CHAPTER

9 Structure of Solids

Crystalline and Amorphous Solids : Classification of Solids on the Basis of Regular or Haphazard Arrangement of the Building Constituents.

1. Crystalline solids. In crystalline solids the building constituents (atoms, ions or molecules) arrange themselves in a *three dimensional recurring regular geometric pattern* which extends to very large distance compared to the inter-particle distances. Thus the crystalline solids have *long-range order.*

Crystalline solids exist as crystals and hence these are also called simply **crystals.** These crystals may be big or small. Some crystals are so tiny that their crystalline shape can be seen with a microscope only. A crystalline solid has a sharp melting point.

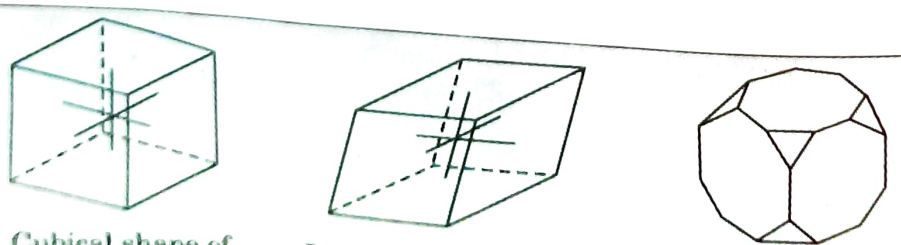
2. Amorphous solids. The word amorphous is a Greek word which means *shapeless*. Thus in these solids the arrangement of different building constituents is *not regular* but *haphazard i.e.* the constituents are arranged at random in the same disorderly way as in liquids. It is for this reason that amorphous substances like glass, pitch and resins are regarded as *super-cooled liquids* or *as intermediate between solids and liquids.* An amorphous substance does not have a sharp melting point.

Differences between Crystalline and Amorphous Solids

These two classes of solids differ from one another in the following properties.

1. Geometrical shape. The crystals of every crystalline solid have a *define geometrical shape* due to definite and orderly arrangement of particles in three-dimensional shape, *e.g.* crystals of NaCl have a *cubical shape*, those of *calcite* ($CaCO_3$) have *rhombohedral shape* while those of *copper* metal have an *octahedral shape.* (Fig. 9.1).

For a given crystal the angles at which the surfaces or faces intersect are always the same.



Cubical shape of NaCl

Rhombohedral shape of calcite ($CaCO_3$)

Octahedral shape of copper metal

Fig. 9.1. Shapes of some crystalline solids.

Most of the crystalline solids are *poly crystals. i.e.* they contain aggegate of many inter-locking small crystals. Such solids have irregular shape but their internal structure is regular. *Mono crystals* (*i.e.* single crystals) are sometimes found in nature. They can also be prepared by artificial means. Sugar is an example of a crystal composed of many single crystals.

An amorphous solid does not have any orderly pattern of arrangement of particles and, therefore, does not have any definite geometrical shape.

2. Melting point. There are many crystalline solids which do not change directly to the liquid state and also there are many crystalline solids which decompose before going into the liquid state. The crystalline solids which directly change into liquid state do so at a definite temperature *i.e.* the melting point of such crystalline solids is *definite*.

Amorphous substances like glass do not have definite melting point.

3. Cleavage planes. When a crystal of a crystalline solid is hammered, it readily breaks up into smaller crystals along particular planes which are called *cleavage planes*. These planes are inclined to one another at a particular angle for a given crystalline solid. Thus the magnitude of this angle varies from substance to substance.

Amorphous substances do not have such well-defined cleavage planes.

4. Anisotropic and isotropic properties. Magnitude of some of the physical properties of crystalline solids like refractive index, coefficient of thermal expansion, electrical and thermal conductivities etc. is different in different directions within the crystal, *e.g.* the coefficient of thermal expansion of a crystal of AgI is positive in one direction and negative in the other direction. Such properties are called *anisotropic properties* and the phenomenon is referred to as *anisotropy*. These properties are due to the fact that the orderly arrangement of particles in crystalline solids is different in different directions.

The above said properties of isomorphous substances are the same in all directions as those of liquids and gases, *i.e. amorphous substances have isotropic properties*. This is because of the fact that in isomorphous solids, as in liquids and gases, the arrangement of particles is random and, therefore their isotropic properties are the same in all the directions.

5. Symmetry. Crystalline solids have crystal symmetry, *i.e.* when a crystalline solid is rotated about an axis, its appearance does not change (*i.e.* remains the same).

Amorphous substances do not have symmetry.

Various Types of Symmetry Found in Crystals

Symmetry is a very important property of crystals. Only three of these are described here. (1) *Centre of symmetry* (2) *Axis of symmetry,* and (3) *Plane of symmetry.*

1. Centre of symmetry. *It is such an imaginary point within the crystal that any straight line drawn through it will intersect the faces, edges or solid angles of the crystal at equal distances on opposite sides.* A crystal may have either one or no centre of symmetry. It can never have more than one centre of

symmetry. A cubical crystal like NaCl crystal has one centre of symmetry as shown in Fig. 9.2.

