *a* means without and *morph* means form. Thus the word *amorphous* means without form. Sodium chloride and sucrose are common examples of crystalline solids while glass, fused silica, rubber and high molecular mass polymers are some examples of amorphous solids.

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

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

8.2.2 Classification of Crystalline Solids

In crystalline solids the constituent particles are arranged in an ordered arrangement and are held together by different types of attractive forces. These forces could be coulombic or electrostatic, covalent, metallic bonding or weak intermolecular in nature. The differences in the observed properties of the solids are due to the differences in the type of forces between the constituting particles. The types of forces binding the constituent particles can be used as a basis for classification of crystalline solids. On this basis, the crystalline solids can be classified into four different types- ionic, molecular, covalent and metallic solids. The characteristics and the properties of different types of solids are compiled in Table 8.1.

Table 8.1: Characteristics and properties of different types of solids.

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

Sodium chloride is an example of an ionic solid because in this case the sodium ions and chloride ions are attracted to each other by electrostatic interactions. Iodine on the other hand is an example of a molecular solid because in this the molecules are held together by

weak van der Waals forces. Diamond, with strong covalent bonds between the constituent carbon atoms is an example of covalent solids while in metals a large number of positive cores of the atoms are held together by a sea of electrons.

8.3   Properties of Crystalline Solids

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

- Solids are rigid in nature and have well defined shapes

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

- Solids are almost incompressible.

You are familiar with a number of crystalline solids like sugar, rock salt, alum, gem stones, etc. You must have noticed that such solids have smooth surfaces. These are called 'faces' of the crystal. These faces are developed in the process of crystal formation by ordered arrangements of the constituent particles. It is generally observed that the faces of crystals are developed unequally. The internal angle between a pair of faces is called **interfacial angle** and is defined as the angle between the normals to the intersecting faces. An important characteristic of crystalline solids is that irrespective of the size and shape of the crystal of a given substance, the interfacial angle between a pair of faces is always the same. This fact was stated by Steno as *the law of constancy of interfacial angles* (Fig. 8.2).
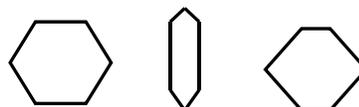
Fig. 8.2   *The constancy of interfacial angles*

8.3.1 Melting Point of a Solid

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

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

Intext Questions 8.1

a) Differentiate between solid, liquid and gaseous state.

....

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

....

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

....

8.4 Close Packed Structures of Solids

In the process of the formation of a crystal the constituent particles get packed quite closely. The crystal structures of the solids can be described in terms of a close packing of identical spheres as shown in Fig. 8.3. These are held together by forces of attraction. Let us learn about the possible close packed structures of solids and their significance.
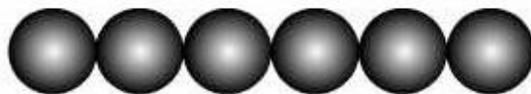

Fig. 8.3 : *Arrangement of identical spheres in one dimension*

A linear horizontal arrangement of identical spheres in one dimension forms a row (Fig. 8.3). A two dimensional close packed structure can be obtained by arranging a number of such rows to form a layer. This can be done in two possible ways. In one of these, we can place these rows in such a way that these are aligned as shown in (Fig. 8.4 (a)). In such an arrangement each sphere is in contact with four other spheres. This arrangement in two dimensions is called **square close packing.**
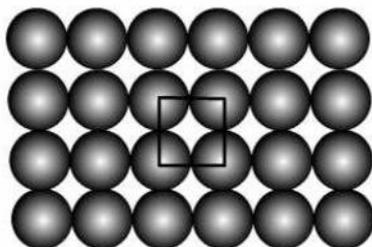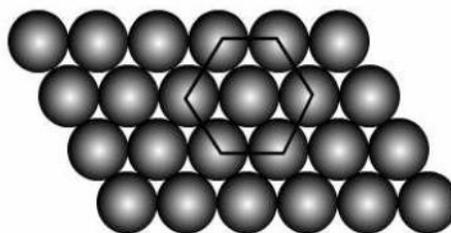
(a)   (b)

Fig. 8.4 : *(a) Square close packing and (b) hexagonal close packing of identical spheres in two dimensions*

In the other way we can place the spheres of the second row in the depressions of the first row and so on so forth (Fig. 8.4(b)). You may notice that in such an arrangement each sphere is in contact with six other spheres. Such an arrangement in two dimensions is called hexagonal **close packing.** In such a packing, the spheres of the third row are aligned with the first row. You may also have noticed that in the hexagonal close packed the spheres are more effectively packed. In Fig. 8.4 an equal number of identical spheres are arranged in two different types of packing.

