Study of Crystals.

(1) Crystal: It is a homogeneous portion of a crystalline substance, composed of a regular pattern of structural units (ions, atoms or molecules) by plane surfaces making definite angles with each other giving a regular geometric form.

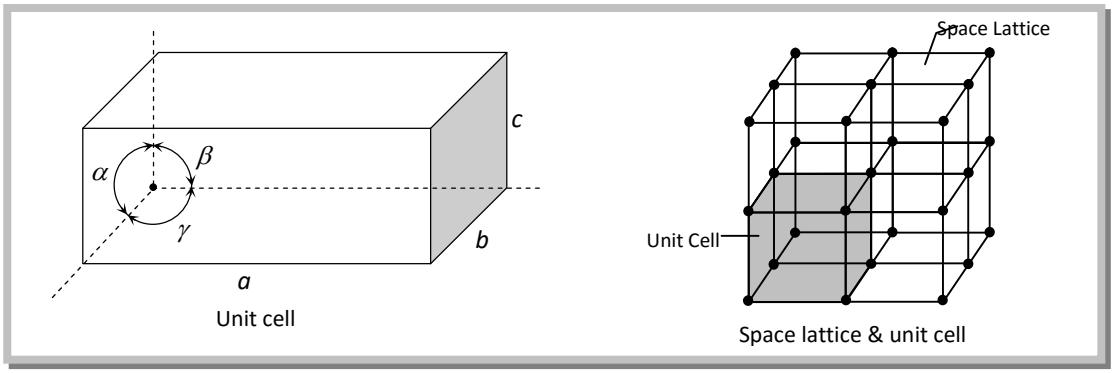
(2) Space lattice and Unit cell: A regular array of points (showing atoms/ions) in three dimensions is commonly called as a space lattice, or lattice.

(i) Each point in a space lattice represents an atom or a group of atoms.

(ii) Each point in a space lattice has identical surroundings throughout.

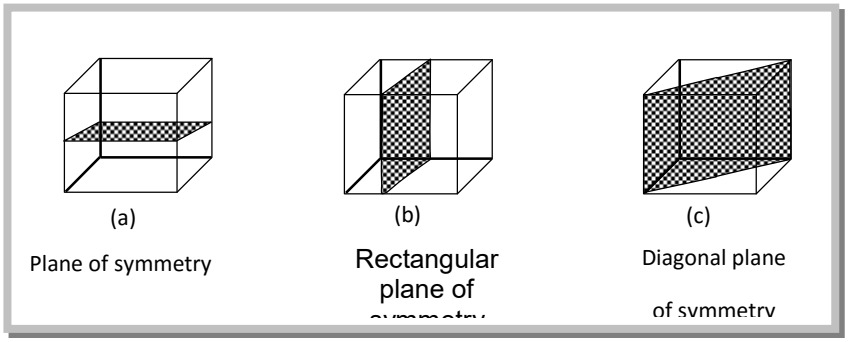
A three dimensional group of lattice points which when repeated in space generates the crystal called unit cell.

The unit cell is described by the lengths of its edges, a, b, c (which are related to the spacing between layers) and the angles between the edges, α, β, γ.



(3) Symmetry in Crystal systems: Law of constancy of symmetry: According to this law, all crystals of a substance have the same elements of symmetry. A crystal possess following three types of symmetry:

(i) Plane of symmetry: It is an imaginary plane which passes through the center of a crystal can divides it into two equal portions which are exactly the mirror images of each other.



(ii) Axis of symmetry : An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution i.e., in a rotation through 360°. Suppose, the same appearance of

crystal is repeated, on rotating it through an angle of 360°/n, around an imaginary axis, is called an n-fold axis where, n is known as the order of axis. By order is meant the value of n in $2\pi / n$ so that rotation through $2\pi / n,$ gives an equivalent configuration. For example, if a cube is rotated about an axis passing perpendicularly through the center so that the similar appearance occurs four times in one revolution, the axis is called a four – fold or a tetrad axis, [Fig (iii)]. If similar appearance occurs twice in one complete revolution i.e., after 180°, the axis is called two-fold axis of symmetry or diad axis [Fig (i)]. If the original appearance is repeated three times in one revolution i.e. rotation after 120°, the axis of symmetry is called three-fold axis of symmetry or triad axis [Fig (ii)]. Similarly, if the original appearance is repeated after an angle of 60° as in the case of a hexagonal crystal, the axis is called six-fold axis of symmetry or hexad axis [Fig (iv)].

