Unit

1

The Solid State

The vast majority of solid substances like high temperature superconductors, biocompatible plastics, silicon chips, etc. are destined to play an ever expanding role in future development of science.

Objectives

After studying this Unit, you will be able to

- describe general characteristics of solid state;
- distinguish between amorphous and crystalline solids;
- classify crystalline solids on the basis of the nature of binding forces;
- define crystal lattice and unit cell;
- explain close packing of particles;
- describe different types of voids and close packed structures;
- calculate the packing efficiency of different types of cubic unit cells;
- correlate the density of a substance with its unit cell properties;
- describe the imperfections in solids and their effect on properties;
- correlate the electrical and magnetic properties of solids and their structure.

From our earlier studies, we know that liquids and gases are called *fluids* because of their ability to flow. The fluidity in both of these states is due to the fact that the molecules are free to move about. On the contrary, the constituent particles in solids have fixed positions and can only oscillate about their mean positions. This explains the rigidity in solids. These properties depend upon the nature of constituent particles and the binding forces operating between them. The correlation between structure and properties helps in the discovery of new solid materials with desired properties. For example, carbon nanotubes are new materials that have potential to provide material that are tougher than steel, lighter than aluminium and have more conductive property than copper. Such materials may play an expanding role in future development of science and society. Some other materials which are expected to play an important role in future are high temperature superconductors, magnetic materials, biodegradable polymers for packaging, biocompliant solids for surgical implants, etc. Thus, the study of this state becomes more important in the present scenario.

In this Unit, we shall discuss different possible arrangements of particles resulting in several types of structures and explore why different arrangements of structural units lend different properties to solids. We will also learn how these properties get modified due to the structural imperfections or by the presence of impurities in minute amounts.

1.1 General Characteristics of Solid State

In Class XI you have learnt that matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure, which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. These are **intermolecular forces** which tend to keep the molecules (or atoms or ions) closer, and the thermal energy, which tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

 (i) They have definite mass, volume and shape.
 (ii) Intermolecular distances are short.
 (iii) Intermolecular forces are strong.
 (iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
 (v) They are incompressible and rigid.

1.2 Amorphous and Crystalline Solids

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. The arrangement of constituent particles (atoms, molecules or ions) in a crystal is ordered and repetitive in three dimensions. If we observe the pattern in one region of the crystal, we can predict accurately the position of particles in any other region of the crystal however far they may be from the place of observation. Thus, crystal has a long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. Glass, rubber and many plastics do not form crystals when their liquids solidify on cooling. These are called amorphous solids. The term amorphous comes from the Greek word *amorphos*, meaning no form.The arrangement of constituent particles (atoms, molecul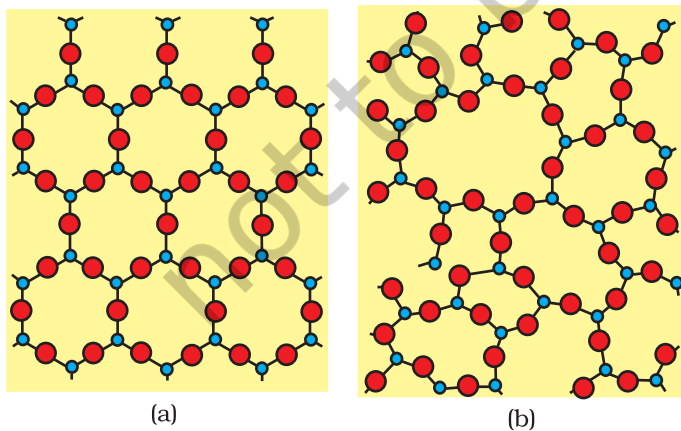es or ions) in such a solid has only *short range order*. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Regular patterns are scattered and in between the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

(a)   (b)

Fig. 1.1: *Two dimensional structure of (a) quartz and (b) quartz glass*

Crystalline solids have a sharp melting point. At a characteristic temperature they melt abruptly and become liquid. On the other hand, amorphous solids soften, melt and start flowing over a range of temperature and can be moulded and blown into various shapes. Amorphous solids have the same structural features as liquids and are conveniently regarded as extremely viscous liquids. They may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called *pseudo solids* or *super cooled liquids*.

