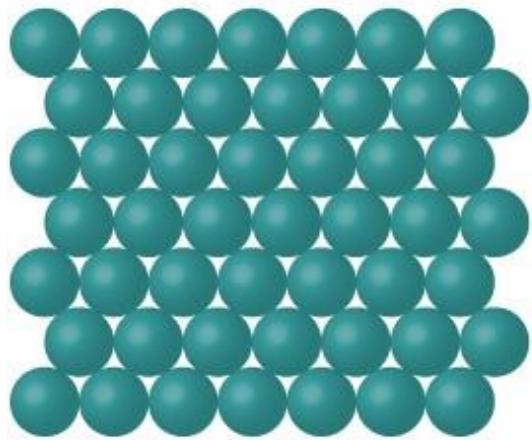
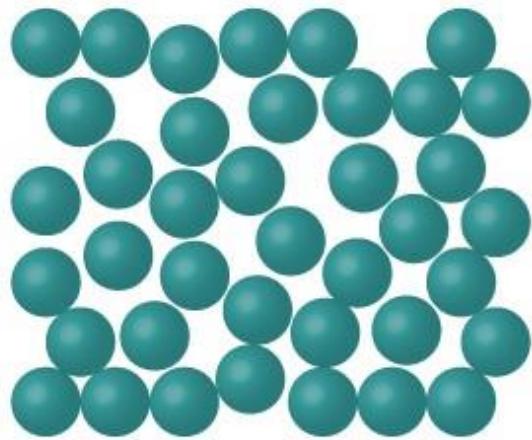


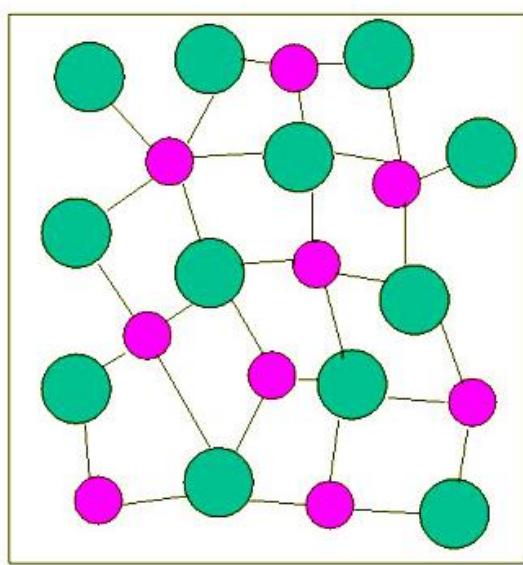
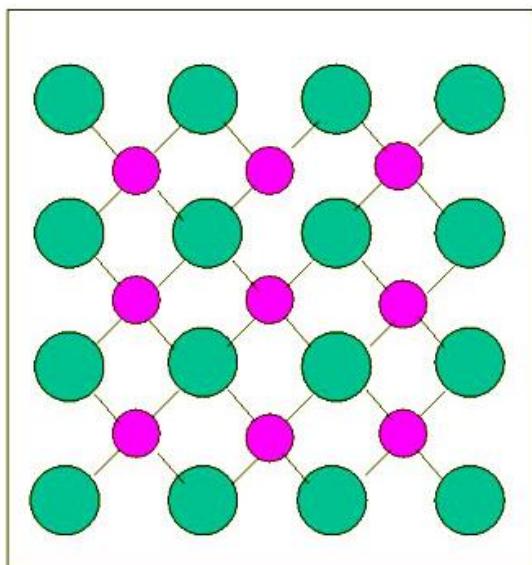
Crystalline and Amorphous Solids