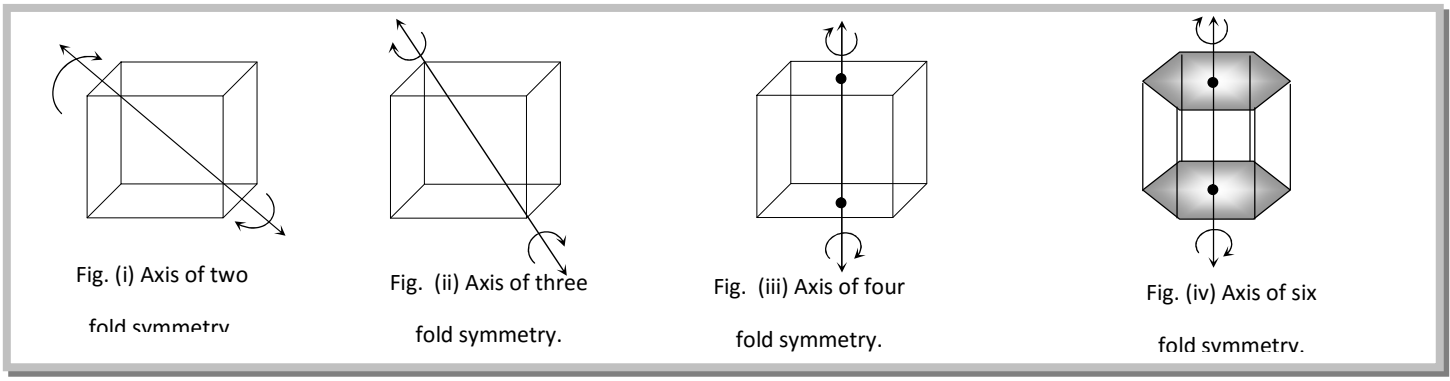


Fig. (i) Axis of two fold symmetry

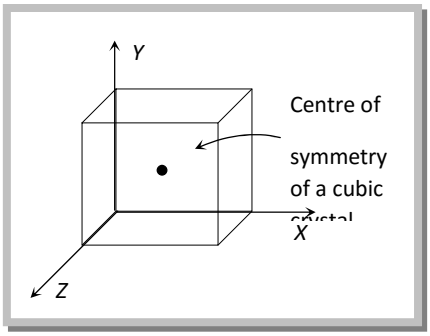
Fig. (ii) Axis of three fold symmetry.

Fig. (iii) Axis of four fold symmetry.

Fig. (iv) Axis of six fold symmetry.

(iii) Centre of symmetry: It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.

Note: Only simple cubic system have one center of symmetry. Other system do not have center of symmetry.



(4) Element of symmetry:

(i) The total number of planes, axes and center of symmetries possessed by a crystal is termed as elements of symmetry.

(ii) A cubic crystal possesses total 23 elements of symmetry.

(a) Plane of symmetry (3 + 6) = 9

(b) Axes of symmetry (3 + 4 + 6) = 13

(c) Centre of symmetry (1) = 1

Total symmetry = 23

(5) Formation of crystals: The crystals of the substance are obtained by cooling the liquid (or the melt) of the solution of that substance. The size of the crystal depends upon the rate of cooling. If cooling is carried out slowly, crystals of large size are obtained because the particles (ions, atoms or molecules) get sufficient time to arrange themselves in proper positions.

$$\text{Atoms of molecules} \xrightarrow{\text{Dissolved}} \text{cluster} \xrightarrow{\text{dissolved}} \text{dissolved embryo} \overset{\rightarrow \underset{\text{(unstable)}}{\text{nucleus}}}{} \rightarrow \text{crystal}$$

(If loosing units dissolves as embryo and if gaining unit grow as a crystals).

