

Solid state

(Part 1)

(For B.Sc 1st year)

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Introduction:

Solid is one of the four fundamental states of matter (the others being liquid, gas, and plasma). The atoms in a solid are closely packed together and contain the least amount of kinetic energy. A solid is characterized by structural rigidity and resistance to a force applied to the surface. Unlike a liquid, a solid object does not flow to take on the shape of its container, nor does it expand to fill the entire available volume like a gas. The atoms in a solid are bound to each other, either in a regular geometric lattice (crystalline solids, which include metals and ordinary ice), or irregularly (an amorphous solid such as common window glass). Solids cannot be compressed with little pressure whereas gases can be compressed with little pressure because the molecules in a gas are loosely packed.

Nature of 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.

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. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Amorphous solids on the other hand are isotropic in nature. It is because there is no long range order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarized in below Table.

Property	Crystalline solid	Amorphous solid
1. Shape	Definite characteristic geometrical shape	Irregular shape
2. Melting point	Melt at a sharp and characteristic temperature.	Gradually soften over a range of temperature
3. Cleavage point	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
4. Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion
5. Anisotropy	Anisotropic in nature.	Isotropic in nature
6. Nature	True solids.	Pseudo solids or super cooled liquids
7. Order in arrangement of constituent particles.	Long range order	Only short range order

Crystal lattice and unit cell

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, a regular three dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 1.5.

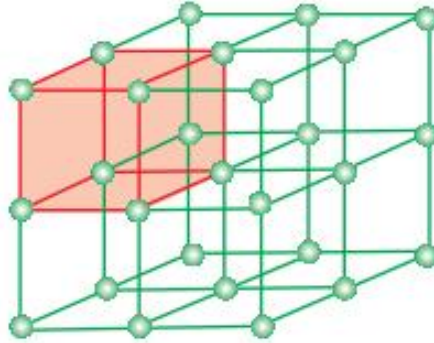


Fig. 1.5: A portion of a three dimensional cubic lattice and its unit cell.

There are only 14 possible three dimensional lattices. These are called Bravais Lattices (after the French mathematician who first described them). The 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. Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A 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. 1.6.

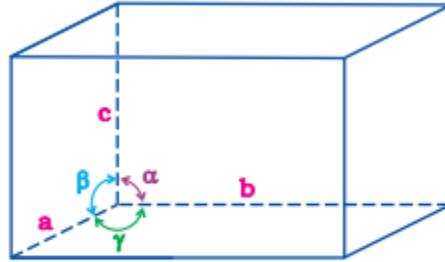


Fig. 1.6: Illustration of parameters of a unit cell

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.

In all, there are seven types of primitive unit cells (Fig. 1.7).