Amorphous solids are *isotropic* in nature. Their properties such as mechanical strength, refractive index and electrical conductivity, etc., are same in all directions. It is because there is no *long range* order in them and arrangement of particles is not definite along all the directions. Hence, the overall arrangement becomes equivalent in all directions. Therefore, value of any physical property would be same along any direction.
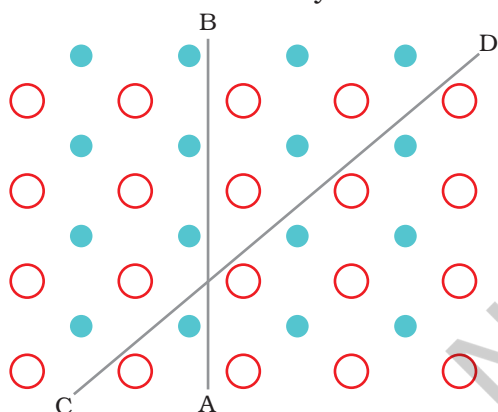

Fig. 1.2: *Anisotropy in crystals is due to different arrangement of particles along different directions.*

Crystalline solids are **anisotropic** in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. This figure shows a simple two-dimensional pattern of arrangement of two kinds of atoms. Mechanical property such as resistance to shearing stress might be quite different in two directions indicated in the figure. Deformation in CD direction displaces row which has two different types of atoms while in AB direction rows made of one type of atoms are displaced. The differences between the crystalline solids and amorphous solids are summarised in Table 1.1.

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic enthalpy of fusion	They do not have definite enthalpy of fusion

Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Besides crystalline and amorphous solids, there are some solids which apparently appear amorphous but have microcrystalline structures. These are called polycrystalline solids. Metals often occur in polycrystalline condition. Individual crystals are randomly oriented so a metallic sample may appear to be isotropic even though a single crystal is anisotropic.

Amorphous solids are useful materials. Glass, rubber and plastics find many applications in our daily lives. Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Intext Questions

1.1 Why are solids rigid?

1.2 Why do solids have a definite volume?

1.3 Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

1.4 Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

1.3 Classification of Crystalline Solids

In Section 1.2, we have learnt about amorphous substances and that they have only short range order. However, most of the solid substances are crystalline in nature. For example, all the metallic elements like iron, copper and silver; non-metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids.

Crystalline solids can be classified in various ways. The method depends on the purpose in hand. Here, we will classify crystalline solids on the basis of nature of intermolecular forces or bonds that hold the constituent particles together. These are — (i) Van der waals forces; (ii) Ionic bonds; (iii) Covalent bonds; and (iv) Metallic bonds. On this basis, crystalline solids are classified into four categories viz., molecular, ionic, metallic and covalent solids. Let us now learn about these categories.

1.3.1 Molecular Solids

Molecules are the constituent particles of molecular solids. These are further sub divided into the following categories:

(i) *Non polar Molecular Solids*: They comprise either atoms, for example, argon and helium or the molecules formed by non polar covalent

bonds, for example, H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) *Polar Molecular Solids*: The molecules of substances like HCl, SO_2, *etc.* are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room temperature and pressure. Solid SO_2 and solid NH_3 are some examples of such solids.

(iii) *Hydrogen Bonded Molecular Solids*: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

1.3.2 Ionic Solids

Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

1.3.3 Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

1.3.4 Covalent or Network Solids

A wide variety of crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal. They are also called **giant molecules**. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points and may even decompose before melting. They are insulators and do not conduct electricity. Diamond (Fig. 1.3) and silicon carbide are typical examples of such solids. Although Graphite (Fig. 1.4) also belongs to this class of crystals, but it is soft and is a conductor of electricity. Its exceptional properties are due to
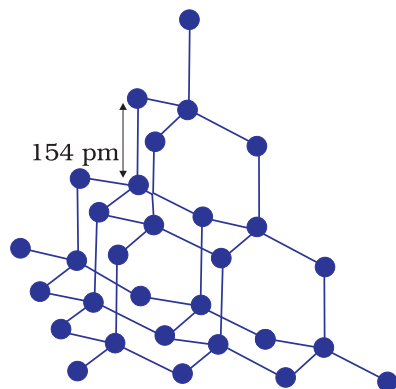
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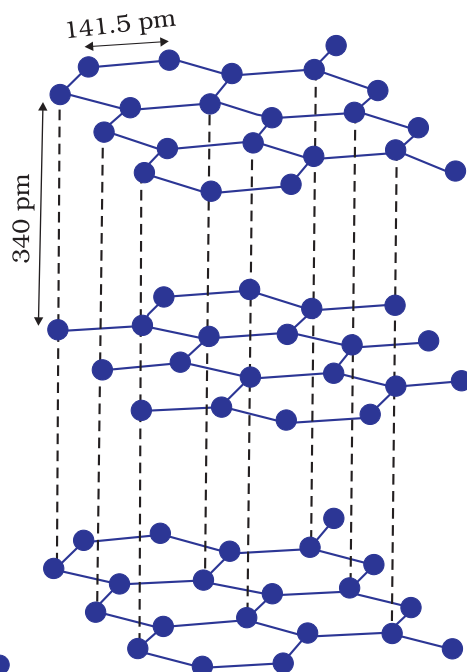*Fig. 1.3: Network structure of diamond*

