

only at the corners of the unit cell). The angles between the three axes X , Y and Z are called *interfacial angles*. The primitives and interfacial angles constitute the lattice parameters of the unit cell (also called *geometrical constants*). By knowing the lattice parameters of the linear dimensions a , b and c as well as interfacial angles α , β , γ between them, the form and actual size of the unit cell can be known. But if we do not know actual values of primitives but only their ratio and the values of interfacial angles, then we can only determine the form of the unit cell and not its actual size.

2.7. CRYSTAL SYSTEMS

The space lattice of a crystal is described by means of a 3-dimensional coordinate system in which the coordinate axes coincide with any three edges of the crystal intersecting at one point. To describe basic crystal structure seven different coordinate systems of reference axes are required (Refer Fig. 2.12).

The Seven Basic Crystal Systems

S. No.	System	Relation between primitives	Interfacial angles	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	CaF_2 , NaCl
2.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	FeSO_4 , Na_2SO_4
3.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$
4.	Tetragonal	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma = 90^\circ$	SnO_2 , NiSO_4
5.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	BaSO_4 , MgSO_4
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaSO_4
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	SiO_2 , AgI

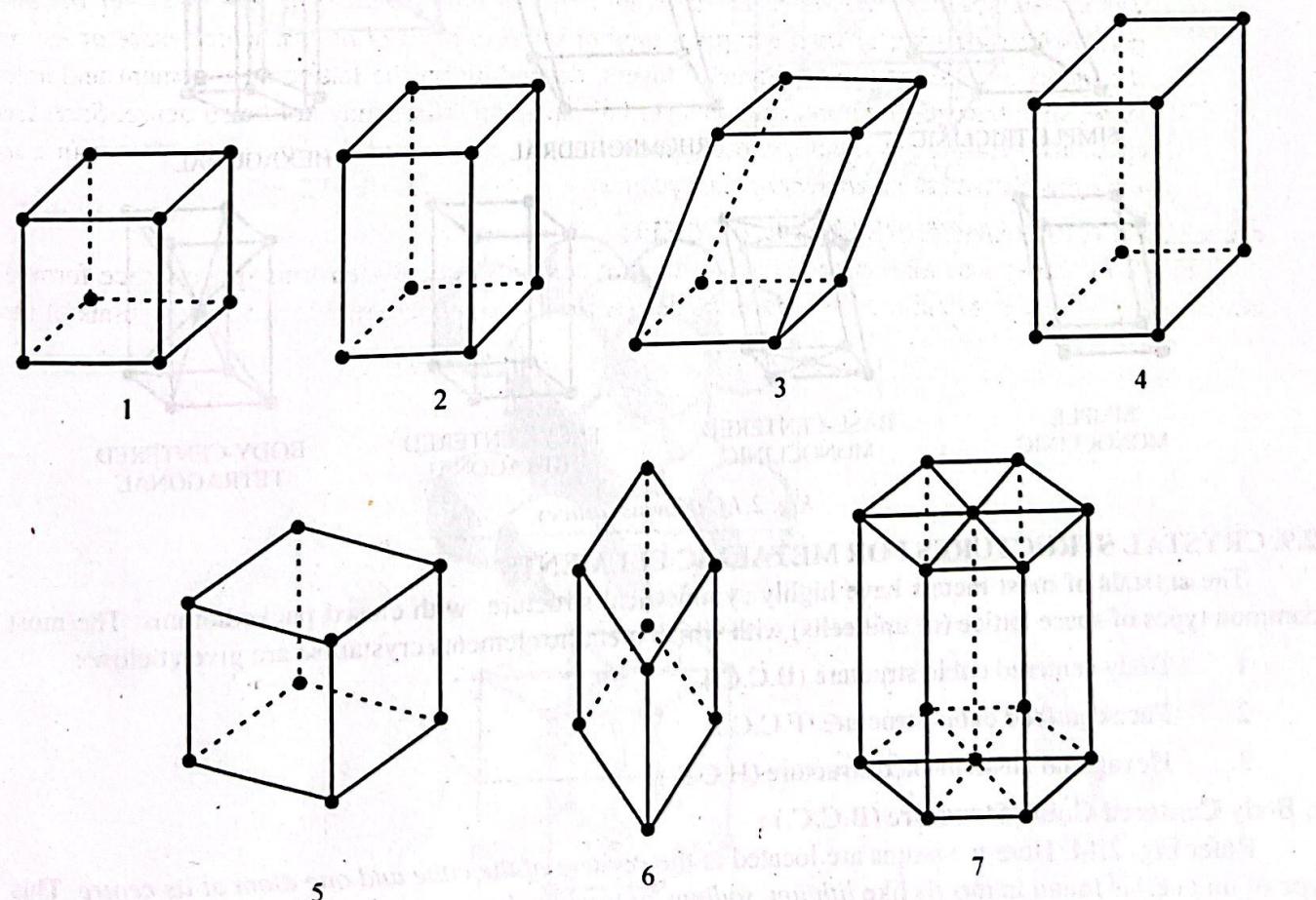


Fig. 2.12. Basic crystal systems.

MONOCLINIC

BASE-CENTERED
MONOCLINIC

FACE-CENTERED
TETRAGONAL

BODY-CENTERED
TETRAGONAL

Fig. 2.13. Bravais lattices.

2.9. CRYSTAL STRUCTURES FOR METALLIC ELEMENTS

The crystals of most metals have highly symmetrical structure with closed packed atoms. The most common types of space lattice (or unit cells) with which metallic elements crystallise are given below :

1. Body centered cubic structure (B.C.C.)
2. Face centered cubic structure (F.C.C.)
3. Hexagonal close-packed structure (H.C.P.).

1. Body Centered Cubic Structure (B.C.C.) :

Refer Fig. 2.14. Here the atoms are located at the *corners of the cube and one atom at its centre*. This type of unit cell is found in metals like *lithium, sodium, potassium, barium, vanadium, molybdenum* etc.

2. Face Centered Cubic Structure (F.C.C.) :

Refer Fig. 2.15. Here the atoms are located at the corners of the cube and one atom at the centre of each face. This type of unit cell is found in metals like copper, silver, gold, calcium, aluminium, lead etc.

3. Hexagon Close Packed Structure (H.C.P.) :

Refer Fig. 2.16. Here the unit cell has an atom at each of the twelve corners of the hexagonal prism, one atom at the centre of each of the two hexagonal faces and three atoms in the body of the cell. This type of unit cell is found in metals like zinc, lithium, magnesium, beryllium etc.

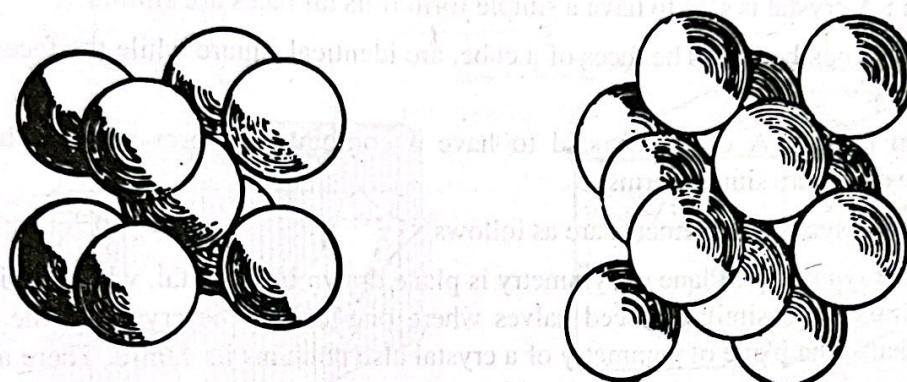


Fig. 2.14. B.C.C.

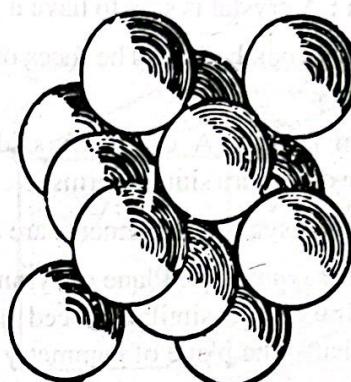


Fig. 2.15. F.C.C.

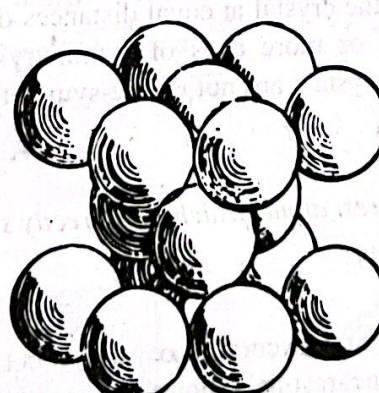


Fig. 2.16. H.C.P.

opposite ends.

2.11. CO-ORDINATION NUMBER

It is defined as the number of nearest atoms which are directly surrounding a given atom.

Let us consider the following cases :

1. Simple Cubic (S.C.) Structure :

Here there are atoms one each at the corners of a unit cell. Any corner atom has four nearest neighbours in the same plane plus two nearest neighbours are exactly above and other exactly below that of corner atom, giving a total of six nearest neighbouring atoms. Thus the co-ordination number of S.C. structure is *six*.

2. Body Centered Cubic (B.C.C.) Structure :

Here there are 8 atoms, one each at the corners of a unit cell, one atom is at the centre of the cube. For any corner atom of the unit cell, the nearest atoms are the body centered atoms and the corresponding to corner atom of the unit cell, there are 8 unit cells in neighbour, which are having 8-body centered atoms. Thus the co-ordination number of B.C.C. structure is *eight*.

3. Face Centered Cubic (F.C.C.) Structure :

The co-ordination number of such structure is *twelve*. Hence the nearest neighbours of any corner

atom are the face-centered atoms of surrounding unit cells. Any corner atom has four such atoms in its own plane, four in a plane above it and four in a plane below it, giving a total of twelve neighbouring atoms.

2.12. ATOMIC RADIUS

Atomic radius is defined as half the distance between nearest neighbours in a crystal of a pure element. It is possible to calculate the atomic radius by assuming that atoms are spheres in contact in a crystal if the structure and the lattice parameters are known.

- (i) Simple cubic (S.C.) structure : Refer Fig. 2.17 (a, b). In this structure atoms touch each other along the lattice.

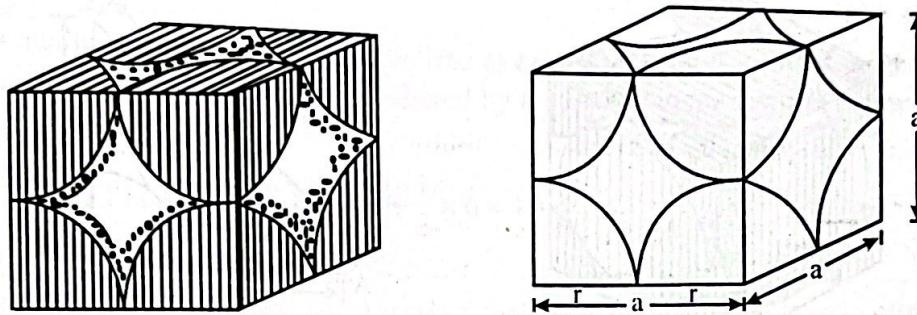


Fig. 2.17. Simple cubic structure.

Therefore, $a = 2r$

or $r = \frac{a}{2}$

- (ii) Body centred cubic (B.C.C.) structure : Refer Fig. 2.18 (a, b). In this structure the atoms touch each other along the diagonal of the cube. Therefore, diagonal of the cube (AC) in this case is $4r$.

Also $AC = \sqrt{AB^2 + BC^2}$

But $AB = \sqrt{a^2 + a^2} = a\sqrt{2}$

$$AC = 4r = \sqrt{(a\sqrt{2})^2 + a^2}$$

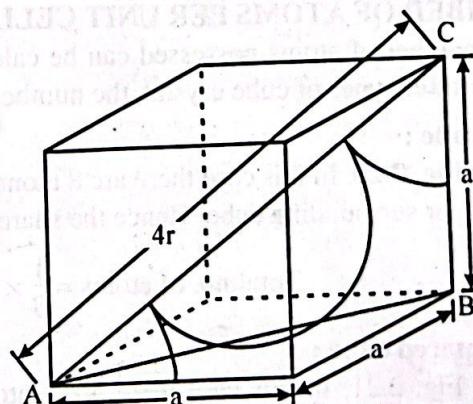
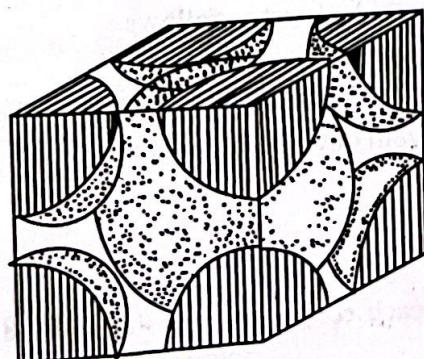


Fig. 2.18. Body centred cubic structure.

or

$$4r = \sqrt{2a^2 + a^2} = a\sqrt{3}$$

or

$$r = \frac{\sqrt{3}}{4}a$$

Conversely,

$$a = \frac{4r}{\sqrt{3}}$$

- (iii) **Face centered cubic (F.C.C.) structure :** Refer Fig. 2.19 (a, b). In this case atoms touch each other along the diagonal of any face of the cube. Obviously the length of diagonal of the face = $4r$.

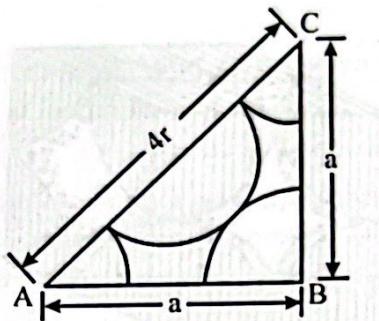
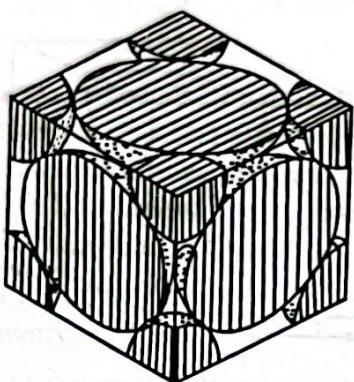


Fig. 2.19. Face centred cubic structure.

Also

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

$$(4r)^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$r^2 = \frac{2a^2}{16}$$

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

$$\text{Conversely, } a = \frac{4r}{\sqrt{2}}$$

2.13. NUMBER OF ATOMS PER UNIT CELL

The number of atoms possessed can be calculated if the arrangement of atoms inside the unit cell is known. For three types of cube crystal, the number of atoms are calculated as follows :

1. Simple cube :

Refer Fig. 2.20. In this case there are 8 atoms one at each corner of the cube and all of them are shared by adjoining or surrounding cube. Hence the share of cube = 1/8th of each corner atom.