A three dimensional structure can be generated by placing such two dimensional layers on top of each other. Before we move on to the three dimensional packing let us look at the hexagonal close packed layer some what more closely (Fig. 8.5).
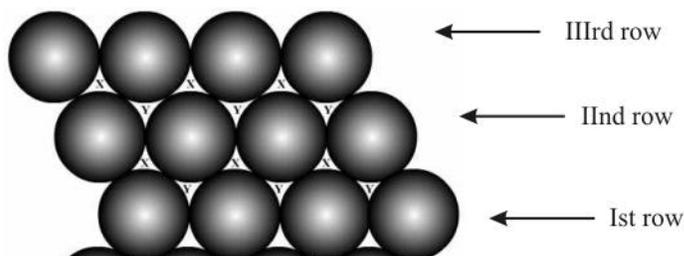

Fig. 8.5 : *A hexagonal Close Packed layer showing two types of triangular voids.*

You may note from Fig 8.5 that in a hexagonal close packed layer there are some unoccupied spaces or voids. These are triangular in shape and are called **trigonal voids**. You can further note that there are two types of triangular voids, one with the apex pointing upwards and the other with the apex pointing downwards. Let us call these as X type and Y type voids respectively as marked in the Fig. 8.5.

Close Packed Structures in three dimensions

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

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

2. In other, the spheres of the second layer are in such a way that these are on the depressions of the first layer. The first possibility is similar to square close packing discussed above and is accompanied by wastage of space. In the second possibility when we place the second layer into the voids of the first layer, the spheres of the second layer can occupy either the X or Y type trigonal voids but not both. You may verify this by using coins of same denomination. You would observe that when you place a coin on the trigonal void of a given type, the other type of void becomes unavailable for placing the next coin (Fig. 8.6).
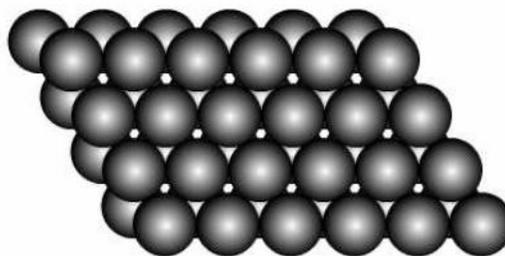

Fig.8.6 : *Two layers of close packed spheres , the second layer occupies only one type (either X or Y) of triangular voids in the first layer.*

In this process, the sphere of second layer covers the trigonal voids of the first layer. It results into voids with four spheres around it, as shown in Fig. 8.7(a). Such a void is called a **tetrahedral void** since the four spheres surrounding it are arranged on the corners of

Notes

a regular tetrahedron, Fig. 8.7(b). Similarly, the trigonal voids of the second layer will be placed over the spheres of the first layer and give rise to tetrahedral voids.
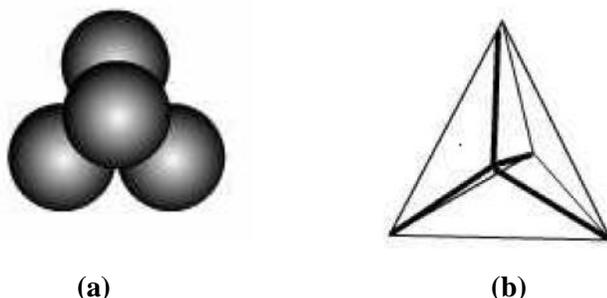

(a)   **(b)**

Fig. 8.7 : *A tetrahedral void*

In a yet another possibility, the trigonal voids of the first layer have another trigonal void of the opposite type (B type over C and C type over B type) from the second layer over it. This generates a void which is surrounded by six spheres, Fig.8.9 (a). Such a void is called an **octahedral void** because the six spheres surrounding the void lie at the corners of a regular octahedron, Fig.8.8 (b).
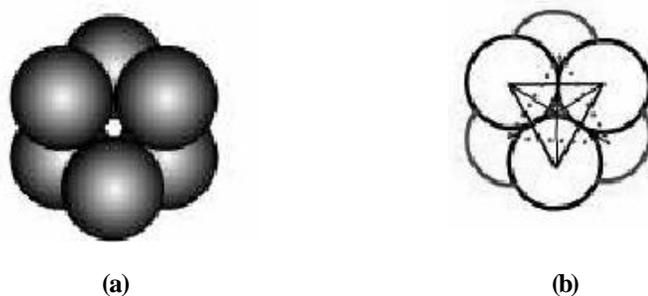

