1. Crystallography

Crystal structures: BCC, FCC and HCP - Directions and planes - Linear and planar densities- Crystal imperfections- Edge and screw dislocations - Grain and twin boundaries - Burgers vector and elastic strain energy - Slip systems, plastic deformation of materials - X-ray diffraction – Bragg's law - Powder X-ray diffraction.

1.1. Introduction

Materials differ from one another in their properties. 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 difference in properties of the various solids are due to their structures. The behaviour of a solid material is related to its crystal structure.

1.2. Classification

Based on the crystal structure, the solid materials are classified as Crystalline and non-crystalline materials. The former is one in which the atoms are arranged in regular and systematical manner while the latter is arrange din an irregular manner.

Crystalline material is either a single crystal or polycrystals. Here, single crystal refers to the material is composed of single crystal. While the poly crystal consists of collection of crystals separated by well-defined boundaries such as each of the crystal is oriented in different direction.

Eg: Metallic crystals such as Iron, cooper, aluminium, tungsten, etc., and non-metallic crystals such as carbon, germanium, silicon, etc.,

The non-crystalline materials is also referred as amorphous material. Eg: Glass, rubber and plastics.

1.3. Basic crystallographic terms

Crystals

Crystal is a regular polyhedral form bounded by smooth surfaces, which is formed by chemical compound under the action of its interatomic forces, when passing from the state of liquid (or) gas to that of a solid, under suitable conditions.

The phase change from liquid (or) gas to solid is called crystallization.

Lattice

Lattice is defined as an array of points. fig.1.1 (a) which are imaginarily kept to represent the position of atoms in the crystal such that every lattice point has got the same environment as that of the other and hence one lattice point cannot be distinguished from the other lattice point. It is an imaginary concept.

Space lattice (or) crystal lattice

A three dimensional collection of points in space are called space lattice (or) crystal lattice. The environment about any particular point is in every way the same.

Lattice points

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

Lattice Planes

A set of parallel and equally spaced planes in a space lattice, which are formed with respect to the lattice points are called lattice planes.
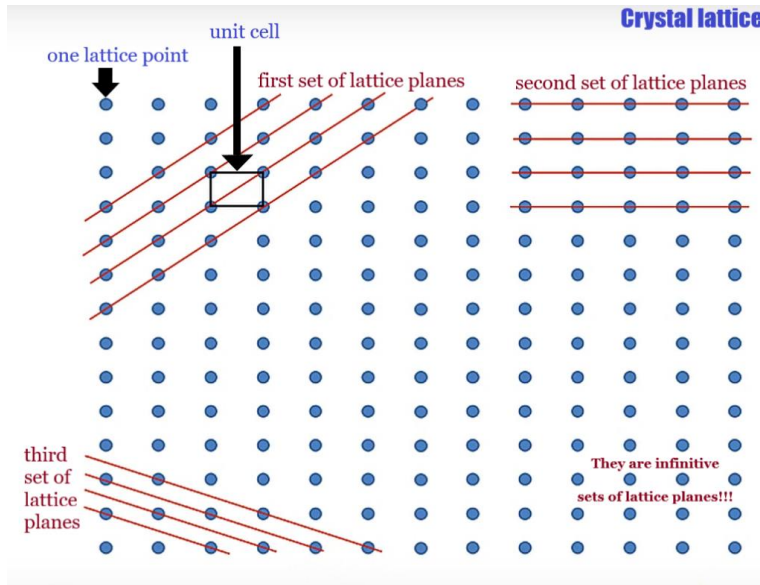

Fig 1.1 (a)

Basis (or) Motif

Basis (or) Motif is an unit assembly of atoms (or) molecules which are identified with respect to the position of lattice points, identical in composition, arrangement and orientation.

Crystal Structure

The crystal structure is formed by the addition of basis to every lattice point of the lattice

i.e., Space lattice + Basis => Crystal structure

basis   (Bravais) lattice   crystal structure
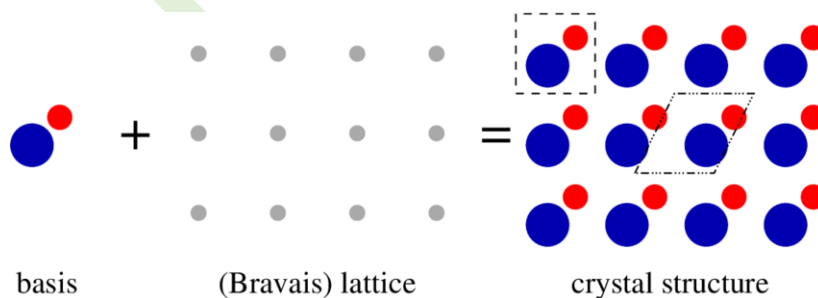
Unit cell

The unit cell is defined as the smallest geometric figure, the translational repetition of which in all over the three dimensions gives actual crystal structure. Fig 1.2 (a) & (b).

(a)   (b)
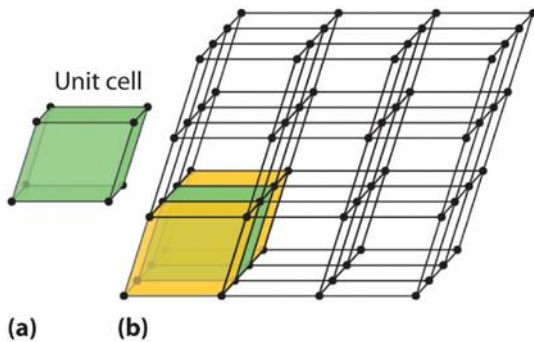
Lattice parameters (or) Unit cell parameters

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 on the axes.

These three quantities a, b and c are also called the fundamental translational vectors (or) axial lengths. The angles between (a, b), (b, c) and (c, a) are denoted by γ, α and β respectively. These three angles (γ, α and β) are called interfacial angles (fig. 1.3a).
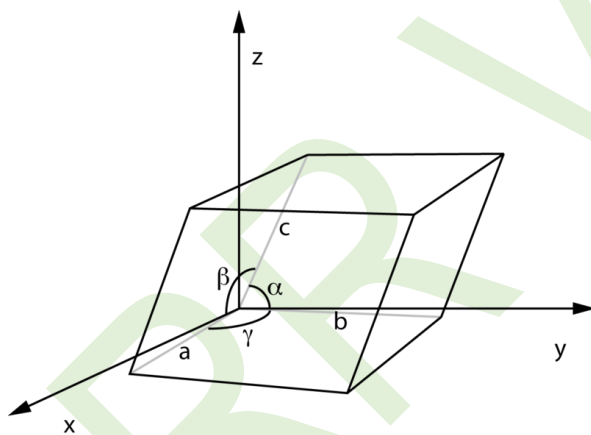

Fig 1.3 (a)

Both the intercepts (a, b, c) and interfacial angles (α, β, γ) constitute the lattice parameters (or) cell parameters of the unit cell.

Primitive cell

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

Example: Simple Cubic (SC)

Non-primitive cell

It there are more than one lattice points in a unit cell, it is called a non-primitive cell.

Example: BCC and FCC contain more than one lattice points per unit cell. Fig. 1.3 (b)
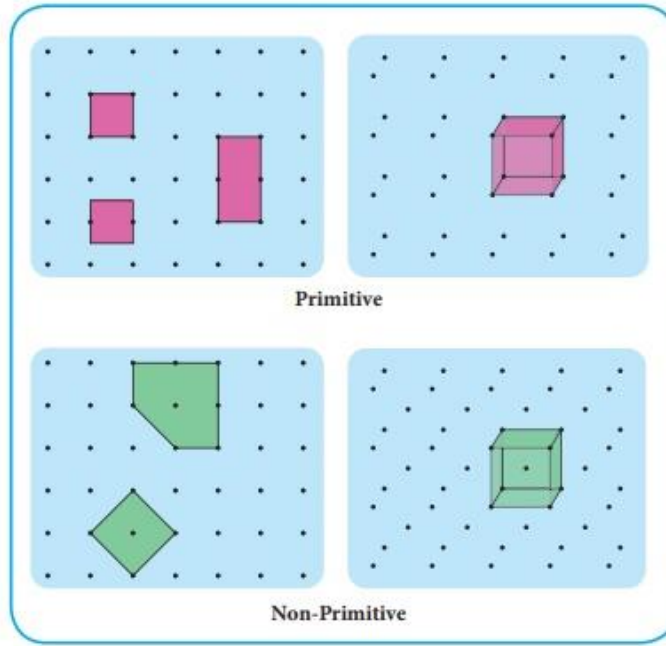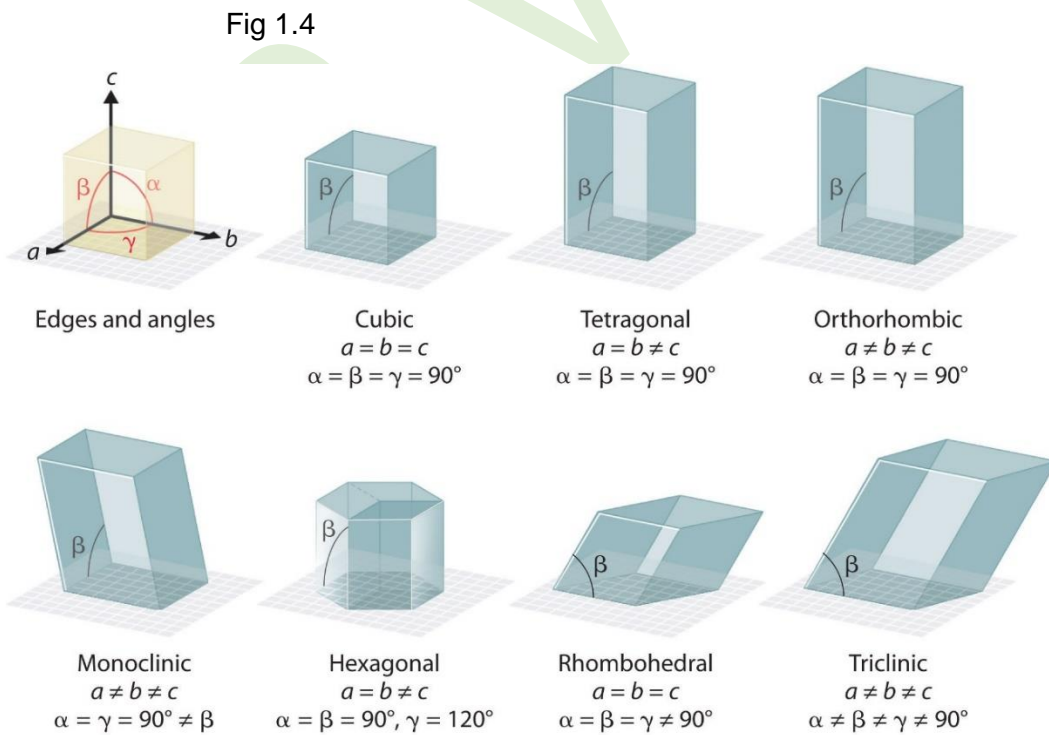
Fig 1.3(b)

1.4. Crystal systems

There are seven crystal systems namely cubic, tetragonal, orthorhombic, monoclinic, triclinic, rhombohedral and hexagonal.

Fig 1.4

Edges and angles	Cubic	Tetragonal	Orthorhombic
	$a = b = c$	$a = b \neq c$	$a \neq b \neq c$
	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$

Monoclinic	Hexagonal	Rhombohedral	Triclinic
$a \neq b \neq c$	$a = b \neq c$	$a = b = c$	$a \neq b \neq c$
$\alpha = \gamma = 90° \neq \beta$	$\alpha = \beta = 90°, \gamma = 120°$	$\alpha = \beta = \gamma \neq 90°$	$\alpha \neq \beta \neq \gamma \neq 90°$

1. Cubic system

Here, all the three axial lengths of the unit cell are equal and they are perpendicular to each other i.e., a = b = c and α= β= γ = 90°.

Example: Iron, Copper, NaCl, CaF_2.

2. Tetragonal system

In this system, two axial lengths of the unit cell are equal and third axial length is either longer or shorter. Al the three axis are perpendicular to eachother. a = b ≠ c and α= β= γ = 90°.

Example: White tin, Indium

3. Orthorhombic system

Here, three axial lengths of the unit cell are not equal but they are perpendicular to eachother. a ≠ b ≠ c and α= β= γ = 90°.

Example: Sulphur, Topaz

4. Monoclinic system

Here, three axial lengths of unit cell are not equal. Two axes are perpendicular to each other and third axis is obliquely inclined. a ≠ b ≠ c and α= β = 90°; γ ≠ 90°

Example: Sodium sulphide, Ferrous sulphate

5. Hexagonal system

Here, two axial lengths of unit cell are equal and lying in one plane at angle 120° with each other. The third axial length (vertical) is either longer or shorter than other two and it is perpendicular to this plane. a = b ≠ c and α= β= 90° γ = 120°

Example: quartz, Tourmaline

6. Rhombohedral system (Trigonal)

Here, three axial lengths of the unit cell are equal. They are equally inclined to each other at an angle other than 90°. a = b = c and α= β= γ ≠ 90°.

Example: calcite

7. Triclinic system

Here, three axial lengths of unit cell are not equal and all the three axes are inclined obliquely to each other. a ≠ b ≠ c and α ≠ β ≠ γ ≠ 90°

Example: Copper sulphate, Potassium dichromate

1.5. Bravais Lattice

Bravais introduces the concept of space lattice. He showed that there are only 14 ways of arranging points in space such that the environment looks same from each point.