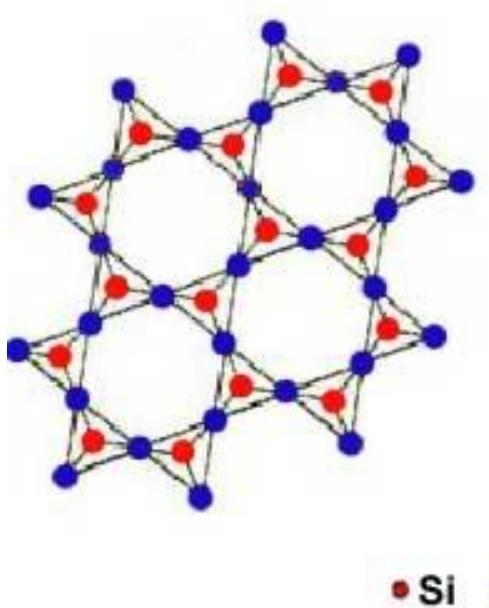
Crystalline



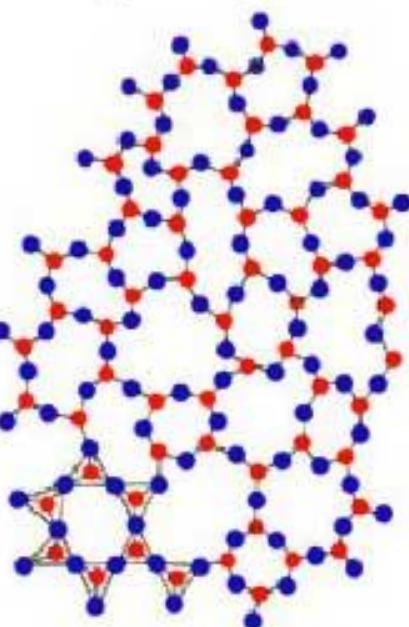
Amorphous



**Crystalline SiO₂
(Quartz)**



**Amorphous SiO₂
(Glass)**



• Si • O

Lattice points and space lattice:

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

are integers and \vec{a} and \vec{b} are fundamental translation vectors.
ray of points is a two-dimensional lattice.

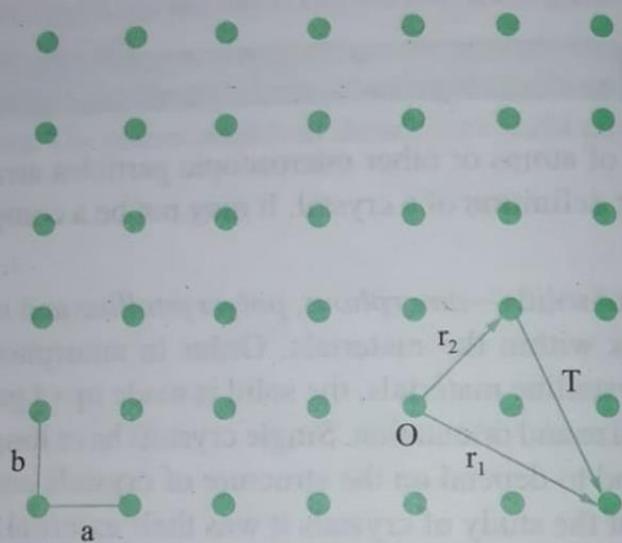
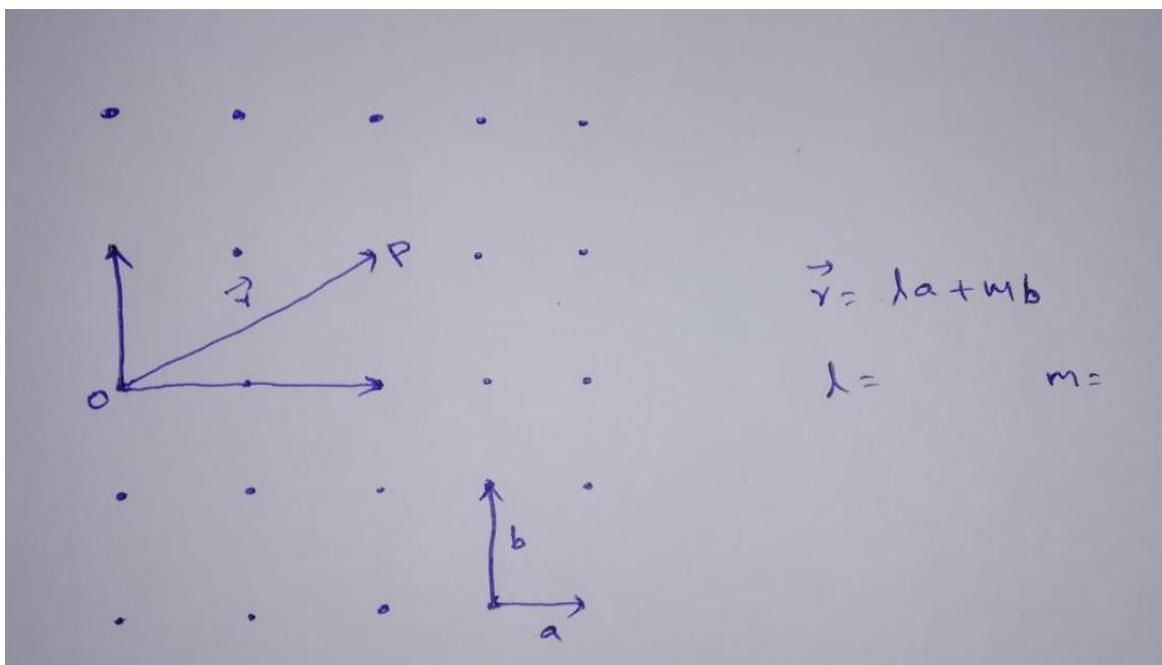


Fig. 4.1 Two-dimensional array of points

mensional lattice:

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$



The term 'identical surroundings' means that the lattice has the same appearance when viewed from a point \mathbf{r} in the lattice as it has when viewed from any other point \mathbf{r}' with respect to some arbitrary origin. This is possible only if the lattice contains a small group of points, called *pattern unit*, which repeats itself in all directions by means of a *translation operation T* given by

$$\mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (1.1)$$

where n_1, n_2 and n_3 are arbitrary integers and the vectors \mathbf{a}, \mathbf{b} and \mathbf{c} are called the *fundamental translation vectors*. Thus, we have

$$\mathbf{r}' = \mathbf{r} + \mathbf{T} = \mathbf{r} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (1.2)$$

In a perfect lattice, Eq. (1.2) holds good, i.e., point \mathbf{r}' can be obtained from \mathbf{r} by the application of the operation (1.1). However, in an imperfect lattice, it is not possible to find \mathbf{a}, \mathbf{b} and \mathbf{c} such that an arbitrary choice of n_1, n_2 and n_3 makes \mathbf{r}' identical to \mathbf{r} . The translation vectors \mathbf{a}, \mathbf{b} and \mathbf{c} are also called the *crystal axes* or *basis vectors* and shall be described later.

Fig. 1.1. Primitive ($\mathbf{a}_1, \mathbf{b}_1$) and non-primitive ($\mathbf{a}_2, \mathbf{b}_2$) translation vectors in a two-dimensional lattice.

Consider, for simplicity, a part of a two-dimensional lattice as shown in Fig 1.1. The translation vectors \mathbf{a} and \mathbf{b} can be chosen in a number of ways. Two such possi-

where two sets $\mathbf{a}_1, \mathbf{b}_1$ and $\mathbf{a}_2, \mathbf{b}_2$ of translation vectors are drawn. Considering first the translation vectors \mathbf{a}_1 and \mathbf{b}_1 , the point \mathbf{R}' can be obtained from \mathbf{R} using the translation operation given by

$$\mathbf{T} = 0\mathbf{a}_1 + 1\mathbf{b}_1$$

which contains integral coefficients. Thus \mathbf{R}' is related to \mathbf{R} by the equation

$$\mathbf{R}' = \mathbf{R} + \mathbf{T} = \mathbf{R} + 0\mathbf{a}_1 + 1\mathbf{b}_1$$

Such translation vectors which produce a translation operation containing integral coefficients are called primitive translation vectors. Referring to the second set of translation vectors \mathbf{a}_2 and \mathbf{b}_2 , the point \mathbf{R}' can be obtained from \mathbf{R} by using the equation

$$\mathbf{R}' = \mathbf{R} + \frac{1}{2}\mathbf{a}_2 + \frac{1}{2}\mathbf{b}_2$$

which contains non-integral coefficients of \mathbf{a}_2 and \mathbf{b}_2 . Such translation vectors for which the translation operation contains non-integral coefficients are called non-primitive translation vectors. Either type of translation vectors may be used to describe the structure of a crystal inspite of the fact that

Basis and Crystal structure:

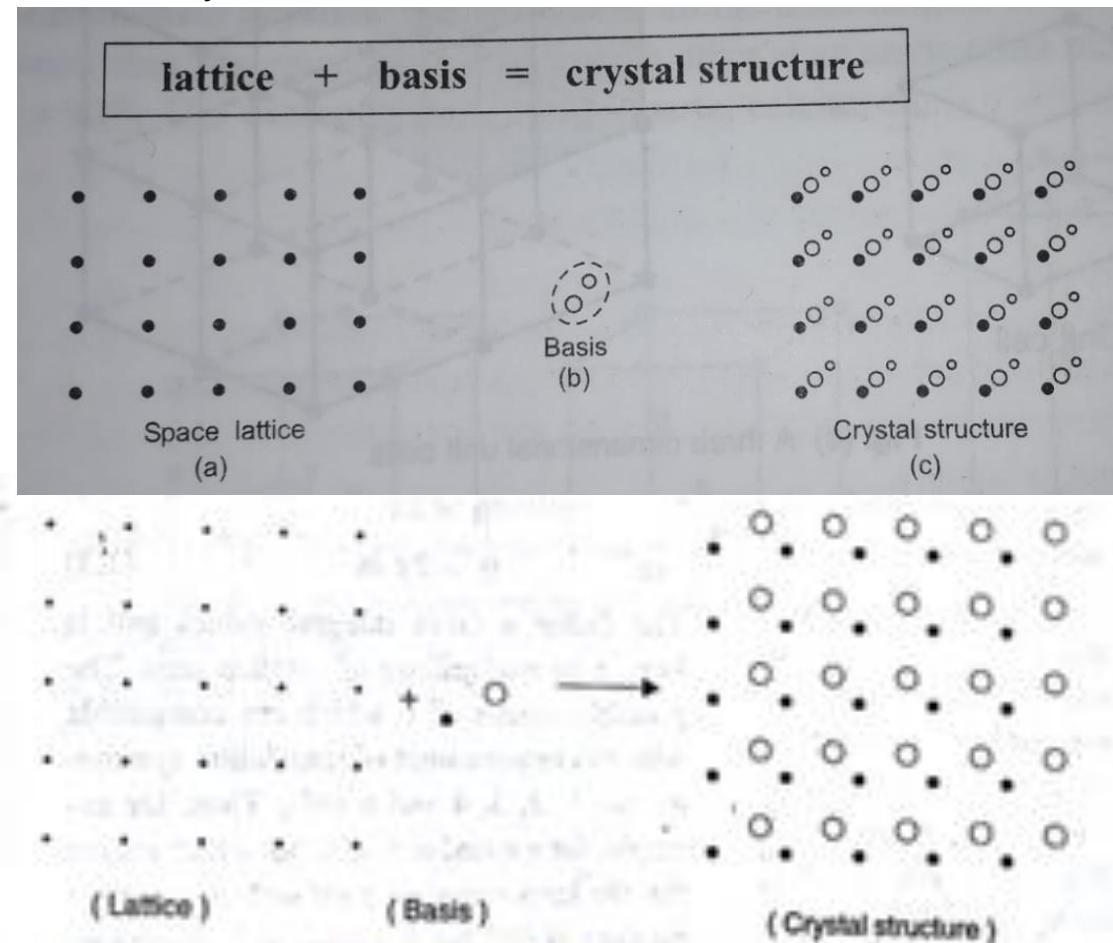
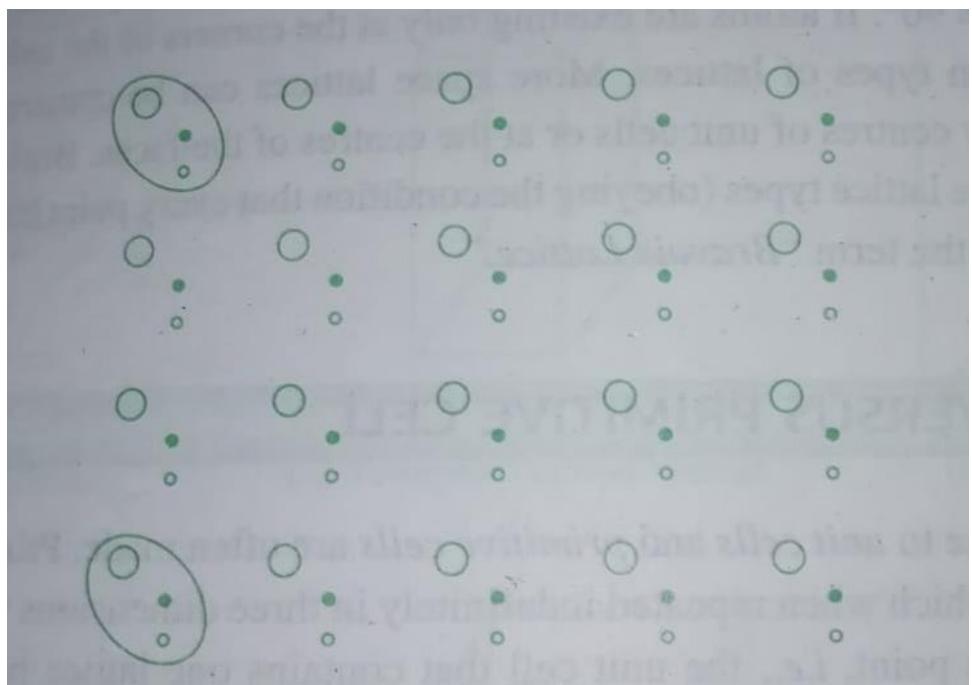
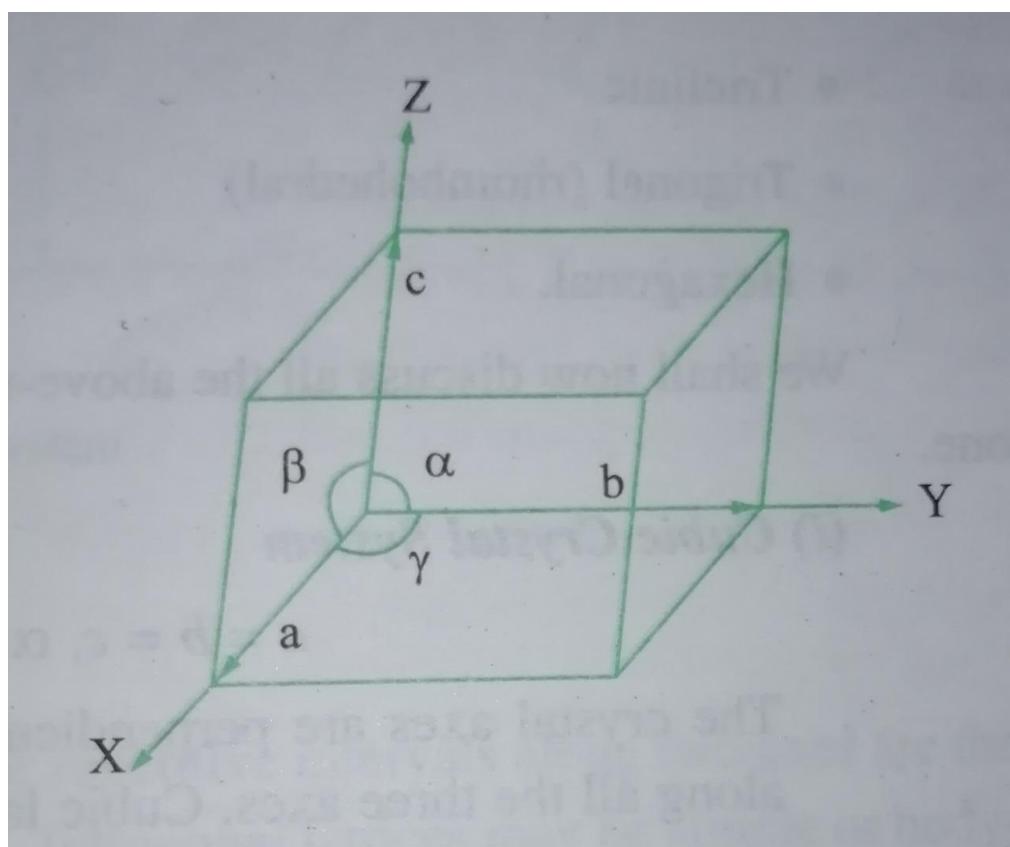


