3 The Solid State

3.1 INTRODUCTION

Characteristics of Solids

Solids are characterized by their high density and low compressibility compared with those of the gas phase. The values of these properties for solids indicate that the molecules (or ions) in them are relatively close together. Solids can very easily be distinguished from liquids by their definite shape, considerable mechanical strength and rigidity. These properties are due to the existence of very strong forces of attraction amongst the molecules (or ions) of the solids. It is because of these strong forces that the structural units (atoms, ions, etc.) of the solid do not possess any translatory motion but can have only vibrational motion about their mean positions.

Crystals and Amorphous Solids

Solids can generally be classified into two broad categories: crystals and amorphous substances. The outstanding characteristics of a crystal are its sharp melting point and its flat faces and sharp edges which, in a well developed form, are usually arranged symmetrically. These properties are the result of a high degree of internal order which extends throughout the crystal (a definite pattern constantly repeating in space), i.e. there exists what is known as the *long range order.* The pattern is such that having observed it in some small region of the crystal, it is possible to predict accurately the positions of particles in any region of the crystal, however far it may be from the region under observation. But amorphous solids, such as glass, do not have this ordered arrangement. In many ways they are more closely related to liquids than to crystalline solids and are, therefore, regarded as supercooled liquids with high viscosity. In this chapter, we shall discuss the subject of crystalline structure.

3.2 FACES, EDGES AND INTERFACIAL ANGLE OF A CRYSTAL

Crystals are bound, as stated earlier, by surfaces which are usually planar. These surfaces are called *faces* and where two faces intersect an *edge* is formed. The angle between the normals to the two intersecting faces is the *interfacial angle.*

In general, the shape of a crystalline solid depends upon the conditions (temperature, rate of growth, extent of stirring and impurities) which exist during the period of growth, e.g., NaCl crystallizes in a cubic form from an aqueous solution and in an octahedral form from an aqueous solution containing some urea.

The first quantitative measurements on crystals were made by N. Stensen who measured the angles between the faces of quartz crystals of different shapes. He found that inspite of the differences in shape, the angles between corresponding faces were always the same. Later, when crystals of many other substances were observed, each was found to have characteristic angles between faces. The statement that *the angles between the corresponding faces of various crystals of the same substance are constant* is sometimes called the first law of crystallography.

3.3 HAÜY'S IDEA AND SPACE LATTICE

The Basic Unit of a Crystal

At about the same time as Stensen's work, Robert Hooke speculated that all observed forms of crystals could be pictured as consisting of regular arrangements of small spherical particles. Hooke's idea was extended by Haüy. In 1784, as the result of a fortunate accident, he began a study of the cleavage of calcite crystals and found that regardless of external appearance of crystals, he would obtain the rhombohedral unit in each case. Based on similar cleavage studies of many other crystals, Haüy concluded that the continued cleavage will result in a basic unit, the shape of which was related to the external shape of the crystal. The macroscopic crystal can be generated by stacking this basic unit one upon the other.

Space Lattice

Rather than drawing the entire unit of pattern it is much more convenient to represent the unit of pattern by a point. Each point then represents the position of an atom, ion, molecule or group of ions or molecules. The regular three-dimensional arrangement of the identical points in space gives rise to what is known as a *space lattice.* The definition of a space lattice is strictly a geometrical concept and represents *a three-dimensional translational repetition of the centres of gravity of the units of pattern in the crystal.* This means that if a straight line is drawn through any two points, it will pass at equal intervals through a succession of similar points. Since the arrangement of these points is regular, it implies that the environment around any point is the same as that around any other point in the lattice. It should be kept in mind that the lattice points need not represent the actual atoms in the crystal but represent the spatial arrangement of the units of pattern. These units of pattern can be anything, for example:

(i) In metals or inert gases, each lattice point may represent the position of each atom.

(ii) In a crystal of methane, each lattice point may represent the centre of a methane molecule.

(iii) In ionic crystals, the lattice points may represent ions or ion-pairs. In the former, it is more convenient to consider a lattice of positive ions independently of a lattice of negative ions; then the two can be interlocked to give an adequate representation of the crystal. In the ion-pair case, a point equidistant between a positive and a negative ion can be considered to be a lattice point, thus having a single lattice to represent the ionic crystal.

