

CEMA-CC-4-9-TH:

PHYSICAL CHEMISTRY 3

CRYSTAL STRUCTURE

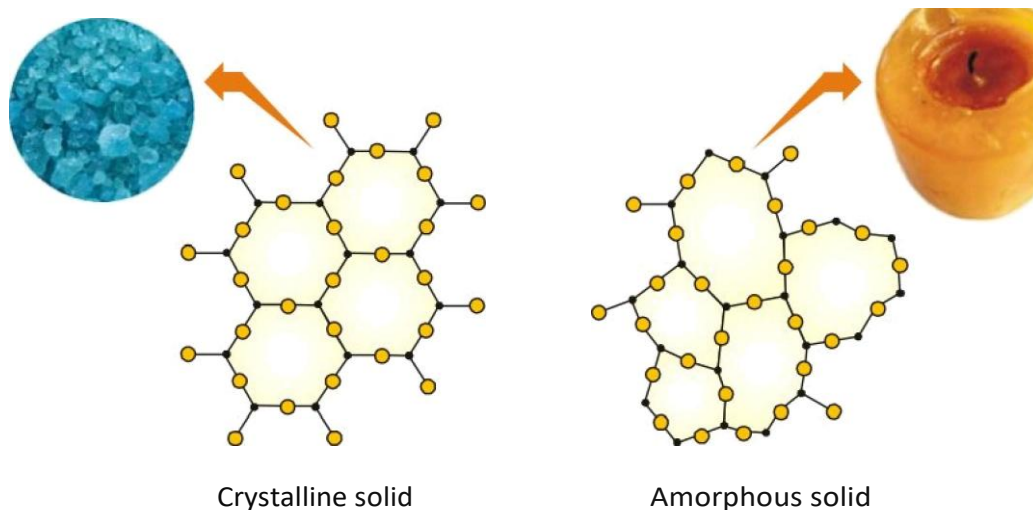
TYPES OF SOLIDS

solids are of two types : (a) **Crystalline solids**; also called true solids

(b) **Amorphous solids**

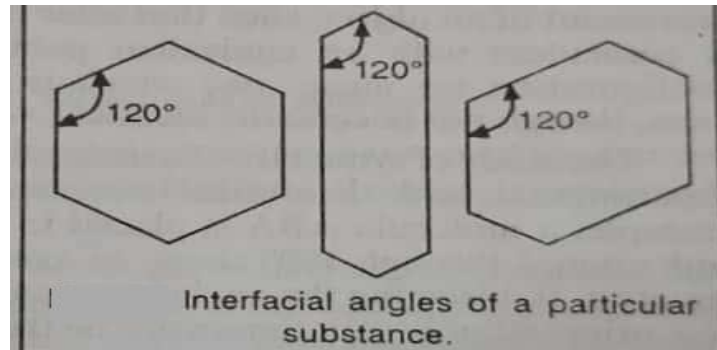
A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the crystal lattice. Sugar and salt are crystalline solids.

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



TERMINOLOGY OF CRYSTALLINE STATE

- (i) **Crystallography**: The branch of science which deals with the study of structure, geometry and properties of crystal and crystalline substances is known as Crystallography.
- (ii) **Crystal faces**: The crystals of a substance bound by plane surfaces are called faces.
- (iii) **Edges**: The point of intersection of two adjacent faces is called an edge.
- (iv) **Interfacial angle**: The angle between two intersecting faces is known as interfacial angle.



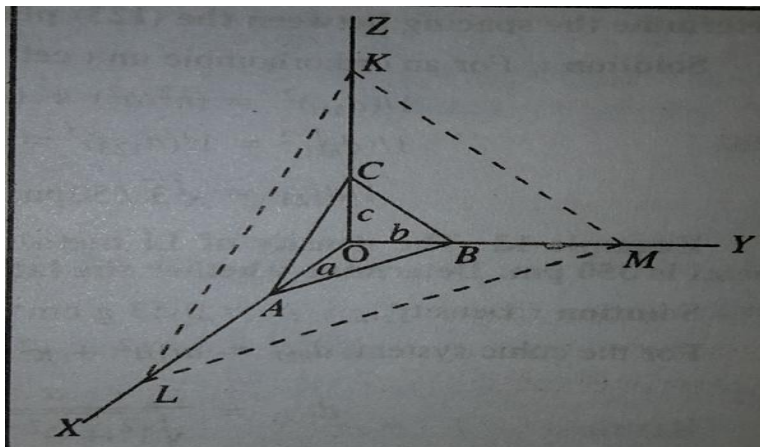
LAWS OF CRYSTALLOGRAPHY

Crystallography is based on three fundamental laws.