(a)   **(b)**

Fig. 8.8 : *An octahedral void*

A closer look at the second layer reveals that it has a series of regularly placed tetrahedral and octahedral voids marked as 't' and 'o' respectively in fig. 8.9.
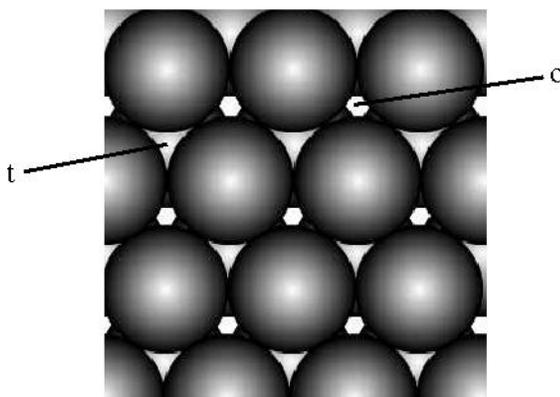

Fig. 8.9 : *The top view of the second layer showing the tetrahedral and octahedral voids.*

Now when we place the third layer over the second layer, again there are two possibilities i.e., either the tetrahedral or the octahedral voids of the second layer are occupied. Let us

take these two possibilities. If the tetrahedral voids of the second layer are occupied then the spheres in the third layer would be exactly on top (i.e., vertically aligned) of the first or A layer The next layer (4th layer) which is then placed would align with the B layer. In other words, every alternate layer will be vertically aligned. This is called AB AB …. pattern or AB AB …. repeat. On the other hand if the octahedral voids of the second layer are occupied, the third layer is different from both the first as well as the second layer. It is called the C layer. In this case the next layer, i.e., the fourth layer, howsoever it is placed will be aligned with the first layer. This is called ABC ABC …. pattern or ABC ABC.. …. repeat. In three dimensional set up the AB AB …. pattern or repeat is called **hexagonal closed packing** (hcp) (Fig. 8.10 (c)) while the ABC ABC …. pattern or repeat is called c**ubic closed packing** (ccp) (Fig. 8.10 (a)**)**.

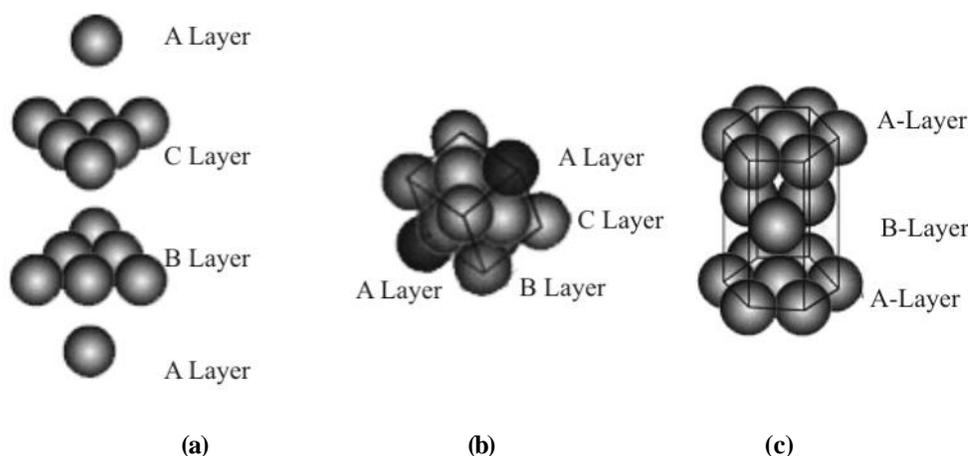   **(a)**   **(b)**   **(c)**

Fig.8.10 *: a) Cubic closed packing (ccp) as a result of ABC pattern of close packed spheres; b) the layers in a) tilted and brought closer to show fcc arrangement c) hexagonal closed packing (hcp) as a result of ABAB pattern of close packed spheres.*

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

In the close packed structures (hcp and ccp) discussed above each sphere is in contact with six spheres in its own layer (as shown in Fig 8.5) and is in contact with three spheres each of the layer immediately above and immediately below it. That is each sphere is in contact with a total of twelve spheres. This number of nearest neighbor is called its **coordination number**. The particles occupying the interstices or the voids will have a coordination number depending on the nature of the void. For example an ion in a tetrahedral void will be in contact with four neighbors i.e., would have a coordination number of four. Similarly the atom or ion in an octahedral void would have a coordination number of six.

