CRYSTAL PHYSICS
Crystallography Space lattice, Unit Cell & Lattice parameters

Introduction

The matter which surround us is found to exist in three states viz, solids, liquids and gases.

All these materials are composed of atoms and molecules. The constituent particles, atoms or molecules of matter are held together through forces of attraction. *The attractive forces which hold the constituent particles of a substance together are called bonds.*

We know that, some solids are brittle, some are ductile, some are malleable, some are strong, some are weak, some are good conductors of heat and electricity, some are bad conductors of heat and electricity, some are magnetic, some are non-magnetic and so on. The reason for these different properties of the solids is due to their structure. That is, the behavior of the solid materials is closely related to the structure of the material.

Classification of Solids

If we examine the solid materials with which we daily come across, we shall find that most of them do not have any characteristic difference in their outward appearance. But, if we examine them under a microscope we shall find these materials have different internal atomic structures.

Based on the internal atomic structure, the solids can be classified into two categories namely

I. *Crystalline*

II. *Non-crystalline or Amorphous solids.*

Crystalline solids (Crystals)

Crystalline solids or crystals are those, in which the constituent atoms or molecules are arranged in an orderly fashion throughout in a three dimensional pattern.

Each atom or molecule is fixed at a definite point in space at a definite distance from and in a definite angular orientation to all other atoms or molecules surrounding it. Therefore, crystalline solids have well defined geometrical form (pattern), i.e., they have well defined faces and angles between them. Further when crystal breaks, the broken pieces are all having regular shape. *The crystalline solids have directional properties and therefore they are called anisotropic substances.* A crystalline material may be either in the form of a single crystal, (where the solid contains only one crystal) or an aggregate of many small crystals or grains separated by well defined grain boundaries also known as *polycrystalline solid.*

Few examples for crystalline solids: **Copper, silver, Aluminium, iron** etc.

Crystallography: *The study of the geometric form and other physical properties of crystalline solids by using X-rays, electron beams and neutron beams etc., is termed as the science of crystallography.*

Examples for single crystals: **Sugar, common salt (NaCl), diamond** *etc. These single crystals are produced artificially from their vapour or liquid state.*

Amorphous solids (Non-crystalline solids)

"Amorphous" means "without form".

In amorphous solids, the constituent particles, atoms or molecules are not arranged in an orderly fashion, i.e., the same atomic groups are arranged more randomly.

These solids have no directional properties and therefore they are called isotropic substances. These amorphous solids do not have a sharp melting point.
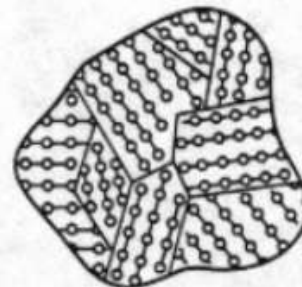
Examples: Plastics, rubber and glass.
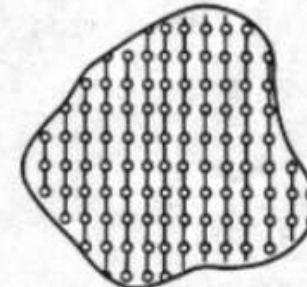
Note:

Super cooled liquids

The materials like glass, which exhibit some of the properties of a solid like hardness, definite shape etc., but are not crystalline, are regarded as super cooled liquids.
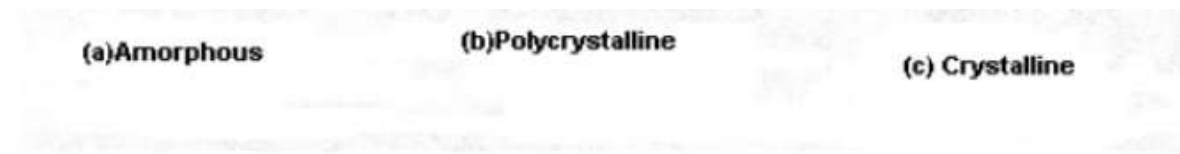

(a)Amorphous   (b)Polycrystalline   (c) Crystalline
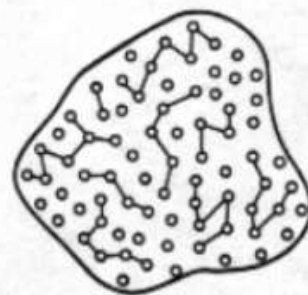
(a)Amorphous   (b)Polycrystalline   (c) Crystalline

Fig.1

Difference between crystalline and non-crystalline material

Sr. No.	Crystalline material	Non-crystalline material
1	They have definite and regular geometrical shapes which extend throughout the crystal.	They do not have definite geometrical shape.
2	They are anisotropic.	They are isotropic.
3	They are most stable.	They are less stable.
4	They have sharp melting point. Examples: Diamond, NaCl, KC1	They do not have sharp melting point. Examples: Glasses, plastics, rubber

Crystal Structure

The crystal structure gives the arrangement and disposition of atoms within a crystal. *Determination of crystal structure with the help of X-rays is known as X-ray crystallography.* X-rays are most widely used to study the crystal structure because the wavelength of X-rays (10^{-12} to 10^{-10} m) is most comparable with the inter-atomic distances.