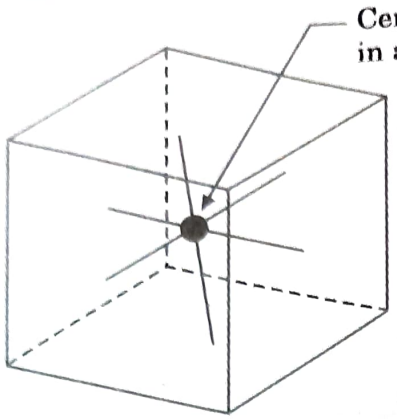


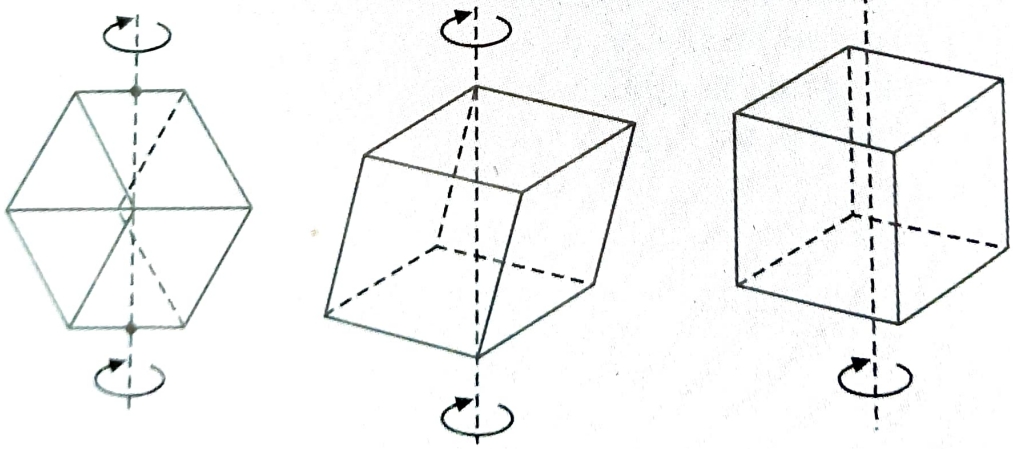
Fig. 9.2. Centre of symmetry in a cubical crystal.

2. Axis of symmetry. *It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during its complete rotation.*

In all there are thirteen axes of symmetry possessed by a cubical crystal like NaCl as shown below :

(*a*) *Six axes of two-fold symmetry.* Each of these six axes is called *diad axis.* When the crystal is rotated about any of these axes, it presents the same appearance two times in a complete rotation. One of such axes is shown in Fig. 9.3(*a*). Each of these three axes intersects at the middle points of the two opposite edges of the cube.

(*b*) *Four axes of three-fold symmetry.* Each of these axes is called *triad axis.* When the crystal is rotated about any of these axes, it presents the same appearance *three times* in a complete rotation. One of such axes is shown in Fig. 9.3(*b*). Each of these four axes intersects at the two opposite solid angles (*i.e.* corners) of the cube.



(*a*) Axis of two-fold symmetry (Six)

(*b*) Axis of three-fold symmetry (Four)

(*c*) Axis of four-fold symmetry (Three)

Fig. 9.3. Thirteen axes of symmetry in a cubical crystal.

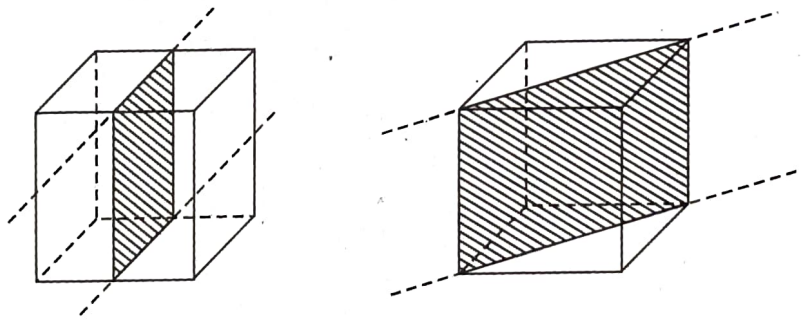
(*c*) *Three axes of four-fold symmetry.* Each of these three axes is called *tetrad axis*. When the crystal is rotated about any of these axes, it presents the same appearance *four times* in a complete rotation. One of such axes is shown in Fig. 9.3(*c*). Each of these three axes intersects at the middle points of the two opposite faces of a cube. All the three axes are at right angles to one another.

3. Plane of symmetry. *It is an imaginary plane which divides a crystal into two such parts that one is the exact mirror image of the other.* In other words, a plane of symmetry divides the crystal into two identical and similarly placed halves.