Unit Cell

The basic idea of Haüy that the crystals can be generated by stacking together the basic units is equivalent to considering the crystal in terms of a lattice. Thus, by connection of the lattice points, a series of parallelepipeds of the type shown in Fig. 3.3.1 can be obtained. Each of these parallelepipeds contains a complete unit of pattern of the crystal. By translation or stacking of the parallelepipeds the entire crystal structure can be generated. Such a parallelepiped can be drawn from any crystal lattice, and is called a *unit cell*.

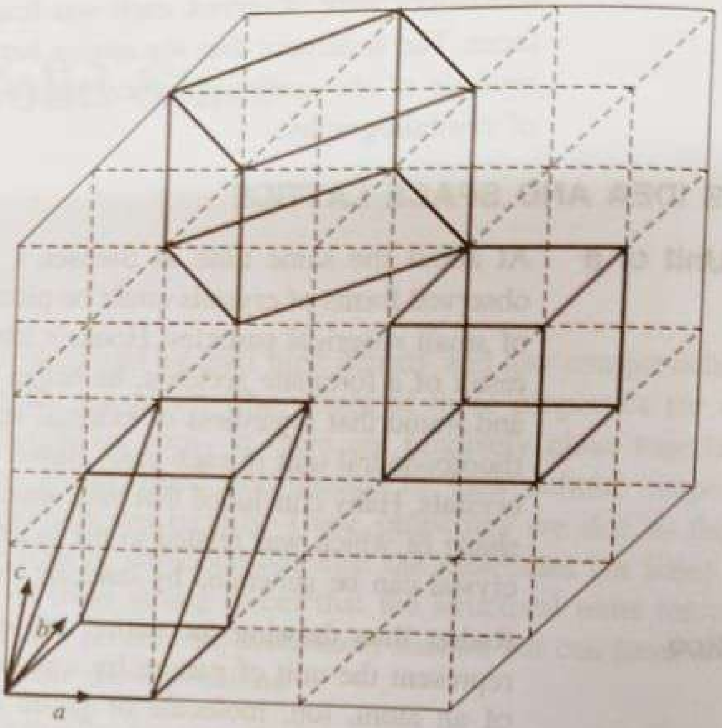

Fig. 3.3.1 Crystal lattice and unit cell

3.4 CRYSTAL SYSTEMS

Unit Cells in a Two-Dimensional Lattice

As stated earlier, in a space lattice or a crystal lattice there exist identical points in space. For example, in a 1-dimensional lattice, we will have a set of points arranged at equal distances along a straight line. The only parameter in this case is the minimum repeat distance. In a 2-dimensional planar lattice, we will have to specify the values of two basis vectors which give the repeat distances along two axes and the angle between these axes. From these parameters a unit pattern or unit cell can be constructed, with which the entire planar lattice can be formed by repeated translations of the unit cell. The values of the two basis vectors in a planar lattice may be same or different, and the angle between them may be 90°, 60° or any value other than these two. These possibilities lead to the existence of just five possible types of planar lattices, each characterized by its unit cell as shown in Fig. 3.4.1.

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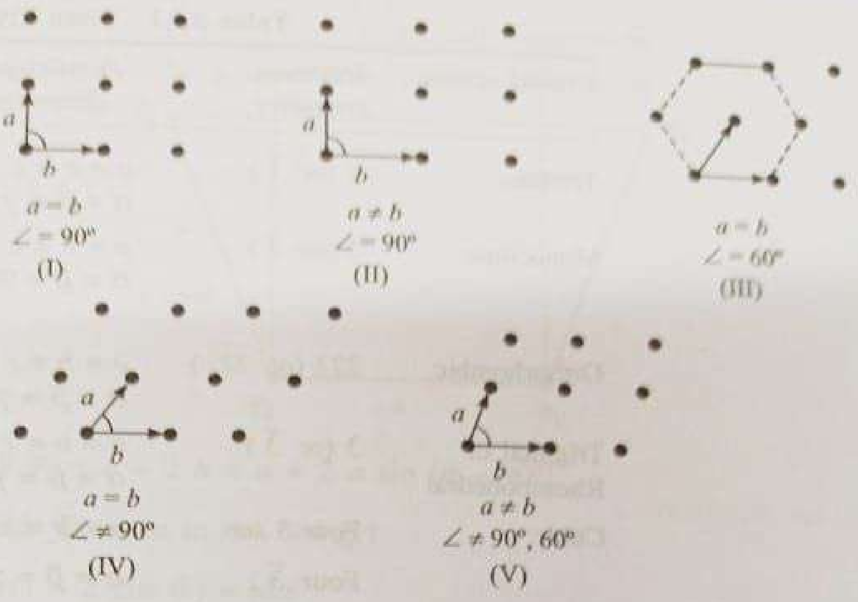
It should be noticed that for some lattices the unit cell can be chosen in more than one way. This is shown in Fig. 3.4.1(III). For the same lattice points, the unit cell may be a parallelogram, an equilateral triangle or a regular hexagon with a lattice point in its centre. In the first two unit cells, namely, parallelogram and equilateral triangle, all lattice points lie at the corners of the unit cells. Such unit cells are called *primitive unit cells* and are represented by the symbol P. The third one, i.e. hexagon, in which one lattice point also lies at the centre, is known as *nonprimitive unit cell*.