Hence, there are only 14 types of space lattices which can be possibly developed from out '7' crystal systems as shown in table. We can understand that simple (P) is related to primitive cell which means, lattice points are at all 8 corners of the unit cell. Body centred (I) has lattice points at all 8 corners of the unit cell and one lattice point at the body centre. Face centred (F)

has lattice points at all 8 corners of the unit cell and one lattice point at each face centre of 6 faces of the cube. Base centred (C) has lattice points at all 8 corners of the unit cell and 2 lattice points each at the centre of two faces opposite to each other.

These 14 types of space lattice are known as Bravais lattices.

BRAVAIS LATTICE

| S.No	Crystal System	Bravais Lattice	Unit cell Parameters	Examples
1.	Cubic	Simple (P) Body centered (I) Face centered (F)	$a = b = c$ $\alpha = \beta = \gamma = 90^o$	NaCl, CaF_2 $NaClO_3$
2.	Tetragonal	Simple (P) Body centered (I)	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$	$NiSO_4$, SnO_2 Indium, White tin
3.	Orthorhombic	Simple (P) Base centered(C) Body centered (I) Face centered (F)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$	KNO_3, $BaSO_4$ $MgSO_4$, Sulphur Topaz
4.	Monoclinic	Simple (P) Base centered (C)	$a \neq b \neq c$ $\alpha = \beta = 90^o : \gamma \neq 90^o$	Na_2So_4, $FeSo_4$ NO_2SO_3
5.	Triclinic	Simple (P)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^o$	$CuSo_{4'}$, $K_2Cr_2O_7$
6.	Trigonal (Rhombohedral)	Simple (P)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^o$	$CaSo_4$, Bi, Sb Calcite
7.	Hexagonal	Simple (P)	$a = b \neq c$ $\alpha = \beta = 90^o$ $\gamma = 120^o$	Tourmaline Quartz
	Total Bravais lattice	14		

CUBIC
$a = b = c$
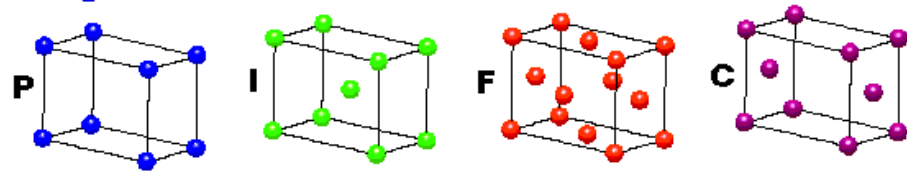$\alpha = \beta = \gamma = 90°$
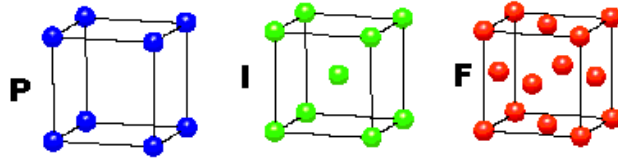
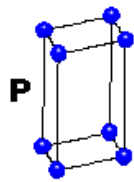**TETRAGONAL**
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
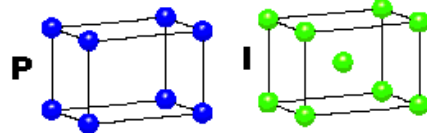
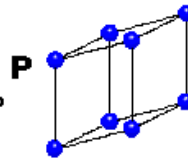**ORTHORHOMBIC**
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

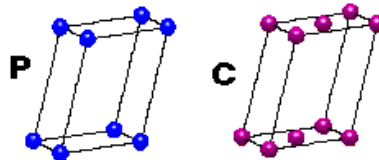**TRIGONAL**
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

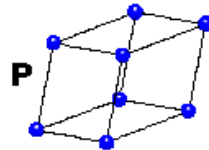**MONOCLINIC**
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Fig. 1.5

1.6. Characteristics of unit cell

Assuming one atom to one lattice point, the unit cell is characterized by the following parameters:

    i. Number of atoms per unit cell
    ii. Coordination number
    iii. Nearest neighbouring distance
    iv. Atomic radius
    v. Packing factor

(i) **Number of atoms per unit cell (or) effective number**

The total number of atoms present in (or) shared by a unit cell is known as number of atoms per unit cell.

(ii) Coordination number

It is the number of nearest atoms directly surrounding a particular atom in a crystal. The coordination number gives the information about the packing of atoms in a structure. It tells whether the crystal structure is closely packed or loosely packed. If the coordination number

is high, then the structure is more closely packed. If it is low, then the structure is loosely packed.

(iii) Nearest neighbouring distance (2r)

It is the distance between the centres of two nearest neighbouring atoms. It is expressed in terms of the length of edge of the unit cell 'a' and it is *2r* in simple cubic
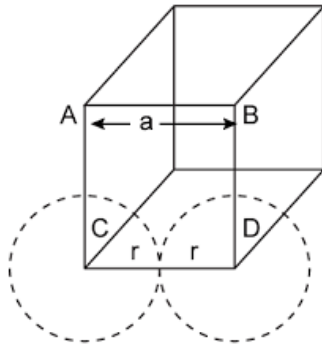

Fig. 1.6

(iv)Atomic radius (r)

It is half of the distance between two nearest neighbouring atoms in the crystal. It is denoted by *'r'*. It is usually expressed in terms of cube edge *'a'* (lattice parameter). For a simple cubic unit cell, the atomic radius is $r = \dfrac{a}{2}$

(v) Packing factor

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total volume of the unit cell (V)

i.e., Packing Factor = $\dfrac{\text{Volume occupied by the total number of atoms per unit cell} = v}{\text{Total Volume of the unit cell} \qquad\qquad V}$

i.e., PF = $\dfrac{\text{Number of atoms per unit cell x Volume of one atom}}{\text{Total volume of the unit cell}}$

It is also known as *density of packing*

The packing factor tells us how closely the atoms are stacked in the unit cell. A high packing factor indicates that atoms are very closely packed and therefore there is very little unoccupied space.

On the other hand, a low packing factor indicates loose packing of atoms and hence there is relatively more unoccupied space.

1.7. Crystal structures – BCC, FCC and HCP

BODY CENTRED CUBIC STRUSTURE (BCC)

In this type of crystal structure the unit cell has one atom at each corner of the cube and one at body center of the cube which gives its total contribution to the unit cell. Fig .1.7. shows the arrangement of lattice points in a BCC unit cell
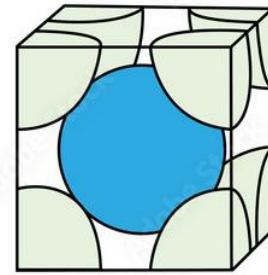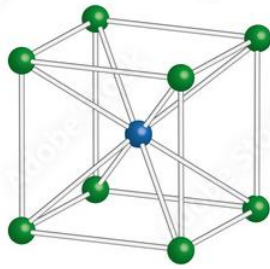
Fig. 1.7

Let us determine the characteristics of the BCC structure:

Number of atoms per unit cell (or) Effective Number

The total number of atoms present in (or) shared by an unit cell is known as number of atoms per unit cell

Number of atoms per unit cell:

Each and every corner atom is shared by 8 adjacent unit cells.

$\therefore$ The total number of corner atoms per unit cell = $\dfrac{1}{8} \times 8 = 1$

Number of body centered atoms per unit cell:

The body centered atom is shared by that particular unit cell alone and is not shared by any other unit cell.

$\therefore$ The number of body centered atoms per unit cell = $\dfrac{1}{1} \times 1 = 1$

$\therefore$ Total number of atoms = Total Number of corner atoms +

Per unit cell in BCC = Total number of body centered atoms = 1 + 1 = 2
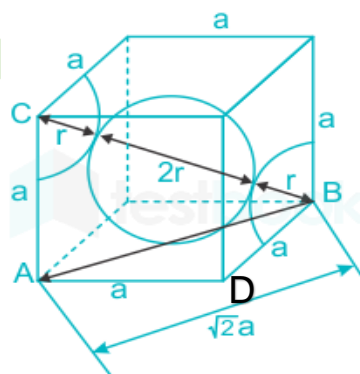
Atomic radius

Fig.1.8.

In BCC structure, the corner atoms do not touch each other. But each corner atom touches the body centered atom along the body diagonal as shown in fig 1.7. Therefore the two corner atoms (B&C) situated at the opposite ends can be joined by drawing a diagonal as shown in figure 1.8. From the geometry of the fig.1.8, we can write

$(BC)^2 = (BA)^2 + (AC)^2$

$\qquad = (BD)^2 + (DA)^2 + (AC)^2$ (or)

$(BC)^2 = a^2 + a^2 + a^2 = 3a^2$

$BC = a\sqrt{3}$ (1)

From fig. 5.11 the diagonal of the cube $BC = 4r$ (2)

∴ From equations (1) & (2), we can write $4r = a\sqrt{3}$

(or) Atomic radius $r = \dfrac{a\sqrt{3}}{4}$

Co-ordination number

Co-ordination number is the number of nearest neighbouring atoms to a particular atom.
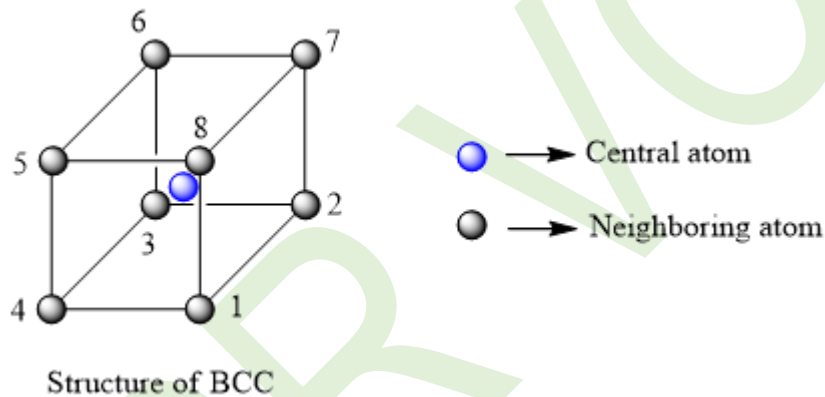

Structure of BCC

Fig. 1.9.

In BCC structure, there will be one body centered atom at the center of the unit cell and eight atoms at the 8 corners of the unit cell as shown in fig.1.9. The corner atoms do not touch each other. But each corner atom touches the body centered atom along the body diagonal. Thus, for an atom X at the body centre obviously, there are 8 nearest neighbors (corner atoms).

Hence the coordination number for body centered cubic is 8.

Atomic Packing Factor (APF)

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total number of the unit cell (V).

In body centered cubic structure,

The number of atoms per unit cell = 2

$\therefore$ Volume of 2 atoms (Spherical) $= 2 \times \dfrac{4}{3} \pi r^3$

We know the radius of atom in BCC is $r = \dfrac{a\sqrt{3}}{4}$

$\therefore$ Volume occupied by the atoms per unit cell (v) $= \dfrac{8\pi}{3} \left[\dfrac{a\sqrt{3}}{4} \right]^3 = \pi a^3 \dfrac{\sqrt{3}}{8}$

Volume of the unit cell for a cubic system (V) $= a^3$

$\therefore$ Atomic Packing Factor (APF) $= \dfrac{\pi a^3 \dfrac{\sqrt{3}}{8}}{a^3}$

(or) $APF = \pi \dfrac{\sqrt{3}}{8} = 0.68$

Therefore, we can say that 68% volume of the unit cell of BCC is occupied by atoms and remaining 32% volume is vacant.

Thus the packing density is 68%

Since the packing density is greater than simple cubic, it has tightly packed structured, when compared to SC.

Examples: Tungsten, Chromium and Molybdenum

Face Centred Cubic Structure (FCC)

In this type of crystal structure, the unit cell has one atom at each corner of the cube and one atom at the centre of each face. This structure is closely-packed because each atom has 12 nearest neighbours. This type of structure is more common in metals.
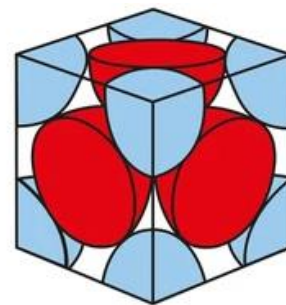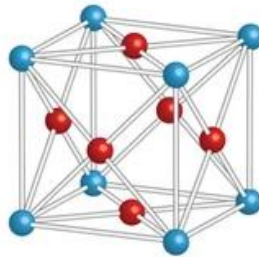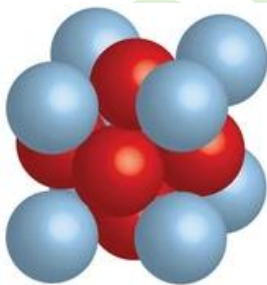

Fig. 1.10

Number of atoms per unit cell (or) Effective number

The total number of atoms present in (or) shared by a unit cell is known as number of atoms per unit cell.

Number of corner atoms per unit cell:

Each and every corner atom is shared by 8 adjacent unit cells.

$\therefore$ The total number of corner atoms per unit cell $= \dfrac{1}{8} \times 8 = 1$

Number of face centered atoms per unit cell:

Each face centered atom is shared by only two unit cells, which lie on either side of the atom. Similarly we have six face centered atoms in a unit cell.