In all, there are nine planes of symmetry possessed by a cubical crystal like NaCl as shown below :

(*a*) *Three rectangular planes of symmetry.* One such rectangular plane of symmetry is shown in Fig. 9.4(*a*). There are in all three such rectangular planes of symmetry which are at right angles to each other.

(*b*) *Six diagonal planes of symmetry.* One such diagonal plane of symmetry is shown in Fig. 9.4 (*b*). There are in all *six* such diagonal planes of symmetry which pass diagonally through the cube.



(*a*)
Rectangular planes of symmetry (Three)

(*b*)
Diagonal planes of symmetry (Six)

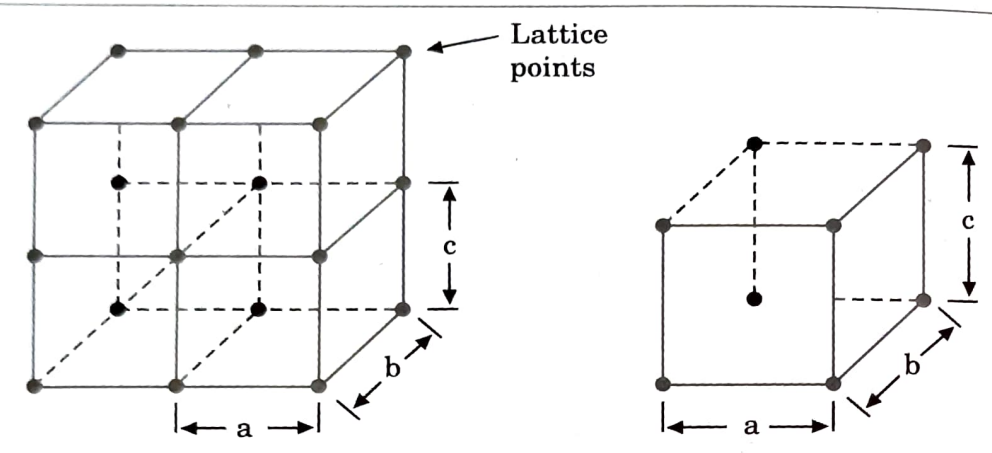
Fig. 9.4. Nine planes of symmetry for a cubical crystal like NaCl.

Crystal Lattice and Unit Cell

The internal structure of crystals (*i.e.* the arrangement of the particles *viz.* atoms, molecules or ions of which the crystal is composed) has been determined by *X-ray diffraction, electron diffraction, neutron diffraction* etc. methods. These methods have shown that the constituent particles are situated at strictly definite positions in space. In crystals, the constituent particles are represented by points. These points are called **lattice points** or **lattice sites** and the arrangement of points in the crystal is called **crystal lattice** or simply **crystal**. Crystal lattice is also called by other names like **space lattice** or **lattice array.** Thus a crystal lattice can be defined as follows :

A crystal lattice is an array of points which show how the constituent particles (atoms, ions or molecules) of a crystal are arranged at different sites in three-dimensional space.

In other words *a crystal lattice is an infinitely extended regular arrangement of different constituent particles of a crystal.* Each point in a crystal lattice has the same environment as any other similar point. A crystal lattice with cubic structure with three-dimensional net work is shown in Fig. 9.5 (*a*).



(*a*) A crystal lattice with cubic structure

(*b*) Unit cell of crystal lattice with cubic structure

Fig. 9.5. Crystal lattice and unit cell.

The crystal lattice like that shown in Fig. 9.5 (*a*) is actually composed of many small parts of the lattice. This smallest part has all the characteristic features of the entire crystal and is called **unit cell.** Thus a unit cell of a crystal lattice can be defined in the following ways :

(*i*) *A unit cell is the smallest unit of the crystal which, when repeated again and again, gives the crystal of the given substance.*

(*ii*) *A unit cell is the smallest sample that represents the picture or definite pattern of the entire crystal.*

(*iii*) *A unit cell of a crystal lattice is the smallest block or geometrical figure from which the entire crystal can be built up by its translational repetition in three dimensions.*

Thus the entire crystal consists of a large number of unit cells adjacent to one another in all three dimensions. The unit cell of the crystal lattice shown in Fig. 9.5 (*a*) is shown in the same figure at (*b*).

A unit cell of a crystal possesses all the structural properties of the given crystal. A large number of unit cells of the crystal combine together to arrange themselves in a regular order and thus form the crystal lattice.

It may be noted that the properties of crystalline solids depend not only on their composition and external conditions, but also on their internal structure. For example, although diamond and graphite are composed of the same substance viz., carbon, they have different properties. The difference in their properties is due to the difference in their internal structure.

Seven Crystal Systems

Depending on the nature of the constituents (which may be atoms, molecules or ions) of which a given crystal is composed, we have different types of crystal. The shape of a given crystal can be described by the lengths of the three sides or edges (a, b and c) of its unit cell and the three angles (α, β and γ) between the three axes of the unit cell. The lengths of the sides of the unit cell are called *primitives* or *crystal axes* and the angles between the three axes are called *interfacial angles* (See Fig. 9.6).