Fundamental crystallographic terms (definitions)

a) Lattice

Lattice is defined as an array of points such that every lattice point has got the same environment or every point is indistinguishable from the other lattice point. It is an imaginary concept.

b) Space lattice or crystal lattice

Definition - 1: *A three dimensional collection of points in space is called a space lattice or crystal lattice. The environment about any particular point is in every way the same.* That is, space lattice is an idealized geometrical (imaginary) concept by which crystal structures can be described.
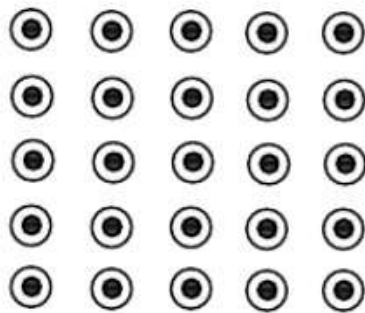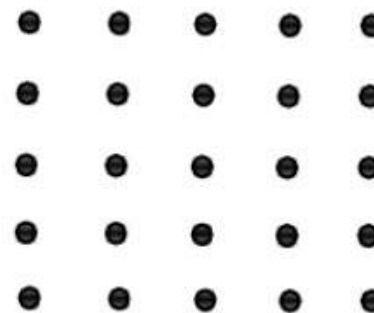
Figure 2

Figure 3

c) Lattice points

Lattice points denote the position of atoms or molecules in the crystal.

d) Basis or Motif

A crystal structure is formed by associating with every lattice point a unit assembly of atoms or molecules (i.e., one or more atoms or molecules) identical in composition, arrangement and orientation. This unit assembly is called the basis or pattern or motif. The logical relation is

Space lattice + Basis = Crystal structure.

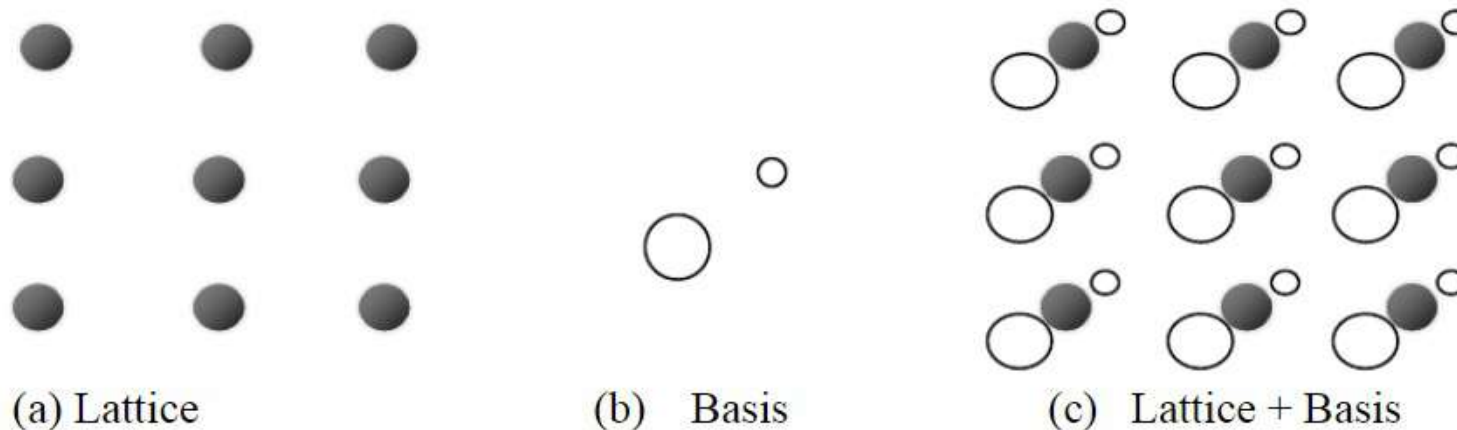(a) Lattice   (b) Basis   (c) Lattice + Basis

Fig.4.

The number of atoms in the basis may be as low as one. Examples are Aluminium and Barium. In NaCl and KCl the basis is two atoms and in CaF_2 the basis is three atoms. But, there are structures for which the basis exceeds 1000 atoms.

Note: A crystal lattice refers to the geometry of a set of points in space. The crystal structure refers to the actual arrangement of atoms or molecules in the space.

e) Lattice planes

A set of parallel and equally spaced planes in a space lattice which include all lattice points are called as lattice planes.

The different ways of drawing the lattice planes for the array of figure 3 are shown in figure 5.
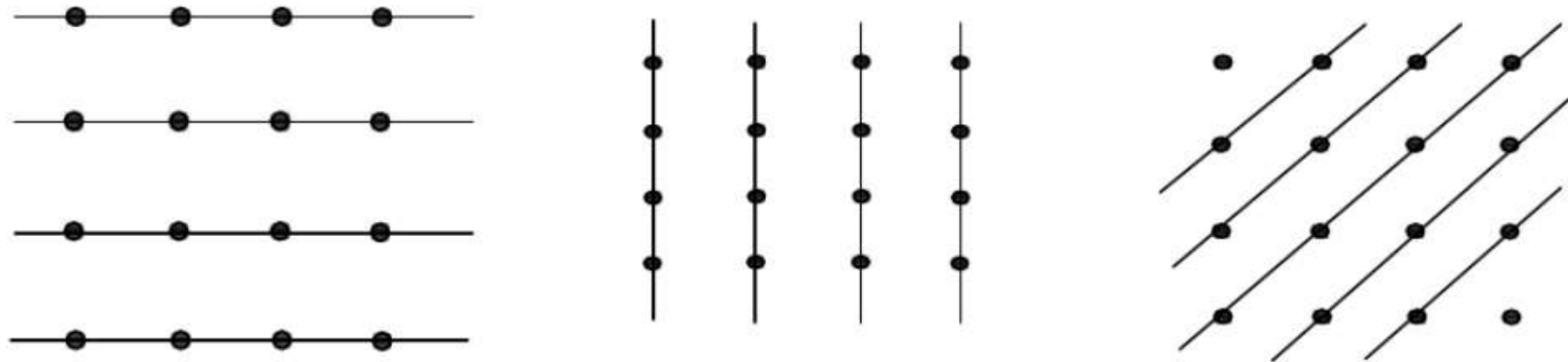

Fig 5

f) Unit cell: The unit cell is the smallest block or geometric figure from which the entire crystal is built up by repetition in three dimensions.