(6) Crystal systems: Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged. Thus, there can be only 14 different space lattices. These 14 types of lattices are known as Bravais Lattices. But on the other hand Bravais showed that there are only seven types of crystal systems. The seven crystal systems are:

(a) Cubic

(b) Tetragonal

(c) Orthorhombic

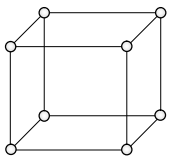
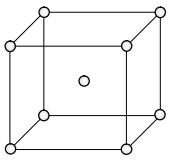
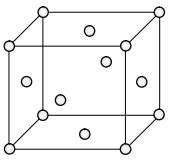
(d) Rhombohedral

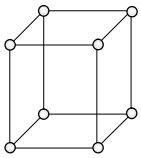
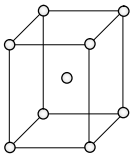
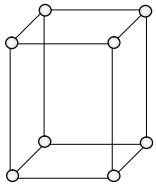
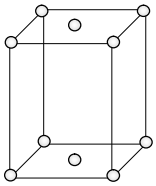
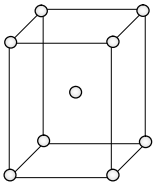
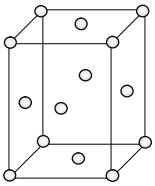
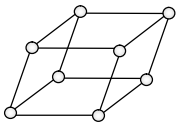
(e) Hexagonal

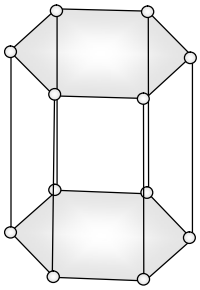
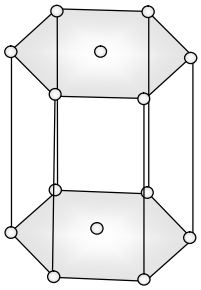
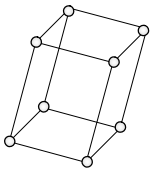
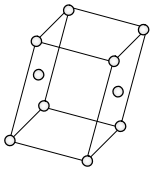
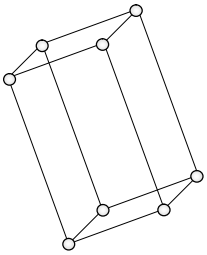
(f) Monoclinic

(g) Triclinic

Bravais lattices corresponding to different crystal systems

Crystal system	Space lattice			Examples
Cubic $a = b = c$, Here a, b and c are parameters (dimensions of a unit cell along three axes) size of crystals depend on	Simple: Lattice points at the eight corners of the unit cells. 	Body centered: Points at the eight corners and at the body centered. 	Face centered: Points at the eight corners and at the six face centers. 	Pb, Hg, Ag, Au, Cu, ZnS, diamond, $KCl, NaCl, Cu_2O, CaF_2$ and alums. etc.

parameters. $\alpha = \beta = \gamma = 90^o$ $\alpha\beta$ and γ are sizes of three angles between the axes.				
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^o$	Simple: Points at the eight corners of the unit cell. 	Body centered : Points at the eight corners and at the body center 		SnO_2, TiO_2, ZnO_2, $NiSO_4$ $ZrSiO_4$. $PbWO_4$, white Sn etc.
Orthorhombic (Rhombic) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	Simple: Points at the eight corners of the unit cell. 	End centered: Also called side centered or base centered. Points at the eight corners and at two face centers opposite to each other. 	Body centered : Points at the eight corners and at the body center 	Face centered: Points at the eight corners and at the six face centers. 	KNO_3, K_2SO_4, $PbCO_3$, $BaSO_4$, rhombic sulphur, $MgSO_4.7H_2O$ etc.
Rhombohedral or Trigonal $a = b = c$, $\alpha = \beta = \gamma \neq 90^o$	Simple : Points at the eight corners of the unit cell 				$NaNO_3$, $CaSO_4$, calcite, quartz, As, Sb, Bi etc.

Hexagonal $a = b \neq c$, $\alpha = \beta = 90^o \ \ \gamma = 120^o$	Simple: Points at the twelve corners of the unit cell out lined by thick line. 	or Points at the twelve corners of the hexagonal prism and at the centers of the two hexagonal faces. 	$ZnO,\ PbS,\ CdS,$ $HgS,$ graphite, $Mg,\ Zn,\ Cd$ ice, etc.
Monoclinic $a \neq b \neq c$, $\alpha = \gamma = 90^o, \beta \neq 90^o$	Simple : Points at the eight corners of the unit cell 	End centered: Point at the eight corners and at two face centers opposite to the each other. 	$Na_2SO_4.10H_2O,$ $Na_2B_4O_7.10H_2O,$ $CaSO_4.2H_2O,$ Monoclinic sulphur etc.
Triclinic $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^o$	Simple: Points at the eight corners of the unit cell. 		$CaSO_4.5H_2O,$ $K_2Cr_2O_7,\ H_3BO_3$ etc.

Note: Out of seven crystal systems triclinic is the most unsymmetrical ($a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90$).