∴

$$\text{Total no. of atoms} = \frac{1}{8} \times 8 = 1$$

2. Body centered cube :

Refer Fig. 2.21. In this case there are 8 atoms one at each corner and are shared by 8 surrounding cubes, plus one centre atom at the centre of the cube.

∴

$$\text{Total no. of atoms} = \frac{1}{8} \times 8 + 1 = 2$$

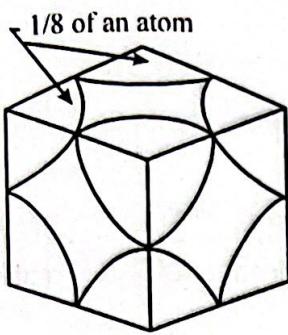


Fig. 2.20.

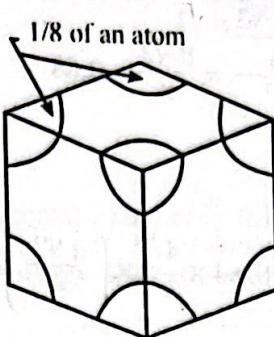


Fig. 2.21.

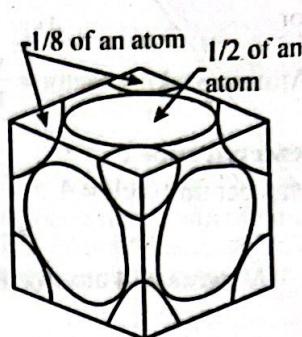


Fig. 2.22.

3. Face centered cube :

Refer Fig. 2.22. In this case there are 8 atoms one at each corner of the cube plus 6 face centered atoms at 6 planes of the cube. Each corner atom is shared by 8 surroundings cubes, and each face centered atom is shared by 2 surroundings cubes.

$$\therefore \text{Total no. of atoms} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 1 + 3 = 4$$

2.14. ATOMIC PACKING FACTOR (A.P.F.)

Atomic packing factor (also known as density of packing) is defined as the *ratio of the volume of atoms per unit cell to the total volume occupied by the unit cell*.

$$\text{A.P.F.} = \frac{\text{Volume of atoms per unit cell}}{\text{Volume of the unit cell}} = \frac{v}{V}$$

1. Simple cube :

Atoms per unit cell = 1

Volume of one atom $v = \frac{4\pi r^3}{3}$ where r is the atomic radius

$$\begin{aligned} v &= \frac{4\pi}{3} \cdot \left(\frac{a}{2}\right)^3 \\ &= \frac{4\pi}{3} \cdot \frac{a^3}{8} = \frac{\pi a^3}{6} \end{aligned}$$

$$\therefore \text{Atomic packing factor} = \frac{v}{V} = \frac{\frac{\pi a^3}{6}}{a^3} = \frac{\pi}{6} = 0.5238 \approx 0.52$$

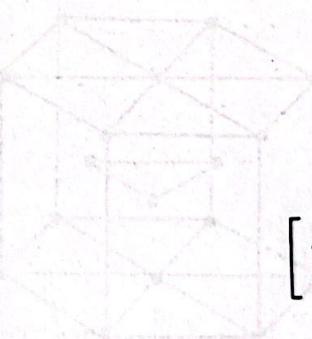
2. Body centered cube :

Atoms per unit cell = 2

$$\begin{aligned} \text{Volume of atoms, } v &= 2 \times \frac{4\pi r^3}{3} = 2 \times \frac{4}{3} \pi \left(\frac{a\sqrt{3}}{4}\right)^3 \\ &= 2 \times \frac{4}{3} \pi a^3 \times \frac{3\sqrt{3}}{64} = \frac{\pi a^3 \sqrt{3}}{8} \end{aligned}$$

$$\text{Volume of the unit cell, } V = a^3$$

$$\left[\because r = \frac{a\sqrt{3}}{4} \right]$$



$$\therefore \text{Atomic packing factor} = \frac{v}{V} = \frac{\frac{\pi a^3 \sqrt{3}}{8}}{a^3} = \frac{\pi \sqrt{3}}{8} = 0.68$$

3. Face centered cube :

Atoms per unit cell = 4

$$\text{Volume of 4 atoms} = 4 \times \frac{4}{3} \pi r^3 = 4 \times \frac{4}{3} \pi \times \left(\frac{a\sqrt{2}}{4} \right)^2$$

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

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

$$\text{Volume of unit cell, } V = a^3$$

$$\therefore \text{Atomic packing factor} = \frac{v}{V} = \frac{\frac{\pi a^3 \sqrt{2}}{6}}{a^3} = \frac{\pi \sqrt{2}}{6} = 0.74$$

4. Hexagonal closed packed (H.C.P.) structure

Fig. 2.23 shows a specific hexagonal structure of magnesium.

The unit cell contains ;

- One atom at each corner,
- one atom each at the centre of the hexagonal faces, and
- three more atoms within the body of the cell.

Each atom touches three atoms in the layer below its plane, six atoms in its own plane, and three atoms in the layer above. Hence coordination number of this structure is 12.

Further, the atoms touch each other along the edge of the hexagon. Thus, $a = 2r$.

The top layer contains seven atoms. Each corner atom is shared by six surrounding hexagon cells and the centre atom is shared by two surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

$$\therefore \text{Total number of atoms in a unit cell} = \frac{3}{2} + \frac{3}{2} + 3 = 6$$

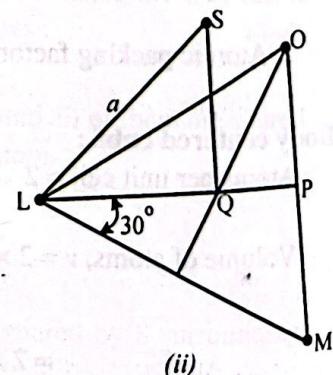
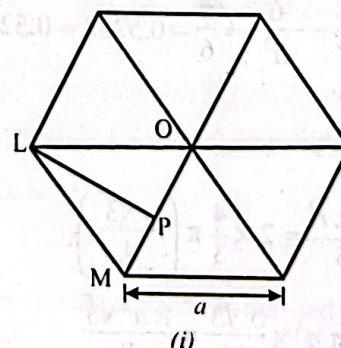
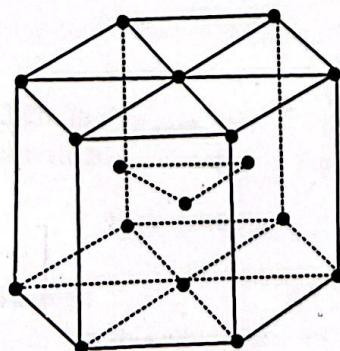


Fig. 2.23. Ideal hexagonal close packed structure.

Fig. 2.24. Bottom layer of H.C.P. structure.

Calculation of $\frac{c}{a}$ ratio for an ideal hexagonal close packed structure :

Let, c = Height of the unit cell, and

a = Edge of the unit cell.

The three body atoms lie in a horizontal plane at $\frac{c}{2}$ from the orthocentres of alternate equilateral triangles at the top or base of the hexagonal cell. These three atoms just rest on the atoms at the corners of the triangles.

Refer Fig. 2.24.,

$$\text{In } \Delta LMP, \quad LP = LM \cos 30^\circ = a \cos 30^\circ = \frac{a\sqrt{3}}{2}$$

$$\text{In } \Delta LQS, \quad LS^2 = LQ^2 + QS^2$$

$$\text{Here, } LQ = \frac{2}{3} LP = \frac{2}{3} \times \frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$

Substituting the appropriate values in eqn. (i), we get

$$a^2 = \left(\frac{a}{\sqrt{3}} \right)^2 + \left(\frac{c}{2} \right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

$$\frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2a^2}{3}$$

or

$$\frac{c^2}{a^2} = \frac{8}{3},$$

or

$$\frac{c}{a} = \sqrt{8/3}$$

Volume of unit cell,

$$V = \text{Area of the base} \times \text{Height of cell}$$

$$= \text{Six times the area of } \Delta LOM \times c$$

$$= 6 \left(\frac{1}{2} \times OM \times LP \right) \times c = 6 \times \left(\frac{1}{2} \times a \times \frac{a\sqrt{3}}{2} \right) \times c$$

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

or

Volume of all the atoms in a unit cell,

$$v = 6 \times \frac{4}{3} \pi r^3$$

$$= 6 \times \frac{4}{3} \pi \left(\frac{a}{2} \right)^3 = \pi a^3$$

or

$$\therefore \text{Atomic packing factor, A.P.F.} = \frac{v}{V} = \frac{\pi a^3}{\frac{3\sqrt{3}}{2} a^2 c} = \frac{2\pi}{3\sqrt{3}} \times \frac{a}{c} = \frac{2\pi}{3\sqrt{3}} \times \frac{\sqrt{3}}{8} = 0.74$$

Table 2.3. Comparison of Cell Properties of Some Crystal Structures

S. No.	Properties	Diamond cube (D.C.)	Simple cube (S.C.)	Body centered cube (B.C.C.)	Face centered cube (F.C.C.)	Hexagonal close packed (H.C.P.)
1.	Volume of unit cell	a^3	a^3	a^3	a^3	$\frac{3}{2}\sqrt{3}a^2c$
2.	Number of atoms per unit cell	8	1	2	4	6
3.	Number of atoms per unit volume	$\frac{8}{a^3}$	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$	$\frac{4}{\sqrt{3}a^2c}$
4.	Number of nearest neighbours (coordination number)	4	6	8	12	12
5.	Nearest neighbour distance (2r)	$\frac{a\sqrt{3}}{4}$	a	$\frac{a\sqrt{3}}{2}$	$\frac{a\sqrt{2}}{2}$	a
6.	Atomic radius	$\frac{a\sqrt{3}}{8}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$
7.	Atomic packing factor	$\frac{\pi\sqrt{3}}{16} = 0.34$	$\frac{\pi}{6} = 0.52$	$\frac{\pi\sqrt{3}}{8} = 0.68$	$\frac{\pi\sqrt{2}}{6} = 0.74$	$\frac{\pi\sqrt{2}}{6} = 0.74$
	Examples	Germanium, silicon and carbon	Polonium	Sodium, lithium and chromium	Aluminium, copper, silver and lead	Magnesium, zinc and cadmium

Table 2.4. Crystal Structures of Representative Compounds

Compound	Molecular weight	Density (kg/m ³) $\times 10^3$	Crystal structure	Lattice constant Å
ZnS	97.43	4.1	Zinc blende	5.41
CdS	144.416	4.6	Zinc blende	5.82
AgI	334.79	5.7	Zinc blende	6.47
NaCl	58.44	2.18	Sodium chloride	5.63
LiH	7.947	2.5	Sodium chloride	4.08
KBr	119.011	2.7	Sodium chloride	6.59
AgBr	187.779	6.5	Sodium chloride	5.77
CsCl	168.362	4.0	Caesium chloride	4.11
NH ₄ Cl	53.497	1.5	Caesium chloride	3.87

Example 2.7. Copper has F.C.C. structure and the atomic radius is 1.278 \AA . Calculate the density of copper crystal. Given atomic weight of copper = 63.5. Avogadro's number = 6.023×10^{23} .

Solution : Here $r = 1.278 \text{ \AA}$

In case of F.C.C. structure number of atoms in unit cell = 4

$$\therefore \text{Mass of each atom of copper} = \frac{63.5}{6.023 \times 10^{23}}$$

$$\text{Lattice constant, } a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.278}{\sqrt{2}} = \frac{4 \times 1.278}{1.414} \text{ \AA} = 3.615 \text{ \AA} = 3.615 \times 10^{-8} \text{ cm}$$

$$\text{Mass of the unit cell} = \frac{4 \times 63.5}{6.023 \times 10^{23}}$$

$$\text{Density} = \frac{\frac{4 \times 63.5}{6.023 \times 10^{23}}}{(3.615 \times 10^{-8})^3} = \frac{4 \times 63.5 \times 10^{24}}{6.023 \times 10^{23} \times (3.615)^3} = 8.92 \text{ gm/cm}^3 \quad (\text{Ans.})$$

Example 2.8. NaCl crystal has F.C.C. structure. The density of NaCl is 2.18 cm^3 . Calculate the distance between two adjacent atoms.

Solution : Molecular weight of NaCl = $23 + 35.5 = 58.5$

$$\begin{aligned} \text{Mass of NaCl molecule} &= \frac{58.5 \text{ (molecular weight)}}{6.02 \times 10^{23} \text{ (Avogadro's number)}} \\ &= 9.718 \times 10^{-23} \end{aligned}$$

$$\begin{aligned} \text{Number of molecules per unit volume} &= \frac{\text{Mass of unit volume of NaCl}}{\text{Mass of a NaCl molecule}} = \frac{2.18}{9.781 \times 10^{-23}} \\ &= 2.444 \times 10^{22} \text{ molecules/cm}^3 \end{aligned}$$

Since NaCl is diatomic,

$$\text{Number of atoms per unit volume of NaCl} = 2 \times 2.444 \times 10^{22} = 4.49 \times 10^{22}$$

If a = Distance between adjacent atoms in NaCl,

and n = Number of atoms along the edge of 1 cm cube,

Then, the length of an edge of a unit cube = na

$$\text{and} \quad \text{volume of unit cube} = n^3 a^3 = 1 \text{ cm}^3$$

$$\text{Since} \quad n^3 = 4.49 \times 10^{22}$$

$$\therefore 4.49 \times 10^{22} \times a^3 = 1$$

$$\text{or} \quad a = \left[\frac{1}{4.49 \times 10^{22}} \right]^{1/3} = 2.81 \times 10^{-8} \text{ cm} = 2.81 \text{ \AA} \quad (\text{Ans.})$$

Example 2.9. If density of NaCl is 2.163 g/cm^3 and its molecular weight 58.45, find the spacing between planes parallel to the cubic lattice faces of NaCl crystal. Given the Avogadro's number is $6.02 \times 10^{23} \text{ molecules/g-mole}$.

Solution : Since the Avogadro's number represents the number of molecules in one gram-molecular weight of the substance, it means that there are 6.02×10^{23} molecules in 58.45 gram of NaCl.

$$\text{No. of molecules/gram} = \frac{6.02 \times 10^{23}}{58.45} = 1.03 \times 10^{22}$$

$$\text{No. of molecules/cm}^3 = 1.03 \times 10^{22} \times 2.163 = 2.23 \times 10^{22}$$

Since there are two atoms to a molecule,

$$\text{No. of atoms/cm}^3 = 2 \times 2.23 \times 10^{22} = 4.46 \times 10^{22}$$

Since, NaCl crystal lattice consists of a multitude of cubes with atoms at the centres, there will be $(4.46 \times 10^{22})^{1/3} = 3.54 \times 10^7$ atoms in a row, 1 cm long. The spacing between atoms and hence rows or planes is

$$d = \frac{1}{3.54 \times 10^7} = 2.825 \times 10^{-8} \text{ cm} = 2.825 \text{ Å} \quad (\text{Ans.})$$

Example 2.10. Calculate the number of atoms per unit cell of a metal having the lattice parameter 2.9 Å and density 7.87 g/cm³. Atomic weight of the metal is 55.85 and Avogadro's constant is 6.0238×10^{23} .