- *The unit cell may be considered as the brick of a wall where the latter represents the crystal. We know that, the shape of the wall depends upon the shape and arrangement of the brick. Similarly the shape of the crystal will depend upon the shape of the unit cell and the arrangement of atoms within the unit cell.*

- *Translation: Motion of a body in which all the points in the body follow parallel paths.*

- *Other terms used to represent a unit cell: The unit cell is also known as basic cell or basic unit or fundamental unit or fundamental elementary pattern or building block or lattice unit.*
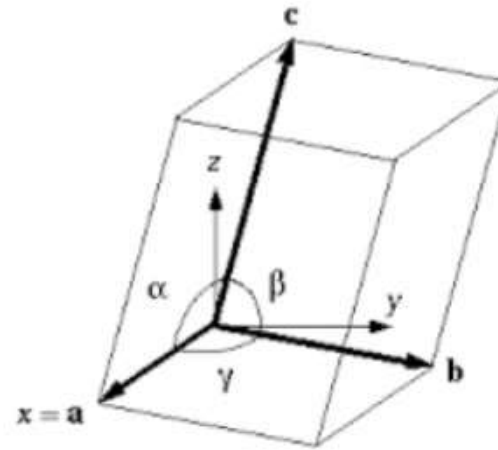
g) Lattice parameters

Fig. 6. Lattice Parameters

The figure 6 shows a unit cell of a three dimensional crystal lattice. *The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.* The intercepts *a*, *b* and *c* are nothing but the edges of the unit cell, (i.e., the distance between two lattice points) which defines the dimensions of a unit cell. *These intercepts are known as its primitives or characteristic intercepts along the axes.* These three quantities *a*, *b* and c are also *called the fundamental translational vectors.* The angles between *(a, b)*, *(b, c)* and *(c, a)* are denoted by γ, α and β respectively.

The three angles (α, β and γ) are called interfacial angles. Both, the intercepts and interfacial angles constitute the lattice parameters of the unit cell.

The form and actual size of the unit cell can be determined if the values of intercepts and interfacial angles are known.

h) Primitive cell P

A primitive cell is the simplest type of unit cell which contains one lattice point per unit cell (contains lattice points at its corner only).

Example: Cubic cell.

If there is more than one lattice point it is called a non-primitive cell.

Example: BCC and FCC contain more than one lattice point per unit cell.

If the number of lattice points per unit cell is two (BCC), three and four (FCC) the unit cell is called doubly primitive, triply primitive and quadruple primitive respectively.

Multiple Choice Questions

Q.1 A crystal Lattice refers to the geometry of a set of-----

a) Points in Space

b) Atoms in Space

c) Molecules in Space

d) Elements In space

Q.2 A unit Assembly of atoms or molecules identical in composition is called as-

a) Basis

b) Unit cell

c) Lattice

Bravais lattices, Cubic systems: SC, BCC & FCC

Crystal System

On the basis of the lengths and directions of the axes of the symmetry, all the crystals may be classified into seven systems.

The shapes of the unit cells are shown in Fig. Of these seven crystal systems, the cubic system is the simplest and most symmetrical in which $a = b = c$ and $\alpha = \beta = \gamma = 90°$. It is interesting to note that more than half of the naturally occurring crystals belong to the cubic system.

According to the different values of the lattice parameter, seven crystal systems can be formed as follows:

S. No.	Crystal System	Basic Vectors	Interfacial Angles
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
2.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$
3.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
4.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
5.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
6.	Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

Bravais Space Lattice:

In 1845, Bravais showed that there are only 14 ways of arranging points in space so that the environment looks the same from each point. These 14 lattices are called Bravais space lattices, each of which has the same collection of symmetry elements at the lattice points. They are shown below
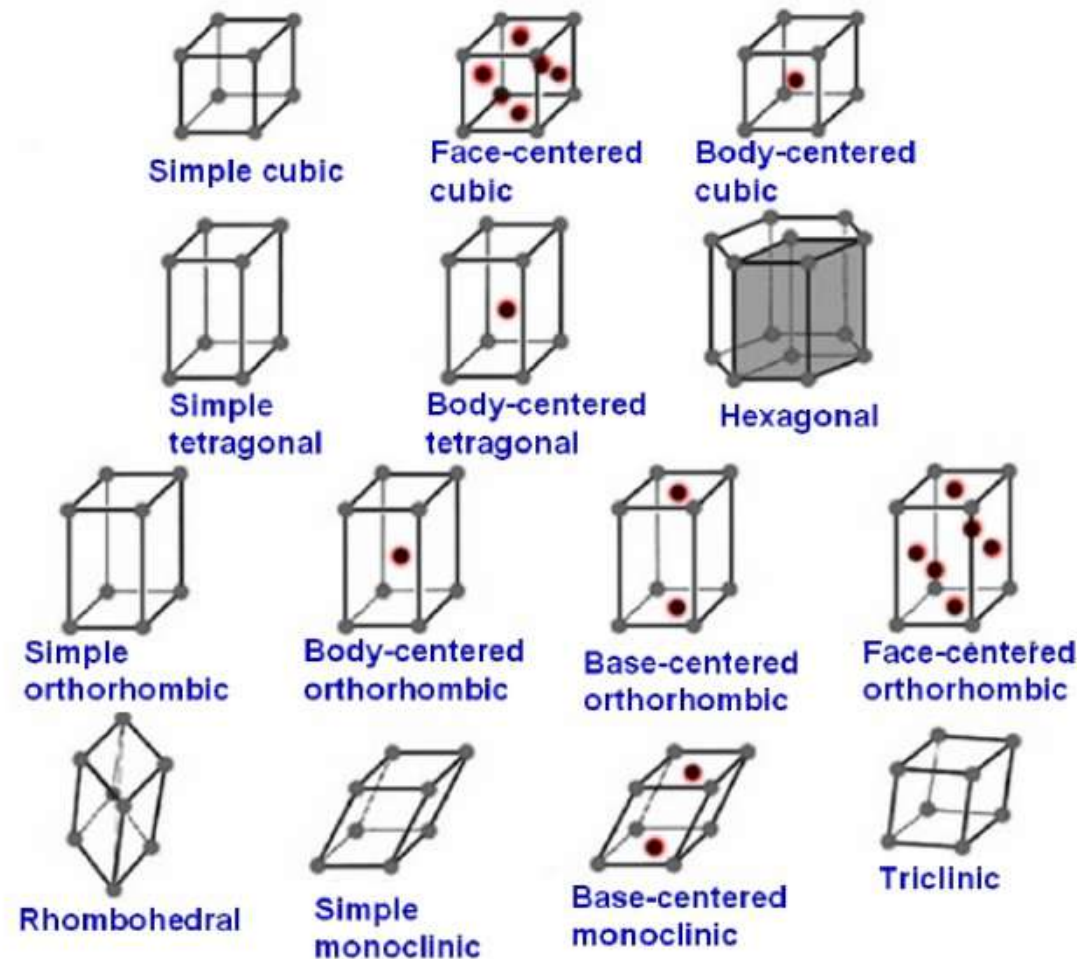