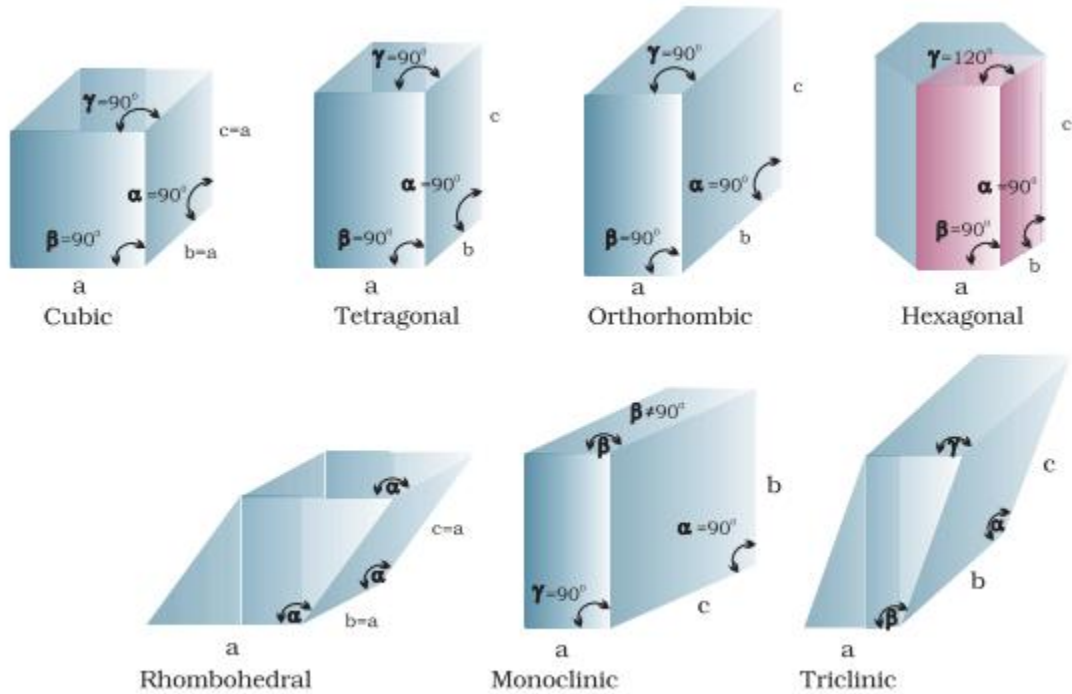


Fig. 1.7: Seven primitive unit cells in crystals

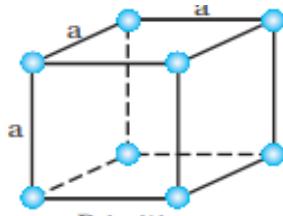
Their characteristics along with the centred unit cells they can form have been listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

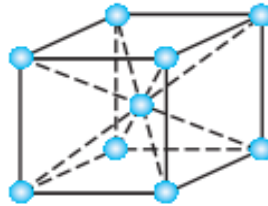
Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , CaSO_4
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (cinnabar)

Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3

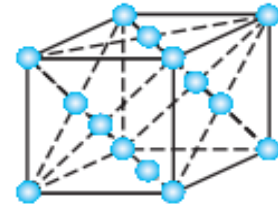
Unit cells of 14 types of Bravais Lattices



Primitive
(or simple)

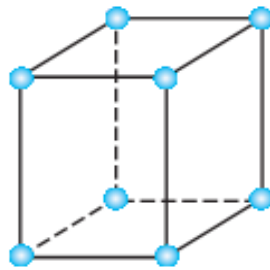


Body-centred

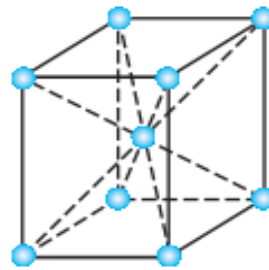


Face-centred

The three cubic lattices: all sides of same length, angles between faces all 90°

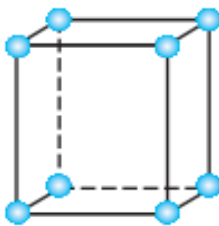


Primitive

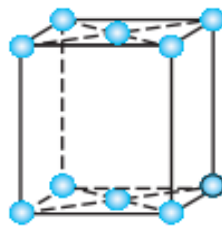


Body-centred

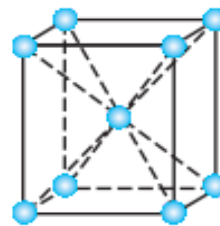
The two tetragonal: one side different in length to the other, two angles between faces all 90°