$\therefore$ The total number of face centered atoms per unit cell $= \dfrac{1}{2} \times 6 = 3$

$\therefore$ Total number of atoms   = Total Number of corner atoms +

  per unit cell in FCC Total number of face centered atoms   = 1 + 3 = 4

Atomic radius

In FCC structure, the corner atoms do not touch each other. But each corner atom touches the face centered atoms along the **diagonal of the face of the cube** as shown in fig. 1.11. Therefore, the two corner atoms (A and C) situated at the opposite ends of the same face can be joined by drawing a diagonal as shown in fig.1.11.
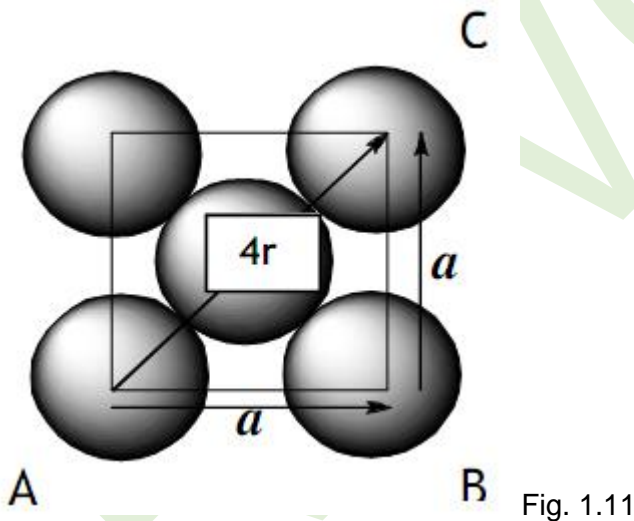

Fig. 1.11

From the geometry of the fig.5.13. We can write

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

$$= a^2 + a^2$$

$$(AC)^2 = 2a^2$$

$$\therefore AC = a\sqrt{2} \tag{1}$$

But from fig.5.14 the diagonal of the cube

$$AC = 4r \qquad\qquad (2)$$

$\therefore$ From equations (1) and (2) we can write $4r = a\sqrt{2}$

$\therefore$ Atomic radius $r = \dfrac{a\sqrt{2}}{4}$

Co-ordination Number

Co-ordination number is the number of nearest neighbouring atoms to a particular atom.
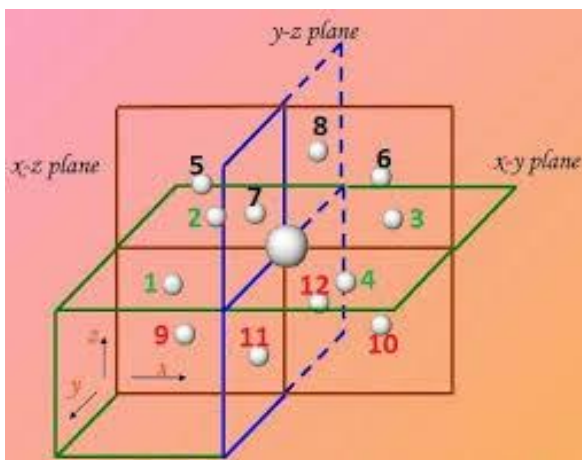
Fig 1.12

In this system, there are 8 corner atoms, and six face centered atoms one at the center of each face. To calculate the coordination number, for FCC, let us consider a XY plane as shown in fig. 1.12. in XY plane it has 4 face centered atoms (1,2,3,4) as nearest neighbours.

In a YZ plane which lie just above this corner atom, it has 4 more face centered atoms (5,6,7,8) as nearest neighbours and similarly in a XZ plane which lie just below this corner atom it has 4 more face centered atoms, (9,10,11,12) as nearest neighbours. The total number of nearest atoms to any corner atom is 4+4+4=12.

Hence the coordination number for face centered cubic is 12.

Atomic Packing Factor (APF)

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total volume of the unit cell (V).

In face centered cubic structure,

The number of atoms per unit cell =4

We know the radius of the atom in FCC $r = \dfrac{a\sqrt{2}}{4}$

$\therefore$ Volume occupied by the atoms per unit cell (v) $= 4 \times \dfrac{4}{3}\pi r^3 = \dfrac{16}{3}\pi \left[a\dfrac{\sqrt{2}}{4} \right]^3 = \dfrac{\pi a^3 \sqrt{2}}{6}$

Volume of the unit cell for a cubic system (V) = a^3

$\therefore$ Atomic packing factor (APF) $= \dfrac{\dfrac{\pi a^3 \sqrt{2}}{6}}{a^3} = \pi \dfrac{\sqrt{2}}{6}$

$$APF = 0.74$$

Therefore, we can say that 74% volume of the unit cell of FCC is occupied by atoms and remaining 26% volume is vacant.

Thus, the packing density is 74%

Since the packing density is very high, the FCC structure has closely (or) tightly packed structure.

Examples: Copper, aluminium, nickel, gold, led and platinum.

Packing fraction of FCC = $\sqrt{2}$ x Packing fraction of SC

Hexagonal Closed Packed Structure

(c) hexagonal close packing

unit cell

atom centres
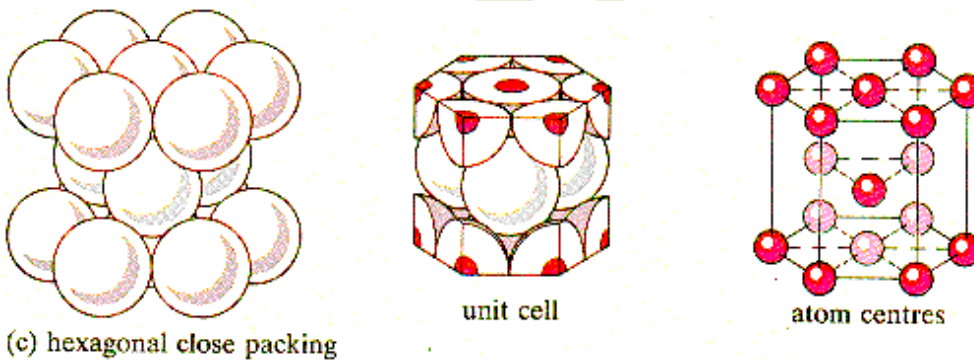
Fig. 1.13

In this type of crystal structure, the unit cell has one atom at each of the twelve corners of the hexagonal crystal, one atom at the center of the two hexagonal faces and three atoms symmetrically arranged in the body of the cell.

This structure is called close packed structure. Each atom has twelve nearest neighbours, six in its plane, and three in the plane above and three in the plane below. Metallic crystals usually have closed packed structure.

The unit cell of hexagonal close packed structure is shown in Fig.1.14. There are three layers of atoms in it. At the bottom layer (B_L) the central atom has six nearest neighbouring atoms in the same plane. Further the middle layer (M_L) which is at a distance c/2 from the bottom layer has three atoms as shown in Fig.1.16. Top layer (T_L) is similar to the bottom layer in the arrangement of atom and it is at a distance from the bottom layer.

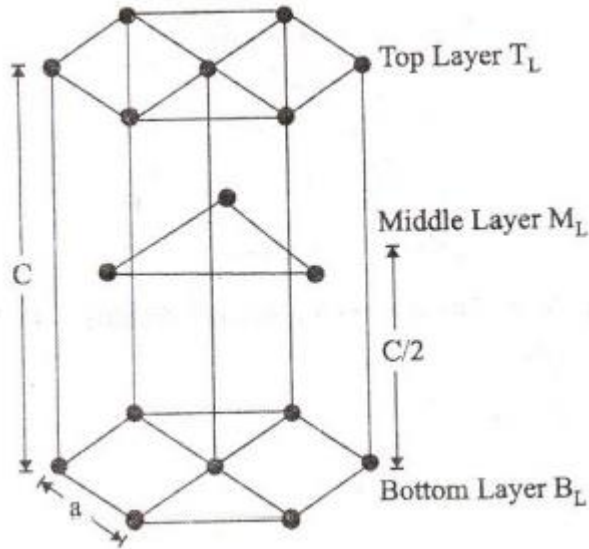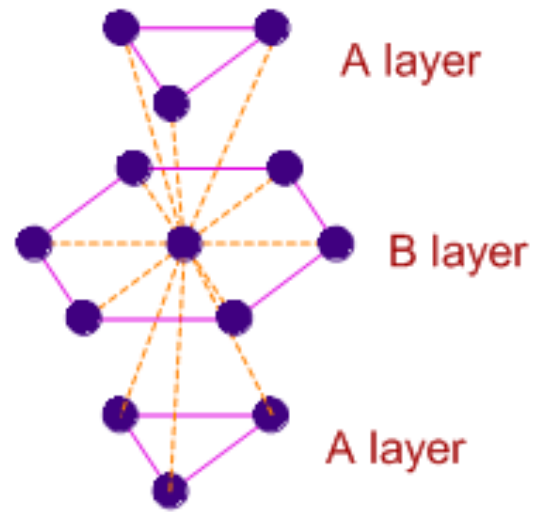Fig. 1.14   Fig. 1.15

Number of atoms per unit cell

$\therefore$ The number of corner atoms per unit cell = $\frac{1}{6} \times 12 = 2$

Number of base centered atoms per unit cell:

Each base atom is shared by two unit cells as shown in figure 1.14. Similarly we have two base centered atoms in an unit cell.

$\therefore$ The number of base centered atoms per unit cell = $\frac{1}{2} \times 2 = 1$

Number of middle layer atoms per unit cell:

The 3 atoms situated at the middle layer, within the body of the unit cell are fully contributing to that particular unit cell alone i.e., they are not shared by any other unit cells.

$\therefore$ The total number of middle layer atoms per unit cell = 3

$\therefore$ The total number of atoms per unit cell in HCP structure (N) = Number of corner atoms +

Number of Base atoms +

Number of middle layer atoms

i.e., **N = 3+2+1 = 6 atoms**

Atomic radius

Consider any two corner atoms in a hexagon closed packed structure. It has to be noted that each and every corner atom touches each other, therefore they are the nearest neighbours. From the below figure 1.18, we can write we can write a = 2r (or) r = a/2

Calculation of c/a ratio:

We know that 'c' is the height of the unit cell of HCP structure and 'a' is the distance between two neighbouring atoms. Now, consider a triangle ABO in the bottom layer (Fig 1.16.)

Here A, B & O are the lattice points and exactly above these atoms at a perpendicular distance 'c'/2 the next layer atoms lies at C,
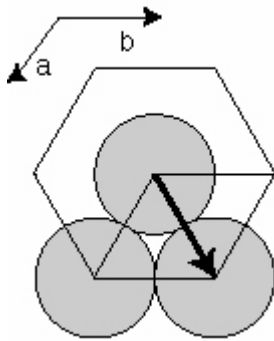
Fig. 1.16   Fig. 1.17

In $\triangle$ ABN, cos 30° = AN / AB
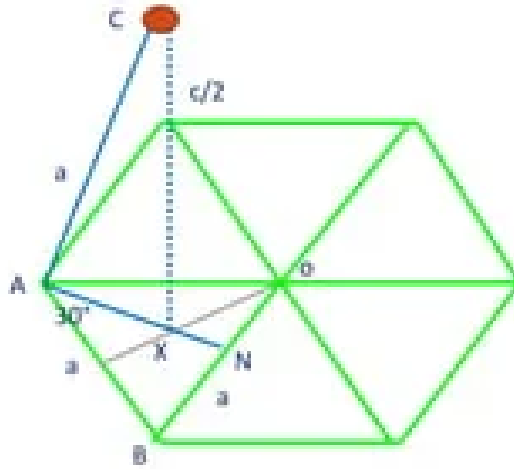
$\therefore$ AN = AB cos 30° = $\dfrac{a\sqrt{3}}{2}$

i.e., AN = $\dfrac{a\sqrt{3}}{2}$ $\left[\because AB = a; \cos 30° = \dfrac{\sqrt{3}}{2}\right]$ (1)

But from Fig 5.18. (b), AX = $\dfrac{2}{3} AN$ (2)

$\therefore AX = \dfrac{2}{3} \times \dfrac{a\sqrt{3}}{2}$ = $\dfrac{2}{\sqrt{3 \times \sqrt{3}}} \times \dfrac{a\sqrt{3}}{2}$

AX = $\dfrac{a}{\sqrt{3}}$ (3)

In $\triangle$ AXC, AC² = AX² +CX²   (4)

Substituting the values for AC =a; AX = $\dfrac{a}{\sqrt{3}}$ and CX = $\dfrac{C}{2}$ in equation (4), we get

a² = $\left[\dfrac{a}{\sqrt{3}}\right]^2 + \left[\dfrac{c}{2}\right]^2$ (5)

(or) $a^2 = \dfrac{a^2}{3} + \dfrac{c^2}{4}$ (or) $\dfrac{c^2}{4} = a^2 + \dfrac{a^2}{3}$

(or) $\frac{c^2}{4} = \frac{2a^2}{3}$ (or) $\frac{c^2}{a^2} = \frac{8}{3}$ (or) $\frac{c}{a} = \sqrt{\frac{8}{3}}$ = 1.633   (6)

Packing Factor

Volume of all atoms in a unit cell (*v*)

Nearest neighbouring distance , 2r = a

Atomic radius r = a/2

Number of atoms per unit cell , *n* = 6

Volume of all 6 atoms in the unit cell *v* = $6 \times \frac{4}{3}\pi r^3$

$$\text{(or) } v = 6 \times \frac{4}{3}\pi \left[\frac{a}{2}\right]^3 = \pi a^3$$

Volume of the unit cell (V)

Area of the base = 6 x Area of triangle AOB

Area of triangle AOB = $\frac{1}{2}$ (BO)(AN)

Substituting for BO = *a* and AY = $\frac{a\sqrt{3}}{2}$ we have

Area of traingle AOB = $\frac{1}{2} \times \frac{a^2\sqrt{3}}{4} = \frac{a^2 3\sqrt{3}}{2}$

Volume of the unit cell of HCP = Base area x Height

$$\therefore V = \frac{a^2 c 3\sqrt{3}}{2}$$

Now, Packing Factor = $\frac{v}{V}$ = $\dfrac{\pi a^3}{\dfrac{a^2 c 3\sqrt{3}}{2}} = \frac{2\pi}{3\sqrt{3}}\left[\frac{a}{c}\right] = \frac{2\pi}{3\sqrt{3}}\left[\frac{a}{c}\right] = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

74% of the volume is occupied by the atoms and the remaining 26% volume is vacant.