(i) **Steno's Law of constancy of interfacial angles:** This law states that angle between adjacent corresponding faces is inter-facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal. The size and shape of crystal depend upon the conditions of crystallisation.

(ii) **Hauy's Law of rational indices:** This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a, b, c or some simple whole number multiples of them e.g., $na, n'b, n''c$, where n, n' and n'' are simple whole numbers. The whole numbers n, n' and n'' are called Weiss indices.

Let OX, OY and OZ represent the three crystallographic axes and let ABC be a unit plane. The unit intercepts will then be a, b and c . According to the above law, the intercepts of any face such as KLM , on the same three Axes will be simple whole number multiples of a, b and c respectively.



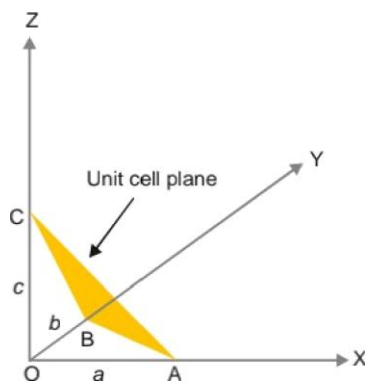
(iii) **Law of constancy of symmetry:** According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and centre of symmetry.

MILLER INDICES

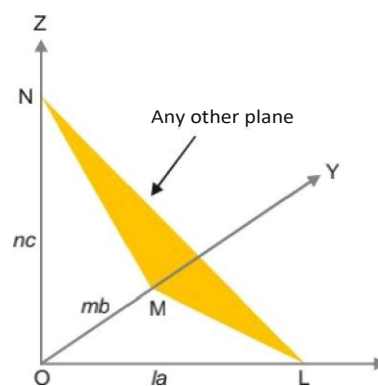
We know that crystal lattice consists of unit cells arranged in parallel planes. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. These planes cut the three axes along the three crystallographic axes (OX, OY, OZ). Hauy proposed that a given crystal plane could 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.

For illustration, let us consider a crystal system with the axes OX , OY and OZ . In the below figure(a) ABC represents a unit cell surface while LMN in Figure(b) depicts another crystal plane under study. The intercepts of the unit cell plane are OA , OB and OC which have the lengths a , b and c respectively. The intercepts of the plane under study are OL , OM and ON . These can be expressed as multiples of the intercepts a , b , c , i.e., la , mb and nc . Here l , m , n are either integral whole numbers or fractions of whole numbers. The reciprocals of these numbers are written together in brackets (h , k , l) to give the Miller indices of the plane under study.



(a) A unit cell plane intercepts the axes to give intercepts a , b and c



(b) Any other plane intersects the axes to give intercepts

Equal to la , mb and nc

How to Find Miller Indices?

- (1) Write the intercepts as multiples of a , b , c , say, la , mb and nc .
- (2) Take reciprocals of l , m , and n ,
- (3) Clear fractions to get whole numbers h , k , l ,
- (4) Miller indices of the plane are (h , k , l).

SOLVED PROBLEM 1. Determine the Weiss and Miller indices for a plane when the intercepts along the axes are (i) $2a$, $3b$ and $2c$ and (ii) a , $-2b$, $3c$

SOLUTION (i) The unit cell intercepts are a , b , c

The intercepts of the given plane are $2a$, $3b$, $2c$

Weiss indices are 2 , 3 , 2

The lengths of the intercepts in terms of unit cell intercepts are 2 , 3 , 2

The reciprocals are $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{2}$

Clear fractions by multiplying with 6 which gives the whole numbers 3 , 2 , 3

Thus the Miller indices of the given plane are (3, 2, 3).

SOLUTION (ii) Weiss indices are 1, -2, 3

Miller indices are $6, \overline{3}, 2$

SOLVED PROBLEM 2: A face makes intercepts 2a and 3b on the X-axis and Y-axis respectively and does not cut the z-axis at all. What are the Weiss indices and Miller indices of the face?