Fig. 1.4: Structure of graphite

its typical structure. Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

The different properties of the four types of solids are listed in Table 1.2.

Table 1.2: Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conduc- tivity	Melting Point
(1) Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high

| (4) | Covalent or network solids | Atoms | Covalent bonding | SiO_2 (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$ | Hard

Soft | Insulators

Conductor (exception) | Very high |

Intext Questions

1.6 Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

1.7 Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

1.8 Ionic solids conduct electricity in molten state but not in solid state. Explain.

1.9 What type of solids are electrical conductors, malleable and ductile?

1.4 Crystal Lattices and Unit Cells

You must have noticed that when tiles are placed to cover a floor, a repeated pattern is generated. If after setting tiles on floor we mark a point at same location in all the tiles (e.g. Centre of the tile) and see the marked positions only ignoring the tiles, we obtain a set of points. This set of points is the scaffolding on which pattern has been developed by placing tiles. This scaffolding is a space lattice on which two-dimensional pattern has bee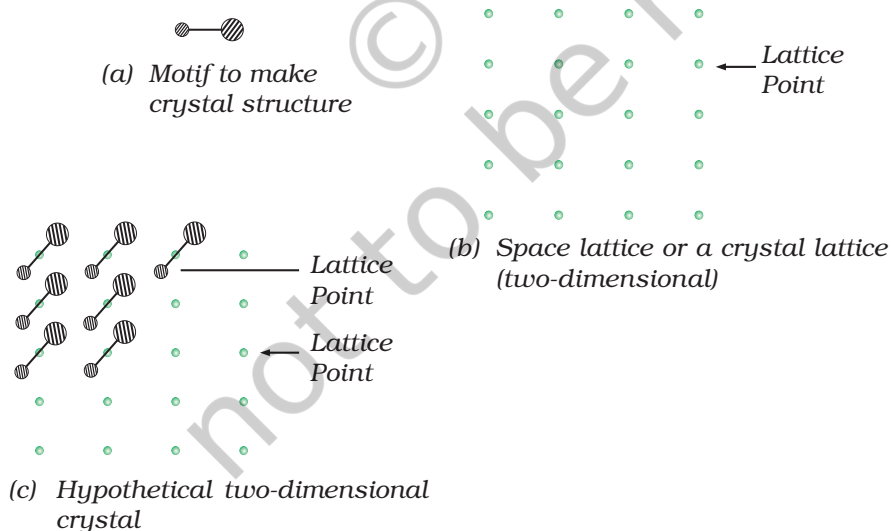n developed by placing structural units on its set of points (i.e. tile in this case). The structural unit is called basis or motif. When motifs are placed on points in space lattice, a pattern is generated. In crystal structure, motif is a molecule, atom or ion. A space lattice, also called a crystal lattice, is the pattern of points representing the locations of these motifs. In other words, space lattice is an abstract scaffolding for crystal structure. When we place motifs in an identical manner on points of space lattice,

(a) Motif to make crystal structure

(b) Space lattice or a crystal lattice (two-dimensional)

(c) Hypothetical two-dimensional crystal

Fig. 1.5: (a) Motif (b) Space lattice (two-dimensional (c) Hypothetical two-dimensional crystal structure

we get crystal structure. Fig. 1.5 shows a motif, a two-dimensional lattice and a hypothetical two-dimensional crystal structure obtained by placing motifs in the two-dimensional lattice.

Spacial arrangement of lattice points gives rise to different types of lattices. Fig 1.6 shows arrangement of points in two different lattices.