Intext questions 8.2

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

....

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

....

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

....

8.5 Crystal Lattices and Unit Cells

You know, the crystalline solids have long-range order and the closely packed constituent particles are arranged in an ordered three dimensional pattern. The structure of the crystalline solids can be represented as an ordered three dimensional arrangement of points. Here each point represents the location of a constituent particle and is known as **lattice point** and such an arrangement is called a **crystal lattice** or **space lattice** or simply a **lattice.**

To understand the meaning of the term lattice let us first take a repetitive pattern in two dimension. In the crystal structure of sodium chloride in two dimensions the Na^+ and Cl^- ions are arranged in an ordered fashion as shown in Fig.8.11 (a). If the position of each ion is represented as a point then the same crystal can be represented as an array of such points in two dimensions (Fig.8.11 (b)). It is called a two dimensional lattice
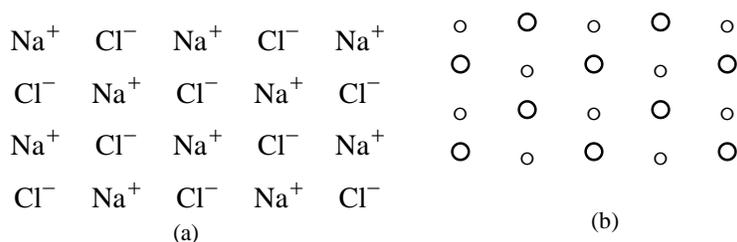
Na^+ Cl^- Na^+ Cl^- Na^+

Cl^- Na^+ Cl^- Na^+ Cl^-

Na^+ Cl^- Na^+ Cl^- Na^+

Cl^- Na^+ Cl^- Na^+ Cl^-

(a)

(b)

Fig. 8.11: *(a) A two dimensional arrangement of ions in sodium chloride (b) the 2D lattice corresponding to the arrangement of ions in (a).*

Similarly, in three dimensions, the crystal structure of a solid is represented as a three dimensional array of lattice points. Remember that the lattice points represent the positions of the constituent particles of the solid (Fig. 8.12).
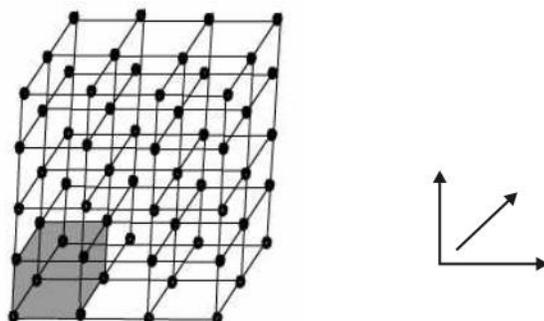

Fig. 8.12: *Schematic representation of a three dimensional crystal lattice.*

In a crystal lattice we can select a group of points which can be used to generate the whole lattice. Such a group is called **repeat unit** or the **unit cell** of the crystal lattice. The shaded region in the Fig. 8.12 represents a unit cell of the crystal lattice. The unit cell is characterized by three distances along the three edges of the lattice and the angles between them as shown in the figure. We can generate the whole crystal lattice by repeating the unit cell in the three directions.

On the basis of the external appearance the known crystals can be classified into seven types. These are called **crystal systems**. In terms of the internal structure also the crystal lattices contain only seven types of unit cells. The seven crystal systems and the definition of their unit cells in terms of their unit distances and the angles are compiled in Table 8.2. The seven simple unit cells are given in Fig. 8.13.

Table 8.2: The seven crystal systems and their possible lattice types.

