

# Solid State

## TYPES OF SOLIDS

Broadly speaking, solids are of two types :

- (a) Crystalline solids; also called true solids
- (b) Amorphous solids

A **crystalline solid** exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the **crystal lattice**. Sugar and salt are crystalline solids.

An **amorphous solid** (Gr *amorphous* = no form) has atoms, molecules or ions arranged at random and lacks the ordered crystalline lattice. Examples are rubber, plastics and glass. In their disordered structure, amorphous solids resemble liquids. Thus glasses are to be regarded as super-cooled or highly viscous liquids. The liquid nature of glass is sometimes apparent in very old window panes that have become slightly thicker at the bottom due to gradual downward flow

## SYMMETRY OF CRYSTALS

In addition to the angles, another important property of crystals is their symmetry. Symmetry in crystals may be due to a plane, a line or a point. Accordingly there are three types of symmetry elements associated with a crystal. These are called the **Elements of Symmetry**.

### (1) Plane of Symmetry

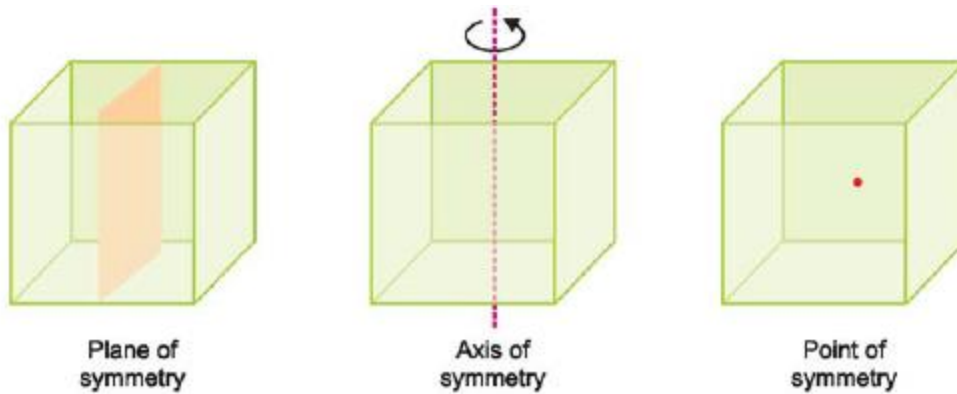
A crystal is said to have a plane of symmetry if it can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other.

### (2) Axis of Symmetry

An axis of symmetry is an imaginary line drawn through the crystal such that during rotation of the crystal through  $360^\circ$ , the crystal presents exactly the same appearance more than once. If similar view appears twice, it is called an axis of two fold symmetry or **diad axis**. If it appears thrice, it is an axis of three fold symmetry or **triad axis**, and so on.

### (3) Centre of Symmetry

It is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side. It is noteworthy that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.



## MILLER INDICES

We know that crystal lattice consists of unit cells arranged in parallel planes. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. These planes cut the three axes along the three crystallographic axes (OX, OY, OZ). Haüy proposed that a given crystal plane could be described in terms of intercepts along the axes (Law of Rational intercepts). The reciprocals of these intercepts are small whole numbers. These numbers,  $h$ ,  $k$  and  $l$  are called **Miller indices** after the name of the British scientist W.H. Miller. Thus Miller indices of a plane may be defined as **the reciprocals of the intercepts which the plane makes with the axes.**

Ex. 1. Suppose the plane intercept the axes

At 1, 2, 3

Miller indices ?

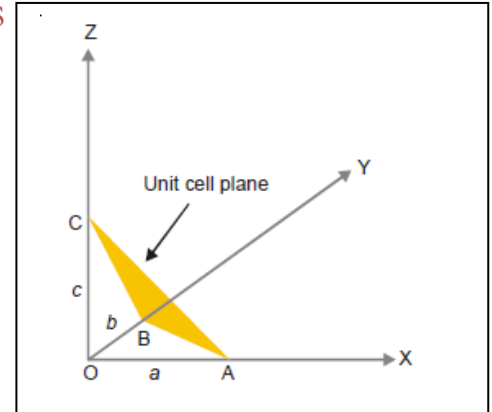
$$\langle 1/1, 1/2, 1/3 \rangle = \langle 1, 0.5, 0.33 \rangle$$

Make all to a whole number

$$\langle 6, 3, 2 \rangle$$

This is the miller indices

$$\langle h, k, l \rangle = \langle 6, 3, 2 \rangle$$



Ex. 2. Suppose

Another plane intercept at

2a. 3b. 3c along x, y, z axes

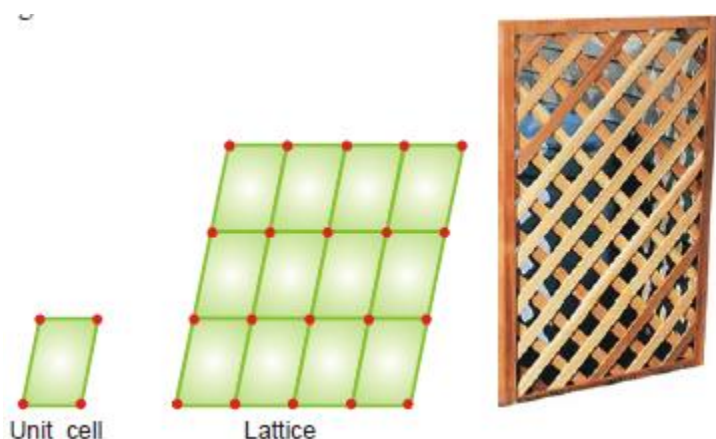
$$\text{Miller indices : } a/2a, b/3b, c/3c = \frac{1}{2}, \frac{1}{3}, \frac{1}{3}$$