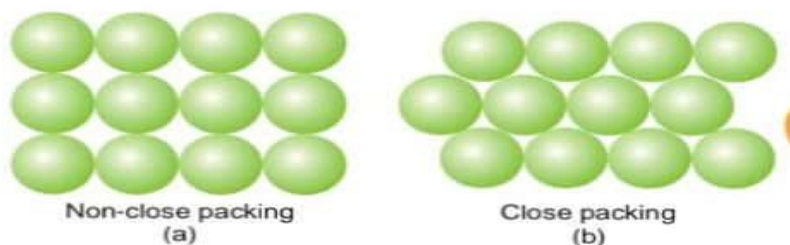
Solution: Intercepts 2a, 3b, ∞c

Weiss indices 2, 3, ∞

Miller indices (3, 2, 0)

CLOSE PACKING IN CRYSTALS

The individual atoms in a metallic crystal lattice can be thought of as hard spheres. The spherical atoms are packed together in the lattice very efficiently in geometrical arrangements so as to leave minimum interspaces. A layer of uniform spheres can be arranged either as in figure (a) or (b). Clearly the second of the patterns uses space more efficiently. Here the spheres fit into the hollows between the adjacent spheres. Thus the vacant spaces (voids) between the spheres are smaller than in the first pattern. The metallic crystals are of the second type i.e., **close packing**.



As clear from figure (b), each sphere in a closely packed layer is in contact with four others. Thus each ball touches six other at the corners of a hexagon. Three dimensional metallic crystals consist of closely packed layers stacked one over the other. The spheres forming the second layer fill the holes or voids in the first layer and the spheres of the third layer fill the voids in the second layer. Depending upon the geometrical arrangements of spheres in the three layers, the close-packed metallic crystals are of two types :

(a) **Hexagonal close-packed (hcp)**

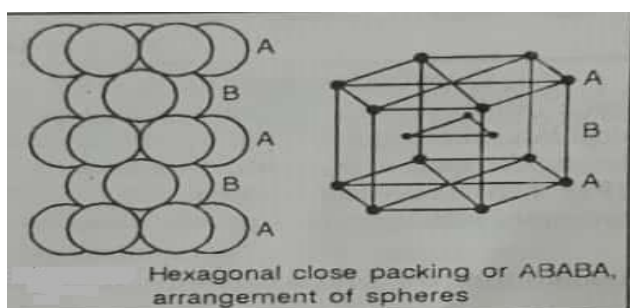
(b) **Cubic close-packed (ccp)**

Hexagonal Close-Packed Structure

The hexagonal close-packed structure of metallic crystals is shown in figure (below). It consists of three layers of spherical atoms packed one over the another. The bottom layer (A) and the top layer (A) have three spheres in similar orientation. The middle layer (B) consists of six spherical

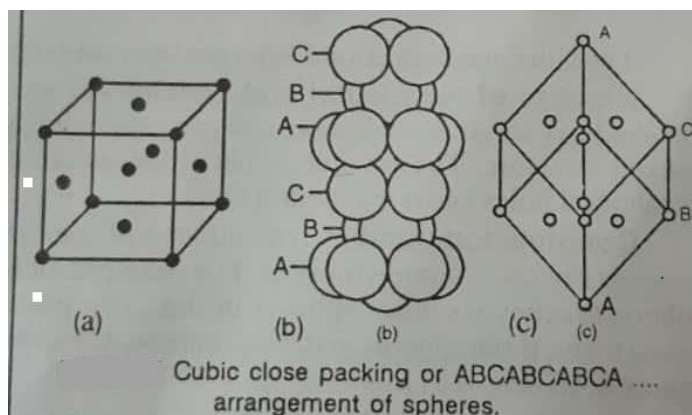
atoms. The three spheres in the top and the bottom layer fit into the same voids on either side of the middle layer. It is noteworthy that each sphere in the structure is in contact with 12 neighbouring spheres, six in its own layer, three in the layer above and three in the layer below. Thus the coordination number of the close-packed structure is 12. In the overall close-packed structure, the layers repeat in the manner ABABAB.

The examples of metals having hexagonal close-packed structures are Ba, Co, Mg and Zn.