Here the packing fraction of FCC and HCP are same and they are known as closely packed structures.

Examples: Magnesium, Zinc, Titanium, Zirconium, beryllium and cadmium.

Properties	BCC	FCC	HCP
Volume of unit cell	a³	a³	$\dfrac{3\sqrt{3}a^2 c}{2}$
No. of atoms per unit cell	2	4	6
Co-ordination number	8	12	12

Atomic radius (r)	$\dfrac{\sqrt{3}a}{4}$	$\dfrac{\sqrt{2}a}{4}$	$\dfrac{a}{2}$
Packing factor	0.68	0.74	0.74
Examples	Iron, Barium, Tungsten	Copper, Aluminium, Nickel	Magnesium, Zinc, Titanium

1.5 Direction in Crystal

It is always useful to have a convention or standardized procedure to specify the directions in a crystal. The procedure of finding the directions inside the crystal is explained below

1. Consider any lattice point that lies on the line as origin.
2. Write down the position vector of the next nearest point on the line in terms of the fundamental translation vector $\vec{a}$, $\vec{b}$ and $\vec{c}$ of the unit cell of the crystal, say,

$$\vec{r} = r_1 \times \vec{a} + r_2 \times \vec{b} + r_3 \times \vec{c}$$

3. Now the components of position vector $\vec{r}$ along the three directions of a, b, c are r_1, r_2, r_3 respectively. Then the crystal direction is denoted by $[r_1, r_2, r_3]$. Let us apply this procedure to find the directions of OP, OQ and OR of an orthorhombic unit cell ($a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$) as shown in figure 1.18 taking O as origin.
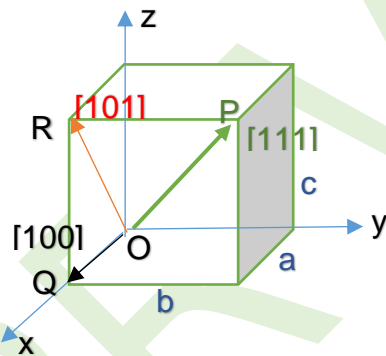
Fig. 1.18

Direction of OP

Position vector of $OP = \overrightarrow{OP} = 1 \times \vec{a} + 1 \times \vec{b} + 1 \times \vec{c}$

Therefore, $r_1 = 1$; $r_2 = 1$; $r_3 = 1$

Hence, direction of OP is represented as [111]

Direction of OQ

Position vector of $OQ = \overrightarrow{OQ} = 1 \times \vec{a} + 0 \times \vec{b} + 0 \times \vec{c}$

Therefore, $r_1 = 1$; $r_2 = 0$; $r_3 = 0$

Hence, direction of OP is represented as [100]

Direction of OR

Position vector of $OR = \overrightarrow{OR} = 1 \times \vec{a} + 0 \times \vec{b} + 1 \times \vec{c}$

Therefore, $r_1 = 1$; $r_2 = 0$; $r_3 = 1$

Hence, direction of OP is represented as [101]

It should be understand that the direction of [222], [333], [444]… will all coincide with [111]. In such cases the lowest combination of integers i.e., [111] is used to specify the direction. If any of the integer is negative for example -3, it should be written as $\vec{3}$ which is read as 3 bar. Given three integers of direction, a family of directions with different possible combinations of them, both positive and negative, is represented with brackets of the type < >..

1.6. Planes in crystal
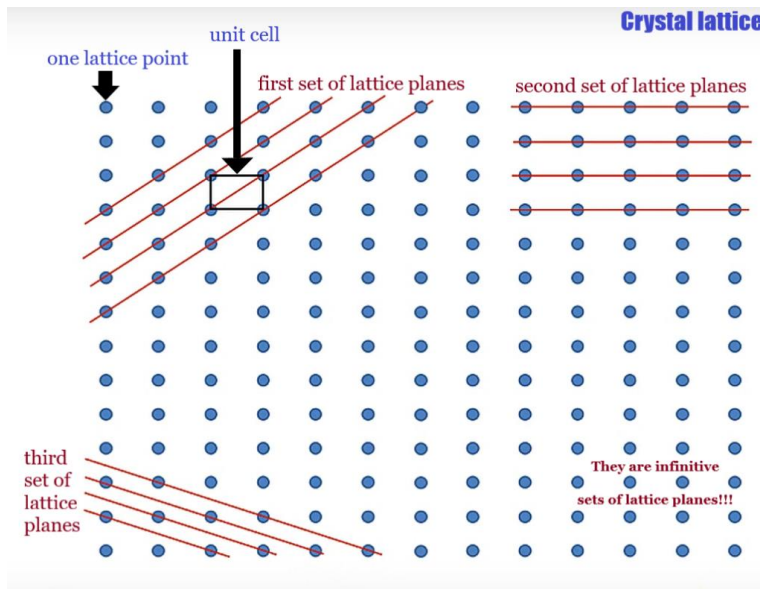
A crystal lattice is considered as a collection of a set of parallel equidistant plane passing through lattice points. These planes are known as lattice planes. These set of planes may be chosen in many different ways as shown in the above figure.

Miller indices

Definition: Miller indices are three possible integers that have the same ratio as the reciprocals of the intercepts of the plane concerned on the three axes.

Procedure: consider a crystal plane. Let us find its Miller indices as follows:

(1) Find the intercepts of the plane along the coordinate axes *X, Y, Z.* The intercepts are measured as the multiples of axial lengths.

(2) Take the reciprocal of these intercepts.

(3) Reduce the reciprocals in to whole numbers. This can be done by multiplying each reciprocal by the number obtain from LCM of the denominators.

(4) Write these integers within parentheses to get Miller indices.

Features:

(1) If a plane is parallel to any one of the coordinate axes, then its intercept will be infinity. Hence the miller indices for that particular axis is zero.

(2) The plane passing through the origin has non-zero intercepts

(3) All equally spaced parallel planes have the same Miller indices (*h k l*)

(4) This (*h k l)* indices define a set of parallel plane than a particular plane

(5) Miller indices is not only the ratio of indices but the notation to find all such planes

(6) If a plane cuts the axis on the negative side, then a bar is put just above the particular miller index.

Consider a cubic crystal of 'a' as side of a cube and a plane ABC as shown in figure. Let this plane belong to a family of planes whose miller indices are [*h k l*]. A normal ON is drawn ⊥r from the origin of the cube to the plane ABC. Let ON represents the interplanar spacing (d) of this family of plane.

The plane ABC makes OA, OB & OC as intercepts on crystallographic axes OX, OY & OZ respectively. α', β' and γ' are the angles between the crystallographic axes. We know that the miller indices of a plane are the smallest integers of the reciprocals of the intercepts.

But here, Intercepts are expressed as reciprocals of miller indices

Of the plane. $i.e.,$ OA: OB: OC $= \frac{1}{h} : \frac{1}{k} : \frac{1}{l} = \frac{a}{h} : \frac{a}{k} : \frac{a}{l}$

$\therefore OA = \frac{a}{h} ; OB = \frac{a}{k} ; OC = \frac{a}{l}$ [Multiply by lattice constant 'a')

From the Geometry of right angles OAN, OBN & OCN, we have

$$cos\acute{\alpha} = \frac{ON}{OA} = \frac{d}{\frac{a}{h}} = \frac{dh}{a}$$

$\text{III}^{\text{rly}} cos\acute{\beta} = \frac{ON}{OB} = \frac{d}{\frac{a}{k}} = \frac{dk}{a}$ & $cos\acute{\gamma} = \frac{ON}{OC} = \frac{d}{\frac{a}{l}} = \frac{dl}{a}$ (blue - α', Red - β' and Black - γ')

The law of direction cosines is $cos^2\acute{\alpha} + cos^2\acute{\beta} + cos^2\acute{\gamma} = 1$

Substituting the values, $\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$

i.e., $\frac{d^2}{a^2}(h^2 + k^2 + l^2) = 1$ (or) $d^2 = \frac{a^2}{h^2+k^2+l^2}$

$\therefore d = \frac{a}{\sqrt{h^2+k^2+l^2}}$
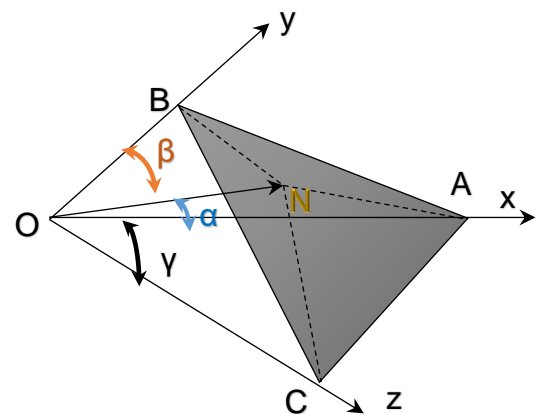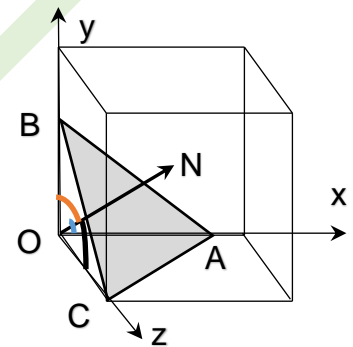
Some of the Miller indices with cubic crystal planes

z [001]   z   [010]

Density of crystal

$$\text{Density of the crystal } (\rho) = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Mass of the unit cell (M)} = \frac{\text{Atomic mass}}{\text{Avogardo number}} \times \text{Number of atoms per unit cell}$$

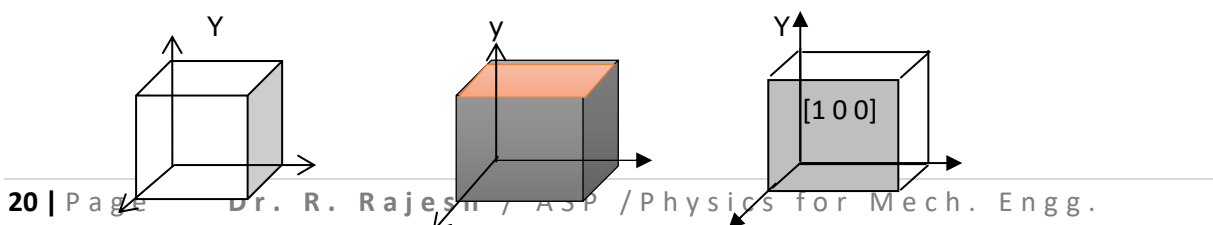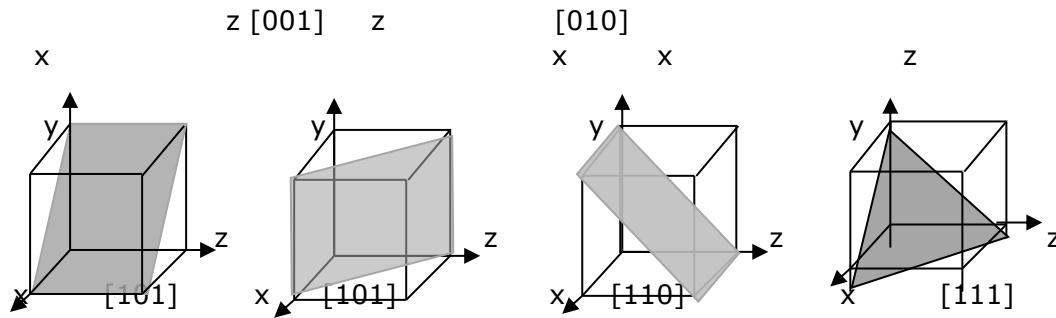(or) $\dfrac{M}{N_A} \times n$; (or) $\rho = \dfrac{nM}{a^3 N_A}$

Linear density and planar density

Linear density is defined as number of atoms per unit length whose centers on the direction vector for specific crystallographic direction.

This is defined as the number of atoms per unit length along a specific crystal direction.

$$\frac{\text{Number of atoms centred on direction vector}}{\text{Length of direction vector}}$$

The unit of linear density is m^{-1}, nm^{-1}.

The planar density of a crystal is the density of atoms in a crystal plane. This is defined as the number of atoms per unit area on a crystal plane. This effects significantly the rate of plastic deformation.