Fig.7. Bravais Lattices

For cubic system, three types of Bravais lattices are possible, viz.:

(i) Simple cubic (SC) (e.g. Palladium)

(ii) Body-centered cubic (BCC) (e.g. Molybdenum)

(iii) Face-centered cubic (FCC) (e.g. Ni, Cu, NaCl)

Some Important terms:

1. **Number of atoms per unit cell or Effective number**

   The total number of atoms present in a unit cell is known as number of atoms per unit cell.

2. **Co-ordination number**

   Co-ordination number is the number of nearest neighbours directly surrounding a given atom.

3. **Atomic radius**

   It is defined as half of the distance between to nearest neighbours in a crystal of a pure element.

   It is usually expressed in terms of cube edge *a.* Any two nearest neighbouring atoms touch each other.

4. **Atomic packing factor (Packing density or Density of packing)**

   It is defined as the ratio of the volume of atoms per unit cell to the total volume occupied by the unit cell.

5. **Voids:**

The space in the unit cell which is left unoccupied by atoms is called as the void

$$void = (100 - APF \text{ in } \%)$$

(a) Simple Cubic Structure:
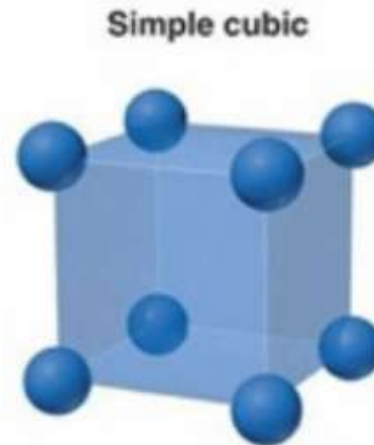

Simple cubic

Fig.8

In simple cubic crystal structure the atoms or molecules are located at the each corner of the cube or the unit cell. Thus there is only one basis atom per unit cell. As it is the cubic crystal structure the lattice constants along the crystallographic axes are equal.

Thus we have $a = b = c$

Also as the for the cubic structure one should have

$\alpha = \beta = \gamma = 90^0$

i. Number of atoms per unit cell:

$\frac{1}{8}$ atom
at 8 corners

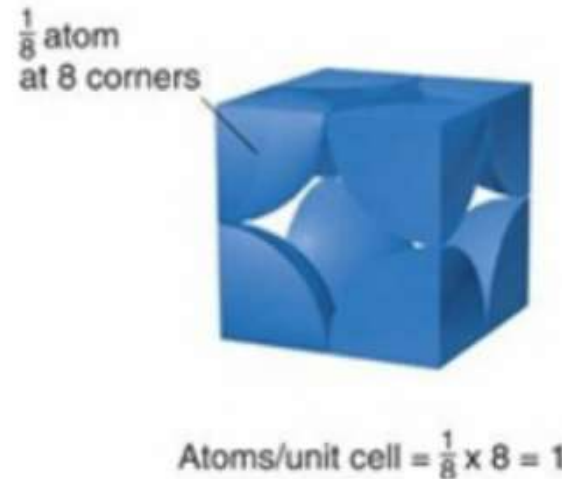Atoms/unit cell $= \frac{1}{8} \times 8 = 1$

Fig.9

The figure 9 shows the unit cell of a simple cubic structure. In this case, there are only 8 atoms, one at each corner of the cube or the unit cell. In actual crystals, each and every corner atom is shared by 8 adjacent unit cells. Therefore, each and every corner atom contributes $1 / 8^{th}$ of its part to one unit cell. Total number of corner atoms $N_c = 8$

∴ The total share of the entire corner atoms/unit cell $= 8 \times 1 / 8 = 1$.

∴ Number of atoms/unit cell $= 1$

In other words, the effective number of lattice points in a simple cubic structure is one. Thus, simple cubic is a primitive cell.

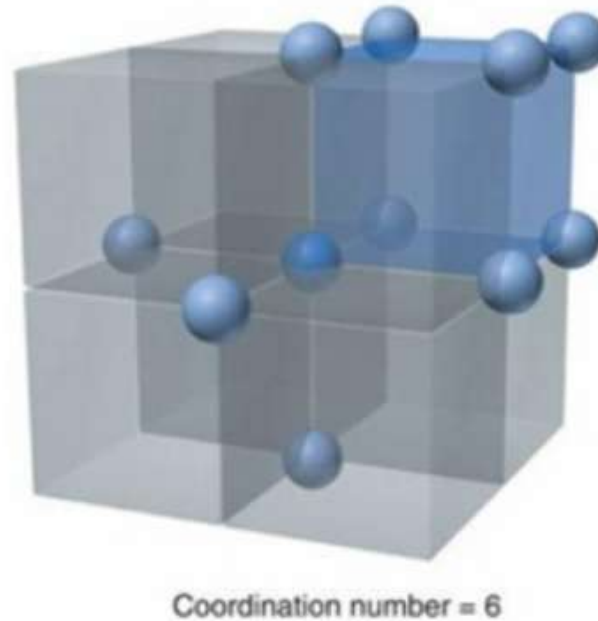## ii.   Co-ordination Number:

Coordination number = 6

Fig.10

Simple cubic unit cell consists of 8 corner atoms. Let us consider any one corner atom as shown in figure 10. For the atom at the centre there are 4 nearest neighbours in its own plane (horizontal plane) and there are 2 more nearest atoms, one directly above and the other one directly below. Except these six atoms all the other atoms lie at greater distances from it. Thus, the coordination number for an atom in simple cubic is 6.

iii. Relation between 'a' and 'r':

Let us consider one face of the simple cubic structure, figure 11. In this structure the atoms touch each other along the edges.
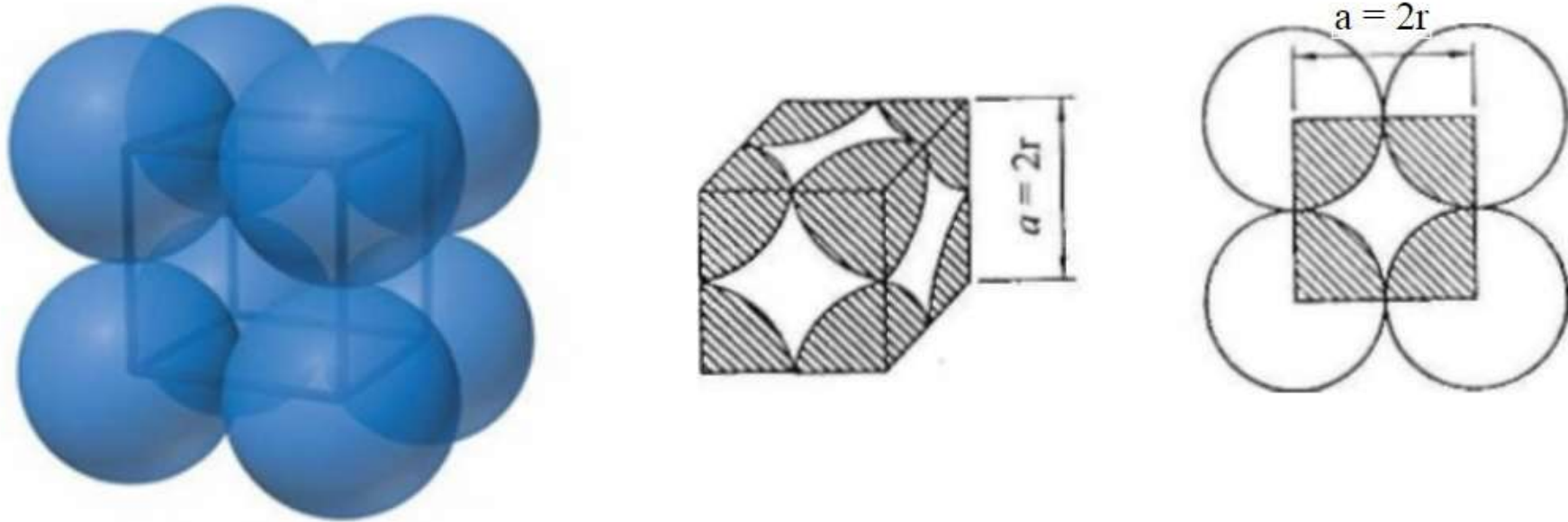

Fig.11: Simple cubic structure

Hence, the nearest neighbour distance is $2r = a$.   Therefore, $r = a/2$.

iv. **Atomic Packing Factor (APF):**

The packing factor or packing density of the simple cubic structure can be calculated as follows:

$$APF = \frac{\text{No. of atoms per unit cell x Volume of one atom}}{\text{Volume of the unit cell}}$$

In simple cubic,

The number of atoms per unit cell = 1

Volume of one atom $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left[\frac{a}{2}\right]^3 \left[\because r = \frac{a}{2}\right]$

Volume of the unit cell $= a^3$

$$APF = \frac{1 \times \frac{4}{3}\pi \left[\frac{a}{2}\right]^3}{a^3}$$

$$APF = \frac{\pi}{6} = 0.52$$

52 % of the volume is occupied by atoms and remaining 48 % volume is vacant.

v. **Void:**

The space in the unit cell which is **left un**occupied by atoms is called as the void

$$\textbf{void} = (100 - APF \text{ in } \%)$$

$$void = (100 - 52) = 48\%$$

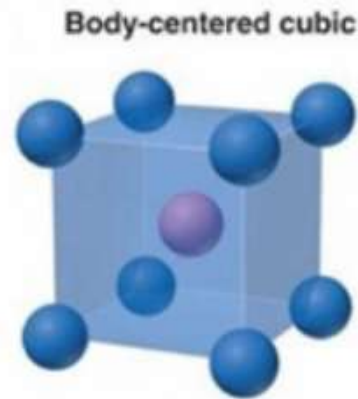## (b) Body Centered Cubic Structure

Fig. 12

In body centered cubic structure, there are 8 atoms at each corner of the unit cell plus one atom at the geometric centre of the unit cell. Thus the corner atom touches the body central atom through the body diagonals. In this way there are two basis atoms, one located at the corner & the other one at the center of the body.

i. Number of Atoms Per Unit Cell:

$\frac{1}{8}$ atom
at 8 corners

1 atom
at center

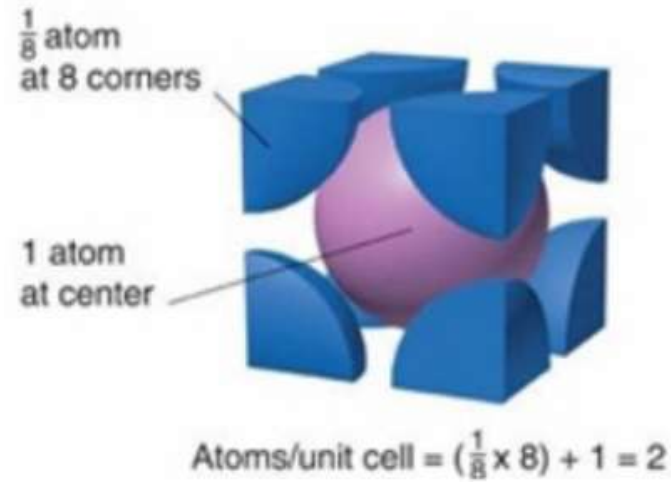Atoms/unit cell = $(\frac{1}{8} \times 8) + 1 = 2$

Fig. 13

In this case, there are 8 atoms one at each corner of the unit cell plus one atom at the centre of the unit cell, figure 10. Each and every corner atom is shared by 8 adjacent unit cells. The atom at the body centre is not shared by any other unit cell. Number of unshared atoms/unit cell = 1.