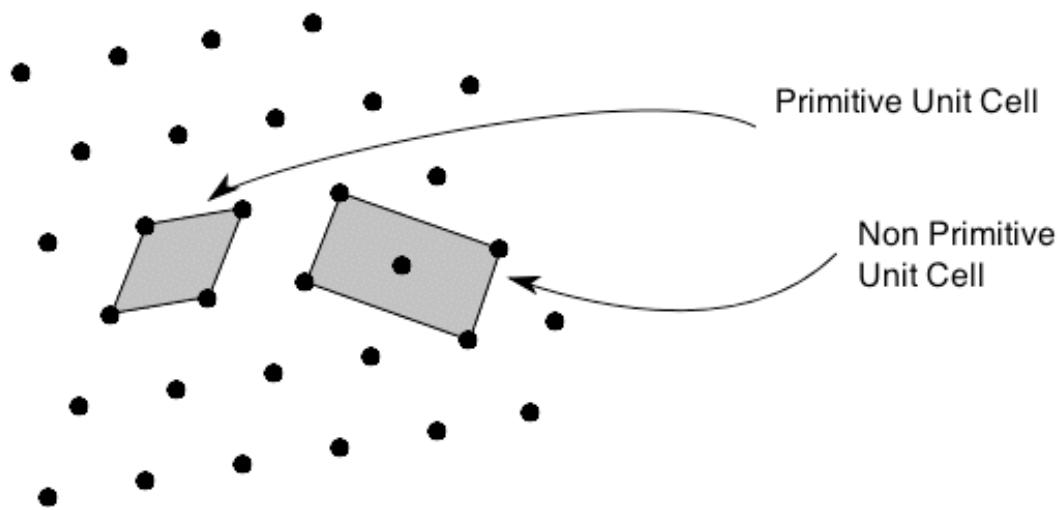
Fig. 1.4. Generation of crystal structure from lattice and basis.