Cubic Close-Packed Structure

The cubic close-packed (ccp) pattern of a metallic crystal is illustrated in figure (below). Its coordination number is also 12. Like the hcp structure, it consists of three layers of spherical atoms lying over one another. There are three spheres in the top layer (C), six in the middle layer (B), and three in the bottom layer (A). However, the overall ccp differs in structure from the hcp structure in respect of the orientation of the three spheres in the top layer. In hcp structure both the top and the bottom layers have the same orientation. But in ccp structure, they are oriented in opposite directions. Therefore, the three spheres in the top layer do not lie exactly on the spheres in the bottom layers. In ccp structure, the layers are repeated in the order ABCABCABC. By turning the whole crystal you can see that the ccp structure is just the face-centred cubic structure. Many metals including Ag, Au, Ca, Co, Cu, Ni, crystallise in ccp structures.

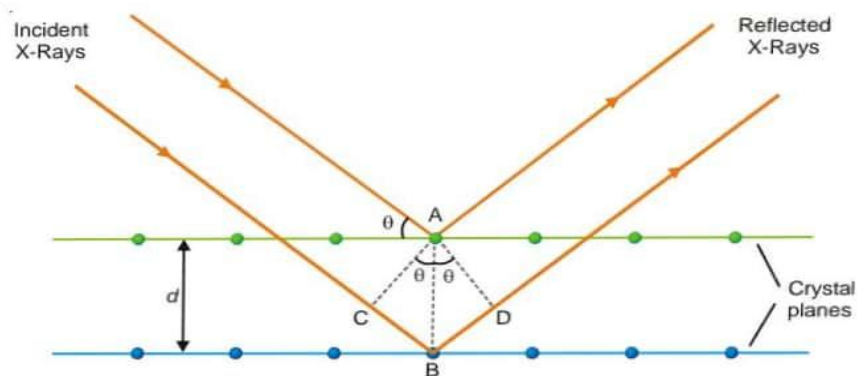


BRAGG'S EQUATION

In 1913 the father-and-son, W.L. Bragg and W.H. Bragg worked out a mathematical relation to determine interatomic distances from X-ray diffraction patterns. This relation is called the [Bragg equation](#). They showed that :

- (1) the X-ray diffracted from atoms in crystal planes obey the laws of reflection.
- (2) the two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.

DERIVATION OF BRAGG EQUATION



Reflection of X-Rays from two different planes of a crystal.

Figure shows a beam of X-rays falling on the crystal surface. Two successive atomic planes of the crystal are shown separated by a distance d . Let the X-rays of wavelength λ strike the first plane at an angle θ . Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane if the extra distance travelled by them ($CB + BD$) is equal to integral number, n , of wavelengths. That is,

$$n\lambda = CB + BD \dots(i)$$

Geometry shows that

$$CB = BD = AB \sin \theta \dots(ii)$$

From (i) and (ii) it follows that

$$n\lambda = 2AB \sin \theta \quad \text{or} \quad n\lambda = 2d \sin \theta$$

This is known as the [Bragg equation](#). The reflection corresponding to $n = 1$ (for a given series of planes) is called the first order reflection. The reflection corresponding to $n = 2$ is the second order reflection and so on.

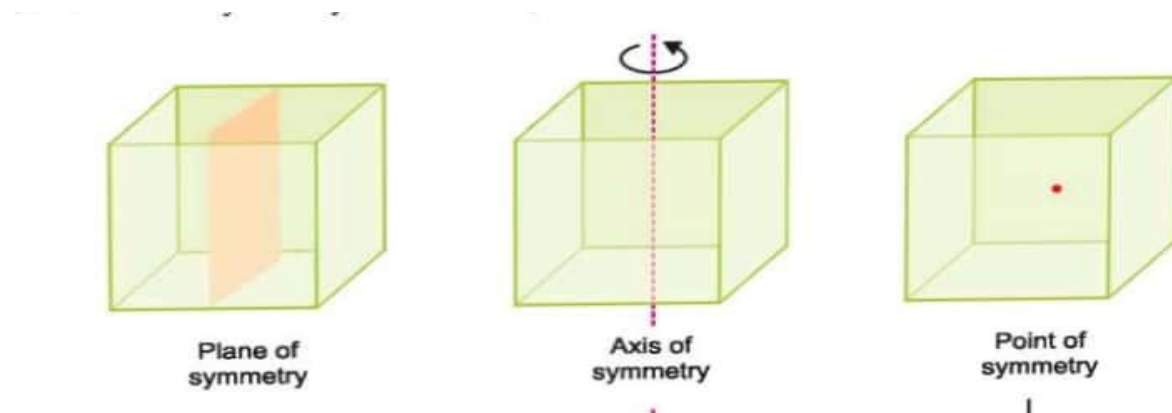
SYMMETRY OF CRYSTALS

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° , 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.