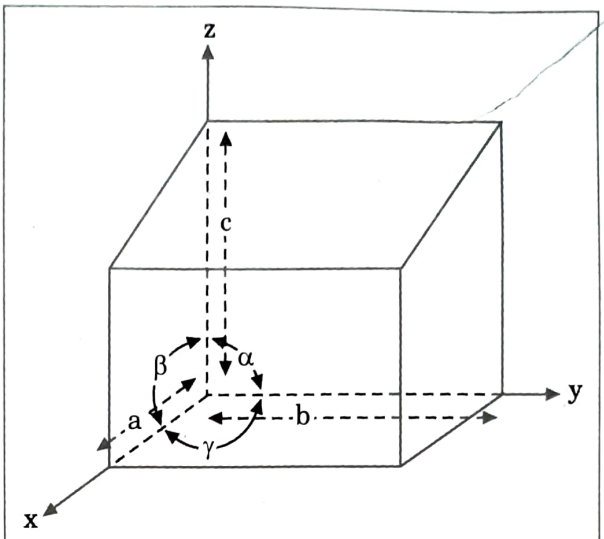
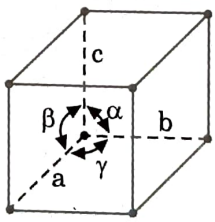
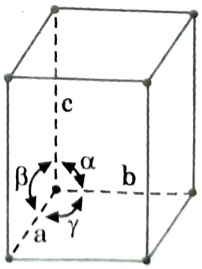
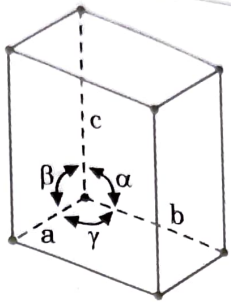
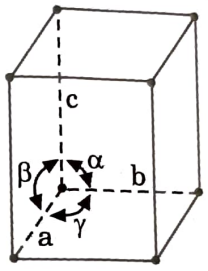
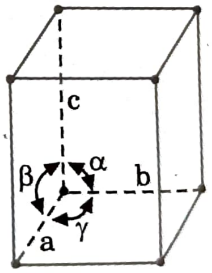
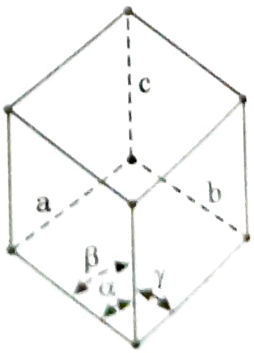


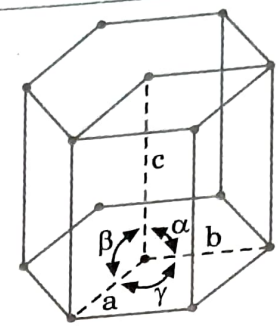
Fig. 9.6. A unit cell with the lengths of its three sides a, b and c and three interfacial angles α, β and γ

There are seven crystal systems corresponding to the seven distinct types of unit cells (sub-units). All these unit cells are parallelopipeds and their shapes are determined by the lengths of three crystal axes, a, b and c and the magnitude of the three interfacial angles α, β and γ. The seven crystal systems are given in Table 9.1.

Table 9.1. Seven systems of crystals

Name of crystal	Relation between crystal axes and interfacial angles	Shape of unit cell of the system and examples of crystals
1. Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	 Examples : NaCl, KCl, CaF_2, $NaClO_2$ alums, diamond
2. Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90°$; $\gamma \neq 90°$	 Examples : $Na_2SO_4.10H_2O$, $NaHCO_3$, $FeSO_4.7H_2O$, monoclinic sulphur (SM)

Name of crystal	Relation between crystal axes and interfacial angles	Shape of unit cell of the system and examples of crystals
3. Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	 Examples : $CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3
4. Tetragonal	$a = b \neq c$ $\alpha = \beta \neq \gamma = 90°$	 Examples : $NiSO_4$, white tin, $SnCl_2$, TiO_2 etc.
5. Orthorhombic or Rhombic	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	 Examples : KNO_3, $BaSO_4$, $MgSO_4.7H_2O$, Rhombic sulphur (SR)
6. Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	 Examples : $CaSO_4$, $NaNO_3$, $KMnO_4$

Name of crystal	Relation between crystal axes and interfacial angles	Shape of unit cell of the system and examples of crystals
7. Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°$; $\gamma = 120°$	 Examples : Graphite, SiO_2, AgI, ice, PbI_2, ZnO

From the above table the following points may be noted :

(*i*) For cubic and trigonal systems, the three edges are of equal lengths while for the remaining five systems the edges are not equal.

(*ii*) All the three interfacial angles are of 90° for cubic, tetragonal and orthorhombic systems while these angles for other systems are not of 90°.