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

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

The unit cell shown in Fig 8.12 and the ones given in Fig.8.13 have the lattice points at the corners only.
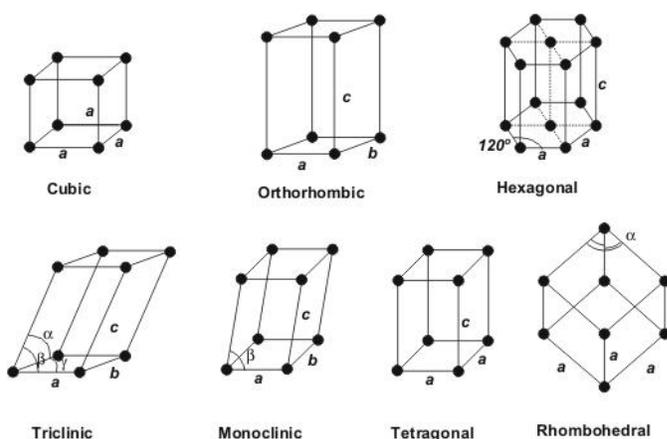

Fig 8.13 : *The primitive unit cells; the relative dimensions of the three repeat distances (a, b and c) and the angles between them (a, s and x) are given in Table 8.2.*

Such unit cells are called **primitive** (P) unit cells. Sometimes, the unit cell of a crystal contains lattice point(s) in addition to the ones at the corners. A unit cell containing a lattice

point each at the centers of its faces in addition to the lattice points at the corners is called a **face centered** (F) unit cell. On the other hand a unit cell with lattice points at the center of the unit cell and at the corners is called a **body centered** unit cell (I). In some cases, in addition to the lattice points at the corners there are two lattice points located at the centers of any two opposite faces. These are called as **end centered** (C) unit cells. The possible lattice types in different crystal systems are also indicated in Table 8.2. The seven crystal systems when combined with these possibilities give rise to 14 lattice types. These are called **Bravais lattices**.

8.5.1 Cubic Unit Cells

Of the seven crystal systems, let us discuss unit cells belonging to the cubic crystal system in somewhat details. As you can see from Table 8.2 that in the cubic crystal system the three repeat distances are equal and all the three angles are right angles. The unit cells of three possible lattice types viz., primitive or simple cubic, body centered cubic and the face centered cubic, belonging to cubic crystal system are shown in Figure 8.14.
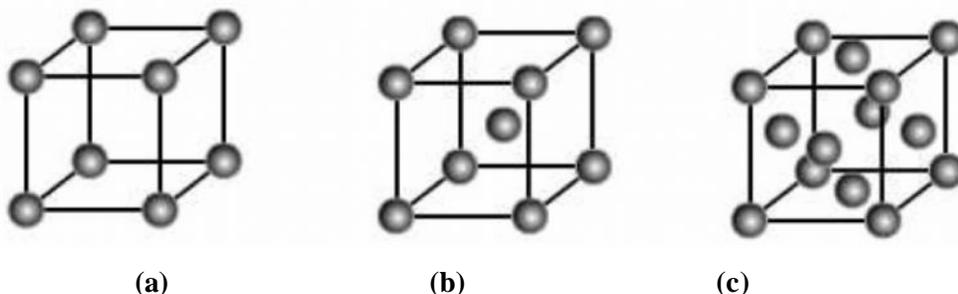

(a)   (b)   (c)

Fig. 8.14: *(a) primitive or simple (b) body centered and (c) face centered cubic unit cells.*

Number of atoms per unit cell

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

Simple Cubic Unit Cell

The simple or primitive unit cell has the atoms at the corners of the cube (Fig. 8.14 (a)). A lattice point at the corner of the unit cell is shared by eight unit cells as you can see from the encircled atom in the Fig 8.15. Therefore, the contribution of an atom at the corner to the unit cell will be 1/8. The number of atoms per unit cell can be calculated as follows:

Fig. 8.15: *A corner lattice point is shared by eight unit cells*

Number of corner atoms = 8

Number of unit cells sharing atoms of the corner = 8

The number of atoms in a simple cubic unit cell $= 8 \times \dfrac{1}{8} = 1$
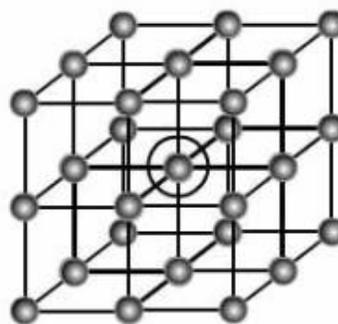
Body Centered Cubic Unit Cell

A body centered cubic (*bcc*) unit cell has lattice points not only at the corners but also at the center of the cube(Fig. 8.14 (b)). The atom in the center of the cube belongs entirely to the unit cell, i.e., it is not shared by other unit cells. The corner atoms, on the other hand, as in the case of simple cubic unit cell, are shared by eight unit cells. Thus the number of atoms per unit cell can be calculated as