It is defined as the number of atoms per unit area

$$\frac{\text{Number of atoms in a plane}}{\text{The area of the plane}}$$

The unit of planar density is m^{-2}, nm^{-2}.

1.8. Crystal imperfections

In an ideal crystal (perfect crystal), the atomic arrangement is perfectly regular and continuous throughout. But in real crystals due to some reasons the regular orientation of atoms may be distributed at a point, along a line or in a region.

Definition

The disturbance occurred in the regular orientation of atoms is called crystal defect or imperfection.

The imperfections or defects are always present in the actual crystal and their effects are often very important in understanding the properties of crystal.

Some properties of crystal defects are **structure sensitive** i.e., properties such as mechanical strength, ductility, crystal growth, magnetic hysteresis, dielectric strength are greatly affected by the relatively minor changes in crystal structure caused by the imperfections.

Some other properties of crystals are **structure-insensitive** i.e., properties such as stiffness and density are not affected by the presence of impurities
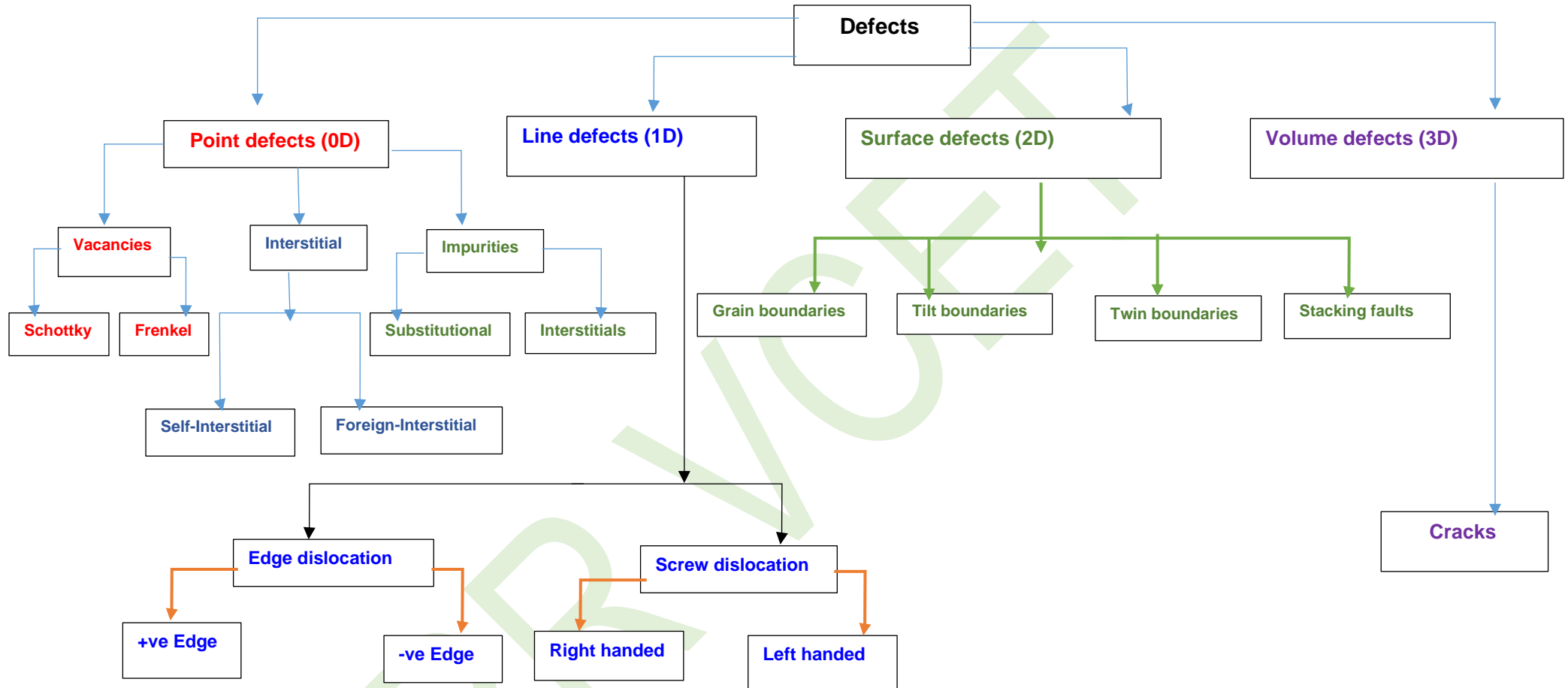
1.9. Point defects

Point defects are crystalline irregularities of atomic dimensions. They are imperfect points like regions in the crystal. One or two atomic diameter is the typical size of a point imperfection.

- Point defect takes place due to imperfect packing of atoms during crystallization
- They produce distortion inside the crystal structures.
- They produce strain only in its surroundings but they do not affect the regularity in other parts of the crystal.

Types of crystal

**(a) Vacancies**

A vacancy is the simplest point defect in a crystal. It refers to a missing atom or vacant atomic site. Whenever on or more atoms are missing from a normally occupied position as shown in figure, the defect caused is known as vacancy.

Vacancies may be single as shown in figure or two or more of them. These defects may arise due to imperfect packing during original crystallisation and thermal vibrations of the atoms at high temperatures.

The atoms surrounding the vacancies are displaced inwards thereby distorting the regularity of arrangement. These are different kinds of vacancies like Frenkel defect, Schottky defect, Colour defect, etc.,

vacancy (missing atom)
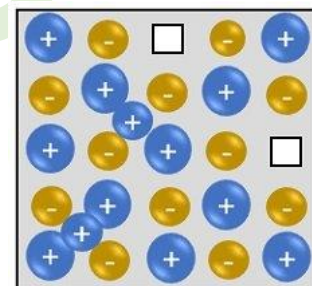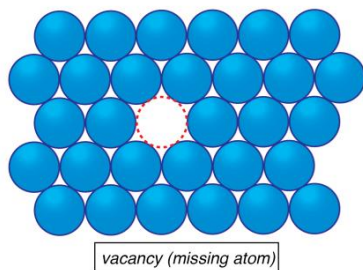
Frenkel Defect

Schottky defect

It refers to the missing of a pair of positive and negative ions in a crystal. Here, two oppositely charges ions are missing from an ionic crystal, therefore a cation-anion divacancy is created. This is known as **Schottky defect or Schottky imperfection or Iron pair imperfection.** Since a pair is missing, electrical neutrality is maintained.

Frenkel defect

A vacancy associated with interstitial impurity is called Frenkel defect. Here a missing atom occupy interstitial position. This defect always occurs in ionic crystal. If a positive ion moves into an interstitial site in an ionic crystal, a cation vacancy is created in normal ion site, this vacancy interstitial pair is known as Frenkel defect. Frenkel defect does not change the overall electrical neutrality of the crystal. The presence of these defects in ionic crystals causes an increase in electrical conductivity.

(b) Interstitial defect

When an extra atom occupies interstitial space (i.e. voids) within the crystal structure without removing parent atom, the defect is called interstitial defect.

An atom can enter into interstitial space or void only if it is smaller than the parent atom otherwise, it will produce atomic distortion or strain because interstitial atom tends to push the surrounding atoms further apart. Interstitial defect has two types

(i) Self-interstitial

If an atom from same crystal occupies interstitial site, then it is called self-interstitial.

(ii) Foreign interstitial

If an impurity atom (foreign atom) occupies interstitial site, then it is called foreign- interstitial.
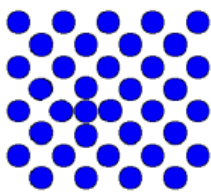
Self-interstitial
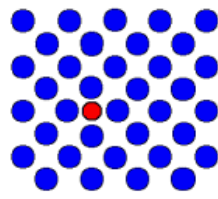
Interstitial
foreign atom

(c) Impurities

When the foreign atoms (impurities) are added to crystal lattices, they are known as impurities. The defect is called impurity defects. They are

(i) Substitutional impurity defect

A substitutional impurity refers to a foreign atom that replaces a parent atom in the lattice. Substitutional impurities change the electrical properties enormously.

Example: *n*-type and *p*-type semiconductors have substitutional impurities from V group and III group elements. A controlled addition of impurity to a very pure semiconductor is the basis of producing many electronic devices like diode and transistors.

During the production of brass alloy, zinc atoms are doped in copper lattice. Here, zinc atoms are called as substitutional impurities.

(ii) Interstitial impurity

An interstitial impurity is a small size atom occupying the empty space (interstitial) in the parent crystal, without dislodging any of the parent atoms from other sites. An atom can enter into interstitial or empty space only when it is substantially smaller than parent atom.

Example: In FCC iron, the atomic radius of iron atom is 0.225 nm. The carbon atoms with atomic radius 0.078 nm can occupy empty spaces in FCC lattice as interstitial impurities.

Substitutional foreign atom | Interstitial foreign atom
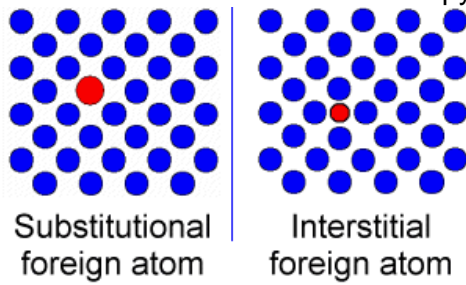
1.10 Line defects or dislocations (1D effect)

The defects due to dislocation or distortion of atoms along a line are known as line defects. These defects are also called dislocations. In the geometrical sense, they are one dimensional defects. In line defects, a portion of a line of atoms is missing or displaced from its regular site.

Types of line defects

(a) Edge dislocation

An edge dislocation arises when one of the atomic planes forms only partially and does not extend through the entire crystal. The atomic plane AB abruptly terminates at B. It is viewed as an extra plane inserted in between a set of parallel planes. The edge of such a plane forms a line defect and it is called an edge dislocation. The atomic row 1 passing through point B has one atom more than row 2 adjacent to it.
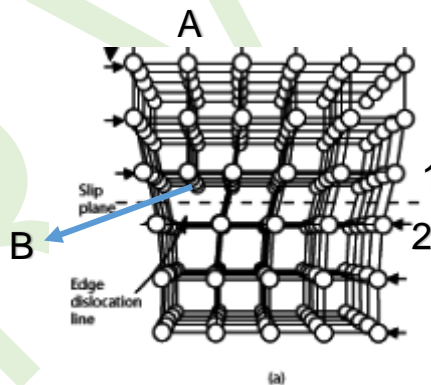
There are two configurations in dislocations:

(i) Positive edge dislocation

If the extra plane of atoms is above the slip plane of the crystal than the edge dislocation is called positive as shown in figure. It is denoted by $\perp$.

(ii) Negative edge dislocation

If the extra plane of atoms is below the slip plane than the edge dislocation is called negative. It is denoted by $\top$.

(b) Screw dislocation

Screw dislocation is due to a displacement of atoms in one part of a crystal relative to rest of the crystal. The displacement terminates within crystal. This dislocation forms a spiral ramp around dislocation line. In a screw dislocation, there is a line of atoms about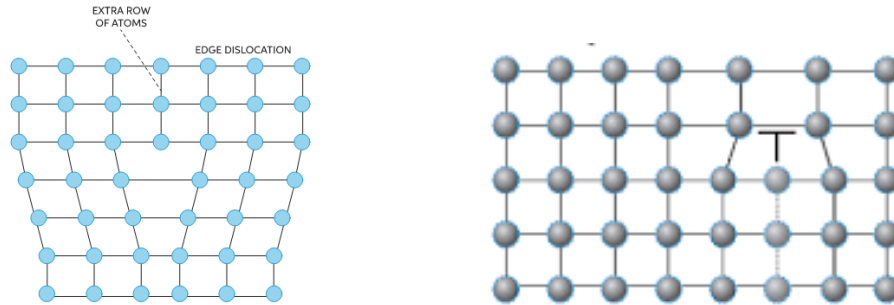 which crystal planes are wrapped to give an effect similar to threads of a screw. The row of atoms marking the termination of the displacement is the screw dislocation. The term screw represents that one part of the crystal is moving in spiral manner about dislocation line. If spiral motion of one part of the crystal is in clockwise direction then dislocation is right handed, on the other hand spiral motion is in anti-clockwise direction then, dislocation is left handed.
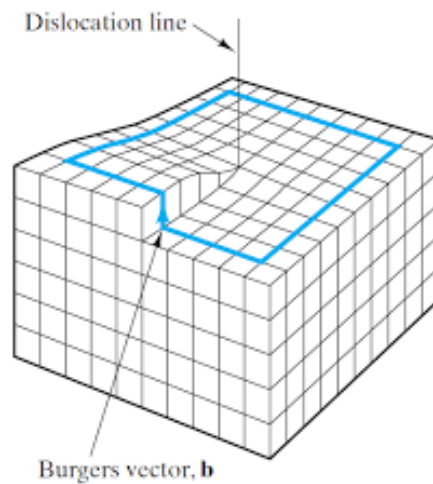
S.No	Edge dislocation	Screw dislocation
1	In edge dislocation, an edge of atomic plane is formed internal to the crystal	In screw dislocation, only distraction the lattice cell in the immediate vicinity is produced.
2	It is perpendicular to Burger's vector	It is parallel to Burger's vector
3	It moves in the direction of the Burger's vector	It moves in a direction perpendicular to the Burger's vector
4	If incomplete plane is above the slip plane then it is known as positive edge dislocation. It is represented by ⊥	If the spiral motion of the dislocation is in clock-wise direction then it is known as right handed screw dislocation
5	If incomplete plane is below the slip plane then it is known as negative edge dislocation. It is represented by ⊤	If the spiral motion of the dislocation is in anti-clockwise direction then it is known as left handed screw dislocation.
6	The amount of force required to form and move an edge dislocation is less	The amount of force required to form and move a screw dislocation is more.