Fourteen Bravais Lattices

It has been shown methametically by Bravais (1848) that there are 14 independent ways of arranging the similar lattice points in a three-dimensional space, *i.e.* there are 14 space lattices in the seven systems of crystals mentioned above. These are : *three cubic, two monoclinic, one triclinic, two tetragonal, four orthorhombic, one rhombohedral* (*trigonal*) and *one hexagonal* as shown in Table 9.2.

Table 9.2. Fourteen Bravais lattices in seven systems of crystals

Crystal system	No. of Bravais lattices	Bravais lattices
1. Cubic	3	(*i*) Simple cubic (sc) lattice (*ii*) Body-centred cubic (bcc) lattice (*iii*) Face-centred cubis (fcc) lattice
2. Monoclinic	2	(*i*) Simple monoclinic lattice (*ii*) End-centred monoclinic lattice
3. Triclinic	1	Simple triclinic lattice
4. Tetragonal	2	(*i*) Simple tetragonal lattice (*ii*) Body-centred tetragonal lattice
5. Orthorhombic or Rhombic	4	(*i*) Simple orthorhombic lattice (*ii*) Body-centred orthorhombic lattice (*iii*) Face-centred orthorhombic lattice (*iv*) End-centred orthorhombic lattice
6. Rhombohedral or Trigonal	1	Simple rhombohedral lattice
7. Hexagonal	1	Simple hexagonal lattice

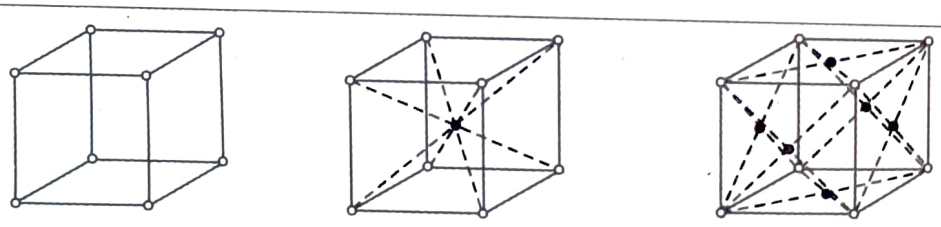
Bravais Lattices of Cubic System

Bravais lattices of the cubic system which is the simplest and also most common are considered in detail as follows. The crystals belonging to cubic system have three kinds of Bravais lattices depending on the positions of the lattice points in the unit cell of cubic system.

1. Simple cubic (sc) lattice. The unit cell of this lattice has atoms (lattice points) only at the corners of the cube [Fig. 9.7(*a*)]. Consequently, these atoms touch along cube edges. This structure is *loosely-packed*, since each atom has only six nearest neighbours. Only one element namely polonium exhibits this structure in a certain temperature region.

2. Body-centred cubic (bcc) lattice. The unit cell of this lattice has one atom at each of the eight corners and one atom at the centre of the body of the cube. [Fig. 9.7(*b*)]. The atom at the centre of the cube belongs entirely to the unit cell. The atoms are in contact along body diagonals. The elements which passess *bcc* lattice are listed below and the value of primitive, *a* (in A°) is also given in parentheses : Ba (= 5.025), α-Fe (= 2.867), Rb (= 5.630), Na (= 4.291), Ti (= 3.306), W (= 3.115), U (= 3.474), Zr (= 3.620).

3. Face-centred cubic (fcc) lattice. The unit cell of this lattice has atoms at the six corners as well as at the centre of each of the six faces of the cube [Fig. 9.7(*c*)]. This structure is close-packed because each atom has 12 nearest neighbours. The atoms are in contact with the diagonal atoms. The elements which crystallise into *fcc* lattice are given below and the value of primitive a (in A°) is also given in parentheses : Al (= 4.049), Cu (= 3.615), Au (= 4.090), γ-Fe (= 3.591), Ni (= 3.524), Pt (= 4.086), Ag (= 4.086).



(*a*) Simple cubic (sc) lattice

(*b*) Body-centered cubic (bcc) lattice

(*c*) Face-centered cubic (fcc) lattice

Fig. 9.7. Three Bravais lattices of cubic system

Classification of Crystalline Solids or Crystals : Types of Crystals

There are three ways to classify the crystals. But in chemistry the crystals are classified on the basis of the nature of the building particles occupying the lattice points (or lattice sites) in the crystal lattice and the nature of the bonds existing between the building particles. This basis of classification gives the following four types of crystals :

1. Ionic crystals. Ionic crystals are those crystals in which the particles forming the crystal are positively and negatively charged ions (*i.e.* cations and anions) which are held together by strong electrostatic force of attraction (*i.e.* by

ionic bonds). Hence the name ionic crystals. Crystals of NaCl, $CuSO_4 . 5H_2O$ etc belong to this class.