Fig. 1.6: *Arrangement of points in two different lattices*

In the case of crystalline solids, space lattice is a three-dimensional array of points. The crystal structure is obtained by associating structurral motifs with lattice points. Each repeated basis or motif has same structure and same spacial orientation as other one in a crystal. The environment of each motif is same throughout the crystal except for on surface.

Following are the characteristics of a crystal lattice:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Fig. 1.7: *Generating hypothetical two-dimensional crystal structure by shifting square in the direction of arrows.*
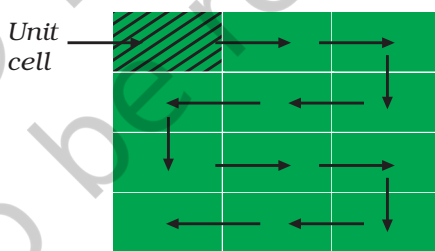
We need only a small part of the space lattice of a crystal to spacify crystal completely. This small part is called unit cell. One can choose unit cell in many ways. Normally that cell is chosen which has perpendicular sides of shortest length and one can construct entire crystal by translational displacement of the unit cell in three dimensions. Fig. 1.7 shows movement of unit cell of a two-dimensional lattice to construct the entire crystal structure. Also, unit cells have shapes such that these fill the whole lattice without leaving space between cells.

In two dimensions a parallelogram with side of length 'a' and 'b' and an angle *r* between these sides is chosen as unit cell. Possible unit cells in two dimensions are shown in Fig. 1.8.
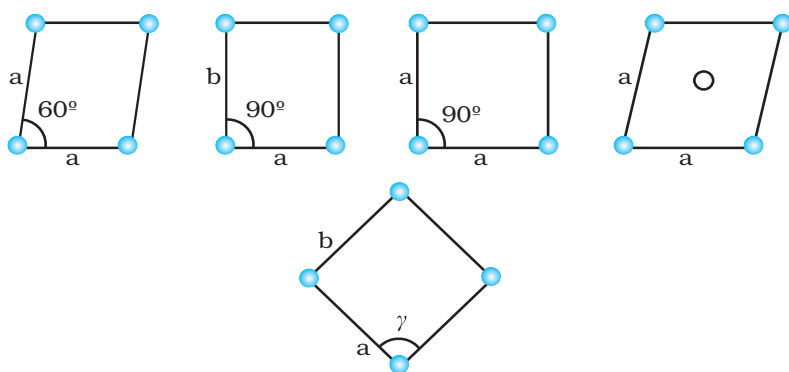
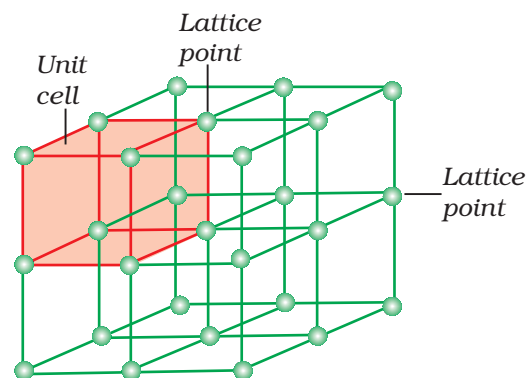Fig. 1.8: *Possible unit cells in two dimensions*

Fig. 1.9: *A portion of a three-dimensional cubic space of a crystal lattice and its unit cell.*
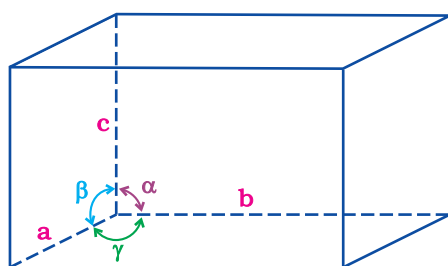

Fig. 1.10: *Illustration of parameters of a unit cell*

A portion of three-dimensional **crystal lattice** and its unit cell is shown in Fig. 1.9.

In the three-dimensional crystal structure, unit cell is characterised by:

 (i) its dimensions along the three edges a, b and c. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α (between b and c), β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters a, b, c, α, β and γ.

These parameters of a typical unit cell are shown in Fig. 1.10.

1.4.1 Primitive and Centred Unit Cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

(a) Primitive Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

(b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a **centred unit cell**. Centred unit cells are of three types:

 (i) *Body-Centred Unit Cells:* Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) *Face-Centred Unit Cells:* Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) *End-Centred Unit Cells:* In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.