Number of corner atoms = 8

Number of unit cells sharing atoms at the corner = 8

$$\therefore \text{Contribution to the unit cell} \quad = 8 \times \frac{1}{8} = 1$$

Number of atoms at the center of the cube = 1

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

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

Face Centered Cubic Unit Cell

A face centered cubic (*fcc*) unit cell has atoms not only at the corners but also at the center of each face. Thus it has eight lattice points at the corners and six at the face centers (Fig. 8.14 (c)). A face centered lattice point is shared by two unit cells, Fig. 8.16. As before,
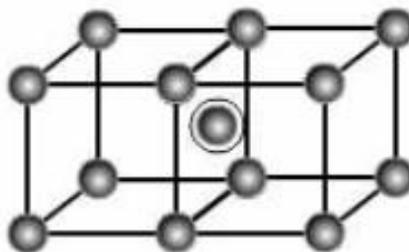
Fig. 8.16: *A face centered lattice point is shared by two unit cells*

Number of corner atoms = 8

Number of unit cells sharing these = 8

Contribution to the unit cell = $8 \times \frac{1}{8} = 1$

Number of atoms at the face center = 1

Number of unit cells sharing a face centered lattice point = 2

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

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

The number of atoms per unit cell in different types of cubic unit cells is given in Table 8.3.

Table. 8.3: atoms per unit cell

Simple cubic	1
Body centered cubic	2
Face centered cubic	4

8.5.2 Structures of Ionic Solids

In case of ionic solids that consist of ions of different sizes, we need to specify the positions of both the cations as well as the anions in the crystal lattice. Therefore, structure adopted by an io nic solid depends on the relative sizes of the two ions. In fact it depends on the ratios of their radii (r+/r-) called **radius ratio**. Here r+ is the radius of the cation and r- is that of the anion. The radius ratios and the corresponding structures are compiled in Table 8.4.

Table 8.4 : The radius ratios (r + /r–) and the corresponding structures

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

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

8.5.2.1 Structures of the Ionic Compounds of MX Type

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

Caesium Chloride Structure

In CsCl the cation and the anions are of comparable sizes (the radius ratio = 0.93) and has a bcc structure in which each ion is surrounded by 8 ions of opposite type. The Cs^+ ions is in the body center position and eight Cl- ions are located at the corners (fig 8.17) of the cube. Thus it has a coordination number of 8.
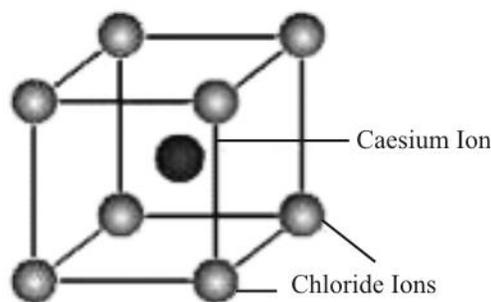

Caesium Ion

Chloride Ions

Fig.8.17: *Caesium chloride structure*

Sodium Chloride Structure

In case of NaCl the anion (Cl-) is much larger than the cation (Na^+) . It has a radius ratio of 0.52 . According to Table 3.3 it should have an octahedral arrangement. In sodium chloride the(Cl-) form a *ccp* (or *fcc*) structure and the sodium ion occupy the octahedral voids. You may visualise the structure having chloride ions at the corners and the face centers and the sodium ions at the edge centers and in the middle of the cube (Fig. 8.18).
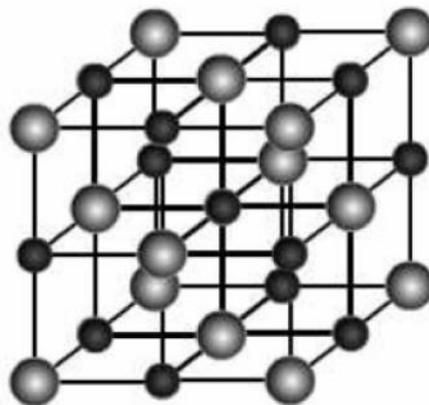