Solution : Let a = Edge of unit cell = lattice parameter of a cube cell,

M = Mass of element per mole = atomic weight of the element,

ρ = Density of the metal,

N_A = Avogadro's number; number of atoms per mole, and

n = Number of atom per unit cell.

Given : $a = 2.9 \text{ Å} = 2.9 \times 10^{-8} \text{ cm}$

$M = 58.85$

$\rho = 7.87 \text{ gm/c.c.}$

$N_A = 6.0238 \times 10^{23}$

Number of atoms per unit cell, n :

Using the relation, $\rho a^3 = \frac{nM}{N_A}$

$$\text{or } n = \frac{\rho a^3 N_A}{M} = \frac{7.87 \times (2.9 \times 10^{-8})^3 \times 6.0238 \times 10^{23}}{55.85} = 2 \quad (\text{Ans.})$$

Since the total number of atoms per unit cell is 2, therefore, the unit cell may be B.C.C. (body centered cubic).

Example 2.11. NaCl crystals have FCC structure. The densit of NaCl is 2.18 g/cm³. Calculate the distance between two adjacent atoms. Atomic weight of sodium = 23 and that of chlorine = 35.5.

Solution : Using the relation :

$$a^3 \rho = \frac{nM}{N_A}$$

Now a is the distance between atoms of the same kind, i.e., equal to the length of the edge of the unit cell. Since NaCl has 4 molecules per unit cell, hence $n = 4$.

$$\text{Also } M = 23 + 35.5 = 58.5 \text{ and } N_A = 6.02 \times 10^{23} \text{ g/mol.}$$

$$\therefore a^3 \times 2.18 = \frac{4 \times 58.5}{6.02 \times 10^{23}}$$

$$\therefore a^3 = \frac{4 \times 58.5}{6.02 \times 10^{23} \times 2.18}$$

$$\text{and } a = 5.628 \times 10^{-8} \text{ cm}$$

Obviously, the distance between adjacent atoms is half of this value.

$$\therefore d = \frac{a}{2} = \frac{5.628 \times 10^{-8}}{2} = 2.814 \times 10^{-8} \text{ cm (Ans.)}$$

Example 2.12. Iron has cubic structure and its atomic weight is 55.84. The density of iron is 7900 kg/m³ and its lattice constant is 2.86 Å. Examine the type of the cubic structure.

Solution : Given : Atomic weight = 55.84; density of iron = 7900 kg/m³; $a = 2.86 \text{ \AA} = 2.86 \times 10^{-10} \text{ m}$.

Type of cubic structure :

Let there be n atoms per unit cell.

$$\text{Then, } 7900 = \frac{n \times \frac{55.84}{6.02 \times 10^{26}}}{(2.86 \times 10^{-10})^3}$$

$$\text{or } n = \frac{7900 \times (2.86 \times 10^{-10})^3 \times 6.02 \times 10^{26}}{55.84} = 2$$

Hence iron has B.C.C. structure. (Ans.)

Example 2.13. Calculate the density of nickel which has F.C.C. structure, given the mass of nickel atom as 58.71 a.m.u. (atomic mass unit) and radius of nickel atom is 1.25 Å. 1 a.m.u. = $1.66 \times 10^{-27} \text{ kg}$.

Solution : Given : Mass of nickel atom = 58.71 a.m.u.

Radius of nickel atom, $r = 1.25 \text{ \AA}$

$$1 \text{ a.m.u.} = 1.66 \times 10^{-27} \text{ kg}$$

Structure of nickel : F.C.C.

Density of nickel :

$$\text{Lattice constant, } a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.25 \times 10^{-10}}{\sqrt{2}} = 3.536 \times 10^{-10} \text{ m}$$

$$\text{Mass of unit cell} = 4 \times 58.71 \times 1.66 \times 10^{-27}$$

$$\therefore \text{Density of nickel} = \frac{4 \times 58.71 \times 1.66 \times 10^{-27}}{(3.536 \times 10^{-10})^3} = 8817 \text{ kg/m}^3 \text{ (Ans.)}$$

2.15. MILLER INDICES

Miller indices is a system of notation of planes within a crystal of space lattice. They are based on the intercepts of plane with the three crystal axes, i.e., edges of the unit cell. The intercepts are measured in terms of the edge lengths or dimensions of the unit cell which are unit distances from the origin along three axes.

Procedure for finding Miller Indices :

The Miller indices of a crystal plane are determined as follows : (Refer Fig. 2.26)

Step 1 : Find the intercepts of the plane along the axes x , y , z (The intercepts are measured as multiples of the fundamental vector). ...4, 2, 3

Step 2 : Take reciprocals of the intercepts

$$\frac{1}{4}, \frac{1}{2}, \frac{1}{3}$$

Step 3 : Convert into smallest integers in the same ratio

...3 6 4

Step 4 : Enclose in parentheses

...(3 6 4)

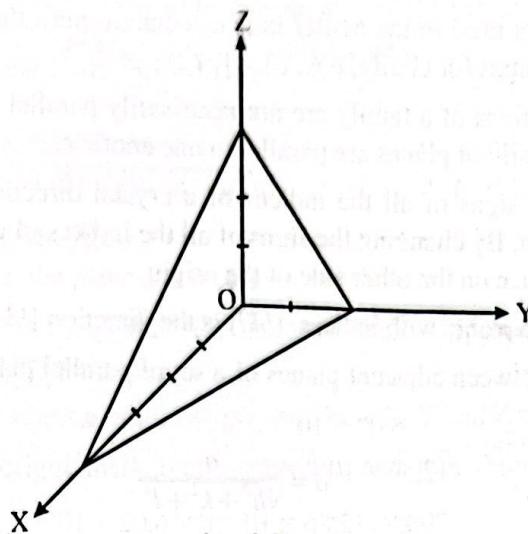


Fig. 2.26.

The factor that results in converting the reciprocals of integers may be indicated outside the brackets, but it is usually omitted.

Important Note : The directions in space is represented by square brackets []. The commas inside the square brackets are used separately and not combined. Thus [1 1 0] is read as "One-one-zero" and not "one hundred ten". Negative indices are represented by putting a bar over digit, e.g., [$\bar{1}$ 1 0]. The general way of representing the indices of a direction of a line is $[x y z]$. The indices of a plane are represented by a small bracket, $(h k l)$. Sometimes the notations $< >$ and $()$ or are also used for representing planes and directions respectively.

The following procedure is adopted for sketching any direction :

1. First of all sketch the plane with the given Miller indices.
2. Now through the origin, draw a line normal to the sketched plane, which will give the required direction.

2.16. IMPORTANT FEATURES OF MILLER INDICES

Some of the important features of Miller indices (particularly for the cubic system) are detailed below:

1. A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞) and therefore, the Miller index for that axis is zero.
2. All equally spaced parallel planes with a particular orientation have same index number $(h k l)$.
3. Miller indices do not only define particular plane but a set of parallel planes.
4. It is the ratio of indices which is only of importance. The planes (211) and (422) are the same.
5. A plane passing through the origin is defined in terms of a parallel plane having non-zero intercepts.
6. All the parallel equidistant planes have the same *Miller indices*. Thus the Miller indices define a set of parallel planes.
7. A plane parallel to one of the coordinate axes has an intercept of infinity.
8. If the Miller indices of two planes have the same ratio (i.e., 844 and 422 or 211), then the planes are parallel to each other.
9. If $(h k l)$ are the Miller indices of a plane, then the plane cuts the axes into a/h , b/k and c/l equal segments respectively.

10. When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas for clarity, e.g., (3, 11, 12).
11. The crystal directions of a family are not necessarily parallel to one another. Similarly, not all members of a family of planes are parallel to one another.
12. By changing the signs of all the indices of a crystal direction, we obtain the antiparallel or opposite direction. By changing the signs of all the indices of a plane, we obtain a plane located at the same distance on the other side of the origin.
13. The normal to the plane with indices (hkl) is the direction $[hkl]$.
14. The distance d between adjacent planes of a set of parallel planes of the indices $(h k l)$ is given by :

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the edge of the cube.

Normally the planes with *low index numbers* have wide interplanar spacing compared with those having *high index numbers*. Moreover, *low index planes* have a higher density of atoms per unit area than the *high index plane*. In fact, it is the *low index planes* which play an important role in determining the physical and chemical properties of solids.

15. The angle between the normals to the two planes $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ is

$$\cos\theta = \frac{(h_1 h_2)/a^2 + (k_1 k_2)/b^2 + (l_1 l_2)/c^2}{\sqrt{(h_1/a)^2 + (k_1/b)^2 + (l_1/c)^2} \sqrt{(h_2/a)^2 + (k_2/b)^2 + (l_2/c)^2}} \text{ for orthorhombic system.} \quad \dots(2.5)$$

$$\text{and } \cos\theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}} \text{ for cubic system.} \quad \dots(2.6)$$

16. A negative Miller index shows that the plane (hkl) cuts the x -axis on the negative side of the origin.
17. Miller indices are proportional to the direction cosines of the normal to all corresponding plane.
18. The purpose of taking reciprocals in the present scheme is to bring all the planes inside a single unit cell so that we can discuss all crystal planes in terms of the planes passing through a single unit cell.
19. Most planes which are important in determining the physical and chemical properties of solids are those with low index numbers.
20. The plane (hkl) is parallel to the line $[uvw]$ if $hu + kv + lw = 0$.
21. Two planes $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ both contain line $[uvw]$ if

$$u = k_1 l_2 - k_2 l_1, v = l_1 h_2 - l_2 h_1 \text{ and } w = h_1 k_2 - h_2 k_1$$

Then both the planes are parallel to the line $[uvw]$ and therefore, their intersection is parallel to $[uvw]$ which defines the zone axis.

22. The plane (hkl) belongs to two zones $[u_1 v_1 w_1]$ and $[u_2 v_2 w_2]$ if $h = v_1 w_2 - v_2 w_1$, $k = v_1 w_2 - v_2 w_1$ and $l = v_1 w_2 - v_2 w_1$.
23. The plane $(h_3 k_3 l_3)$ will be among those belonging to the same zone as $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ if $h_3 = h_1 \pm h_2$, $k_3 = k_1 \pm k_2$ and $l_3 = l_1 \pm l_2$.
24. The angle between the two directions $[u_1 v_1 w_1]$ and $[u_2 v_2 w_2]$ for orthorhombic system is

$$\cos\phi = \frac{u_1 u_2 a^2 + v_1 v_2 b^2 + w_1 w_2 c^2}{\sqrt{u_1^2 a^2 + v_1^2 b^2 + w_1^2 c^2} \sqrt{u_2^2 a^2 + v_2^2 b^2 + w_2^2 c^2}} \quad \dots(2.7)$$

and for cubic system is

$$\cos\phi = \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{u_1^2 + v_1^2 + w_1^2} \sqrt{u_2^2 + v_2^2 + w_2^2}} \quad \dots(2.8)$$

Given Miller Indices how to draw the plane :

For the given Miller indices, the plane can be drawn as follows :

Step-1. Find the reciprocal of the given Miller indices. These reciprocals give the intercepts made by the plane on X, Y and Z axes respectively.

Step-2. Draw the cube and select a proper origin and show X, Y and Z axes respectively.

Step-3. With respect to origin mark these intercepts and join through straight lines. The plane obtained is the required plane.

Following points are worth noting :

- (i) Take lattice constant as one unit.
- (ii) If the intercept for an axis is infinity then proceed parallel to that axis till you reach the next lattice point.
- (iii) Try to get two points and join them first.

Fig. 2.27 (a) and (b) shows important planes of cube. Thick lines with arrows indicate the directions.

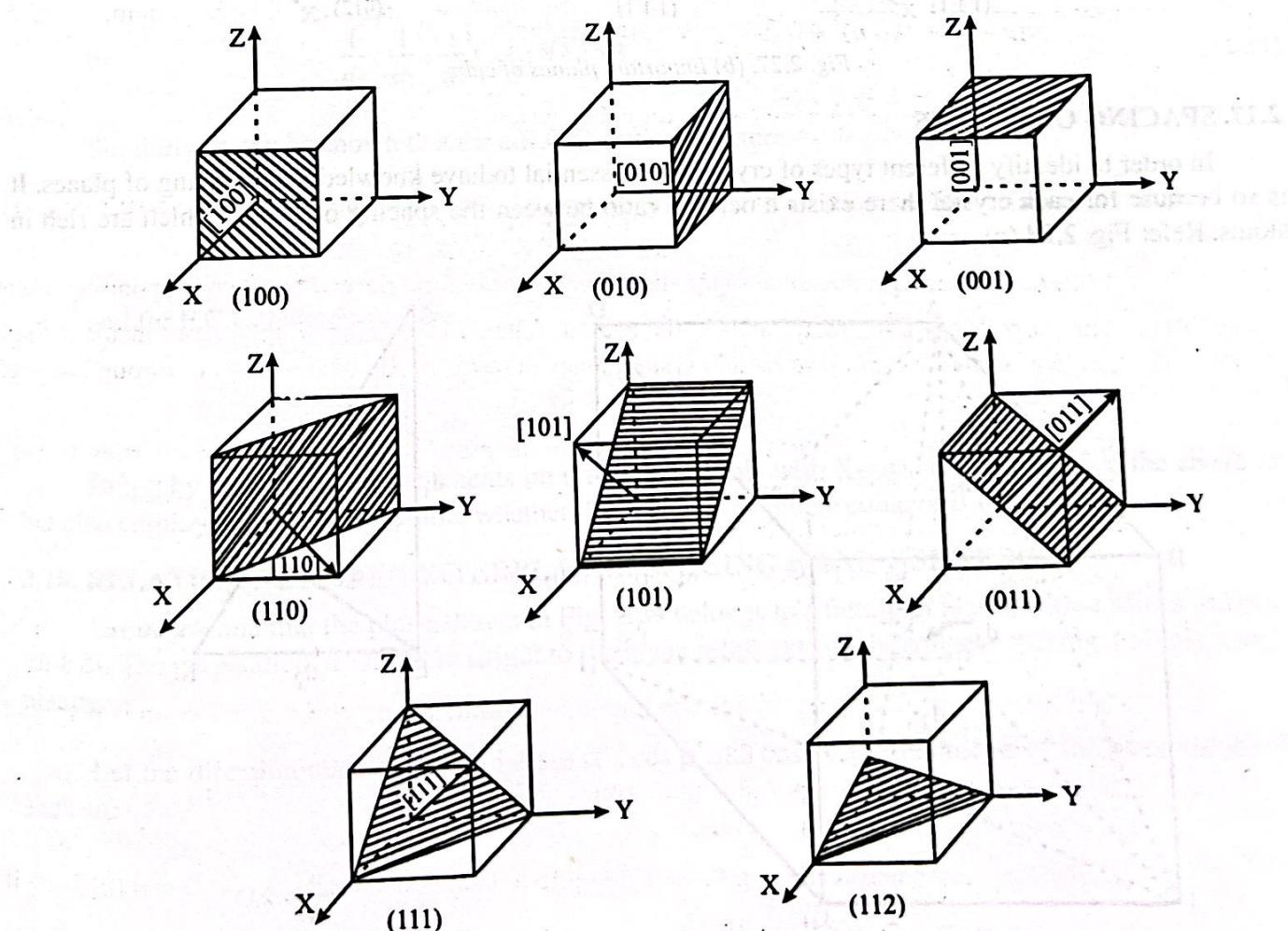


Fig. 2.27. (a) Important planes of cube.