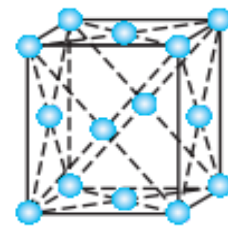
Primitive



End-centred

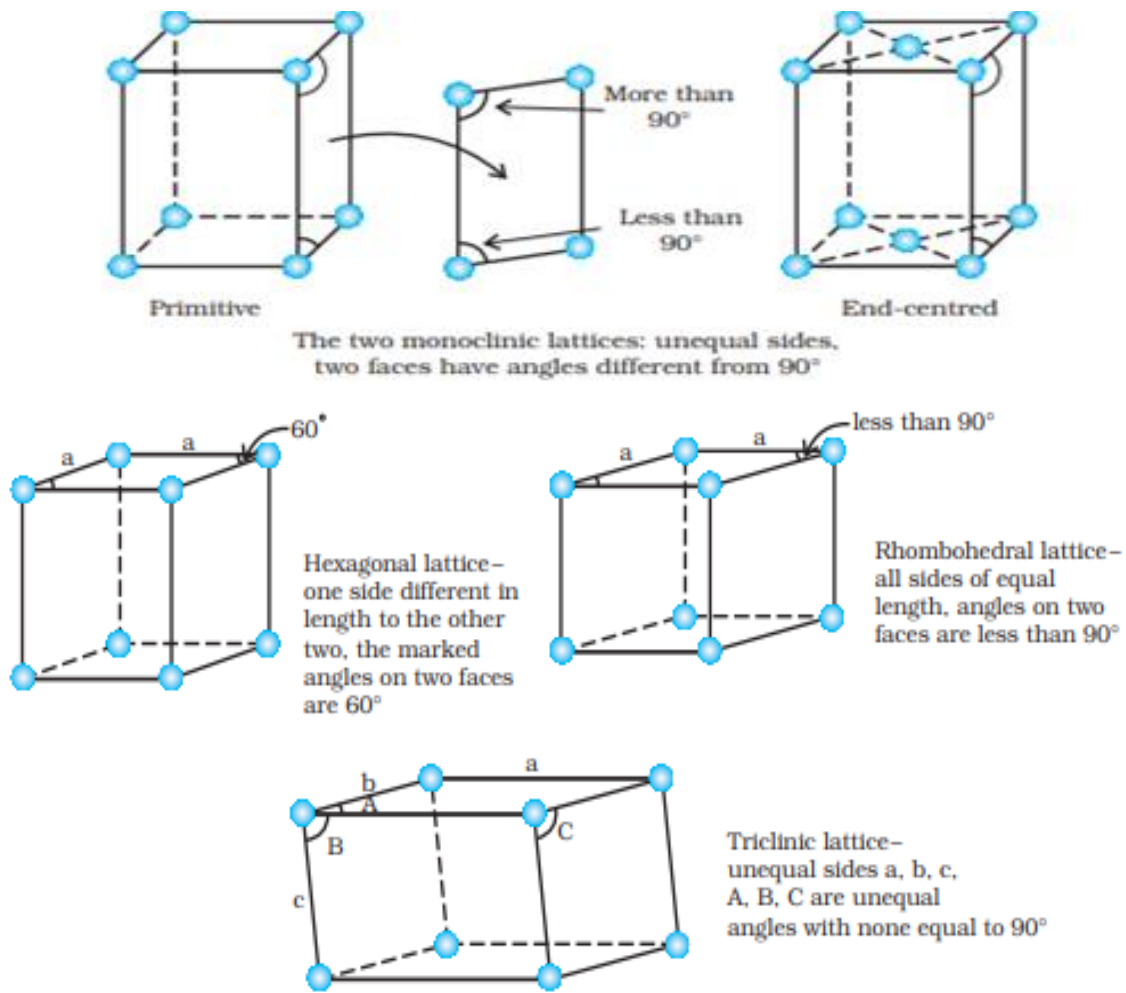


Body-centred



Face-centred

The four orthorhombic lattices: unequal sides, angles between faces all 90°



Number of atoms in a unit cell

We know that any crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). Let us now work out what portion of each particle belongs to a particular unit cell. We shall consider three types of cubic unit cells and for simplicity assume that the constituent particle is an atom.