1.11. Burger's vector

The dislocation lines are expressed by a Burger vector $\vec{b}$. It indicates the amount and direction of shift in lattice on slip plane. The following figure shows a perfect crystal and a crystal with positive edge dislocation. Consider a point starting from E moves in a particular direction as shown (Left side of figure) and it completes atomic distances in the form of circuit called *Burger circuit* or *Burger loop*. If the same circuit is drawn starting from E (as shown in right side) will not complete the circuit due to the presence of dislocation. Hence, if we wish to arrive at starting point E from S. then we must move an extra distance $\vec{b}$ as shown in figure. The vector $\vec{b} = \vec{ES}$ connects end point with starting point is called burger's vector of the dislocation.
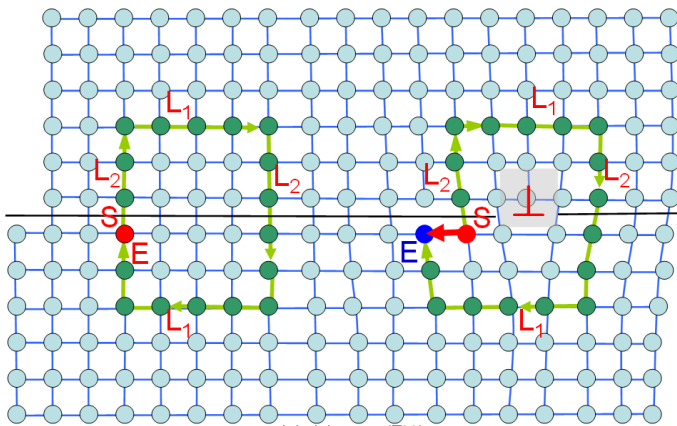
1.12. Surface defects (Plane defects -2D)

The defects on the surface of material are called surface defects or plane defects. They are also known as two dimensional imperfections. Surface defects are due to a change in the stacking of atomic planes on or across a boundary.

Some important internal surface defects are discussed below

(i) Grain boundaries
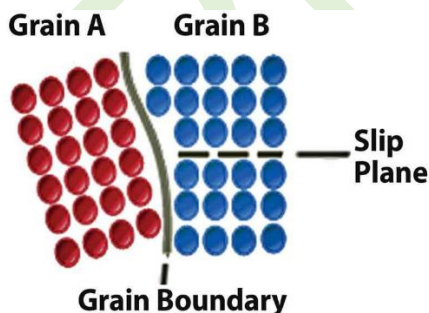
Whenever the grains of different orientations separate the general pattern of atoms and exhibits a boundary, the defect caused is called grain boundary. A grain boundary is formed when two growing grain surfaces meet. The shape of the grain is usually influenced by the presence of surrounding grains. This type of defect generally takes place during the solidification of liquid metal.

(ii) Tilt and twist boundaries

Tilt boundary is another surface imperfection. It is an array of parallel edge dislocation of same sign (i.e., either ⊤ or ⊥) arranged one above other in an array or series. Tilt angle is a type of low angle boundary (less than 10°). By rotation of an axis in the boundary, it is possible to bring the axis of two bordering grains into coincidence, then

Angle of tilt, $\tan\theta = \dfrac{b}{D}$, D – Dislocation spacing; b – Length of Burger's Vector. When θ is

small, then tan θ = θ & hence, $\theta = \dfrac{b}{D}$
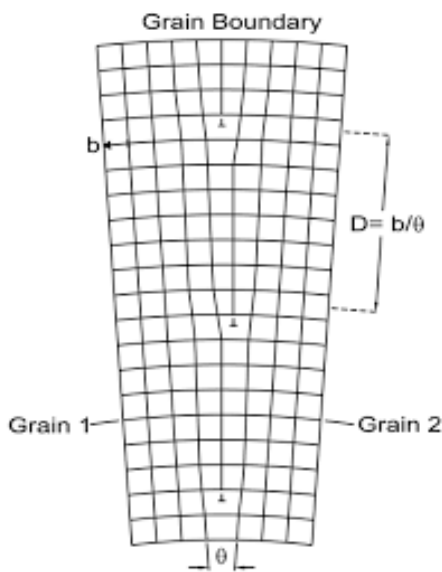
Twist boundaries

Twist boundaries are another type of low angle boundaries. It consists of atleast two sets of parallel screw dislocations lying in the boundary. In twist boundary, the rotation is about an axis normal to boundary.

(iii) Twin boundaries

Twin boundaries are another surface imperfections. If the boundaries in which the atomic arrangement on one side of the boundary is somewhat a mirror image of the arrangement of atoms of the other side. The defect caused is called twin boundary.
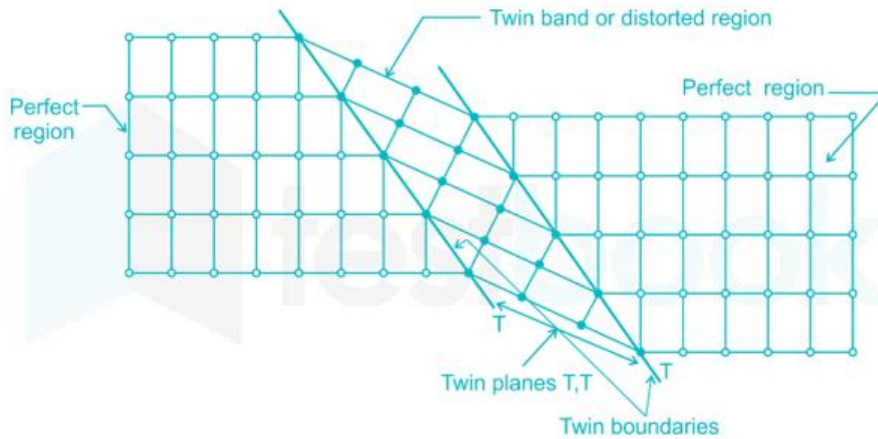
Stacking faults

It is a kind surface imperfection. Whenever the stacking of atoms is not in proper sequence throughout the crystal, defect caused is called stacking fault

Perfect Crystal   Stacking Fault
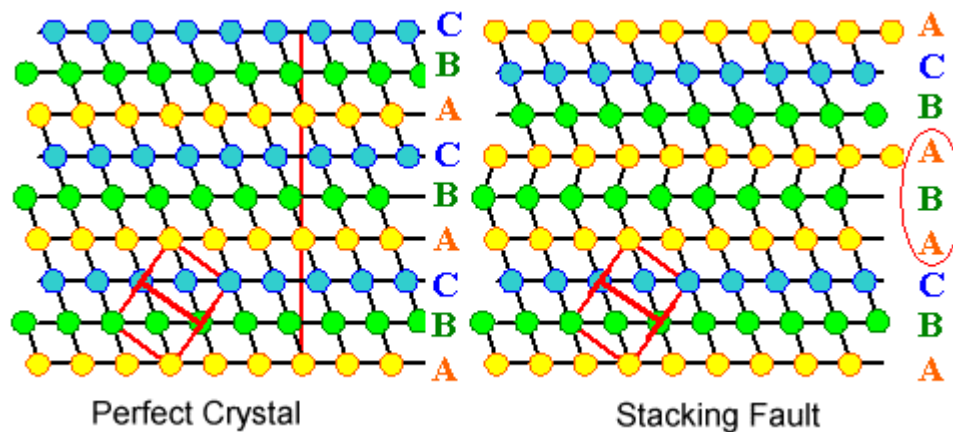
Explanation

The above figure shows the proper and improper sequence of atomic planes. Perfect crystal has a sequence C-B-A-C-B-A while the encircle part of the sequence is change on right side which forms a thin region of a hexagonal close packing in a FCC crystal.

1.13. Elastic strain energy

The dislocation line have distortional energy associated with them since there are compressive and tensile strains around edge dislocations and shear strains around the screw dislocations. The elastic strain energy U per unit length of the dislocation line is given by

$$U = \frac{1}{2}\mu b^2$$

Where μ is the shear modulus of the material and b is the length of Burger's vector. Larger the Burgers vector, longer is the strain energy. For a full dislocation, the Burger vector is

$$\vec{b} = n\vec{r}$$

Where r is the lattice vector and n is any integer number.

The dislocation has a tendency to have smaller Burgers vector and hence least strain energy increases. There can be partial dislocation also, if the Burgers vector is a fraction of a lattice translation.

Deformation of metals

When metals or alloys are stressed (i.e., subject to load), they get deformed.

Deformation is the change in dimension of matter under the action of applied forces

The deformation may be completed temporary that is elastic deformation. It disappears after the deforming load is removed.

The permanent deformation may also occur that is plastic deformation which remains even after the removal of the deforming load.

Elastic deformation

If a metal is loaded, a temporary deformation of the crystals takes place through displacement of the atoms. As the deformation load is removed, the atoms return to their original position and the crystal recovers its original shape.

Stress →

Before loading

Loaded

Load removed
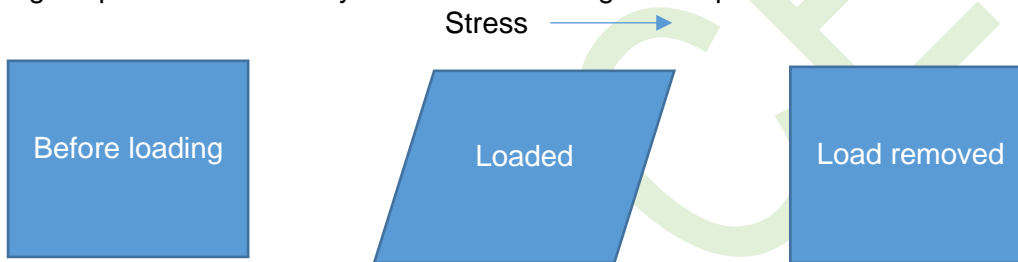
Plastic deformation

Plastic deformation follows elastic deformation

If the deformation load is such that the stresses in the metal piece cross the elastic limit, the specimen gets plastically deformed.

If the deforming load at this stage is removed, the metal piece does not regain its original shape, i.e., a permanent set (plastic strain) is always retained.

Before loading

Loaded
Loaded
Loaded

Load removed
Load removed
Load removed
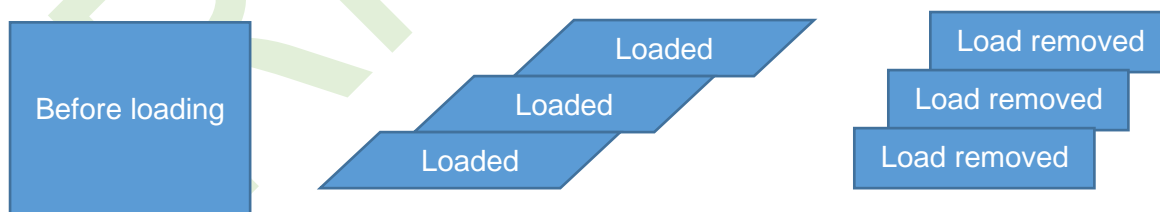
Plastic deformation depends on (i) applied stress (ii) Temperature (iii) Strain rate

Plastic deformation is accompanied by changes in both the internal and external state and it is not reversible.

Permanent deformation distortion of the crystal and microstructure. It is intentionally carried out as in working and shaping processes such as bending, stamping, drawing , spinning, rolling , forging, extruding, etc.,

It is also carried out in order to improve some of the mechanical properties of metals and alloys.

Plastic deformation mechanisms

It occur in two ways: (i) Slip (ii) Twinning

Slip

The deformation by slip takes place one part of the crystal moves or glides over another part along certain planes. The planes over which slip takes place are the planes of greatest atomic density and they are called slip planes. Slip directions are the closest packed directions within the slip planes.

Mechanism of slip

There are 4 stages during plastic deformation of single crystal by the slip

(i) Perfect crystal without slip

(ii) Deformation shear force is applied to the crystal

(iii) Slip taking place along the slip plane

(iv) Permanent deformation when deformation forces are removed.
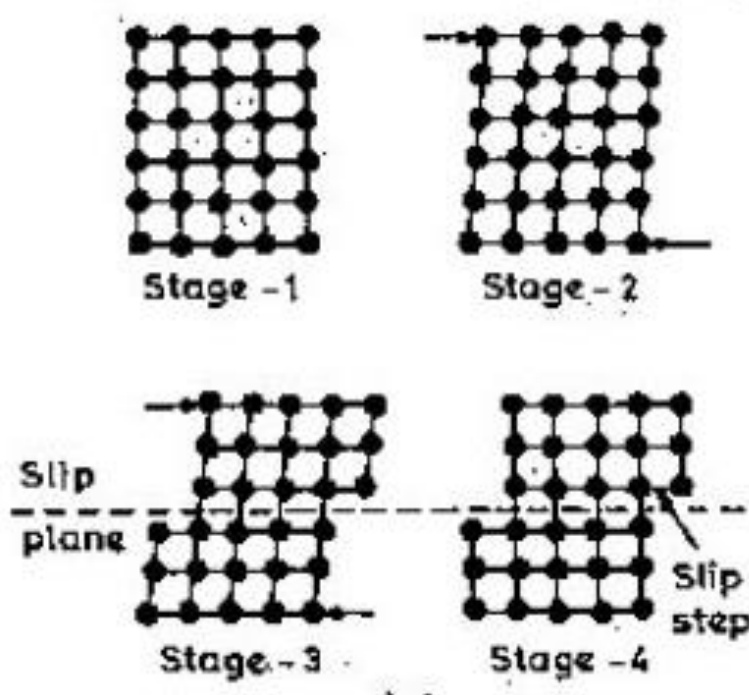
The slip represents a displacement of a part of the crystals relative to another along certain crystallographic planes and a certain crystallographic directions. The particular crystallographic planes where slip occurs are called slip planes. Similarly, the preferable direction along which slip occurs is called the slip direction.