$$= 0.5, 0.33, 0.33 = \langle 3, 2, 2 \rangle$$

## CRYSTAL STRUCTURE

The particles (atoms, ions or molecules) in crystals are highly ordered as is evident from their geometrical shapes, smooth surfaces and specific interfacial angles.

The particles in crystals are arranged in regular patterns that extend in all directions. The overall arrangement of particles in a crystal is called the **Crystal lattice**, **Space lattice** or **Simply lattice**.

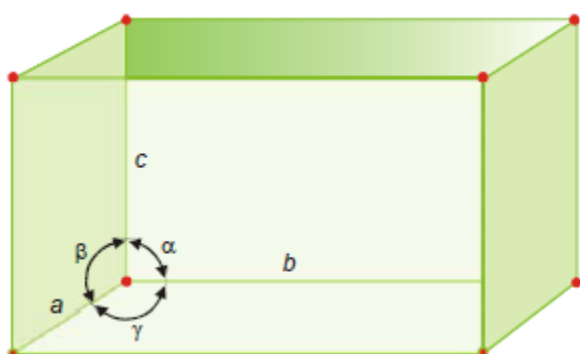


A unit cell has one atom or ion at each corner of the lattice. Also, there may be atoms or ions in faces and interior of the cell. A cell with an interior point is called the **body centered cell**. A cell which does not contain any interior points is known as the **primitive cell**. That is, a **primitive cell** is a **regular three-dimensional unit cell with atoms or ions located at its corners only**.

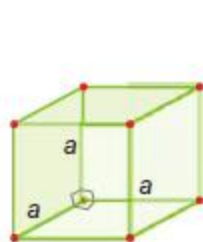
### Parameters of the Unit Cells

In 1850, August Bravais, a French mathematician observed that the crystal lattice of substances may be categorised into seven types. These are called **Bravais lattices** and the corresponding unit cells are referred to as **Bravais unit cells**. The unit cells may be characterised by the following parameters :

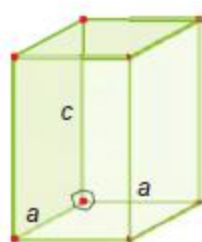
- (a) relative lengths of the edges along the three axes ( $a, b, c$ ).
- (b) the three angles between the edges ( $\alpha, \beta, \gamma$ ).



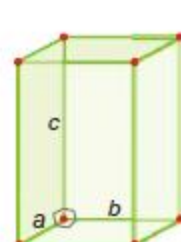
Crystal system	Relative axial length	Angles	Examples
Cubic (isometric)	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{Na}^+\text{Cl}^-$ , $\text{Cs}^+\text{Cl}^-$ , $\text{Ca}^{2+}(\text{F}^-)_2$ , $\text{Ca}^{2+}\text{O}^{2-}$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{PtCl}_6^{2-}$ , $\text{Pb}^{2+}\text{WO}_4^{2-}$ , $\text{NH}_4^+\text{Br}^-$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{SO}_4^{2-}$ , $\text{K}^+\text{NO}_3^-$ , $\text{Ba}^{2+}\text{SO}_4^{2-}$ , $\text{Ca}^{2+}\text{CO}_3^{2-}$ (aragonite)
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$\text{Ca}^{2+}\text{CO}_3^{2-}$ (calcite), $\text{Na}^+\text{NO}_3^-$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\text{AgI}$ , $\text{SiC}$ , $\text{HgS}$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	$\text{Ca}^{2+}\text{SO}_4^{2-}$ , $2\text{H}_2\text{O}$ , $\text{K}^+\text{ClO}_3^-$ , $(\text{K}^+)_4\text{Fe}(\text{CN})_6^{4-}$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{Cu}^{2+}\text{SO}_4^{2-} \cdot 5\text{H}_2\text{O}$ , $(\text{K}^+)_2\text{Cr}_2\text{O}_7^{2-}$



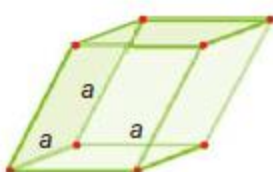
Cubic



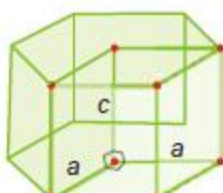
Tetragonal



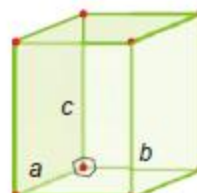
Orthorhombic



Rhombohedral



Hexagonal



Monoclinic

## CUBIC UNIT CELLS

These are the simplest unit cells. These unit cells are particularly important for two reasons. First, a number of ionic solids and metals have crystal lattices comprising cubic unit cells. Second, it is relatively easy to make calculations with these cells because in them all the sides are equal and the cell angles are all  $90^\circ$ .