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.

To describe the structure of a crystal it is convenient to view it as being made of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called the Unit cell.

How to Represent Crystal Lattice and Units Cells ?

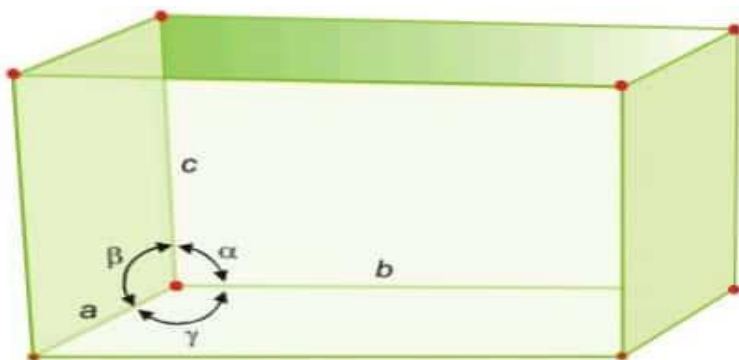
The crystal lattice of a substance is depicted by showing the position of particles (structural units) in space. These positions are represented by bold dots (or circles) and are referred to as lattice points or lattice sites. The overall shape and structure of a crystal system is governed by that of the unit cell of which it is composed.

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 :

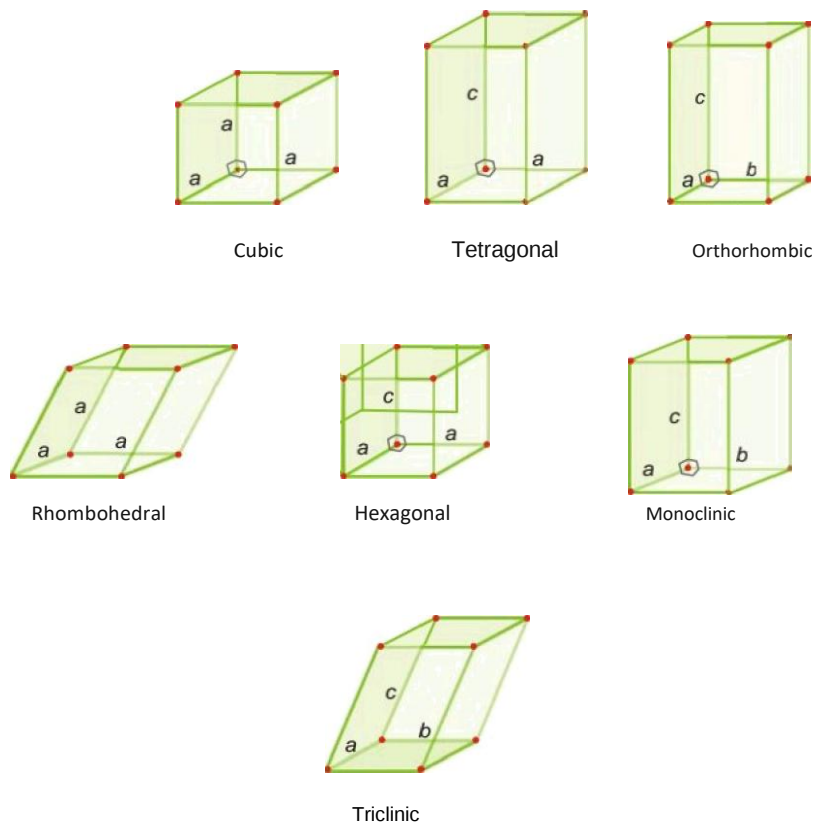
(a) relative lengths of the edges along the three axes (a , b , c). (b) the three angles between the edges (α , β , γ). The parameters of a unit cell can be illustrated as in following figure. Parameters of the **seven Bravais unit cells** are listed in Table 1.