2. Metallic crystals. Metallic crystals are those in which the particles forming the crystals are metallic positive ions (called *positive cores* or *Kernels*) which are surrounded by a *sea of electrons* (also called *electron-gas* or *electron-cloud*) and are held together by metallic bond (Fig. 9.8). The positive metal ions are obtained when the metal atoms lose their valence-shell electrons. The electrons obtained form a *sea of* electrons. These electrons are not bond up with any particular metal ion and hence are free to move throughout the metallic crystal. Due to their mobile nature these electrons are called *mobile* or *delocalised electrons*. It is these mobile electrons which keep the metal positive ions held together.

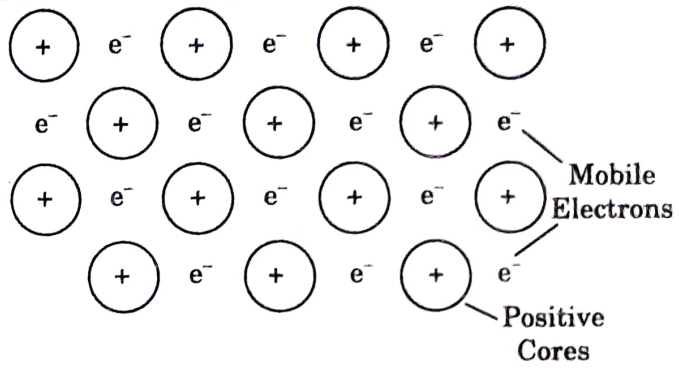


Fig. 9.8. Positive cores surrounded by mobile electrons

3. Atomic or covalent crystals. Atomic crystals are those in which the particles forming the crystal are neutral atoms of the same element (as in diamond) or of different elements (as in SiC) which are held together by covalent bonds. Hence atomic crystals are also called *covalent crystals*. Atomic crystals are of two types :

(*i*) Those in which atoms are bonded with each other by covalent bonds resulting in the formation of *giant molecules*. Examples of giant molecules are *diamond, silicon carbide* (SiC). *aluminium nitride* (AlN) etc.

(*ii*) Those which consist of *separate layers*. Examples of covalent crystals containing separate layers are *graphite*, CdI_2, $CdCl_2$, *BN* etc.

Structure of diamond crystal. The unit cell of the diamond crystal is a *regular tetrahedron* having one C-atom at each of its four corners and one C-atom lying at its centre [Fig. 9.9 (*a*)]. In this unit cell, central carbon atom is linked to the four corner C-atoms by covalent bonds.

The structure of diamond is obtained by uniting a number of such unit cells in such a way that each of the four corner C-atoms of each unit cell is linked with the central C-atom of its own unit cell and with the other three corner C-atoms belonging to three different unit cells [Fig. 9.9 (*b*)]. Thus we find that in the structure of diamond each of the C-atoms is linked with four carbon atoms. The bonds between carbon atoms are covalent bonds which run through the crystal in three dimensions. Each of the corbons in the diamond crystal is sp^3 hybridised and hence each of the four covalent bonds by which each carbon is

linked with the three carbons is $sp^3(C)$—sp^3 (C) σ bond. The tetrahedral arrangement of four C-atoms round the central C-atom gives rise to rigid three *dimensonal network* which runs throughout the crystal. The whole lattice is, therefore, continuous and because of the continuity of C—C covalent bonding, the entire diamond crystal behaves as a single huge or giant three dimensional carbon molecule which is called **macro molecule.**