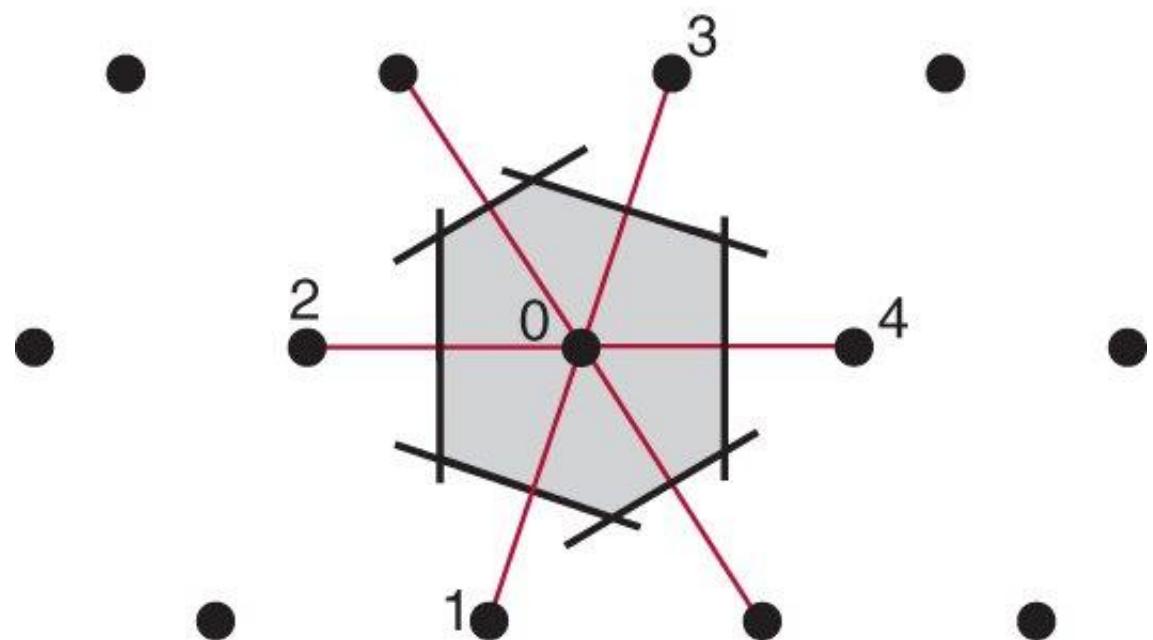
Unit cell

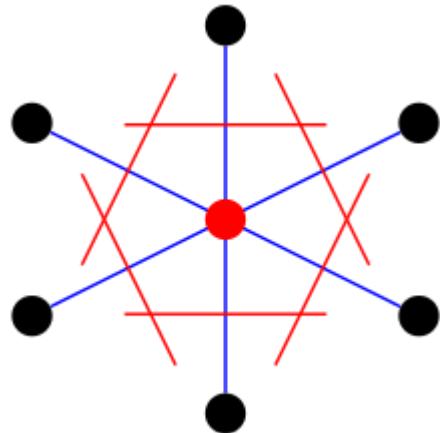


Primitive and non-primitive cell:



Wigner-Seitz cell:





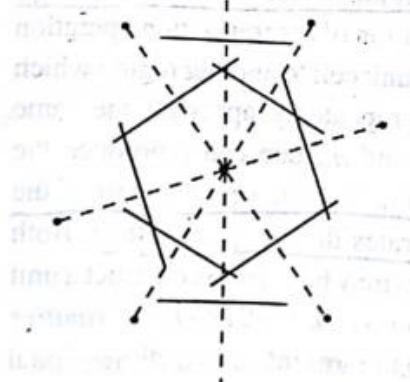
inside and on the surface of the cell and, therefore, the effective number of lattice points in a non-primitive cell is greater than one. A primitive cell can also be constructed using the following procedure :

(i) Connect a given lattice point to all the nearby lattice points.

(ii) Draw normals at the mid-points of lines connecting the lattice points.

The smallest volume enclosed by the normals is the required primitive cell. Such a cell is called *Wigner-Seitz cell* and is shown in Fig. 1.3. The volume of a primitive cell having \mathbf{a} , \mathbf{b} and \mathbf{c} as the fundamental translation vectors or crystallographic axes is given by

$$V = |\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|$$



Crystal systems and Bravais lattices:

Seven Crystal Systems:

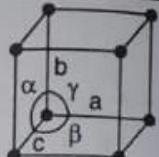
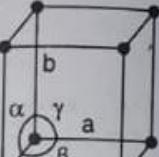
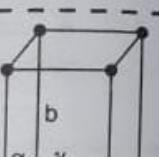
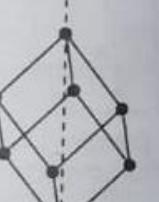
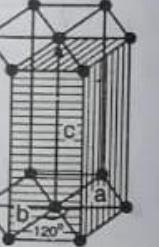
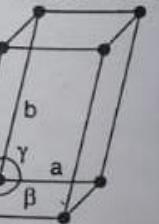
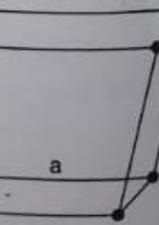
| Table 2 : The Seven Crystal Systems | | Unit cell geometry |
|-------------------------------------|--|--|
| System | Axial lengths and angles | |
| Cubic | $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$ |  |
| Tetragonal | $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ |  |
| Orthorhombic | $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ |  |
| Trigonal (Rhombohedral) | $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$ |  |
| Hexagonal | $a = b \neq c$ $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ |  |
| Monoclinic | $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$ |  |
| Triclinic | $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ |  |