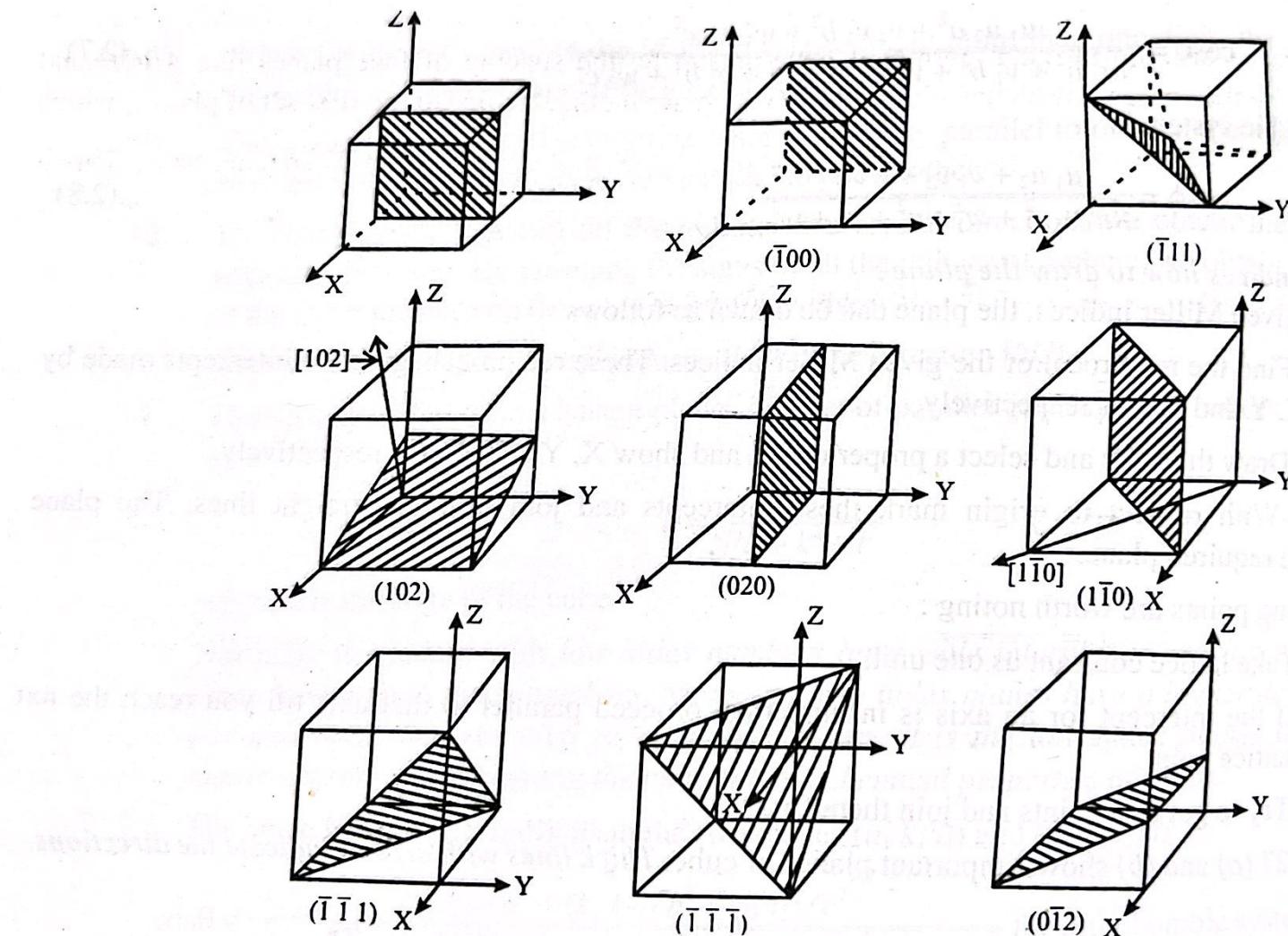


Fig. 2.27. (b) Important planes of cube.

Example 2.14. Obtain the Miller indices of a plane which intercepts at a , $b/2$, $3c$ in a simple cubic unit cell.

Solution : The linear parameters of the plane are a , $b/2$, $3c$. Its numerical parameters are : $1, \frac{1}{2}, 3$

Hence, its Miller indices are :

$$\left(\frac{1}{1}, \frac{1}{\frac{1}{2}}, \frac{1}{3} \right) \quad \dots \text{(Reciprocals)}$$

or

$$\left(1 2 \frac{1}{3} \right)$$

or

$$(3 \ 6 \ 1) \text{ (Ans.)}$$

Example 2.15. Draw the (112) and (111) planes in a simple cubic cell.

OR

Draw the different (111) planes in the unit cell of a simple cubic structure.

Solution : Miller indices of the planes (112) have the following intercepts on the three axes, i.e.,

$$\frac{1}{1}, \frac{1}{1}, \frac{1}{2} \quad \dots[\text{Refer Fig. 2.30 (a)}]$$

Now the axial intercepts of the plane (111) are

$$\frac{1}{1}, \frac{1}{1}, \frac{1}{1}$$

The four (111) triangle planes [Fig. 2.30 (b)] are AFH, CFH, ACH, ACF.

Example 2.16. Draw (110) and (111) planes and [110] and [111] directions in a simple cubic crystal. What do you infer from these diagrams?

Solution : The required planes are shown in Fig. 2.31.

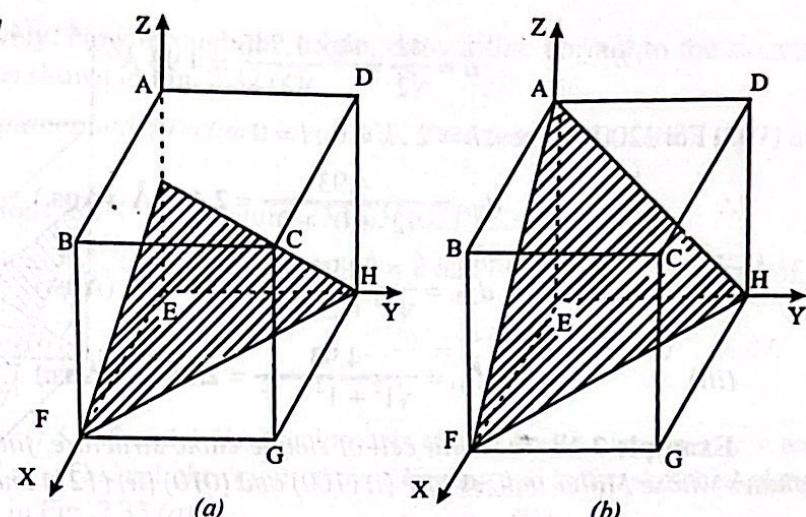


Fig. 2.30.

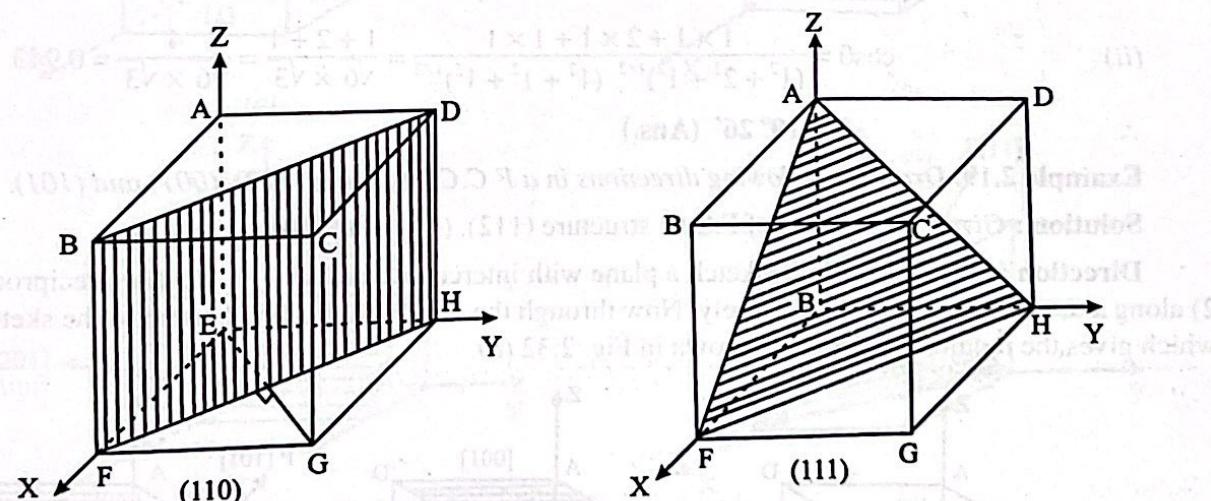


Fig. 2.31.

The direction of (110) is denoted by EG and direction of (111) by EC. (The directions are described by giving the co-ordinates of the first whole number point (x, y) through which they pass). The inference is that direction [110] is perpendicular to the plane (110). So is the case with other pair of direction and plane.

Example 2.17. Lead is the face centered cubic with an atomic radius $r = 1.747 \text{ \AA}$. Find the spacing of (i) (200) planes (ii) (220) planes and (iii) (111) planes.

Solution : Interplanar spacing, d is given by the relation :

$$d = \frac{a}{(\sqrt{h^2 + k^2 + l^2})} \quad \dots[\text{Eqn. (2.9)}]$$

Also, for F.C.C. structure

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.746}{\sqrt{2}} = 4.93 \text{ \AA}$$

(i) For (200) planes, $h = 2, k = 0, l = 0$

$$\therefore d_{200} = \frac{4.93}{\sqrt{2^2 + 0^2 + 0^2}} = 2.465 \text{ \AA} \quad (\text{Ans.})$$

$$(ii) \text{ Similarly } d_{220} = \frac{4.93}{\sqrt{2^2 + 2^2 + 0^2}} = 1.74 \text{ \AA} \quad (\text{Ans.})$$

$$(iii) \quad d_{111} = \frac{4.93}{\sqrt{1^2 + 1^2 + 1^2}} = 2.85 \text{ \AA} \quad (\text{Ans.})$$

Example 2.18. In a unit cell of simple cubic structure, find the angle between the normals to pair of planes whose Miller indices are (i) (100) and (010) (ii) (121) and (111).

Solution : The directions of the two normals are [100], [010] and [121], [111] respectively.

Using the relation

$$\cos\theta = \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{(u_1^2 + v_1^2 + w_1^2)^{1/2} (u_2^2 + v_2^2 + w_2^2)^{1/2}}, \text{ we have}$$

$$(i) \quad \cos\theta = \frac{1 \times 0 + 0 \times 1 + 0 \times 0}{(1^2 + 0^2 + 0^2)^{1/2} (0^2 + 1^2 + 0^2)^{1/2}} = 0$$

$$\therefore \theta = 90^\circ \quad (\text{Ans.})$$

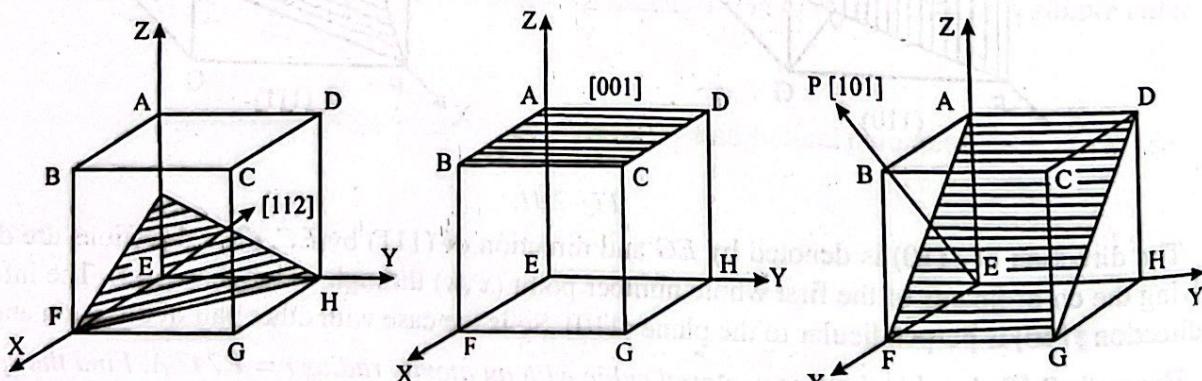
$$(ii) \quad \cos\theta = \frac{1 \times 1 + 2 \times 1 + 1 \times 1}{(1^2 + 2^2 + 1^2)^{1/2} (1^2 + 1^2 + 1^2)^{1/2}} = \frac{1+2+1}{\sqrt{6} \times \sqrt{3}} = \frac{4}{\sqrt{6} \times \sqrt{3}} = 0.943$$

$$\therefore \theta = 19^\circ 26' \quad (\text{Ans.})$$

Example 2.19. Draw the following directions in a F.C.C. structure (112), (001) and (101).

Solution : Given : Directions of F.C.C. structure (112), (001) and (101).

Direction (112) : First of all, sketch a plane with intercepts equal to 1, 1, 0.5 (i.e., reciprocals of 1, 1, 2) along x - x , y - y and z - z axes respectively. Now through the origin draw a line normal to the sketched plane, which gives the required direction as shown in Fig. 2.32 (a).



(a) Direction (112).

(b) Direction (001).

(c) Direction (101).

Fig. 2.32.

Direction (001) : First sketch a plane with intercepts equal to ∞, ∞ and 1 (i.e., reciprocals of 0, 0, 1) along x - x , y - y and z - z axes respectively. Now through the origin, draw a line normal to the sketched plane, which gives the required direction as shown in Fig. 2.32 (b).

Direction (101) : First of all, sketch a plane with intercepts equal to 1, ∞ and 1 (i.e., reciprocals of 1,

0, 1) along x - x , y - y and z - z axes respectively. Now through the origin, draw a line normal to the sketched plane, which gives the required direction as shown in Fig. 2.32 (c).

Example 2.20. Draw the following planes and directions in a F.C.C. structure (321), (102), (201) and (111).

Solution : Given : Planes and directions in F.C.C. structures (321), (102), (201) and (111).

(i) **Plane and direction (321)** : We know that in this case $h = 3$, $k = 2$ and $l = 1$. And reciprocals of h , k and l are

$$\frac{1}{3}, \frac{1}{2}, \frac{1}{1} = 0.3, 0.5, 1$$

Now sketch the plane with intercepts 0.3, 0.5 and 1 (i.e., reciprocals of h , k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.33 (a). Through the origin, draw a line normal to the sketched plane. This gives the required direction as shown in Fig. 2.33 (a).