Twinning

Another important plastic deformation mechanism which occurs in some material is known as twinning. The mechanism of twinning is shown in figure.

Slip and Twinning
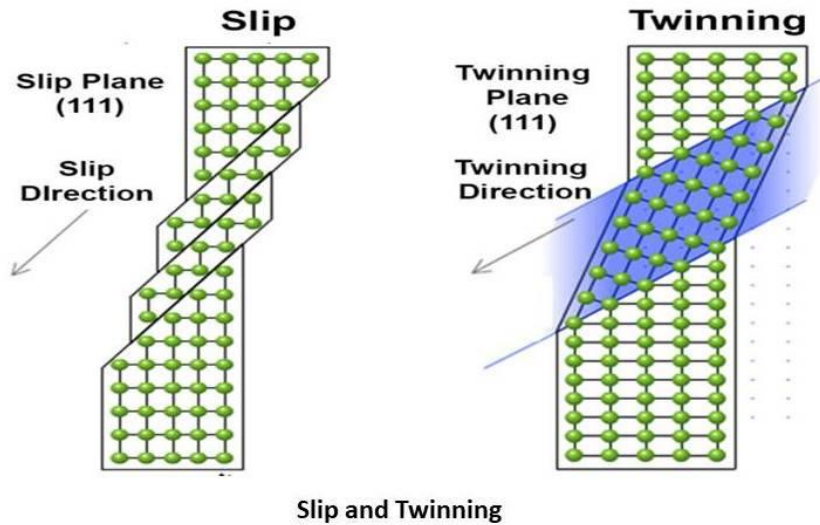
The shear force produce atomic displacements such that the deformed lattice forms a mirror image of the undeformed lattice. That is, the atoms on one side of the plane location is in mirror image position of the atoms on the other side. The crystallographic plane of symmetry between the deformed and undeformed parts of the metal lattice is called the twinning plane. Twinning is a major deformation notably seen in hexagonal closed packed metals like zinc and tin. Twinning also occurs in definite crystallographic planes and direction that depends on the crystal structure.

Types of twins

(i) Mechanical twins:

Twins which are produced by mechanical deformation are called mechanical twins. These twins are produced in BCC and HCP metals under the conditions of decreased temperature and shock loading. Mechanical twins are not formed in FCC metals. These twins can form in a few microsecond while slip takes several seconds to occur.

(ii) Annealing twins:

The twins which are produced by annealing are called annealing twins. These are usually broader. Most of the FCC metals form annealing twins. They are formed because of a change in normal growth mechanism.

Slip systems

The combination of a slip plane and slip direction is known as slip system. Slip direction is the most important factor in slip system.

(i) Slip system in FCC crystals

In FCC metals, plane (111) is the plane of maximum atomic density. There are four possible {111} slip planes namely (111), ($\bar{1}$11), (1$\bar{1}$1) and (11$\bar{1}$). Each plane contains three <110> slip directions. Thus there are 12 slip systems in FCC metals. Here, some panes and direction will always favourable oriented for plastic deformation. Hence, the metals are easily deformed.

(ii) Slip system in BCC crystals

In BCC metals, slip occurs predominately on {110}<111> slip system.{110} planes have highest atomic density. There are six plane in {110} family and each plane has two directions. Thus, there are 12 such slip systems. There are also 12+24 more slip system in BCC metal which are less predominant.

1.14. X-Ray Diffraction

It is well known that, for visible electromagnetic radiation to be diffracted, the spacing between lines in a two-dimensional grating must be of the same order as the wavelength range for light (3900–7800 Å). The same principle holds good for diffraction by the three-dimensional grating of the periodic array of atoms in crystals. The typical interatomic spacing in crystals is 2–3 Å. So, the wavelength of the radiation used for crystal diffraction should be in the same range. X-rays have wavelengths in this range and are, therefore, diffracted by crystals. This property is widely used for the study of crystal structures.

1.15. Bragg's law of X-Ray Diffraction

When electrons moving at high speeds are directed to a metal target, a small percentage of their kinetic energy is converted into x-rays. The x-rays emitted by the target consist of a continuous range of wavelengths, called white radiation, by analogy with white light consisting of a range of wavelengths. The minimum wavelength in the continuous spectrum is inversely proportional to the applied voltage which accelerates the electrons towards the target. If the applied voltage is sufficiently high, in addition to the white radiation, a characteristic radiation of a specific wavelength and high intensity is also emitted by the target. The radiation emitted by a molybdenum target at 35 kV includes both types of radiation. In spectroscopic notation, the characteristic radiations are named K_α, K_β, L_α, etc. K_α radiation has a high intensity and is commonly used in diffraction studies. The wavelengths of this radiation for typical target metals are given below:

Target Metal	Mo	Cu	Co	Fe	Cr
K_α (wavelengths)	0.71 Å	1.54 Å	1.79 Å	1.94 Å	2.29 Å

A beam of x-rays directed at a crystal interacts with the electrons of the atoms in the crystal. The electrons oscillate under the impact and become a new source of electromagnetic radiation. The waves emitted by the electrons have the same frequency as the incident x-rays. The emission is in all directions. As there are millions of atoms in a crystal, the emission in a particular direction is the combined effect of the oscillations of electrons of all the atoms. The emissions will be in phase and reinforce one another only in certain specific directions, which depend on the direction of the incident x-rays, their wavelength as well as the spacing between atoms in the crystal. In other directions, there is destructive interference of the emissions from different sources. The easiest way to visualize the diffraction effects produced by the three-dimensional grating provided by the crystal is to consider the Bragg law.

In the following Figure, a set of parallel planes in a crystal is shown. A beam of x-rays of wavelength λ is directed towards the crystal at an angle θ to the atomic planes. In Bragg law,

the interaction described above between x-rays and the electrons of the atoms is visualized as a process of reflection of x-rays by the atomic planes. This is an equivalent description of the diffraction effects produced by a three-dimensional grating. The atomic planes are considered to be semi-transparent, that is, they allow a part of the x-rays to pass through and reflect the other part, the incident angle θ (called the Bragg angle) being equal to the reflected angle. Referring to above figure, there is a path difference between rays reflected from plane 1 and the adjacent plane 2 in the crystal. The two reflected rays will reinforce each other, only when this path difference is equal to an integral multiple of the wavelength. If d is the interplanar spacing, the path difference is twice the distance d sin θ, as indicated in the above figure. The Bragg condition for reflection can therefore be written as

$2\ d\ \sin\theta = n\ \lambda$ (1)

Where n is an integer and θ is the wavelength of the x-rays used. A first order reflection is obtained, if n = l; a second order reflection occurs if n = 2, and so on.

As sin θ has a maximum value of 1, for a typical value of interplanar spacing of 2 Å, Eq. (1) gives the upper limit of λ for obtaining a first order reflection as 4 Å. There will be no reflection if λ is greater than 4 Å. λ can be reduced indefinitely, obtaining reflections from other sets of planes that have spacing less than 2 Å as well as an increasing number of higher order reflections. A very small wavelength of the order of 0.1 Å is not necessarily an advantage as it tends to produce other effects such as knocking off electrons from the atoms of the crystal and getting absorbed in the process. The wavelengths of the K_α radiation given in the above table for typical target metals lie in the right range. The Bragg equation can be used for determining the lattice parameters of cubic crystals. Let us first consider the value that n should be assigned. A second order reflection from (100) planes should satisfy the following Bragg condition:

$2\ \lambda = 2\ d_{100}\ \sin\theta$

(or) $\lambda = d_{100}\ \sin\theta$ (2)

Similarly, a first order reflection from (200) planes should satisfy the following condition:

$\lambda = 2d_{200}\ \sin\theta$ (3)

We have earlier noted that the interplanar spacing of (100) planes is twice that for (200) planes. So, Eqs. (2) and (3) are identical. For any incident beam of x-rays, the Bragg angle θ would be the same, as the two sets of planes in question are parallel. As Eqs. (2) and (3) are identical, the two reflections ill superimpose on each other and cannot be distinguished. By a similar argument, it can be shown that the third order reflection from (100) planes will superimpose on the first order reflection from (300) planes. In view of such superimposition, there is no need to consider the variations in n separately; instead, we take n to be unity for all reflections from parallel sets of planes such as (100), (200), (300), (400), etc. In a crystal, it may turn out, for example, that there is no (200) plane with atoms on it. Then, what is designated as a (200) reflection actually refers to the second order reflection from (100) planes.

In diffraction studies, in order to increase the probability that crystals with the right orientation for Bragg reflection are available, one of the following procedures is adopted:

(i) A monochromatic x-ray beam of a specific wavelength is combined with numerous possible θ values so that reflection occurs at the right combination that satisfies the Bragg law. This is

done by placing thousands of crystals of random orientation in the path of the beam. The crystals are usually in powder form.

(ii) A single crystal is held stationary in the path of the beam so that θ is kept constant. A white radiation is then directed at the crystal so that numerous values of the wavelength are available, and again the right combination will lead to the diffraction condition. This method is called the Laue technique.

(iii) A single crystal is held in the beam of a monochromatic radiation and is rotated such that at some position of the crystal, the diffraction condition is satisfied. This method is known as the rotating crystal method. Even though this is not the most widely used method, it provides greater certainty in identification, as well as more accurate measurement of the intensities of the reflected beam.
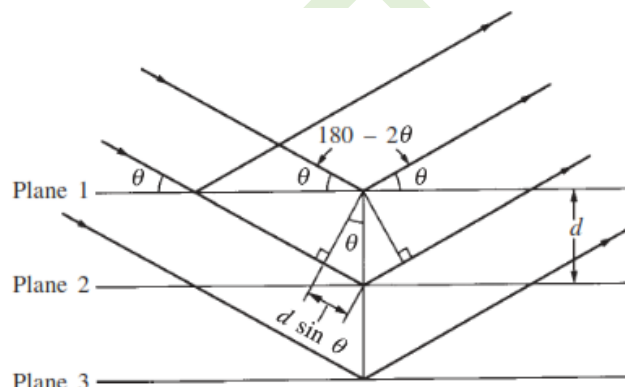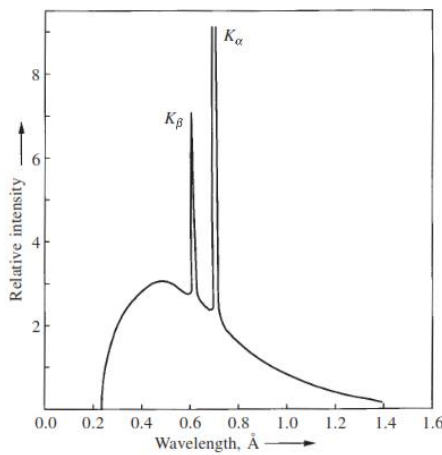

Illustration of the Bragg law.

The spectrum of x-rays emitted from a molybdenum target at 35 kV.

The powder method

The powder method is a widely used experimental technique for the routine determination of crystal structures. It is highly suitable for identification and for determination of the structures of crystals of high symmetry. Here, a monochromatic x-ray beam, usually of K_α radiation, is incident on thousands of randomly oriented crystals in powder form. The powder camera, called the Debye-Scherrer camera, consists of a cylindrical cassette, with a strip of photographic film positioned around the circular periphery of the cassette. The powder specimen is placed at the centre of the cassette in a capillary tube or pasted on a thin wire. The tube, the wire and the paste material must be of some non-diffracting substance such as glass or glue. The x-ray beam enters through a small hole, passes through the powder specimen and the unused part of the beam leaves through a hole at the opposite end. The geometry of the powder method is illustrated in the below figure.

Consider a set of parallel crystal planes making an angle θ with the incident direction. When this angle satisfies the Bragg equation, there is reflection. By virtue of the large number of randomly oriented crystals in the powder, there are a number of possible orientations of this set of planes in space for the same angle θ with the incident direction. So the reflected radiation is not just a pencil beam like the incident one; instead, it lies on the surface of a cone whose apex is at the point of contact of the incident radiation with the specimen. Also, the

interplanar spacing d being the same for all members of a family of crystal planes, they all reflect at the same Bragg angle θ, all reflections from a family lying on the same cone. After taking n = 1 in the Bragg equation, there are still a number of combinations of d and θ that would satisfy the Bragg law. For each combination of d and θ, one cone of reflection must result and, therefore, many cones of reflection are emitted by the powder specimen. If the reflected cones were recorded on a flat film placed normal to the exit beam, they will be in the form of concentric circles. In the powder camera, however, only a part of each reflected cone is recorded by the film strip positioned at the periphery of the cylindrical cassette. The recorded lines from any cone are a pair of arcs that form part of the circle of intersection. When the film strip is taken out of the cassette and spread out, it looks like the figure given below.