Fig. 8.18 : *Sodium chloride structure.*

Zinc Sulphide Structure

In case of zinc sulphide the radius ratio is just = 0.40. According to Table 3.3 it should have an tetrahedral arrangement. In Zinc sulphide structure, the sulphide ions are arranged in a ccp structure. The zinc ions are located at the corners of a tetrahedron, which lies inside the cube as shown in the Fig. 8.19. These occupy alternate tetrahedral voids.
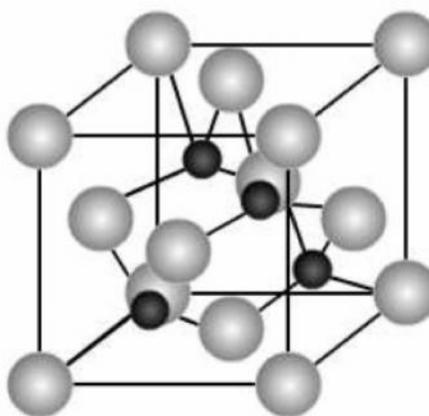

Fig. 8.19 : *Zinc Sulphide structure.*

Calcium fluoride or fluorite structure

In this structure the Ca^{2+} ions form a *fcc* arrangement and the fluoride ions are located in the tetrahedral voids (Fig. 8.20).
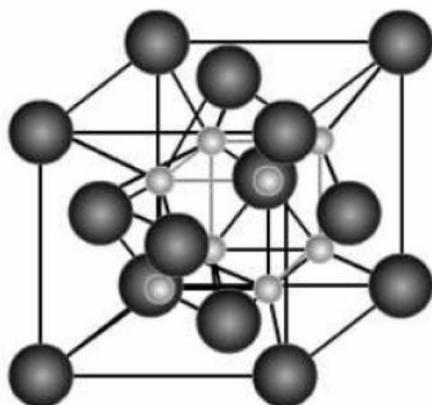
Fig. 8.20 : *Calcium fluoride or Fluorite structure; calcium ions occupy the corners of the cube and face centers The F⁻ ions are on the corners of the smaller cube.*

Antifluorite Structure

Some of the ionic compounds like Na_2O have antifluorite structure. In this structure the positions of cations and the anions in fluorite structures are interchanged. That is why it is called anti fluorite structure. In Na_2O the oxide ions form the ccp and the sodium ions occupy the tetrahedral voids (Fig. 8.21).
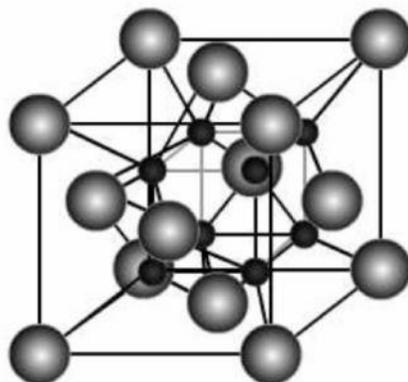

Fig. 8.21: *Antifluorite structure adopted by Na_2O; The oxide ions occupy the corners of the cube and face centers and the Na^+ ions (shown in black) are on the corners of the smaller cube.*

8.6 Defects in Ionic Crystals

You have learnt that in a crystalline solid the constituent particles are arranged in a ordered three dimensional network. However, in actual crystals such a perfect order is not there. Every crystal has some deviations from the perfect order. These deviations are called imperfections or defects. These defects can be broadly grouped into two types. These are **stoichiometric** and **non-stoichiometric** defects depending on whether or not these disturb the stoichiometry of the crystalline material. Here, we would deal only with stoichiometric defects. In such compounds the number of positive and negative ions are in stoichiometric proportions. There are two kinds of stoichiometric defects, these are

- Schottky defects

- Frenkel defects

Schottky defects : this type of defect are due to the absence of some positive and negative ions from their positions. These unoccupied lattice sites are called holes. Such defects are found in ionic compounds in which the positive and negative ions are of similar size e.g., NaCl and CsCl. The number of missing positive and negative ions is equal. The presence of Schottky defects decreases the density of the crystal [Fig. 8.22(a)].