$a = b$, $\angle = 90°$ (I)

$a \neq b$, $\angle = 90°$ (II)

$a = b$, $\angle = 60°$ (III)

$a = b$, $\angle \neq 90°$ (IV)

$a \neq b$, $\angle \neq 90°, 60°$ (V)

Fig. 3.4.1 Five types of unit cells in planar lattice

Unit Cells in a Three-Dimensional Lattice

In a 3-dimensional space lattice, we need to specify the values of three basis vectors which give the three repeat distances along the three axes and three angles as shown in Fig. 3.4.2.

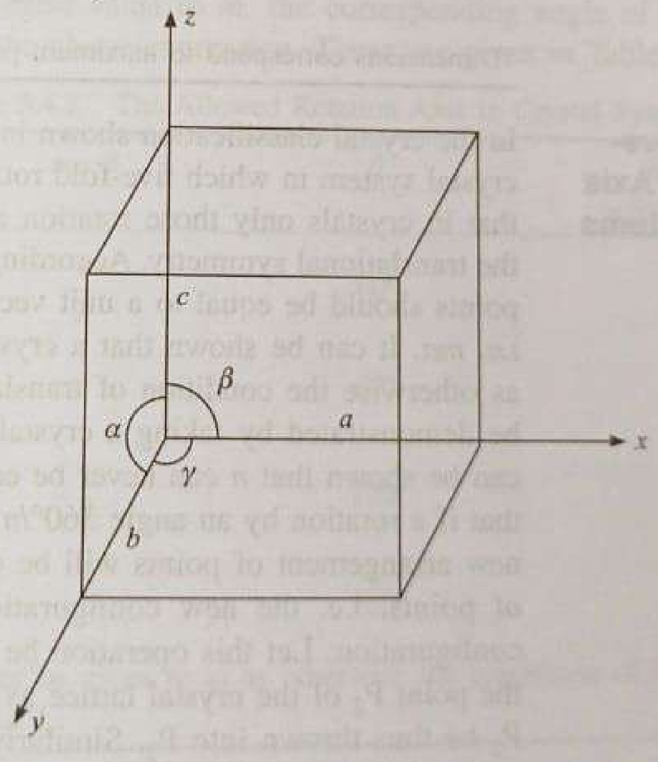


Fig. 3.4.2 Three basis vectors in a 3-dimensional space lattice

Seven Crystal Systems

For a given lattice, there is, in principle, an infinite number of ways in which the three basis vectors a, b and c might be chosen. The choice of the most suitable unit vectors is based on symmetry. If there are no symmetry elements, the three vectors chosen are the shortest ones in three different planes. The morphological study of crystals of different symmetries[†] showed that they could be classified into seven crystal systems based on the presence of certain rotation axes. The results are listed in Table 3.4.1. The schematic shapes of these primitive (symbol: P) crystal systems are shown in Fig. 3.5.4.

[†] *See* Annexure I at the end of this chapter for elementary ideas of symmetry.

Table 3.4.1 Seven Crystal Systems

Crystal system	*Minimum symmetry*	*Parallelepiped dimensions*[†]	*Examples*
Triclinic	1 (or $\bar{1}$)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$
Monoclinic	2 (or $\bar{2}$)	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	S(monoclinic), $CaSO_4 \cdot 2H_2O$, $Na_2SO_4 \cdot 10H_2O$
Orthorhombic	222 (or $\overline{222}$)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	S(rhombic), $BaSO_4$, KNO_3, K_2SO_4
Trigonal or Rhombohedral	3 (or $\bar{3}$)	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	$CaCO_3$, calcite
Cubic	Four 3 (or Four $\bar{3}$)	$a = b = c$ $\alpha = \beta = \gamma = 90°$	NaCl, diamond, Alums, CaF_2
Tetragonal	4 (or $\bar{4}$)	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	TiO_2, Sn(white), $ZrSiO_4$
Hexagonal	6 (or $\bar{6}$)	$a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	SiO_2, graphite PbI_2, Mg, ZnO

†Dimensions correspond to maximum possible symmetry of their respective systems.