parameters of a unit cell

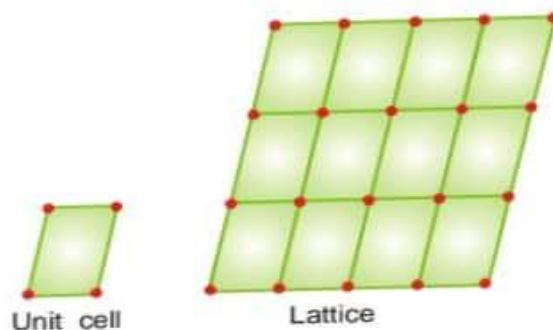
TABLE 1. THE SEVEN UNIT CELLS

Crystal system	Relative axial length	Angles	Examples
Cubic (isometric)	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Na^+Cl^- , Cs^+Cl^- , $\text{Ca}^{2+}(\text{F}^-)_2$, $\text{Ca}^{2+}\text{O}^{2-}$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{PtCl}_6^{2-}$, $\text{Pb}^{2+}\text{WO}_4^{2-}$, NH_4^+Br^-
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{SO}_4^{2-}$, K^+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), Na^+NO_3^-
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	AgI , SiC , HgS
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma \neq 90^\circ$	$\text{Ca}^{2+}\text{SO}_4^{2-}$, $2\text{H}_2\text{O}$, K^+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 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° .



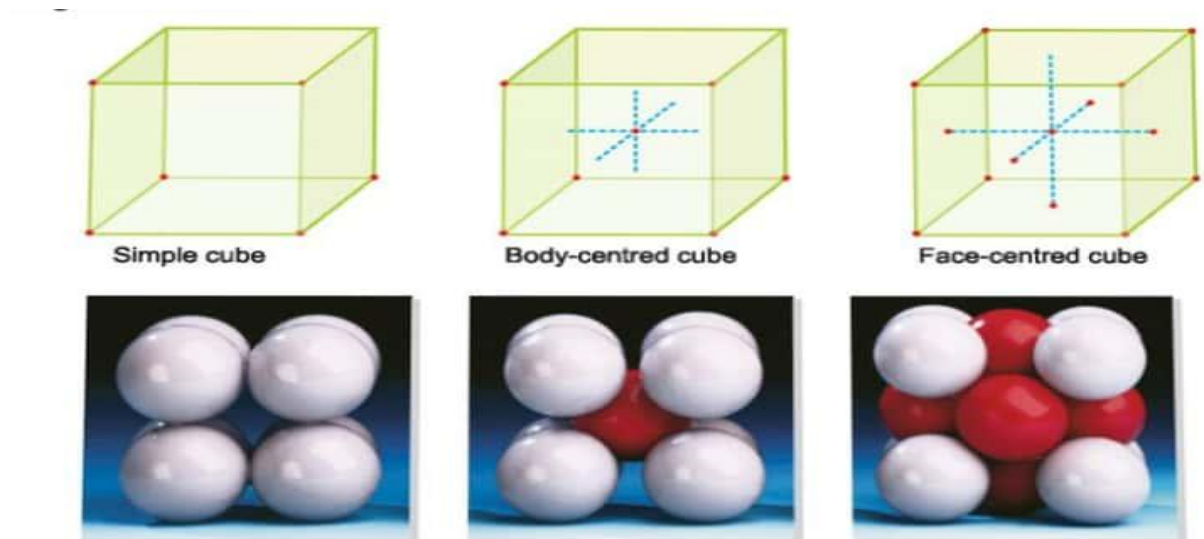
Three types of Cubic Unit Cells

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.



How to Compute Atoms or Points in a Unit Cell ?

In counting the number of atoms (or points) per unit cell, we must keep in mind that atoms on corners of faces are shared with adjoining cells. Therefore the number of atoms in a cubic unit cell may be computed as follows.

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

$$\text{At each corner we have} = 1/8 \text{ atom}$$

$$\text{At 8 corners we have} = 1/8 \times 8 = 1 \text{ atom}$$

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

$$\text{At 8 corners, } 1/8 \text{ each} = 1 \text{ atom}$$

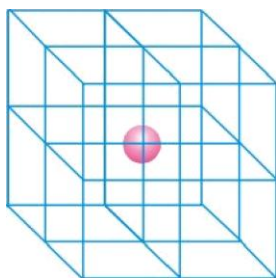
$$6 \text{ face-centred sites, } 1/2 \text{ each} = 3 \text{ atoms}$$

$$\text{Total equivalent atoms} = 1 + 3 = 4$$

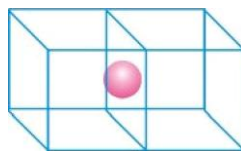
(3) A body centred unit cell contains the equivalent of **two atoms**.

$$\text{At 8 corners at } 1/8 \text{ each} = 1 \text{ atom}$$

central unshared = 1 atom
 Total equivalent atoms = 1 + 1 = 2



(a)



(b)

(a) In the simple cubic cell, each corner atom is shared by 8 cells; (b) In the face-centred cell, each atom in a face is shared by 2 cells.