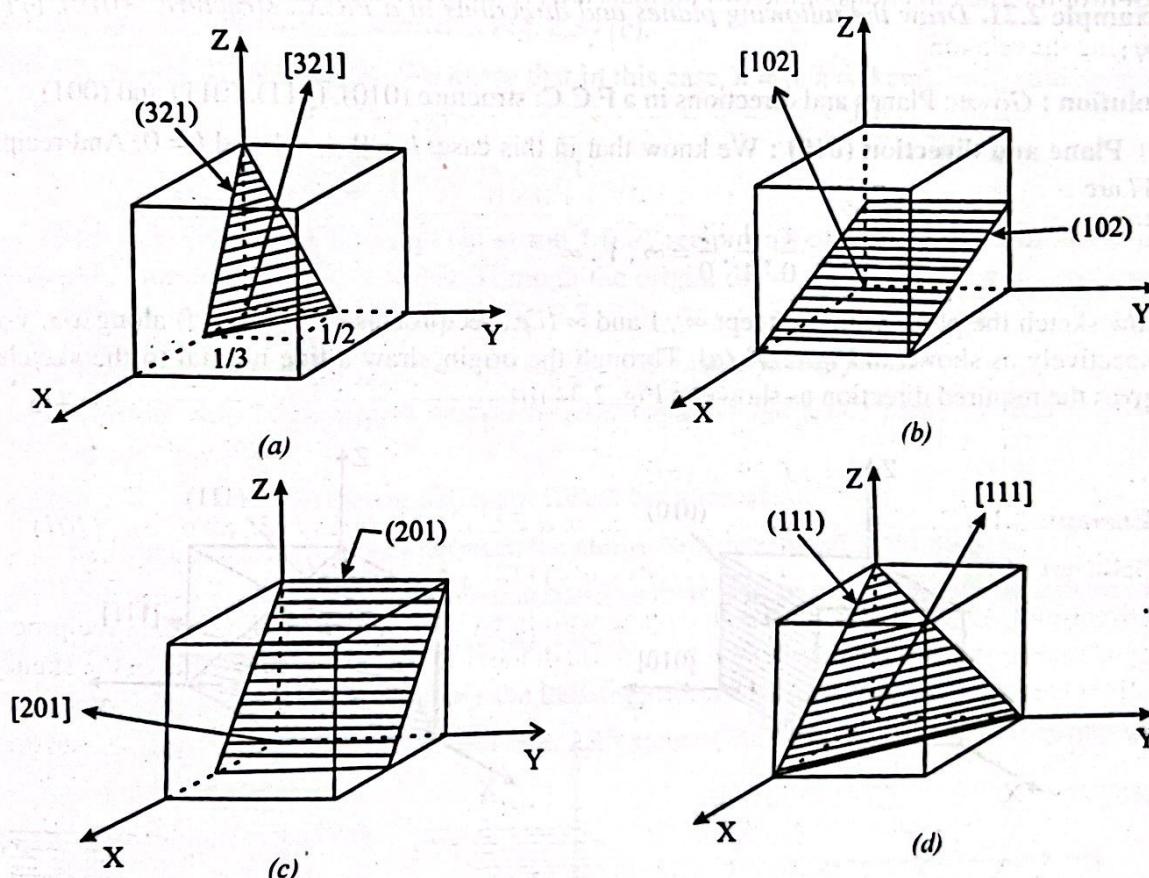


Fig. 2.33.

(ii) **Plane and direction (102)** : We know that in this case $h = 1$, $k = 0$ and $l = 2$ and reciprocals of h , k and l are :

$$\frac{1}{1}, \frac{1}{0}, \frac{1}{2} = 1, \infty, 0.5$$

Now sketch the plane with intercepts 1, ∞ and 0.5 (i.e., reciprocals of h , k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.33 (b). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.33 (b).

(iii) **Plane and direction (201)** : We know that in this case $h = 2$, $k = 0$ and $l = 1$. And intercepts h , k and l are :

$$\frac{1}{2}, \frac{1}{0}, \frac{1}{1} = 0.5, \infty, 1.$$

Now sketch the plane with intercepts $0.5, \infty$ and 1 (i.e., reciprocals h, k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.33 (c). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.33 (c).

(iv) **Plane and direction (111)** : We know that in this case, $h = 1, k = 1$ and $l = 1$. And reciprocals of h, k and l are :

$$\frac{1}{1}, \frac{1}{1}, \frac{1}{1} = 1, 1, 1.$$

Now sketch the plane with intercepts, $1, 1$ and 1 (i.e., reciprocals of h, k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.33 (d). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.33 (d).

Example 2.21. Draw the following planes and directions in a F.C.C. structure : (010), (111), (011) and (001).

Solution : Given : Planes and directions in a F.C.C. structure (010), (111), (011) and (001).

(i) **Plane and direction (010)** : We know that in this case, $h = 0, k = 1$ and $l = 0$. And reciprocals of h, k and l are :

$$\frac{1}{0}, \frac{1}{1}, \frac{1}{0} = \infty, 1, \infty$$

Now sketch the plane with intercept $\infty, 1$ and ∞ (i.e., reciprocals of h, k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.34 (a). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.34 (a).

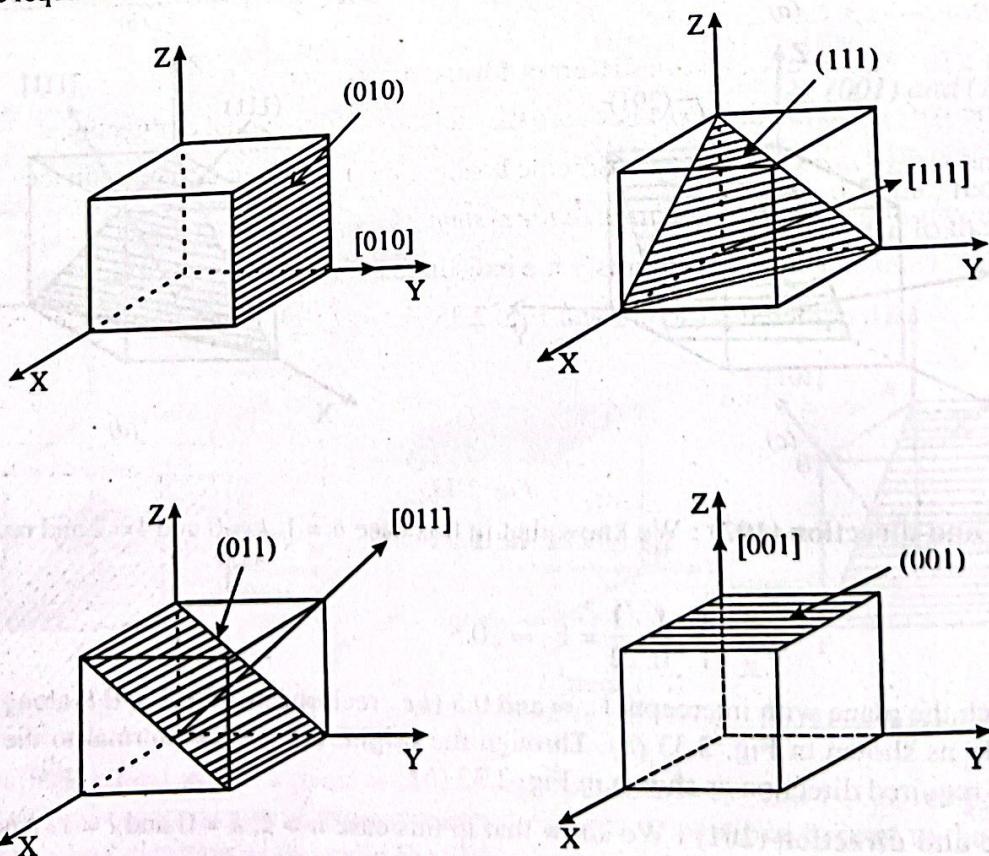


Fig. 2.34.

(ii) **Plane and direction (111)** : We know that in this case, $h = 1$, $k = 1$ and $l = 1$. And reciprocals of h , k and l are

$$\frac{1}{1}, \frac{1}{1}, \frac{1}{1} = 1, 1, 1$$

Now sketch the plane with intercept 1, 1 and 1 (i.e., reciprocals of h , k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.34 (b). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.34 (b).

(iii) **Plane and direction (011)** : We know that in this case, $h = 0$, $k = 1$ and $l = 1$. And reciprocals of h , k and l are

$$\frac{1}{0}, \frac{1}{1}, \frac{1}{1} = \infty, 1, 1$$

Now sketch the plane with intercept ∞ , 1 and 1 (i.e., reciprocals of h , k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.34 (c). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.34 (c).

(iv) **Plane and direction (001)** : We know that in this case, $h = 0$, $k = 0$ and $l = 1$. And reciprocals of h , k and l are

$$\frac{1}{0}, \frac{1}{0}, \frac{1}{1} = \infty, \infty, 1$$

Now sketch the plane with intercept ∞ , ∞ and 1 (i.e., reciprocals of h , k and l) along x - x , y - y and z - z axes respectively as shown in Fig. 2.34 (d). Through the origin, draw a line normal to the sketched plane which gives the required direction as shown in Fig. 2.34 (d).

Example 2.22. (a) Why different materials exist in different structure form ?

(b) How many atoms per square millimeter are there on the (100) plane of lead ? Assume the interatomic distance as 3.499 Å.

Solution : (a) Materials exist in different forms because of :

- (i) The type of bonds that exist between the atoms-Non directional or directional.
- (ii) The size of atoms. In the case of ionic bonding there will be a difference in the size of atoms.
- (iii) The minimum energy condition of the system.
- (iv) The symmetry principle to satisfy the indistinguishability of the space lattice.

(b) Lead has face centered structure and Fig. 2.35 shows (100) plane. The shaded portion shows the portion of the atom.

$$\text{Interatomic distance} = 3.499 \text{ \AA}$$

$$2r = 3.499 \text{ \AA}$$

If a is the side of square then $\sqrt{2}a = 4r$
(length of the diagonal)

$$a = \frac{4r}{\sqrt{2}} = \frac{2 \times 3.499}{\sqrt{2}} = 4.95 \text{ \AA}$$

$$\text{Area of (100) plane} = (4.95 \times 10^{-7})^2 \text{ mm}^2$$

$$\text{No. of atoms in the plane} = 2$$

$$\begin{aligned} \text{Atoms/mm}^2 &= \frac{2}{(4.95 \times 10^{-7})^2} \\ &= 8.2 \times 10^{12} \text{ atoms/mm}^2 \quad (\text{Ans.}) \end{aligned}$$

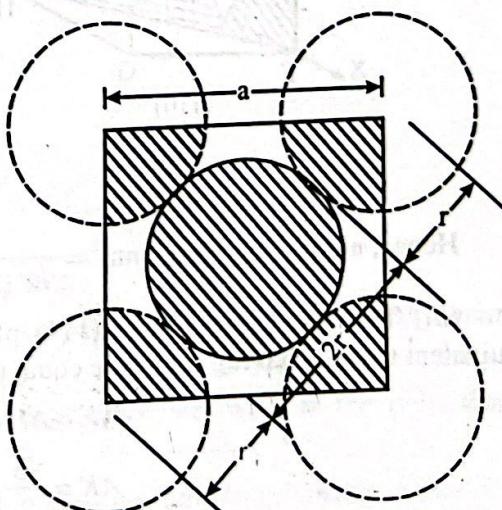
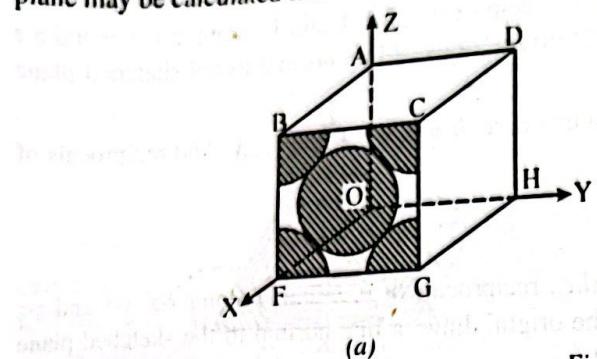


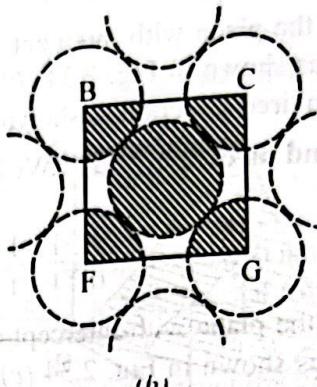
Fig. 2.35.

Example 2.23. How many atoms per mm^2 surface area are there in (i) (100) plane, (ii) (110) plane and (iii) plane for copper which has FCC structure and a lattice constant $a = 3.61 \times 10^{-7} \text{ mm}$.

Solution : (i) Fig. 2.36 shows the two views of (100) plane. The number of atoms/ mm^2 area of the plane may be calculated from the following consideration :



(a)



(b)

Fig. 2.36.