### Three types of Cubic Unit Cells

There are three types of cubic unit cells :

- (1) Simple cubic unit cell
- (2) Body-centred cubic unit cell
- (3) Face-centred cubic unit cell

A **simple cubic unit cell** is one in which the atoms or ions are occupying only the corners of the cube.

A **body-centred cubic unit cell** has one particle at the centre of the cube in addition to the particles at the corners.

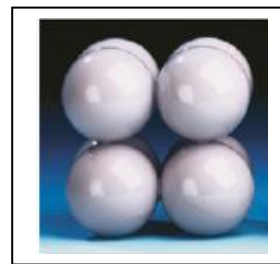
A **face-centred cubic unit cell** has one particle at each of the six faces of the cube apart from the particles at the corners.

Calculation of Number of atoms per unit cell

For simple cubic

(1) Eight unit cells share each corner atom. Therefore the simple cubic unit cell contains the equivalent of one atom.

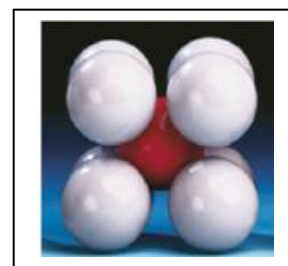
At each corner we have =  $\frac{1}{8}$  atom  
At 8 corners we have =  $\frac{1}{8} \times 8 = 1$  atom



For body centric cubic

A body centred unit cell contains the equivalent of two atoms.

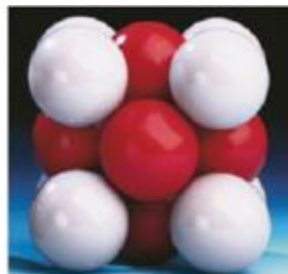
At 8 corners at  $\frac{1}{8}$  each = 1 atom  
central unshared = 1 atom  
Total equivalent atoms =  $1 + 1 = 2$



For Face centric cubic

(2) Each face-centred atom is shared by two unit cells. Therefore the face-centred unit cell contains the equivalent of four atoms.

At 8 corners,  $1/8$  each = 1 atom  
6 face-centred sites,  $1/2$  each = 3 atoms  
Total equivalent atoms =  $1 + 3 = 4$



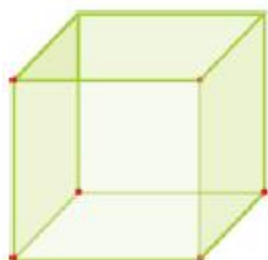
#### Calculation of Mass of the Unit Cell

Mass of the unit cell can be calculated from the number of atoms in the unit cells. For this multiply the mass of one atom by the number of atoms in the unit cell.

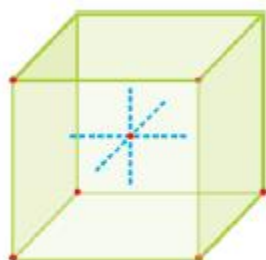
$$\text{Thus the mass of one atom} = \frac{\text{molar mass of the substance}}{\text{Avogadro's number}}$$

#### What is Coordination Number of a Crystal Lattice ?

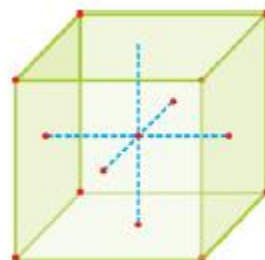
The coordination number of a crystal structure is the number of particles (ions, atoms or molecules) immediately adjacent to each particle in the lattice. It is characteristic of a given space lattice and is determined by inspection of the model. In a simple cubic lattice *e.g.*, NaCl, each particle is surrounded by six other particles and so the coordination number is six. It will be observed that the coordination numbers for body-centred and face-centred cubic lattice are 8 and 12 respectively.



Simple cube



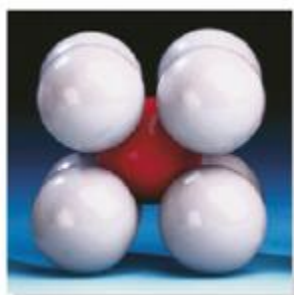
Body-centred cube



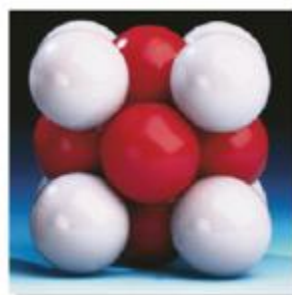
Face-centred cube



Coordination No 6



Coordination No 8



Coordination No 12

**Book :** A. Bhal, B. S. Bahl, G. D. Tuli, Essentials of Physical Chemistry