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.

Thus the mass of one atom = molar mass of the substance / Avogadro's number

SOLVED PROBLEM 1. The unit cell of metallic gold is face-centred cubic. (a) How many atoms occupy the gold unit cell ? (b) What is the mass of a gold unit cell ?

SOLUTION : eight corners at $1/8$ atom each = 1 atom

six faces at $1/2$ atom each = 3 atoms

$\therefore$ 4 atoms occupy the gold unit cell.

Mass of gold atom = molar mass / Avogadro's number

$$\frac{197 \text{ g/mol}}{6.023 \times 10^{23} \text{ atoms/mol}} \times \frac{1}{4}$$

$$= 8.178 \times 10^{-23} \text{ g}$$

SOLVED PROBLEM 2. By X-ray diffraction it is found that nickel crystals are face-centred cubic. The edge of the unit cell is $3.52 \text{ \AA}$. The atomic mass of nickel is 58.7 and its density is 8.94 g/cm^3 . Calculate Avogadro's number from the data.

SOLUTION: Number of atoms in nickel unit cell = 4

Let Avogadro's number = N

Thus the mass of one Ni atom = $58.7 / N$

the mass of one unit cell = $4(58.7 / N)$ g

the volume of one unit cell = $(3.52 \times 10^{-8})^3 \text{ cm}^3$

the density of nickel cell = $4(58.7 / N) \text{ g} / (3.52 \times 10^{-8})^3 \text{ cm}^3 = 8.94 \text{ g/cm}^3$ (given)

$$\therefore N = 6.02 \times 10^{23}$$

INTERSTITIAL VOIDS OR INTERSTITIAL SITES

In hcp and ccp arrangement of spheres, some spaces or sites are left vacant. These sites or holes in a crystal are called interstitial sites or voids. There are two types of interstitial sites.

(i) **Tetrahedral site or void**

(ii) **Octahedral site or void**

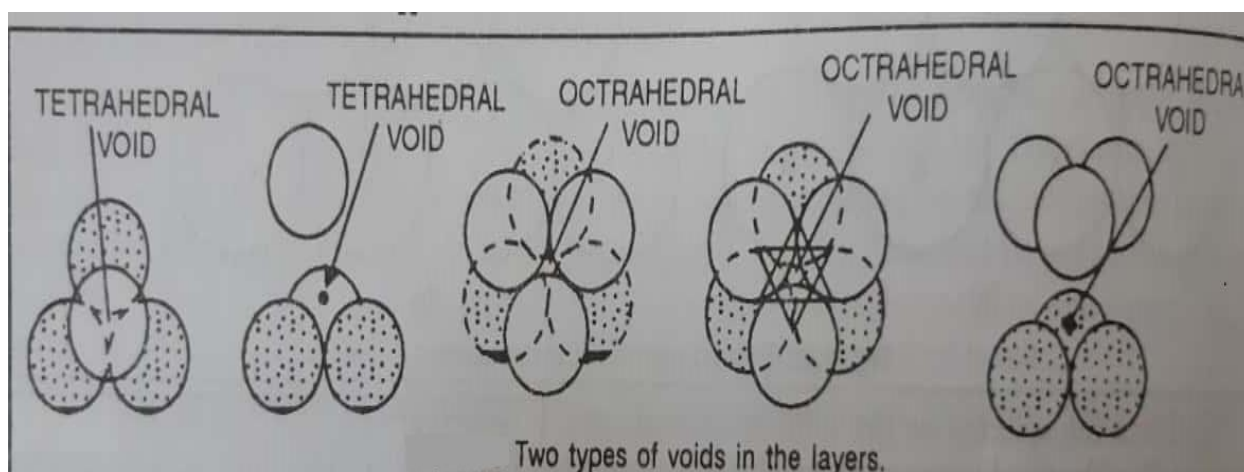
(i) Tetrahedral void : The empty space among four spheres having tetrahedral arrangement is called tetrahedral void or tetrahedral site.