Surface area of face $BFGC$ is

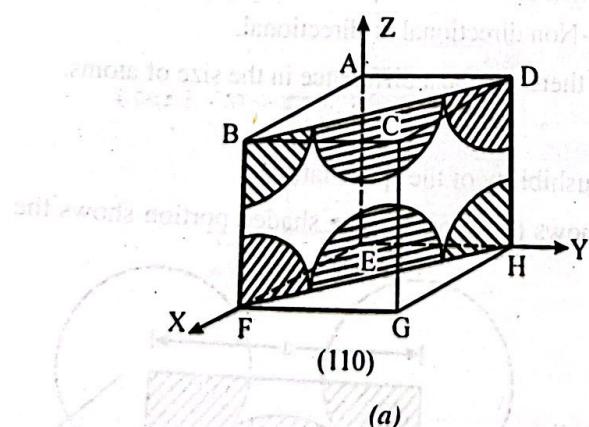
$$a^2 = (3.61 \times 10^{-7})^2 \text{ mm}^2 = 13 \times 10^{-14} \text{ mm}^2$$

Since the (100) plane includes one full atom and four quarter atoms [Refer Fig. 2.36 (b)], therefore, the total number of atoms included $= 1 + (4 \times 1/4) = 2$. Because an area of $13 \times 10^{-14} \text{ mm}^2$ contains 2 atoms, therefore, number of atoms per mm^2 of surface area

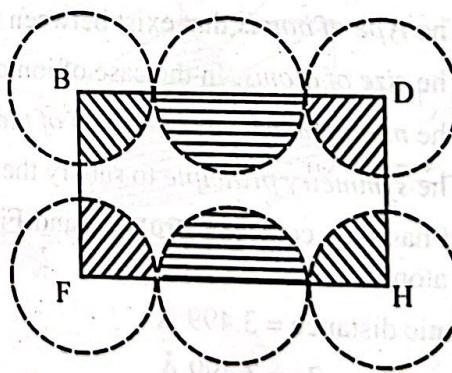
$$= \frac{2}{13 \times 10^{-14}} = 1.54 \times 10^{13} \text{ atoms/mm}^2 \text{ (Ans.)}$$

(ii) Fig. 2.37 shows the (110) plane $BFHD$. As is evident, it contains four quarter atoms and two half atoms. Total number of atoms $= (4 \times 1/4) + (2 \times 1/2) = 2$.

$$\text{Area of plane} = BF \times FH = a \times \sqrt{2} a = \sqrt{2} a^2 = \sqrt{2} (3.61 \times 10^{-7})^2 \text{ mm}^2$$



(a)



(b)

Fig. 2.37.

$$\text{Hence, number of atoms/mm}^2 = \frac{2}{\sqrt{2} (3.61 \times 10^{-7})^2} = 1.08 \times 10^{13} \text{ atoms/mm}^2 \text{ (Ans.)}$$

(iii) The two views of the (111) plane are shown in Fig. 2.38. It may be observed that it is an equivalent triangle having each side equal to the face diagonal of the cube.

$$AF = AH = FH = \sqrt{2} a$$

$$AK = \frac{\sqrt{3}}{2} AH = \frac{\sqrt{3}}{2} \times \sqrt{2} a$$

$$\text{Area of } \triangle AFH = \frac{1}{2} FH \times AK = \frac{1}{2} \times \sqrt{2}a \times \frac{\sqrt{3}}{2} \times \sqrt{2}a = \frac{\sqrt{3}}{2}a^2 = 0.866a^2$$

As seen from Fig. 2.38 (b), it contains three one sixths of an atom and three one-halves. Hence number of atoms

$$= (3 \times 1/6) + (3 \times 1/2) = 2$$

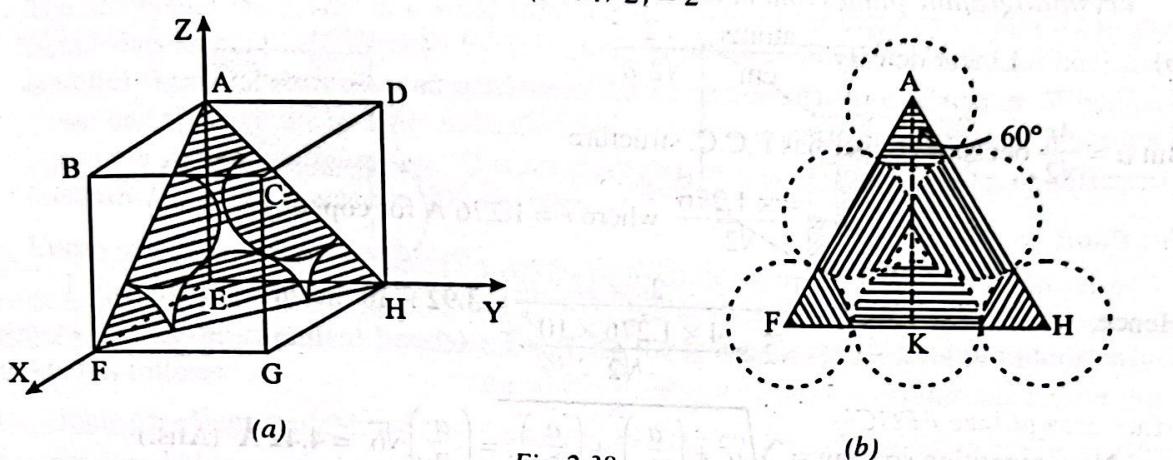


Fig. 2.38.

Hence number of atoms/mm² surface area of (111) plane

$$= \frac{2}{0.866 \times (3.61 \times 10^{-7})^2} = 1.778 \times 10^{13} \text{ atoms/mm}^2 \quad (\text{Ans.})$$

Example 2.24. A F.C.C. unit cell has a lattice constant $a = 4.0 \times 10^{-10}$ m. Calculate the number of atoms per units area on (110) and (111) planes and density of atoms per unit length in directions [110] and [111].

Solution : In plane (110) :

$$\text{No. of atoms} = 2 \times \frac{1}{2} \text{ (centres)} + 4 \times \frac{1}{4} \text{ (corners)} = 1 + 1 = 2$$

Now area of (110) plane $= a \times a \sqrt{2}$

$$\therefore \text{No. of atoms per unit area} = \frac{2}{a^2 \sqrt{2}} = \frac{2}{(4.0 \times 10^{-10})^2 \times \sqrt{2}} = 8.84 \times 10^8 \text{ atoms/m}^2 \quad (\text{Ans.})$$

In plane (111) :

$$\text{No. of atoms} = 3 \times \frac{1}{2} \text{ (centres)} + 3 \times \frac{1}{6} \text{ (corners)} = \frac{3}{2} + \frac{3}{6} = 2 \text{ atoms}$$

$$\text{Area of plane} = \frac{\sqrt{3}}{2} a^2$$

$$\begin{aligned} \therefore \text{No. of atoms per unit area} &= \frac{2}{\frac{\sqrt{3}}{2} a^2} = \frac{4}{\sqrt{3} a^2} = \frac{4}{\sqrt{3} (4.0 \times 10^{-10})^2} \\ &= 1.444 \times 10^{10} \text{ atoms/m}^2 \quad (\text{Ans.}) \end{aligned}$$

2.22.8. X-ray Diffraction Analysis of Crystals

- When visible electromagnetic radiation is to be diffracted the spacing between lines in two dimensional grating must be of the same order as the wavelength range of light (3900-7800 Å).
The same principle is true for diffraction by the three dimensional grating of the periodic array of

atoms in the crystals. The typical interatomic spacing in crystals is 2-3 Å. Therefore, the wavelength of the radiation used for crystal diffraction should be in the same range. X-rays have wavelength in this range and are, therefore, diffracted by crystals. This property is widely used for the study of crystal structures. A beam of X-ray directed at a crystal interacts with the electrons of the atoms that constitute the crystals. The electrons oscillate under the impact. They 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 oscillations of electrons of all the atoms. *These emissions will be in phase and reinforce one another only in certain specific directions, which depends on the direction of incident X-rays, their wavelength as well as the spacing between atoms in the crystal.* In other directions there is a destructive interference of the emissions from different sources.

- The easiest method to visualise the diffraction effects produced by the three dimensional grating provided by the crystal is by considering Bragg's law. *Bragg's law states that for a given X-ray diffraction by regularly spaced atomic centres in a set of parallel planes in a crystal with interplaner spacing 'd' and using homogenous radiation of wavelength λ , reinforcement will occur only at those angles which satisfy the relation.*

$$2d \sin \theta = n \lambda$$

where n is called the *order* and is integer and θ being the glancing angle or angle of incidence; or angle of reflection of diffracted beam.

- The lattice parameters of cubic crystals can be determined by using Bragg's equation. Let us consider the value that n should be assigned. A second order reflection from (100) planes should satisfy the following Bragg's condition :

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

$$d_{100} \sin \theta = \lambda \quad \dots(i)$$

Similarly, a first order reflection from (200) planes will satisfy the equation,

$$2d_{200} \sin \theta = \lambda \quad \dots(ii)$$

We know that interplanar spacing of (100) planes is twice for (200) planes. Therefore, Eqns. (i) and (ii) given above are *identical*. For any incident beam of X-rays, the glancing angle θ would be the same, as the two sets of planes in question are parallel. As Eqns. (i) and (ii) are identical the two reflections will *superimpose* on each other and cannot be distinguished. By a similar reasoning, it can be proved 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 separately. Rather we take it to be unity for all reasons from parallel set of planes.

2.22.6. Bragg's Law

When a beam of monochromatic X-rays falls on a crystal it is scattered by the individual atoms which are arranged in sets of parallel layers. Bragg's reflection takes place when the following *two conditions* are satisfied.

1. X-rays are reflected by the regularly arranged parallel layers of atom in a crystal.
2. The atoms on which X-rays fall become centre of disturbance and develop spherical wavelets whose envelope provides size to the reflected wave front by Huygen's construction.

Bragg's law can be explained as follows :

Refer Fig. 2.56. It represents three layers of a crystal. An X-ray wave front enters the upper left, making an angle θ with the crystal surface. It may be noted that the rays reflected from the second layer travel a greater distance than those from the first layer. In order that reflections from the second and successive layers shall reinforce, it is necessary that these additional distances shall be some integral multiple of the X-ray wavelength λ or $n\lambda$. If we construct the lines LP and LQ perpendicular to the directions of the incident and reflected rays respectively, we see that each of these lines makes an angle θ with line LM whose length is the separation d of the layers. The additional length of the path of the ray reflected from the layer is $(PM + MQ)$, each of which is equal to $d \sin \theta$.

Thus $2d \sin \theta = n\lambda$, where n is the order of spectrum and the value of n may be 1, 2, 3 etc., for first order, second order and third order maxima respectively.

This equation is called **Bragg's law** for diffraction at crystal surfaces and is basis for the determination of crystal structures.

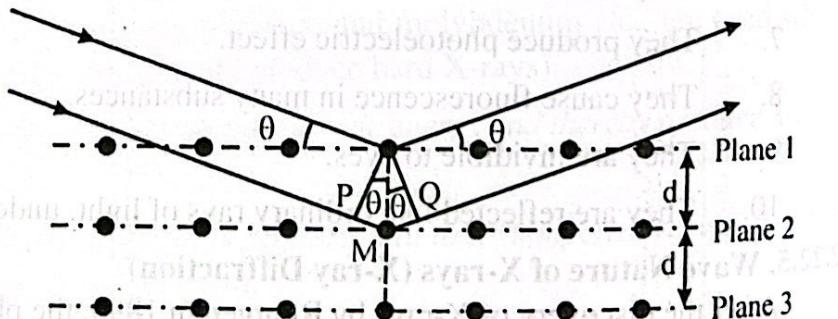


Fig. 2.56. Bragg's law.

Example 2.34. Determine the interplanar spacing when a beam of X-rays of wavelength 1.54 \AA is directed towards the crystal at an angle 20.3° to the atomic plane.

Solution : Wavelength $\lambda = 1.54 \text{ \AA}$

Angle, $\theta = 20.3^\circ$

Interplanar spacing, d :

Using the relation (Bragg's equation)

$$2d \sin \theta = n \lambda$$

$$2d \times \sin 30^\circ = \lambda \quad (\text{for } n = 1)$$

$$\text{or} \quad d = \frac{\lambda}{2 \sin 20.3^\circ} = \frac{1.54}{2 \sin 20.3^\circ} \text{ \AA} = \frac{1.54}{2 \times 0.3469} \text{ \AA} = 2.219 \text{ \AA}$$

$$\text{i.e.,} \quad d = 2.219 \text{ \AA} = 2.219 \times 10^{-10} \text{ m} \quad (\text{Ans.})$$

Example 2.35. The Bragg angle corresponding to the first order reflection from $(1, 1, 1)$ planes in a crystal is 30° when X-rays of wavelength of 1.75 \AA are used. Calculate the atomic spacing.

Solution : We know that, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

where h, k, l are the miller indices,

a is the interatomic distance, and

d is the interplanar distance.

In the case of plane $(1, 1, 1)$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

According to Bragg's law

$$2d \sin \theta = n \lambda$$

$$2d_{111} \sin \theta = n \lambda$$

Here

$$d_{111} = \frac{a}{\sqrt{3}}$$

$$\theta = 30^\circ$$

$$\lambda = 1.75 \text{ \AA}; n = 1$$

Inserting the value in Eqn. (1), we get

$$2 \times \frac{a}{\sqrt{3}} \sin 30^\circ = 1.75 \text{ \AA}$$

$$a = \frac{\sqrt{3}}{2} \times 2 \times 1.75 = \sqrt{3} \times 1.75 \text{ \AA} = \sqrt{3} \times 1.75 \times 10^{-8} \text{ cm}$$

$$= 3.01 \times 10^{-8} \text{ cm} \quad (\text{Ans.})$$

Example 2.36. An X-ray diffraction analysis of a crystal is made with X-rays having wavelength of 0.8 \AA . Reflections are observed at angles (i) 6.45° (ii) 9.15° , (iii) 13° . What interplanar spacings are present in the crystal?

Solution : Bragg's law is given by : $2d \sin \theta = n \lambda$

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

Now

$$\lambda = 0.58 \text{ \AA} = 0.58 \times 10^{-10} \text{ m}$$

1. When $\theta = 6.45^\circ$:

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta} = \frac{0.58 \times 10^{-10}}{2 \sin 6.45^\circ} = 2.58 \times 10^{-10} \text{ m}$$

2. When $\theta = 9.15^\circ$:

$$\frac{d}{n} = \frac{0.58 \times 10^{-10}}{2 \sin 9.15^\circ} = 1.817 \times 10^{-10} \text{ m}$$

3. When $\theta = 13^\circ$:

$$\frac{d}{n} = \frac{0.58 \times 10^{-10}}{2 \sin 13^\circ} = 1.29 \times 10^{-10} \text{ m}$$

Since the value of $\frac{d}{n}$ is twice that in (3), it shows that angles 6.45° and 13° represent the first and second order reflection maxima from one set of parallel planes with a spacing which may be found from (1) by putting $n = 1$ or from (3) by putting $n = 2$.

Considering case (3), we get

$$\frac{d}{2} = 1.29 \times 10^{-10}$$

$$d = 2.58 \times 10^{-10} = 2.58 \text{ \AA}$$

Case (2) has a different value of $\frac{d}{n}$ and must be first order reflection from other set of parallel planes in the crystal. Their interplanar spacing is

$$\frac{d}{1} = 1.817 \times 10^{-10} = 1.817 \times 10^{-10} = 1.817 \text{ \AA} \quad (\text{Ans.})$$

Example 2.37. A beam of X-ray of $\lambda = 0.842 \text{ \AA}$ is incident on a crystal at a glancing angle of $8^\circ 35'$ when the first order Bragg's reflection occurs. Calculate the glancing angle for 3rd order reflection.

Solution : According to Bragg's law : $2d \sin \theta = n \lambda$

For first order reflection, $n = 1$

$$\therefore 2d \sin 8^\circ 35' = \lambda \quad \dots(i)$$

For third order reflection

$$2d \sin \theta = 3 \lambda \quad \dots(ii)$$

From Eqns. (i) and (ii), we get

$$\frac{2d \sin \theta}{2d \sin 8^\circ 35'} = \frac{3 \lambda}{\lambda}$$

$$\sin \theta = 3 \sin 8^\circ 35'$$

or

$$\theta = 26^\circ 35' \quad (\text{Ans.})$$

Example 2.40 For a certain B.C.C. crystal the (110) planes have a separation of 1.181 Å. These (110) planes are indicated with X-rays of wave length 1.540 Å. How many orders of Bragg's reflections can be observed in this case?