Note that the angle between a reflected line lying on the surface of the cone and the exit beam is 2θ. Therefore, the angle included at the apex of the cone is twice this value, 4θ, When the Bragg angle is 45°, the cone opens out into a circle and reflection at this angle will make a straight line intersection with the film strip at the midpoint between the incident and the exit points in the below figure. When the Bragg angle is greater than 45°, back reflection is obtained, that is, the reflected cones are directed towards the incident beam. Bragg angles up to the maximum value of 90° can be recorded by the film of the powder camera, which is not possible on a flat film placed in front of the exit beam. The exposure in a powder camera must be sufficiently long to give reflected lines of good intensity. The exposure time is usually a few hours. After the film is exposed and developed, it is indexed to determine the crystal structure. It is easily seen that the first arc on either side of the exit point corresponds to the smallest angle of reflection. The pairs of arcs beyond this pair have larger Bragg angles and are from planes of smaller spacings, recall that $d = \lambda/(2 \sin \theta)$.

The distance between any two corresponding arcs on the spread out film is termed S, Fig. 4. S is related to the radius of the powder camera R:

$$S = 4R\theta \qquad\qquad (4)$$

where θ is the Bragg angle expressed in radians. For easy conversion of the distance S measured in mm to Bragg angle in degrees, the camera radius is often chosen to be 57.3 mm, as 1 rad = 57.3°. In the powder method, the intensity of the reflected beam can also be recorded in a diffractometer, which uses a counter in place of the film to measure intensities. The counter moves along the periphery of the cylinder and records the reflected intensities against 2θ. Peaks in the diffractometer recording (Fig. 4) correspond to positions where the Bragg condition is satisfied.

(a)

(b)
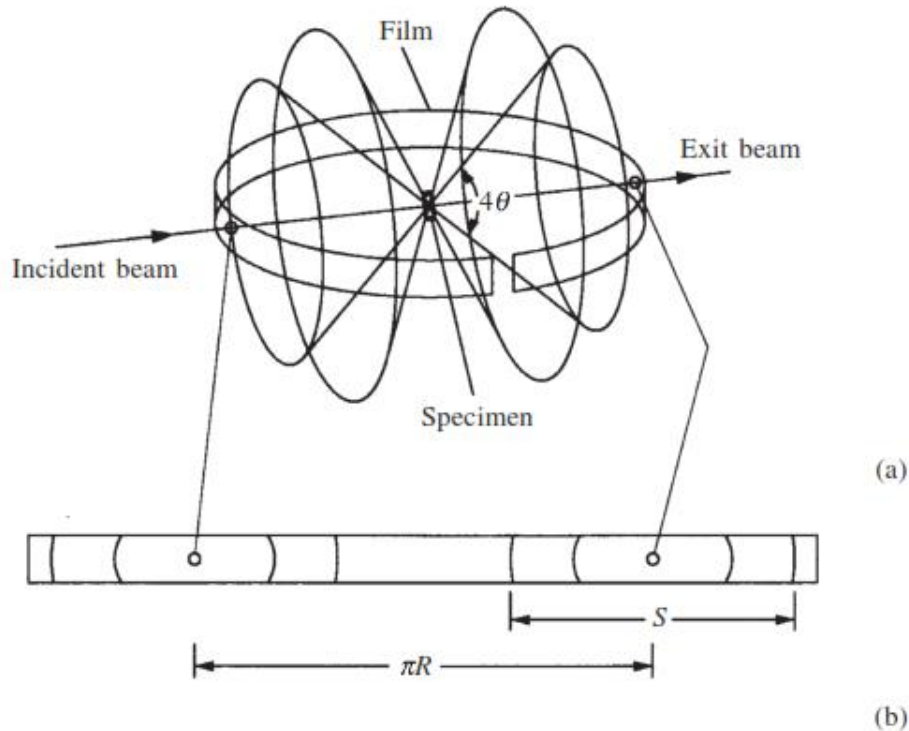
Part – A Question and Answers

1. **What is space lattice?**
   It is an array of points in three dimensions in which every point has an identical surroundings.

2. **What is unit cell?**
   It is the smallest volume of the solid from which the entire crystal structure can be constructed by repetition in three dimension.

3. **Name the seven crystal system.**
   (i) Cubic (ii) Tetragonal (iii) Orthorhombic (iv) Monoclinic (v) Triclinic (vi) Hexagonal (vii) Rhombohedral

4. **What is primitive cell?**
   A primitive cell is the simplest type of unit cell which contains only one lattice point per unit cell

5. **Name the crystal structure of the following: (a) Gold (b) Germanium (c) Barium (d) Zinc**
   (a) FCC (b) Diamond cubic (c) BCC (d) HCP

6. **Bismuth has $a = b = c = 4.74$ Å and angles $\alpha = \beta = \gamma = 60°$. What is its crystal structure?**
   Since $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$. Hence the crystal structure is Rhombohedral (Trigonal)

7. **What are Bravais lattices?**
   There are only 14 ways of arranging points in 3-dimensional space such that the environment looks same from each point. i.e., there are 14 possible types of space lattices out of the seven crystal systems. These 14 space lattices are called Bravais lattices.

8. **Explain the differences between Crystalline & Non crystalline materials.**

S.No	Crystalline	Non crystalline
1	Definite shape & Size	No geometrical shape
2	Anisotropic in nature	Isotropic in nature
3	Long range ordering	Short range ordering
4	They are most stable	They are less stable
5	Examples : NaCl, Cu, Au, etc.,	Examples : Plastic, Rubber, Glass,

9. **Give the important characteristics of unit cell for SC, BCC, FCC, HCP & Diamond?**

Type of Structure	No. of atoms in unit cell	Coordination number	Atomic radius (r)	Atomic packing factor
Simple Cubic	1	6	$\dfrac{a}{2}$	0.52
Body centred Cubic	2	8	$\dfrac{\sqrt{3}a}{4}$	0.68
Face Centred Cubic	4	12	$\dfrac{\sqrt{2}a}{4}$	0.74
Hexagonal Close Packed	6	12	$\dfrac{a}{2}$	0.74
Diamond structure	8	4	$\dfrac{\sqrt{3}a}{8}$	0.34

10. **Define Coordination number?**

It is the number of nearest neighbour atoms directly surrounding a particular atom in a crystal structure

11. **Define atomic radius?**

The half of the distance between nearest neighbouring atoms which is in contact with each other in a crystal is known as atomic radius. (Symbol: r)

12. **Define Atomic Packing fraction? What is its unit?**

It is the ratio of the total volume occupied by the atoms in the unit cell to the total volume of the unit cell

13. **State $\frac{c}{a}$ ratio & packing factor of HCP?**

$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.6333$ & Packing Fraction $= \frac{\pi}{3\sqrt{2}} = 74\%$

14. **What are miller indices?**

Miller indices are three possible integers which have the same ratios as the reciprocals of the plane concerned on the three axes.

15. **State the expression for interplanar spacing for a cubic system in terms of lattice constant and miller indices.**

Interplanar Spacing $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ where a – lattice constant & h, k, l – miller indices

16. **Some of the planes in cubic system:**

z [001]   z [010]

z

x
y
x
[101]

x
y
x
[101]
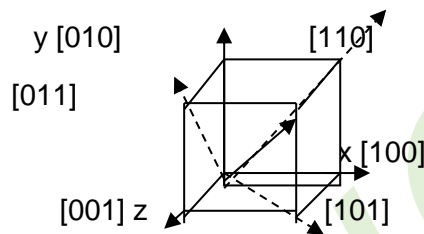
x
y
y
x
[110]

z
x
[111]
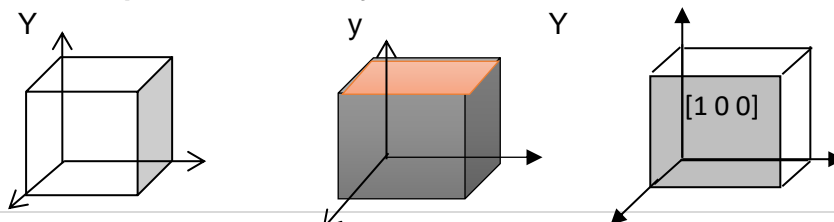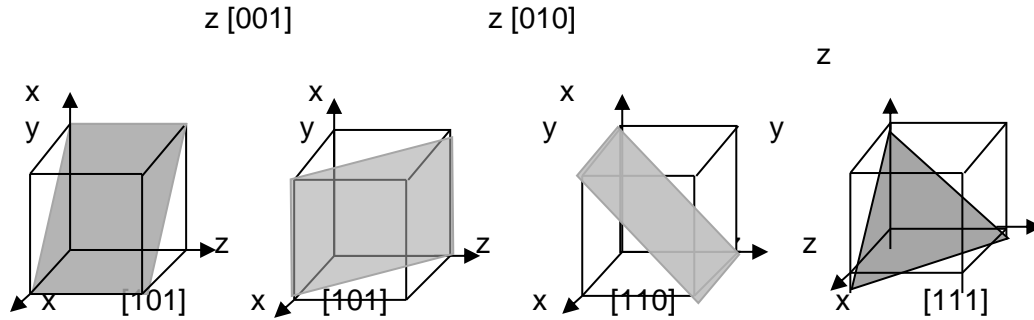
17. What are the characteristics of unit cell?

(i) Number of atoms per unit cell (ii) atomic radius (iii) Coordination number (iv) Atomic packing fraction

18. Some of the Cubic Crystal direction:

y [010]   [110]

[011]

x [100]

[001] z   [101]

19. What are the types of crystal structure? Give the types of Bravais Lattice with example?

S. No	Types of Crystal Structure	Intercepts	Interfacial angles	Example	Bravais lattice
1.	Cubic	a = b = c	α = β = γ = 90°	NaCl, CaF_2	P,I,F
2.	Tetragonal	a = b ≠ c	α = β = γ = 90°	White Tin, Indium	P,I
3.	Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	Sulphur , Topaz	P,C,F,
4.	Monoclinic	a ≠ b ≠ c	α = β = 90° ; γ ≠ 90°	Na_2SO_4 , $FeSO_4$	P,C
5.	Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	$CuSO_4$,$K_2Cr_2O_7$	P
6.	Rhombohedral	a = b = c	α = β = γ ≠ 90°	Calcite , Bi	P
7.	Hexagonal	a = b ≠ c	α = β =90°; γ = 120°	Quartz, Zn, Mg	P

20. Give the relation between the density of the crystal and the lattice constant

$$\rho = \frac{nA}{Na^3}$$ n – No. of atoms per unit cell, N – Avagardo Number , A – atomic weight & a – Lattice   constant.

21. How carbon atoms are arranged in diamond structure?
The *X* atom is located with an origin of (0, 0, 0) and the *Y* atom is located with an origin of (a/4, a/4, a/4) i.e., one quarter of the way along the body diagonal with an interpenetration of two FCC sublattices in a unit cell

22. What are Frenkel and Schottky imperfections?

Frenkel defect is an ionic crystal imperfection that occurs when an ion moves into an interstitial site, thereby creating two defects simultaneously i.e., one vacancy and the other self-interstitial. A pair of ion vacancies in an ionic crystal is termed as Schottky defect.

23. List the different types of point defects?

Schottky defect, Frenkel defect, Substitutional impurities, Interstitial impurities

24. What are the differences between edge and screw dislocation?

Edge dislocation	Screw dislocation
These dislocation arises due to introduction or elimination of an extra plane of atoms	Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of crystal forming a spiral ramp around the dislocation line
Region of lattice disturbance extends along an edge inside a crystal	Region of lattice disturbance extends in two separate planes at right angles to each other
AN edge dislocation can glide and climb	A screw dislocation can glide only
Burger vector is always perpendicular to the dislocation line	Burger vector is parallel to the dislocation line
These are formed during deformation and crystallization	These are also formed during deformation and crystallization

25. What are vacancies?

Vacancies are empty atomic sites. Vacancies may occur as a result of imperfect packing during the original crystallization or they may arise from the thermal vibrations of atoms at higher temperatures.

26. What is burger vector?

The magnitude and direction of the displacement due to edge dislocation are defined by a vector called Burger's vector

27. What are twin boundaries?

If the atomic arrangement on one side of the boundary is the mirror image of the arrangement on the other side the defect is called twin boundaries.

28. What is stacking fault?

It arises due to defect in the stacking of atomic planes. IN some cases part of certain atomic plane will be missing whereas in some other cases a portion of extra atomic plane is present, changing the sequence of arrangement of atoms.

Part –B Questions

1. Define the terms atomic radius and packing factor. Calculate the above for BCC and FCC structures.
2. Calculate the number of atoms per unit cell, coordination number and packing factor for FCC and BCC structures.
3. Describe the structure of a HCP crystal. Give details about its atomic rdius, atomic packing factor and axial ratio.

4. What is packing factor? Prove that the packing fraction of HCP is 0.74
5. Show that the atomic packing fraction of FCC and HCP are same.
6. Explain crystal defects in detailed manner.
7. Write a brief note Bragg's law of X-ray diffraction and explain the X-ray diffraction using powder method