If r is the radius of the sphere that can be fitted in the void, R is the radius of the sphere constituting the void, then for a tetrahedral void,

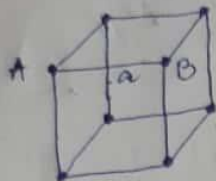
$$r/R = 0.225$$

(ii) Octahedral void: The vacant space formed by two equilateral triangles with apices in opposite direction is called octahedral void or octahedral site.

For an octahedral void, $r/R = 0.414$



Calculation of void space in (i) p-type cubic crystal i.e. simple cubic system



Distance between nearest neighbours A and B, $d = AB = a$.

For, crystals of pure elements, $r = \frac{d}{2}$

But, $d = a$

$\therefore$ Radius, $r = a/2$ or $a = 2r$

Number of spheres per unit cell = 1

volume of the sphere = $\frac{4}{3}\pi r^3$

volume of the cube = $a^3 = (2r)^3 = 8r^3$

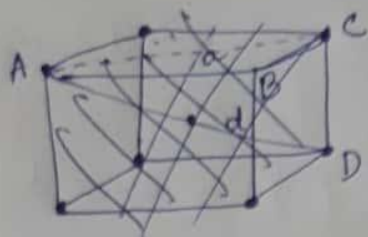
$\therefore$ Fraction occupied i.e. packing fraction

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} = 0.524$$

or % space occupied = 52.4%

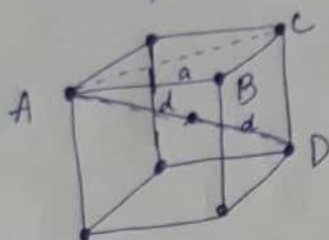
void space = 47.6%

(ii) I-type cubic system i.e. body-centred cubic lattice (bcc) :-



Distance between nearest neighbours, $d = AD/2$

$$\therefore AD = 2d \quad \text{--- (1)}$$



From right angled triangle ABC, we have

$$\begin{aligned} AC^2 &= AB^2 + BC^2 \\ &= a^2 + a^2 = 2a^2 \end{aligned}$$

$$\therefore AC = a\sqrt{2} \quad \text{--- (2)}$$

From right angled triangle, ADC, we have

$$\begin{aligned} AD^2 &= AC^2 + CD^2 \\ &= (a\sqrt{2})^2 + a^2 \end{aligned}$$

$$AD = a\sqrt{3}$$

$$2d = a\sqrt{3} \quad [\because AD = 2d] \quad \text{--- (3)}$$

For crystals of pure elements, radius, $r = \frac{d}{2}$ --- (4)
Substituting the value of 'd' from (3) in (4), we get,

$$r = \frac{a\sqrt{3}}{2 \times 2} = \frac{a\sqrt{3}}{4} \quad \text{or, } a = \frac{4r}{\sqrt{3}}$$

$$\text{Volume of the unit cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

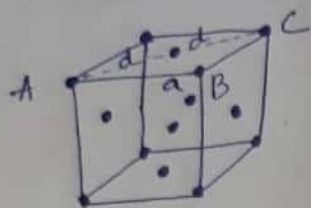
$$\text{No. of spheres per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\text{Vol. of two spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\therefore \text{Fraction occupied is packing fraction} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = 0.68$$

$$\% \text{ space occupied} = 68\%, \text{ void space} = 32\%$$

(iii). F-type cubic system i.e. face-centred cubic lattice



Distance between nearest neighbours,

$$d = \frac{AC}{2}, \therefore AC = 2d \quad \text{--- (1)}$$

From right angled $\triangle ABC$, we have

$$AC^2 = AB^2 + BC^2, \quad AC^2 = a^2 + a^2 = 2a^2$$

$$AC = a\sqrt{2}; \quad 2d = a\sqrt{2} = 4r$$

$$\therefore a = \frac{4}{\sqrt{2}} r, \quad a = 2\sqrt{2} r$$

$$a = 2\sqrt{2} r$$

volume of the unit cell, $a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$

$$\text{No. of spheres in the unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Vol. of 4 spheres} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$$

$\therefore$ Fraction occupied i.e. packing fraction,

$$= \frac{\frac{16}{3} \pi r^3}{16\sqrt{2} r^3} = 0.74$$

$$\text{or, \% space occupied} = 74\%$$

$$\therefore \text{void space} = 26\%$$

[Atomic radius = r

Edge length = a

Nearest neighbour distance = d where $r = \frac{d}{2}$]