Solution : According to Bragg's law

$$2d \sin \theta = n \lambda$$

$$\text{Here } d = 1.181 \text{ Å} = 1.181 \times 10^{-10} \text{ m}$$

$$\lambda = 1.540 \text{ Å} = 1.540 \times 10^{-10} \text{ m}$$

Obviously for highest value of n the maximum value of θ can be 90°, i.e.,

$$n = \frac{2d \sin \theta}{\lambda} = \frac{2 \times 1.181 \times 10^{-10} \times \sin 90^\circ}{1.540 \times 10^{-10}} \approx 1.53$$

Since n can be integer only, however, highest permissible value of n in this case is 1 (i.e., first order reflection).

Example 2.41. A FCC crystal has an atomic radius of 1.246 Å. What are d_{200} , d_{220} and d_{111} spacings?

Solution : For a crystal, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ a , being interatomic distance.

$$\text{For FCC crystal, } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r = 2\sqrt{2} \times 1.245 = 2.492\sqrt{2} \text{ Å}$$

$$d_{200} = \frac{2.492\sqrt{2}}{\sqrt{2^2 + 0^2 + 0^2}} = 1.762 \text{ Å} \quad (\text{Ans.})$$

$$d_{220} = \frac{2.492\sqrt{2}}{\sqrt{2^2 + 2^2 + 0^2}} = 1.246 \text{ Å} \quad (\text{Ans.})$$

$$d_{111} = \frac{2.492\sqrt{2}}{\sqrt{1^2 + 1^2 + 1^2}} = 1.017 \text{ Å} \quad (\text{Ans.})$$

Example 2.42. Monochromatic X-rays of $\lambda = 1.5 \text{ Å}$ are incident on a crystal face having an interplanar spacing of 1.6 Å. Find the various orders in which Bragg's reflections take place.

Solution : According to Bragg's law :

$$2d \sin \theta = n \lambda \quad \text{where } n = 1, 2, 3 \text{ etc.},$$

$$\sin \theta = \frac{\lambda}{2d} = \frac{1.5}{2 \times 1.6} = 0.468$$

(putting $n = 1$)

4.1.6. Imperfections (Defects) in Crystals

The perfectly regular crystal structures that have been considered upto now are called ideal crystals in which atoms are arranged in a regular way. In actual crystals, however, imperfections or defects are always present and their nature and effects are very important in understanding the properties of crystals. These imperfections affect the properties of crystals such as mechanical strength, chemical reactions, electrical properties etc., to a great extent.

Imperfections are found in all crystals unless some special means are used to reduce them to a low level.

The crystallographic defects are *classified* as follows :

1. Point defects or zero dimensional defects :

- (i) Vacancy
- (ii) Schottky imperfections
- (iii) Interstitialcy
- (iv) Frenkel defect
- (v) Compositional defects
 - (a) Substitutional impurity
 - (b) Interstitial impurity
- (vi) Electronic defects

2. Line defects or one dimensional defects :

- (i) Edge dislocation
- (ii) Screw dislocation

3. Surface defects or plane defects or two dimensional defects :

- (i) Grain boundaries
- (ii) Tilt boundaries
- (iii) Twin boundaries
- (iv) Stacking fault

4. Volume defects or three dimensional defects.

4.1.6.1. Point Defects

- Point defects are *imperfect point like regions in a crystal*. The typical size of a point defect is one or two atomic diameters.
- These defects are completely local in effect, e.g., a vacant lattice site.
- *Point imperfections are always present in crystals and their presence results in a decrease in the free energy.*

The point defects may be created as follows :

- (i) By thermal fluctuations

- (ii) By quenching (quick cooling) from a higher temperature.
- (iii) By severe deformation of the crystal lattice; e.g., by hammering or rolling. While the lattice still retains its general crystalline nature, numerous defects are introduced.
- (iv) By external bombardment by atoms or high-energy particles; e.g., from the beam of the cyclotron or the neutrons in a nuclear reactor. The first particle collides with the lattice atoms and displaces them, thereby forming a defect. The number produced in this manner is not dependent on temperature but depends only on the nature of the crystal and on the bombarding particles.

The various point defects are discussed below :

1. **Vacancy.** Refer Fig. 4.8. A vacancy is the simplest point defect and involves a *missing atom within a metal*. These defects may come up as a result of *imperfect packing during the original crystallisation*. They may also arise from thermal vibrations of the atoms at high temperatures.

2. **Schottky imperfections.** Refer Fig. 4.9. These are closely related to vacancies but are found in compounds which must maintain a charge balance. They *involve vacancies of pair of ions of opposite charges*. This type is *dominant in alkali halides*.

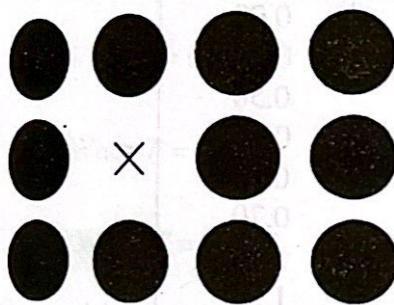


Fig. 4.8. Vacancy.

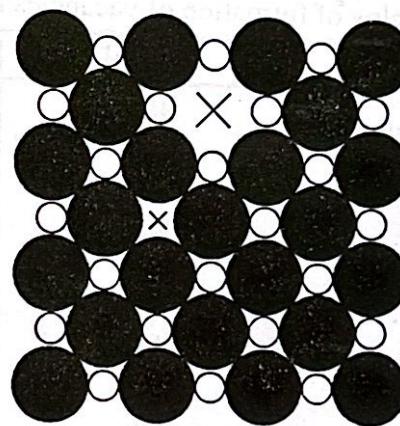


Fig. 4.9. Schottky imperfections.

Both vacancies and schottky defects facilitate atomic diffusion.

3. **Interstitialcy.** Refer Fig. 4.10. It is the addition of an extra atom within a crystal structure particularly if atomic packing factor is low. This results in atomic distortion. The foreign atom may form added alloying agent or simply an impurity. The vacancy and interstitialcy are therefore, inverse phenomena.

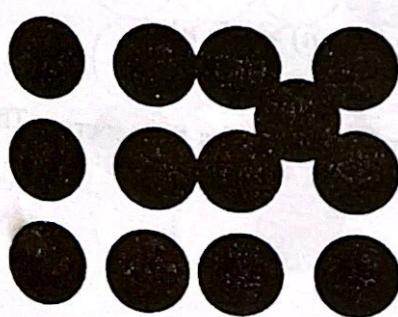


Fig. 4.10. Interstitialcy defect.

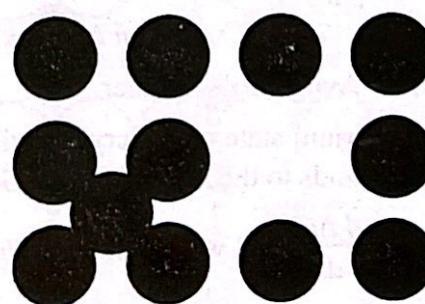


Fig. 4.11. Frenkel defect.

4. **Frenkel defect.** Refer Fig. 4.11. An ion dislodged from the lattice into an interstitial site is called *Frenkel defect*. The interstitialcies and Frenkel defects are *less in number* than vacancies and Schottky

defects, because additional energy is required to force the atom into the new position.

Close-packed structures have fewer interstitialities and Frenkel defects than vacancies and Schottky defects, as additional energy is required to force the atoms in their new positions.

- When an ionic crystal does not correspond to exact stoichiometric formula defect structures are produced. Such defect structures have an appreciable concentration of point imperfections.

4.1.6.2. Line Defects (Dislocations)

- A linear disturbance of the atomic arrangement, which can move very easily on the slip plane through the crystal is known as **dislocation**. The dislocation may be caused during growth of crystals from a melt or from a vapour or they may occur during a slip.
- The line defects, as the name implies, extend along some direction in an otherwise perfect crystal. One such defect can therefore be considered as the boundary between the two regions of a surface which are perfect themselves but out of register with each other.
- In case of crystals it arises when one part of the crystal shifts or slips relative to the rest of the crystal such that displacement terminates within the crystal. However, if the displacement does not terminate within the crystal, but continues throughout the crystal instead, it may not introduce any defect in the crystal.
- This defect is created along a line which is also the boundary between the slipped and unslipped regions of the crystal. The defect is commonly called a "dislocation" and the boundary as the "dislocation line".

Two basic types of dislocations are :

1. Edge dislocation (or Taylor-Orowan dislocation)
2. Screw dislocation (or Burger's dislocation)

These are usually two extreme types of dislocations. Any particular dislocation is usually a mixture of these two extreme types. These may be regarded as the components of a general dislocation.

1. **Edge dislocations.** Refer Fig. 4.13 [(a), (b)].

- An edge dislocation may be described as an extra plane of atoms within a crystal structure. It is accompanied by zones of compression and of tension so that there is a net increase in energy along a dislocation.
- The displacement distance for atoms around the dislocation is called the '**Burger vector**'. This vector is at right angle to the edge dislocation.

Burger's vector (b) is determined by drawing a rectangle in the region being investigated by connecting an equal number of atoms on opposite sides, as shown in the Fig. 4.13. If a certain region contains an edge dislocation, the circuit will fail to close. The dotted line PP' given in the Fig. 4.13 is the Burger's vector.

The edge dislocations are represented by the symbols \perp and T denoting the insertion of extra plane from the top and bottom side of the crystal respectively. These two configurations are called *positive* and *negative* edge dislocations. These symbols also indicate the position of the dislocation line.

Fig. 4.13 (c) shows the atomic view in a edge dislocation.

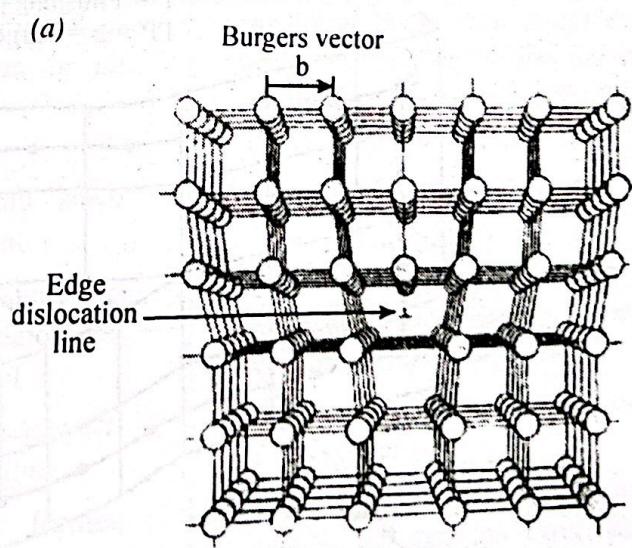
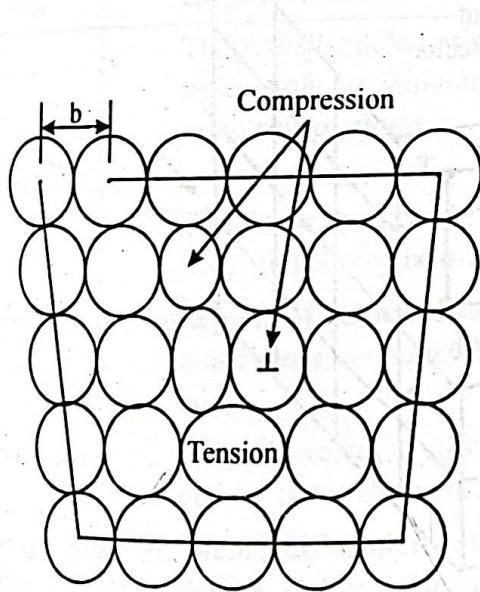
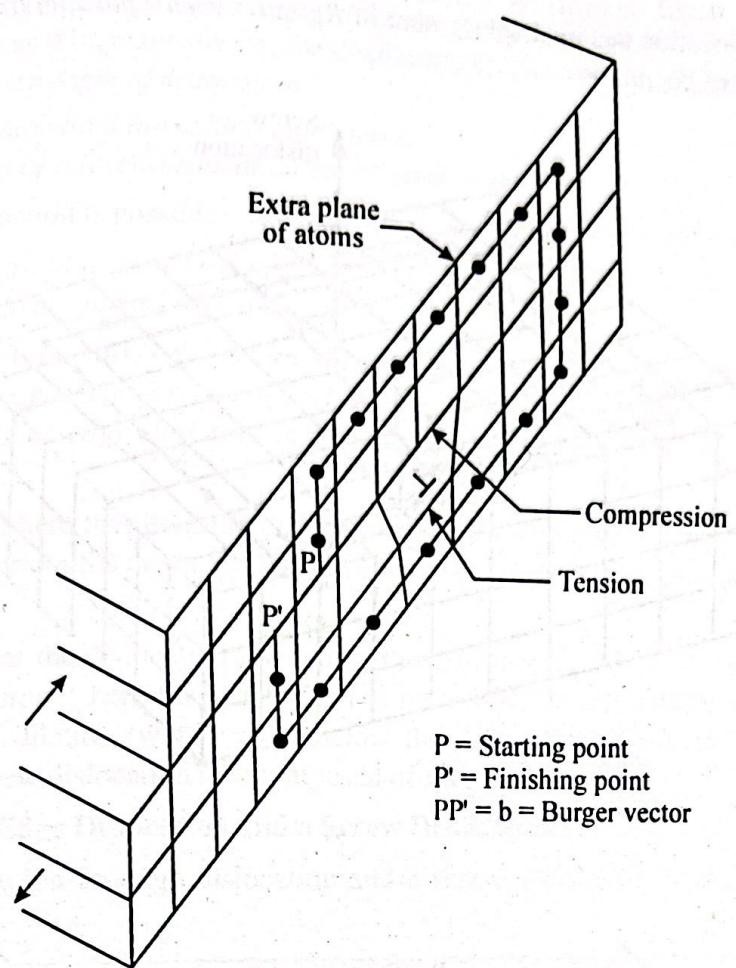
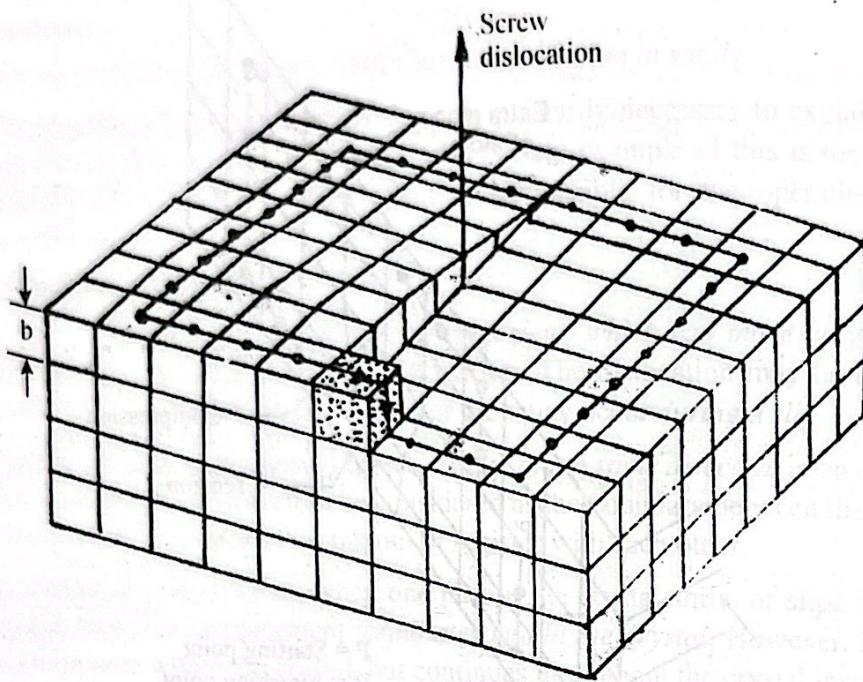


Fig. 4.13. Edge dislocation

2. Screw dislocation : Refer Fig. 4.14 [(a), (b)].

- Screw dislocation may originate from partial slipping of a section of crystal plane.
- In this type of dislocation shear stresses are associated with adjacent atoms and extra energy is involved, along the dislocation. The successive atom planes are transformed into the surface of the helix of screw by this dislocation which accounts for its name as screw dislocation.