The total share of all the corner atoms per unit cell is 8 x 1 / 8= 1.

Hence, total number of atoms/unit cell = 1 + 1 = 2

ii. Co-ordination Number:

In this structure, there will be one atom at the body centre and eight atoms at the 8 corners of the unit cell figure 14. Thus, for an atom at the body centre obviously, there are 8 nearest neighbours (corner atoms). Hence, the co-ordination number of an atom in body centered cubic structure is 8. The corner atoms do not touch each other. But, each corner atom touches the body centre along the body diagonal
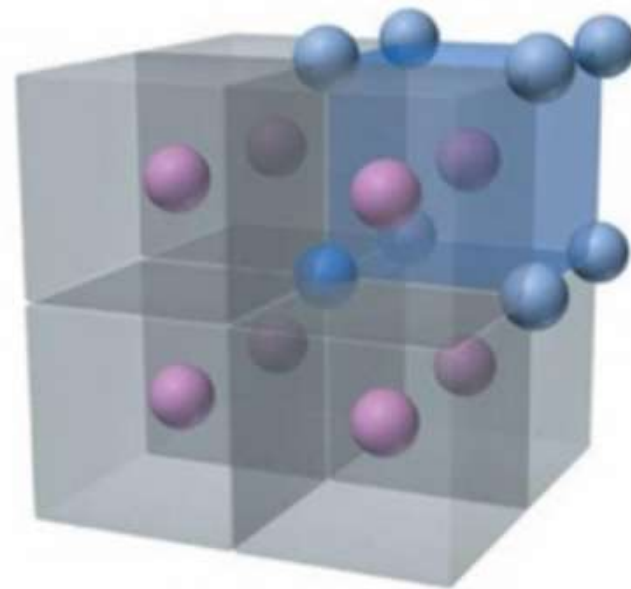
Coordination number = 8

Fig. 14

Alternative method

The coordination number can also be determined in another way as follows.

We know that in a BCC structure, each corner atom is surrounded by eight ether body centered unit cells. Therefore, the nearest adjacent neighbours are the body centered atoms of the eight surrounding unit cells. Thus, the coordination number is 8.

ii. Relation between 'a' and 'r':
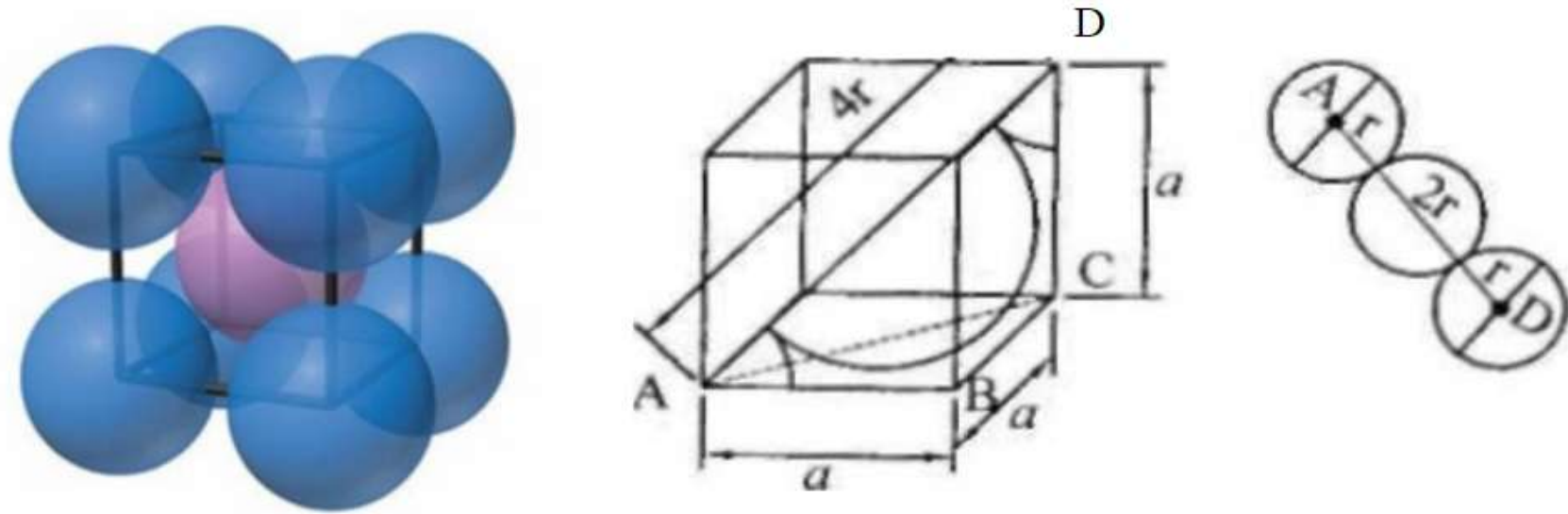
ii. Relation between 'a' and 'r':

Fig.15: Body Centered Cubic structure

In this structure, the corner atoms do not touch each other. But, each corner atom touches the body centered atom along the body diagonal, figure 15. Thus, the diagonal of the cube AD is 4r. But, from the geometry of the cube,

$$(AD)^2 = (AC)^2 + (CD)^2 = (AB)^2 + (BC)^2 + (CD)^2 \ [\because (AC)^2 = (AB)^2 + (BC)^2]$$

$$(AD)^2 = a^2 + a^2 + a^2 = 3a^2 \ [\because AB = BC = CD = a]$$

$$AD = a\sqrt{3} \ ; But \ AD = 4r$$

$$\therefore 4r = a\sqrt{3} \quad OR \quad r = a\frac{\sqrt{3}}{4}$$

iii. Atomic Packing Factor (APF):