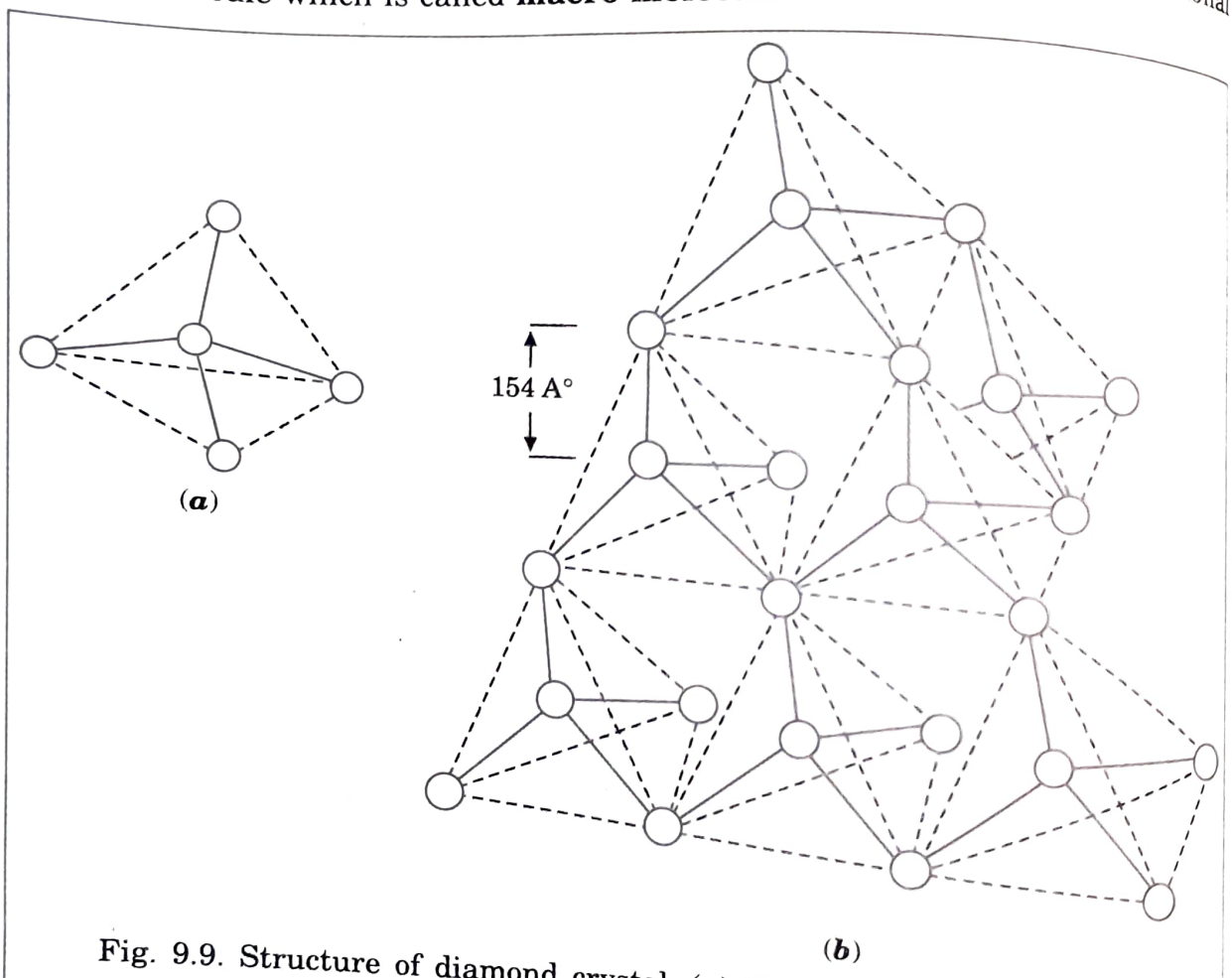


Fig. 9.9. Structure of diamond crystal, (*a*) Unit cell of diamond crystal (*b*) Structure of diamond crystal.

The structure of diamond discussed as above explains some of the properties of diamond as follows :

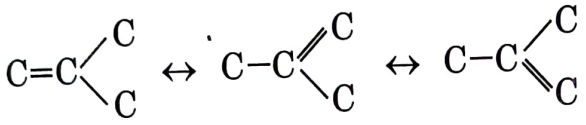
(*i*) *High density.* All the C—C bond distances are equal to 1.54 Å. This C—C bond distance is so short that high density of diamond is well explained.

(*ii*) *Non-conductor of electricity.* We have seen that, since all the four electrons present in the valence-shell of carbon atom are used up in forming four C—C σ bonds, no mobile electrons are left in the diamond crystal to allow the conduction of electricity. Thus diamond crystal is a non-conductor of electricity.

(*iii*) *Extremely hard, high melting point and high boiling point.* We have seen that, since the structure of diamond crystal consists of a large number of C—C covalent bonds, the force acting between carbon atoms is very strong and hence it is very difficult, to break these bonds. This explains the extreme hardness of diamond crystal. Also at the same time, in order to break this large number

of C—C bonds, a large amount of energy is needed. This means that diamond crystal has high melting and boiling point.

Structure of graphite. Graphite has a layer structure, *i.e.* it has a number of flat parallel layers (or planes or sheets) of carbon atoms. In each layer carbon atoms are arranged in a regular flat hexagon as in hexane, napthalene etc. C—C distance in each layer is 1.42Å which is intermediate between the single C—C bond distance (= 1.54Å) and double C=C bond distance (= 1.33Å). Note that the C=C distance in benzene compounds is 1.39Å. Each of the carbon atoms of a given layer is sp^2 hybridised and is thus bonded to the adjacent three carbon atoms of the same layer by three sp^2(C) —sp^2(C) σ-bonds. Each of these three C—C σ-bonds has *two-third single bond character* and *one-third double bond character* which is due to the resonance existing between single and double bonds as shown below :



Since there are four valence electrons in each C-atom, after forming three C—C σ-bonds, each C-atom is left with one spare electron in its $2p_z$ orbital. These $2p_z$ orbitals which are single-filled overlap together to form a delocalised π-system which extends above and below each layer. This π-system gives an aromatic quinone type (*i.e.* hexagonal) structure to graphite as shown in Fig. 9.10.