Frenkel defects : this type of defect arise when some ions move from their lattice positions and occupy interstitial sites. The interstitial sites refer to the positions in between the ions. When the ion leaves its lattice site a hole is created there. ZnS and AgBr are examples of ionic compounds showing Frenkel defects. In these ionic compounds the positive and negative ions are of quite different sizes. Generally the positive ions leave their lattice positions, as these are smaller and can accommodate themselves in the interstitial sites. The Frenkel defects do not change the density of the solids [Fig. 8.22(b)].
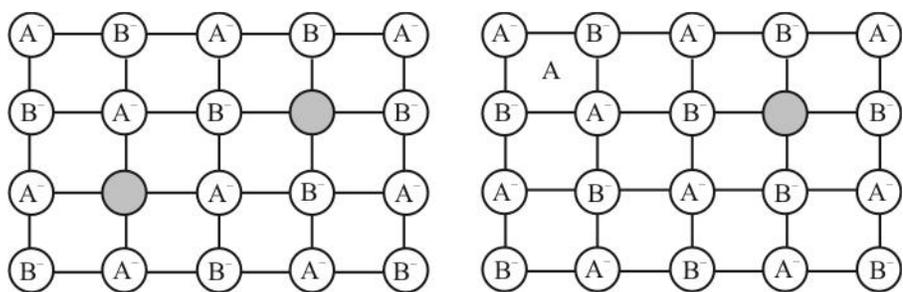

Fig : 8.22: *Stoichiometric defects a) Schottky and b) Frenkel defects*

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

Intext Questions 8.3

a) What do you understand by crystal lattice?

....

b) What is a unit cell ?

....

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

....

What You Have Learnt

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Terminal Exercises

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

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

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

4. What do you understand by coordination number? What would be an ion occupying a\n octahedral void.?

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

a) Schottky defect

b) Frankel defect

Answers to Intext Questions

8.1

1. Solids have definite shape and definite volume.

Liquids have indefinite shape but define volume.

Gases have indefinite shape and indefinite volume.

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

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

8.2

1. Refer to section 8.4

2. Hexagonal close packed

3.   Refer to sections 8.4

8.3

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

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

3.   Four.

SENIOR SECONDARY COURSE
CHEMISTRY
Student's Assignment – 2

Maximum Marks: 50   **Time :** $1\frac{1}{2}$ **Hours**

INSTRUCTIONS

- Answer all the questions on a separate sheet of paper.
- Give the following information on your answer sheet:
    - Name
    - Enrolment Number
    - Subject
    - Assignment Number
    - Address
- Get your assignment checked by the subject teacher at your study centre so that you get positive feedback about your performance.

Do not send your assignment to NIOS

1. (a) Define Lattice energy.

   (b) What an an electrovalent bond.

   (c) State Charles' law and give mathematical expression for it.

   (d) Why do molecular crystals have low melting point?

   (e) Why do you feel cool after a both?

   (f) State valence shell electron pair repulsion theory.

   (g) Write down van der Waal's equation.

   (h) What is Kelvin scale of temperature?

   (i) State Avogadro law.

   (j) Liquids have a definite volume. Explain. $(1 \times 10 = 10)$

2. (a) Name the parameters of a chemical bond and define any one of them.

   (b) List four characteristics of a covalent compound.

   (c) Differenciate π-bond from †-bond.

   (d) Define critical temperature and critical pressure of a gas.

   (e) List the four types of crystalling solids and give one example of each.

   (f) Vapour pressure of a liquid at 25ºC is 35 mm Hg and its normal boiling point is 110ºC. What will be its vapour pressure at 110ºC?

(g) Which assumptions of kinetic theory of gases are wrong?

(h) Write two differences between amorphous and crystalline solids.

(i) How will you calculate the enthalpy of formations of NaCl using Born-Haber Cycle.

(j) At a certain altitude in the atmosphere, density is 10^{-9}th the density of earth's atmosphere at STP and the temperature is $-100°C$. Assuming a uniform atmospheric composition, find the pressure at that attitude. $\hspace{2cm} (2 \times 10 = 20)$

3. (a) Assign the geometry to the following molecule using the VSEPR theory. State reasons for your decisions.

   (i) Phosphorus (V) Chloride (PCl_5)

   (ii) Sulphur (VI) Flouride (SF_6)

   (iii) Boron (III) Flouride (BF_3)

   (b) Explain that HNH bond angle in ammonia is $107°$ while HOH bond angle in water is $104.5°$.

   (c) The carbon-oxygen bond length in CO is shorter than in CO_2 molecule.

   (d) Draw a diagram to show the arrangement of particles in gases, liquids and solids.

   $\hspace{8cm} (3 \times 4 = 12)$

4. (a) Calculate the volume of one mole of oxygen at $27°C$ and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.

   (b) An element has a *bcc* structure and a cell edge of 288 pm. The density of the element is 7.2 g/cm³. How many atoms are present in 208 g of the element? $\hspace{2cm} (4 \times 2 = 8)$