The packing factor or packing density of the body centered cubic structure can be calculated as follows:

$$APF = \frac{\text{No. of atoms per unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}}$$

The no of atoms per unit cell = 2

∴Volume of 2 atoms $= 2 \times \frac{4}{3}\pi r^3 = \frac{8\pi}{3}\left[\frac{a\sqrt{3}}{4}\right]^3 = \pi a^3 \frac{\sqrt{3}}{8} \left[\because r = a\frac{\sqrt{3}}{4}\right]$

Volume of the unit cell = a^3

$$APF = \frac{\pi a^3 \frac{\sqrt{3}}{8}}{a^3}$$

∴ APF = 0.68

∵ 68% of the volume is occupied by atoms and remaining 32 % volume is vacant.

iv. Void:

The space in the unit cell which is **left un**occupied by atoms is called as the void

$$\textbf{void} = (100 - \text{APF in \%})$$

$$void = (100 - 68) = 32\ \%$$
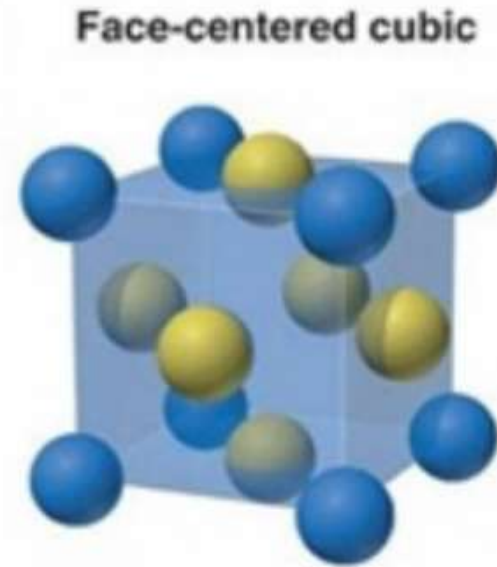
(c) Face Centered Cubic Structure

Fig.16

In face centered cubic structure, there are 8 atoms at each corner of the unit cell. Also we have in addition one atom at the center of the each face of the cube. Thus the corner atom touches the face central atom along the face diagonals. In this way there are two basis atoms, one located at the corner & the other one at the center of the face.
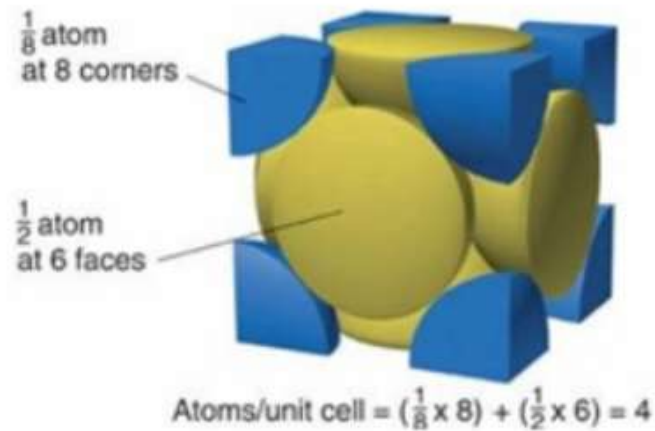
i. Number of atoms per unit cell:

Fig.17

In this case, there are 8 atoms, one at each corner of the unit cell and six atoms at the centers of six faces of unit cell figure 17. The total share of all the corner atoms per unit cell is $8 \times 1/8 = 1$.

Now, consider the atoms at the face centre of the unit cell. Each such atom is shared by only two unit cells, which lie on either side of the plane in which the atom is located. The total share of all the face centered atoms per unit cell = $6 \times 1/2 = 3$. Hence, the total number of atoms/unit cell is $1 + 3 = 4$.

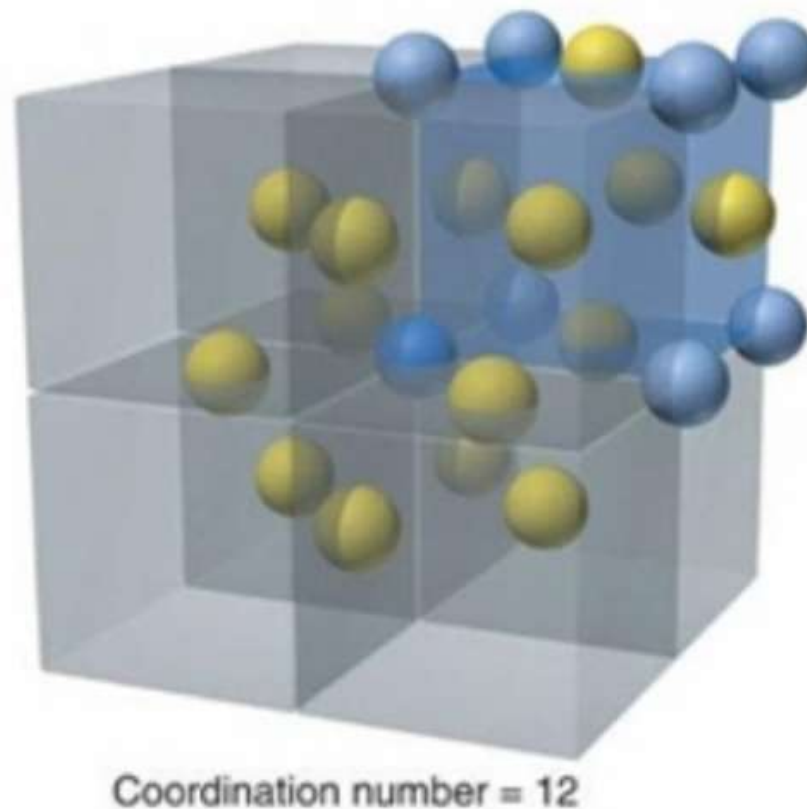## ii.   Co-ordination Number:

Coordination number = 12

Fig.18

In this system, there are 8 corner atoms and six face centered atoms one at the centre of each face. To calculate the coordination number, consider any corner atom (the blue coloured one at the center). In its own plane it has 4 face centered atoms as nearest neighbour. In a plane which lie just above this corner atom, it has 4 more face centre atoms as nearest neighbors' and similarly, in a plane which lie just below this corner atom it has 4 more face centered atoms as nearest neighbours.   The total number of nearest atoms to any corner atoms is 4 + 4 + 4 = 12. Hence, the coordination number is 12.
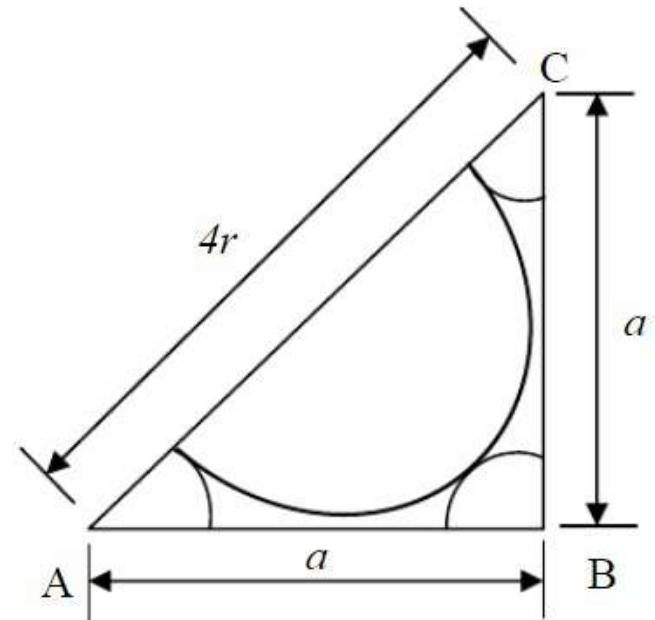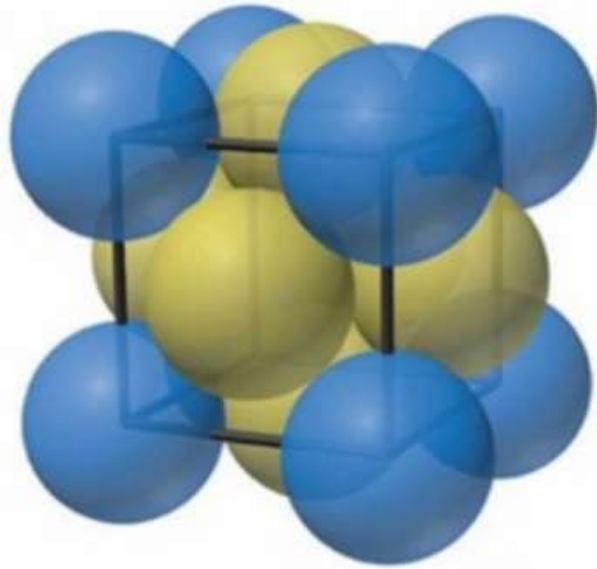
iii. Relation between 'a' and 'r':

Fig.19: Face Centered Cubic structure

In face-centered cubic structure, the atoms touch each other along the diagonal of any face of the cube. The diagonal of the cube AC is 4r.

But, from the geometry of the figure

$$(AC)^2 = (AB)^2 + (BC)^2 = a^2 + a^2 = 2a^2$$

$$\therefore AC = a\sqrt{2} \qquad\qquad [\because AC = 4r]$$

$$4r = a\sqrt{2}$$

Hence $\qquad\qquad r = a\dfrac{\sqrt{2}}{4}$

iv. Atomic Packing Factor (APF):

The packing factor or packing density of the face centered cubic structure can be calculated as follows:

$$APF = \frac{No.\ of\ atoms\ per\ unit\ cell \times Volume\ of\ one\ atom}{Volume\ of\ the\ unit\ cell}$$

The no of atoms per unit cell $= 4$

$$\therefore Volume\ of\ 4\ atoms = 4 \times \frac{4}{3}\pi r^3 = \frac{16\pi}{3}\left[\frac{a\sqrt{2}}{4}\right]^3 = \pi a^3 \frac{\sqrt{2}}{6}\ \left[\because r = a\frac{\sqrt{2}}{4}\right]$$

Volume of the unit cell $= a^3$

$$APF = \frac{\pi a^3 \frac{\sqrt{2}}{6}}{a^3} = \pi\frac{\sqrt{2}}{6}$$

$$\therefore APF = 0.74$$

$\therefore$ 74% of the volume is occupied by atoms and remaining 26 % volume is vacant

v. Void:

The space in the unit cell which is left unoccupied by atoms is called as the void

$$\mathbf{void} = (100 - APF\ in\ \%)$$
$$void = (100 - 74) = 26\ \%$$

Relation between Lattice Constant and Density

Consider a cubic crystal.

Let, the lattice constant of the cell = a

The number of atoms per unit cell = n

The atomic weight of the crystalline substance or compound = A

The density of the unit cell = ρ

The Avogadro's number = N

[Avogadro's number gives the number of molecules per kilogram mole of the substance]

$\therefore$ Mass of each Atom = $\frac{A}{N}$

Hence, Mass of n Atoms (i.e., mass in each unit cell) = $\frac{A}{N}n$

$\therefore$ Density of a unit cell is

$$\rho = \frac{\text{Mass of a unit cell}}{\text{Volume of a unit cell}}$$

$$\rho = \frac{A \times n}{Na^3}$$

$$a^3 = \frac{An}{N\rho}$$

$$a^3 = \frac{Atomic\ weight \times Number\ of\ atoms\ per\ unit\ cell}{Avagadro\ Number \times Density}$$

Hence, using the above equation, we can calculate the lattice constant 'a'.