- A screw dislocation has its displacement of Burger's vector parallel to the linear defect but there is distortion of the plane.



(a)

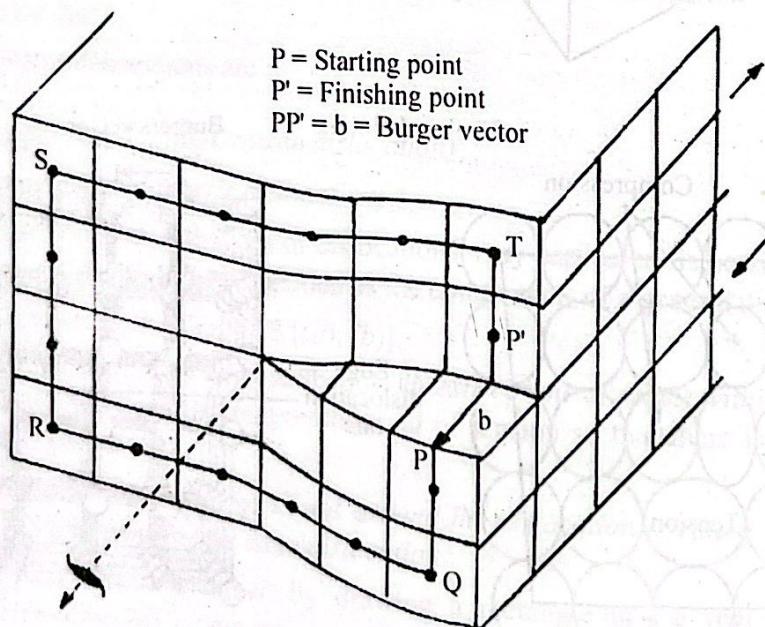


Fig. 4.14. Screw dislocation.

- When the screw dislocation is present in a crystal, the complete planes of atoms normal to the dislocation no longer exist. Rather all the atoms lie on a single surface which spirals from one end of the crystal to the other with dislocation line as the axis of spiral. The displacement of the atoms from their original positions in the perfect crystal is described by the equation :

$$r = \frac{b}{2\pi} \theta \text{ (spiral ramp)}$$

where, r = The displacement along the dislocation line, and

θ = The angle measured from some axis perpendicular to the dislocation line.

It may be noted that as θ increases by 2π , the displacement increases by the factor b ; thus, b is, in this respect, the measure of the strength of dislocation.

- A screw dislocation does not exhibit climb motion.

The following effects of a screw dislocation are of great importance :

- Plastic deformation is possible under low stress, without breaking the continuity of the lattice.
- The force required to form and move a screw dislocation is probably somewhat greater than that required to initiate an edge dislocation.
- Screw dislocation causes distortion of lattice for a considerable distance from the centre of the line and takes the form of spiral distortion of the planes. Dislocations of both types (combinations of edge and screw) are closely associated with crystallization as well as deformation.

It may be mentioned here that both the dislocations are accompanied by the distortion in the crystal which varies with distance from the centre of the dislocation (being severest in the immediate vicinity of the dislocation line).

— The region near the dislocation line where the distortion is extremely large is called the "core of the dislocation"; here the local strain is quite high. In edge dislocation the local strain is composed of dilation (with tension below the dislocation edge and compression above it), whereas in screw dislocation it is composed of shear.

Comparison between an Edge Dislocation and a Screw Dislocation :

The comparison between an edge dislocation and a screw dislocation is spelled out in table given below :

S. No.	Edge dislocation	Screw dislocation
1.	These dislocations arise due to introduction or elimination of an extra row of atoms.	A screw dislocation provides for easy crystal growth because additional atoms and unit cells can be added to step of the screw.
2.	Tensile, compressive and shear stress fields may be present.	Only shear stress field exists.
3.	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.
4.	Burger's vector is always perpendicular to the dislocation line.	Burger's vector is parallel to the dislocation line.
5.	These dislocations are formed during deformation and during crystallisation.	These dislocations are also formed during deformation and during crystallisation.
6.	An edge dislocation (pure) can glide and climb.	A screw dislocation can glide only.

Fig. 4.15 shows the geometry of simple dislocations--Edge dislocation and screw dislocation.

4.1.2. Slip

Slip is defined as a shear deformation that moves atoms by many interatomic distances in one crystal plane over the atoms of another crystal plane. Fig. 4.2 shows the slip process under a shear load (in a single

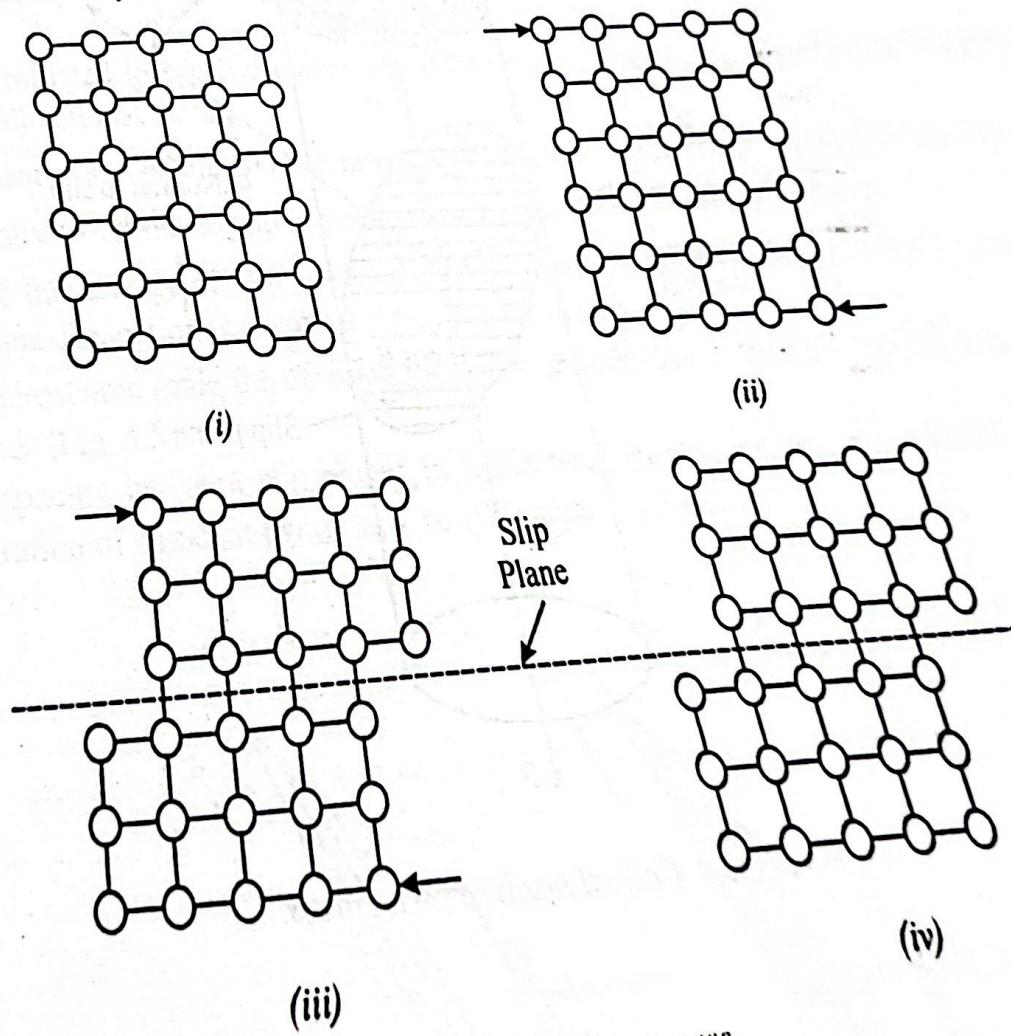


Fig. 4.2. Slip process.

crystal). Because of plastic deformation, the crystal is divided into layers or slip blocks which are displaced in reference to each other and are separated by thin layers in which a considerable displacement of atoms has taken place. These intermediate layers with strongly distorted lattices are called "slip planes". Slip occurs more readily along certain crystal directions and planes than along others. This is shown in Fig. 4.3 where a single crystal HCP metal was deformed plastically.

4.1.4. Twinning

Twinning is that process by which a portion of the crystal takes up an orientation which makes that portion a mirror image of the parent crystal.

Deformation by twinning is most common in HCP metals and its effects on others is to move parts of the grains such that they acquire favourable orientation for the slip to occur. Twinning is produced suddenly and is accompanied with sound. The well known cry of tin is the result of twinning.

Fig. 4.6 shows the classical atomic picture of twinning. The twinning plane is at right angle to the paper. If a shear stress is applied, the crystal will turn about the twinning plane. The region to the left of the twinning plane is underformed. To the right of this plane, the planes of atoms have sheared in such a way as to make the lattice a mirror image across the twin plane. The mechanism of twinning may thus be described

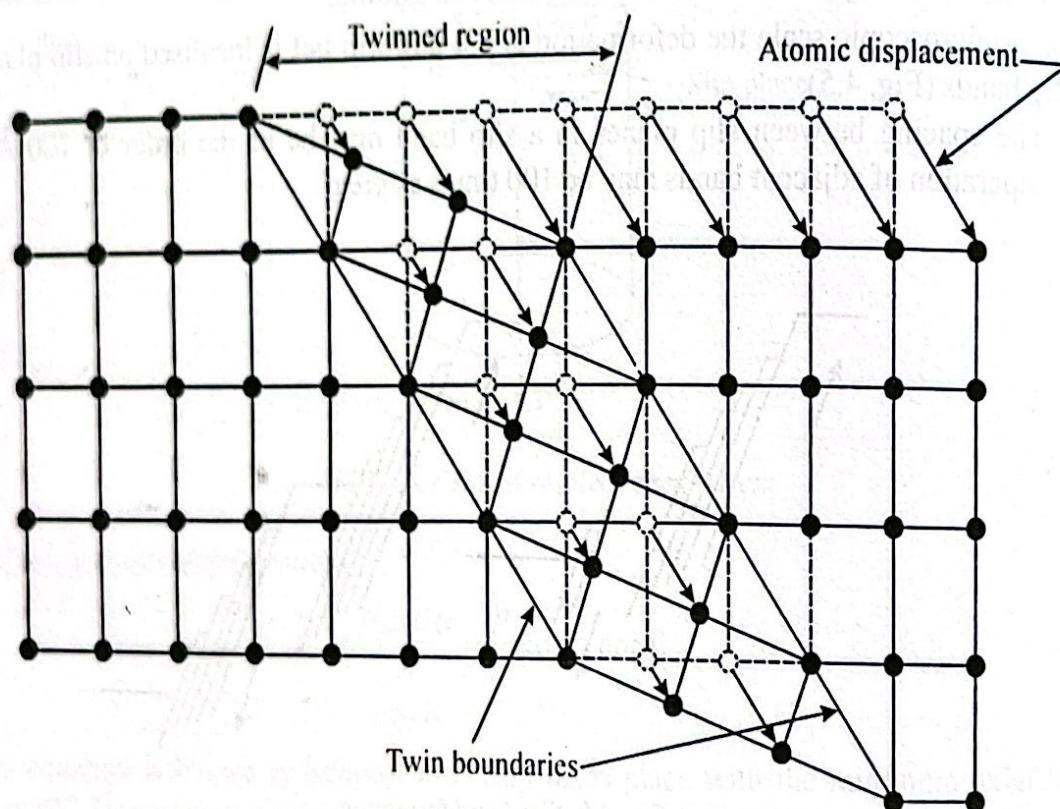


Fig. 4.6. Twinning.

as the simple sliding of one plane of atoms over the next, the extent of movement of each plane being proportional to its distance from the twinning plane. Fig. 4.7 shows the schematic representation of twinning.

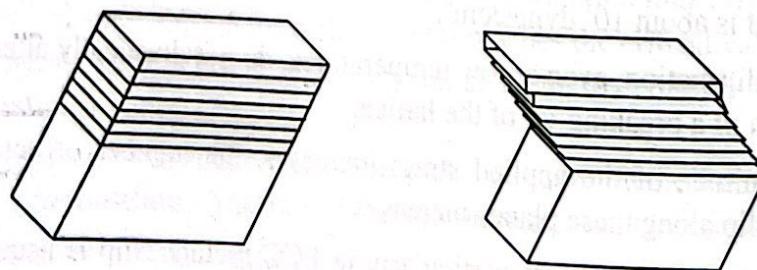


Fig. 4.7. Schematic representation of twinning.

In case of slip, the offset is a multiple of interatomic spacing, but in twinning the offset produced by sliding of one plane against its neighbour is a fraction of a unit slip. This causes a difference in the orientation between the twinned and untwinned regions in the crystal and on polishing and etching these can

4.1.5. Difference between Slip and Twinning

The difference between slip and twinning is given below :

S. No.	Slip	Twinning
1.	It occurs in <i>discrete multiples of atomic spacing</i> .	Atom movements are <i>much less than the atomic spacing</i> .
2.	The orientation of the crystal above and below the slip plane is <i>the same after deformation as before</i> .	Orientation difference takes place <i>across the twin plane</i> .
3.	<i>It occurs over wide planes</i> .	<i>Every atomic plane is involved</i> .
4.	Slip begins when shearing stress on the slip plane in the slip direction reaches a <i>threshold value called the critical resolved shear stress</i> .	<i>There is no critical resolved shear stress for twinning</i> .
5.	<i>It takes place in several milliseconds</i> .	<i>It takes place in a few microseconds</i> .

6.

Slip lines do not appear during any heat treatment.

7.

Slip lines disappear after grinding or other surface finishing operations.

8.

Slip lines may be present in even or odd numbers.

Twin lines appear during the annealing operation of materials.

Twin lines run through the whole depth of the material and hence do not disappear on grinding etc.

Twin lines always occur in pairs.