Absence of Five-Fold Rotation Axis in Crystal Systems

In the crystal classification shown in Table 3.4.1, it can be seen that there is no crystal system in which five-fold rotation axis is present. This is due to the fact that in crystals only those rotation axes are allowed which are consistent with the translational symmetry. According to the latter, the distance between any two points should be equal to a unit vector *a* or an integral multiple of this vector i.e. *ma*. It can be shown that a crystal can never have a five-fold rotation axis as otherwise the condition of translational symmetry is not fulfilled. This may be demonstrated by taking a crystal lattice which has a *n*-fold rotation axis. It can be shown that *n* can never be equal to five. The *n*-fold rotation axis means that if a rotation by an angle 360°/*n* is carried around the rotation axis, then the new arrangement of points will be completely identical to the old arrangement of points, i.e. the new configuration will be indistinguishable from the old configuration. Let this operation be carried out around an axis passing through the point P_2 of the crystal lattice as shown in Fig. 3.4.3 and let the lattice point P_1 be thus thrown into P_3. Similarly, let the lattice point P_2 be thrown into the point P_4 if the rotation operation is carried out around the axis passing through the point P_1 (Fig. 3.4.3).

According to the condition of translational symmetry, the distance between the points P_3 and P_4 must be an integral multiple of the unit vector *a*. Thus, we have

$$P_3P_4 = ma$$

As can be seen from Fig. 3.4.3, the distance between the points P_3 and P_4 is also given by

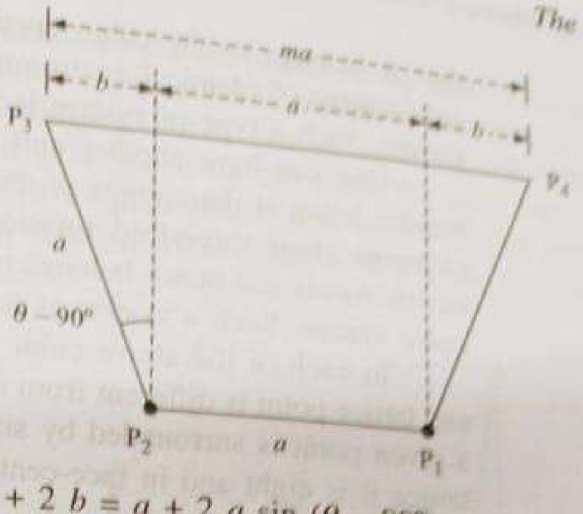


Fig. 3.4.3 Absence of five-fold rotation axis

$$P_3P_4 = a + 2\,b = a + 2\,a \sin\,(\theta - 90^\circ)$$

Equating this distance to *ma*, we get

$$a(1 - 2\cos\theta) = ma$$

or $$\cos\theta = \frac{1-m}{2}$$

By giving an integral value to *m*, the corresponding angle of rotation can be calculated from the above expression. These are given in Table 3.4.2.

Table 3.4.2 The Allowed Rotation Axis in Crystal Systems

m	$\cos\theta$	θ	*Value of n, i.e. order of rotation axis*
0	$\frac{1}{2}$	60°	$\frac{360}{60} = 6$
1	0	90°	$\frac{360}{90} = 4$
2	$-\frac{1}{2}$	120°	$\frac{360}{120} = 3$
3	−1	180°	$\frac{360}{180} = 2$

Higher values cannot be given to *m* as otherwise the magnitude of the value of cos θ becomes greater than 1.

It can be seen from the Table 3.4.2 that the five-fold rotation axis is absent Thus, it can be concluded that a crystal can never have five-fold rotation axis if it has to satisfy the translational symmetry.

THE FOURTEEN BRAVAIS LATTICES

bic System

Consider a cube in which a lattice point exists in the centre of each face as well as at the corners. This unit cell can be repeated to give a space lattice. This unit cell, which is known as non-primitive cell, also has the minimum symmetry elements as that of a simple cubic unit cell (four three-fold rotations axes) and