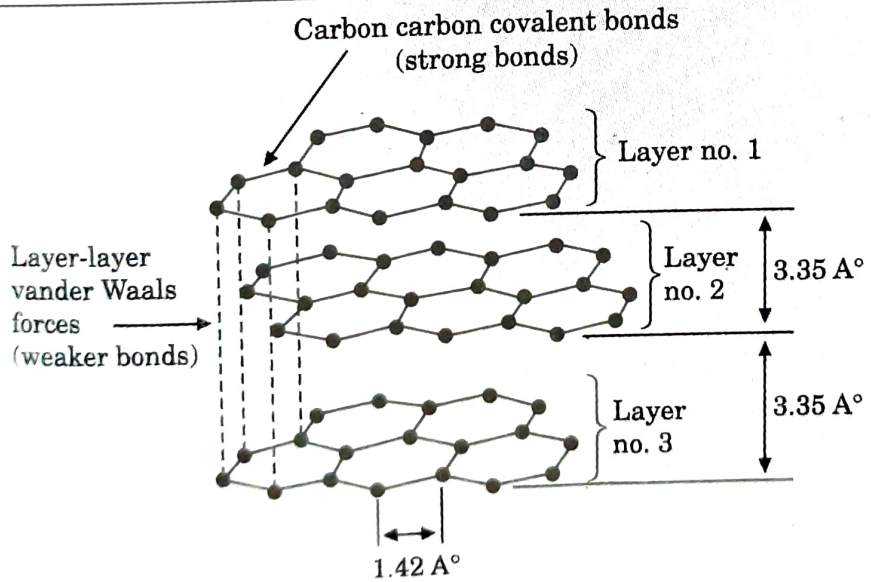
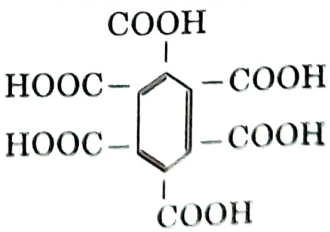


Fig. 9.10. Layer structure of graphite. Black circles indicate carbon atoms.

This hexagonal structure is supported by the fact that when graphite is completely oxidised, it gives a benzene derivative *viz. mellitic acid*, $C_6(COOH)_6$ which is benzene hexacarboxylic acid. The structure of this acid is shown in the margin. The layer structure of graphite as given above explains some of the properties of graphite as follows :



(*i*) *Good conductor of electricity.* In each delocalised π-system the electrons are free to move within the layer and this accounts for the fact that graphite conducts electricity in the plane of the layer but not in the direction perpendicular to its laminal crystals. *Thus graphite is a good conductor of electricity.*

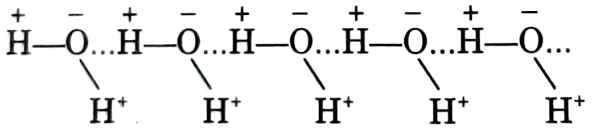
(*ii*) *Soft, flaky and slippery substance.* Every two adjacent layers in graphite are at a distance of 3.35Å. This distance is so large that the possibility of the formation of covalent bonds between the atoms of the adjacent layers is ruled out. These layers are, therefore, loosely linked together by weak *Van der Waals forces*. These van der Waals forces which hold the graphite crystal layers together are so weak that even a slight pressure causes the layers to slide over one another. This explains why (*a*) graphite is a *soft substance* and hence is used as a *solid lubricating agent* (*b*) graphite is *flaky* substance and *feels slippery* between the figures.

(*iii*) *Black and shiny substance.* The arrangement of carbon atoms in each layer causes reflection and absorption of light and hence graphite is *black* and *shiny*.

(*iv*) *Less dense than diamond.* The comparatively more open structure of graphite makes it less dense than diamond (sp. gra. of diamond = 3.52, sp. gra. of graphite = 2.25) but more reactive chemically.

4. Molecular crystals. Molecular crystals are those in which the particles forming the crystal are polar or non-polar whole molecules, except in solidified noble gases in which the particles are *atoms*, which are held together by two types of inter-molecular forces given below :

(*a*) *Dipole-dipole forces.* These forces occur in solids which consist of polar molecules like water molecules (in ice, or even in liquid state). In water the negative end of one molecule attracts the positive end of the neighbouring water molecule as shown below :



(*b*) *van der Waals forces.* These forces are more general and occur in all kinds of molecular crystals.

Both the types of inter-molecular forces mentioned above are much weaker than the electrostatic forces of attraction between cations and anions existing in ionic crystals. The binding energy in molecular crystals is, therefore, less than that in ionic crystals. The molecular crystals are of two types :

(*i*) *Polar molecular crystals* [*See Fig. 9.11*(*a*)]. Examples are water (ice) and sugar.

(*ii*) *Non-polar molecular crystals* [*See Fig. 9.11*(*b*)]. Examples are iodine, sulphur, phosphorus and solid carbon dioxide.

The polar molecular crystals are formed from unsymmetrical molecules containing polar covalent linkages and have comparatively higher melting and boiling points than the non-polar molecular crystals. This is so because in the former there are stronger dipole-dipole forces.