1. Primitive cubic unit cell

Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig. 1.8, four unit cells in the same layer and four unit cells of the upper (or lower) layer. Therefore, only $1/8$ th of an atom (or molecule or ion) actually belongs to a particular unit cell. In

Fig. 1.9, a primitive cubic unit cell has been depicted in three different ways. Each small sphere in Fig. 1.9(a) represents only the centre of the particle occupying that position and not its actual size. Such structures are called open structures. The arrangement of particles is easier to follow in open structures. Fig. 1.9 (b) depicts space-filling representation of the unit cell with actual particle size and Fig. 1.9 (c) shows the actual portions of different atoms present in a cubic unit cell. In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times (1/8) = 1$ atom.

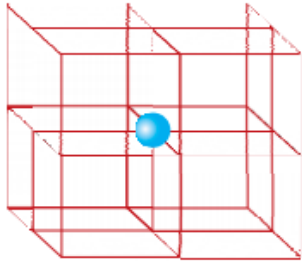


Fig. 1.8: In a simple cubic unit cell, each corner atom is shared between 8 unit cells.

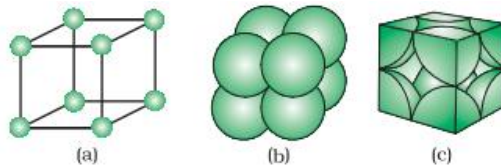


Fig. 1.9: A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

2. Body centred cubic unit cell

A body-centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre.

Fig. 1.10 depicts (a) open structure (b) space filling model and (c) the unit cell with portions of atoms actually belonging to it. It can be seen that the atom at the body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

- (i) $8 \text{ corners} \times 1/8 \text{ per corner atom} = 8 \times (1/8) = 1 \text{ atom}$
 - (ii) $1 \text{ body centre atom} = 1 \times 1 = 1 \text{ atom}$
- \therefore Total number of atoms per unit cell = 2 atoms

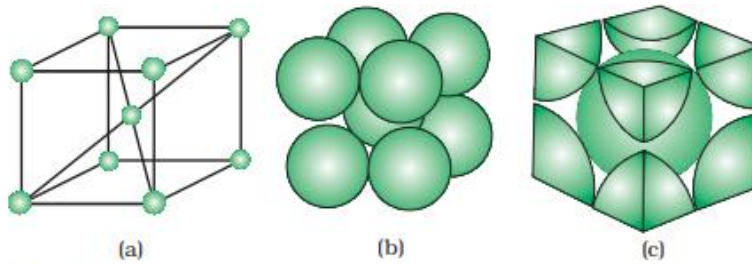


Fig. 1.10: A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

3. Face centred cubic unit cell

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.11 that each atom located at the face-centre is shared between two adjacent unit cells and only 1/2 of each atom belongs to a unit cell. Fig. 1.12 depicts (a) open structure (b) space-filling model and (c) the unit cell with portions of atoms actually belonging to it. Thus, in a face-centred cubic (fcc) unit cell:

- (i) 8 corners atoms \times 1/8 atom per unit cell = $8 \times (1/8) = 1$ atom
 - (ii) 6 face-centred atoms \times 1/2 atom per unit cell = $6 \times 1/2 = 3$ atoms
- \therefore Total number of atoms per unit cell = 4 atoms

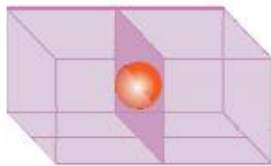


Fig. 1.11: An atom at face centre of unit cell is shared between 2 unit cells

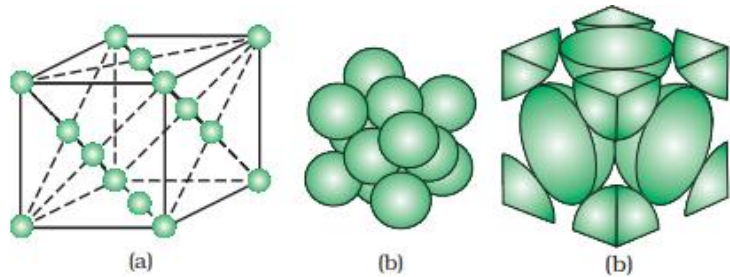


Fig 1.12: A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.