Table 4.1 Seven basis crystal systems with their characteristics

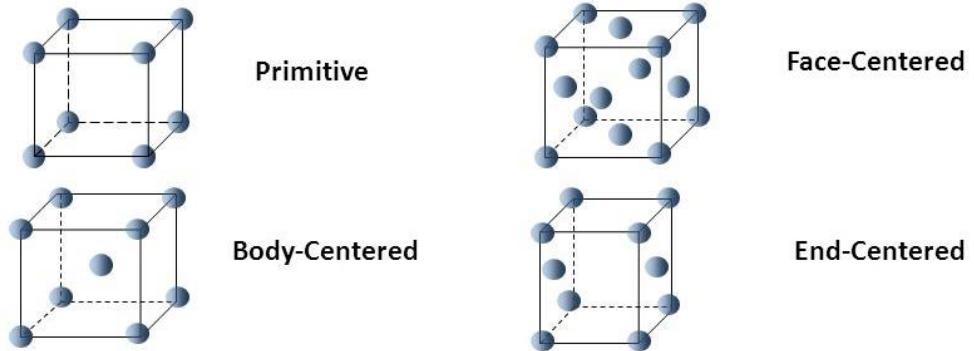
| Sl. No. | Crystal system | Axial lengths of unit cell (a , b and c) | Interaxial angles (α , β and γ) | Examples |
|---------|----------------|--|---|--|
| 1. | Cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90^\circ$ | Au, Cu, NaCl |
| 2. | Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | TiO_2 , SnO_2 , NiSO_4 |
| 3. | Orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | KNO_3 , BaSO_4 , PbCO_3 |
| 4. | Monoclinic | $a \neq b \neq c$ | $\alpha = \beta = 90^\circ \neq \gamma$ | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum), FeSO_4 , Na_2SO_4 |
| 5. | Triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$ | $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ |
| 6. | Trigonal | $a = b = c$ | $\alpha = \beta = \gamma \neq 90^\circ$ | As, Sb, Bi, Calcite |
| 7. | Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ | SiO_2 , Zn, Mg, Cd |

Table 4.4 The seven crystal systems and the fourteen Bravais lattices

| Sl.No. | System | Number of lattices in the system | Space lattices or Bravais lattices | Lattice symbol | Nature of unit cell [Axial length and interaxial angles] |
|--------|--------------|----------------------------------|--|------------------|--|
| 1. | Cubic | 3 | 1. Simple 2. Body centred 3. Face centred | P I F | $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$ |
| 2. | Tetragonal | 2 | 1. Simple 2. Body centred | P I | $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ |
| 3. | Orthorhombic | 4 | 1. Simple 2. Base centred 3. Body centred 4. Face centred | P C I F | $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ |
| 4. | Monoclinic | 2 | 1. Simple 2. Base centred | P C | $a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$ |
| 5. | Triclinic | 1 | 1. Simple | P | $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |
| 6. | Trigonal | 1 | 1. Simple | P | $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$ |
| 7. | Hexagonal | 1 | 1. Simple | P | $a = b \neq c$ $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ |

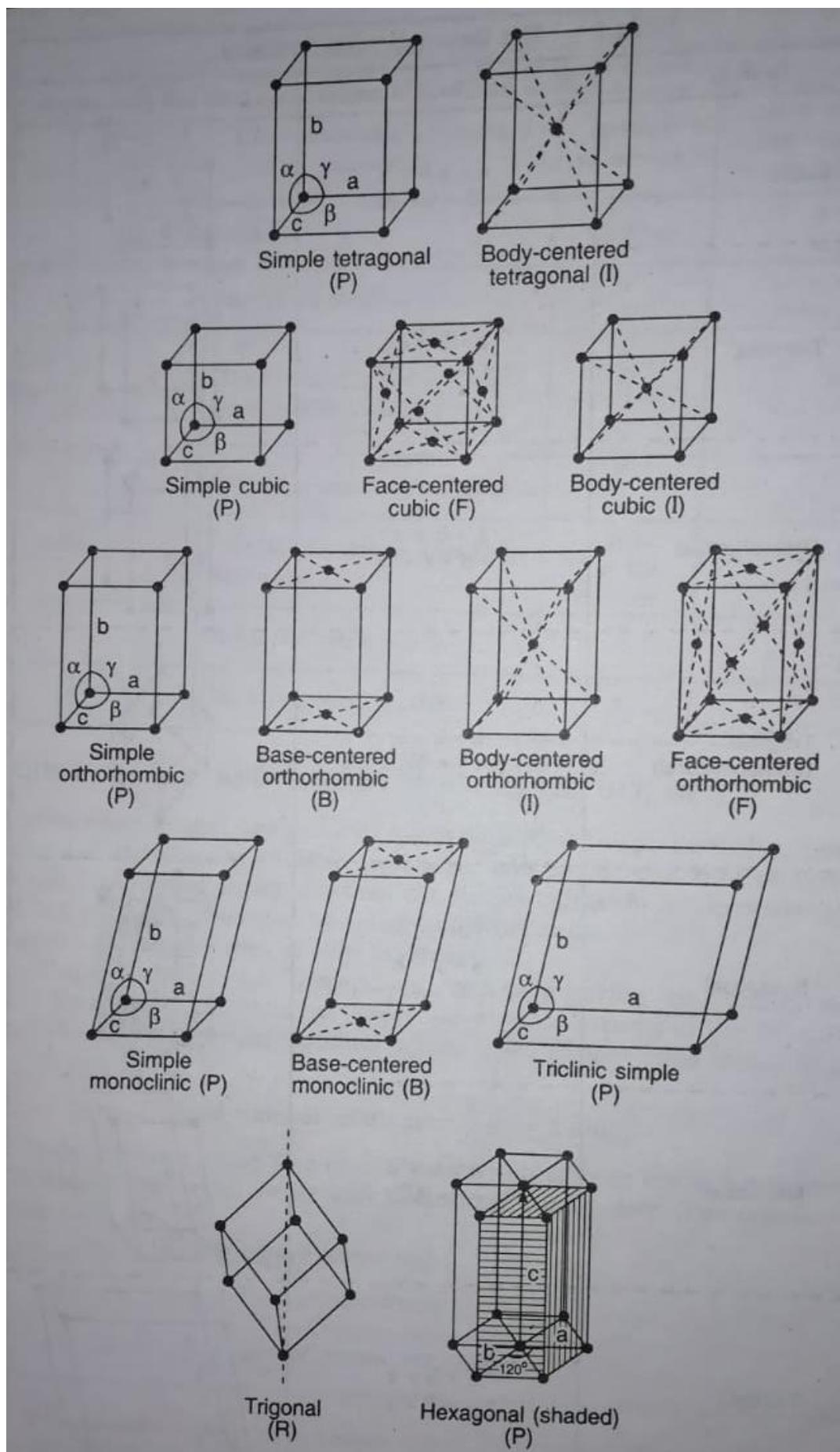
Types of Unit cell:

- **Primitive (P)** unit cells contain only a *single lattice point*.
- **Internal (I)** unit cell contains an atom in the *body center*.
- **Face (F)** unit cell contains atoms in the *all faces of the planes* composing the cell.
- **Centered (C)** unit cell contains atoms *centered on the sides* of the unit cell.



Combining **7 Crystal Classes** (cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, trigonal) with **4 unit cell types (P, I, F, C) symmetry** allows for only **14 types of 3-D lattice.**³

| Bravais lattice cells | Axes and interaxial angles | Examples |
|---|--|---|
| Cubic P Cubic I Cubic F | Three axes at right angles; all equal: $a = b = c; \alpha = \beta = \gamma = 90^\circ$ | Copper (Cu), silver (Ag), sodium chloride (NaCl) |
| Tetragonal P Tetragonal I | Three axes at right angles; two equal: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$ | White tin (Sn), rutile (TiO_2), β -spodumene ($\text{LiAlSi}_2\text{O}_6$) |
| P C I F | Three axes at right angles; all unequal: $a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$ | Gallium (Ga), perovskite (CaTiO_3) |
| Monoclinic P Monoclinic C | Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$ | Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) |
| Triclinic P | Three axes not at right angles, of any lengths: $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$ | Potassium chromate (K_2CrO_7) |
| Trigonal R (rhombohedral) | Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$ | Calcite (CaCO_3), arsenic (As), bismuth (Bi) |
| Trigonal and hexagonal C (or P) | Hexagonal: three equal axes coplanar at 120° , fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$ | Zinc (Zn), cadmium (Cd), quartz (SiO_2) [P] |



Symmetry Operations:

1.5 SYMMETRY OPERATIONS

A *symmetry operation* is that which transforms the crystals to itself, i.e., a crystal remains invariant under a symmetry operation. These operations are *translation*, *rotation*, *reflection* and *inversion*. The translation operation applies to lattices only while all the remaining operations and their combinations apply to all objects and are collectively known as *point symmetry operations*. The inversion operation is applicable only to three-dimensional crystals. These operations are briefly described below:

(i) Translations

The translation symmetry follows from the orderly arrangement of a lattice. It means that a lattice point \mathbf{r} , under lattice translation vector operation \mathbf{T} , gives another point \mathbf{r}' which is exactly identical to \mathbf{r} , i.e.,

$$\mathbf{r}' = \mathbf{r} + \mathbf{T}$$

where \mathbf{T} is defined by Eq. (1.1).

(ii) Rotations

J ——— J ——— J ——— J

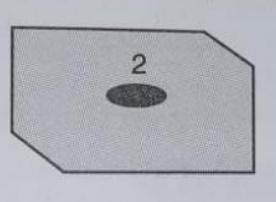
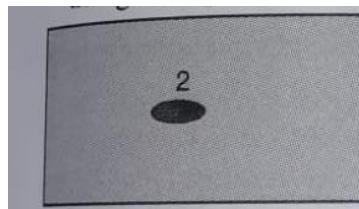
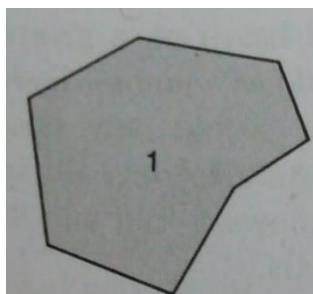
(a) Translation

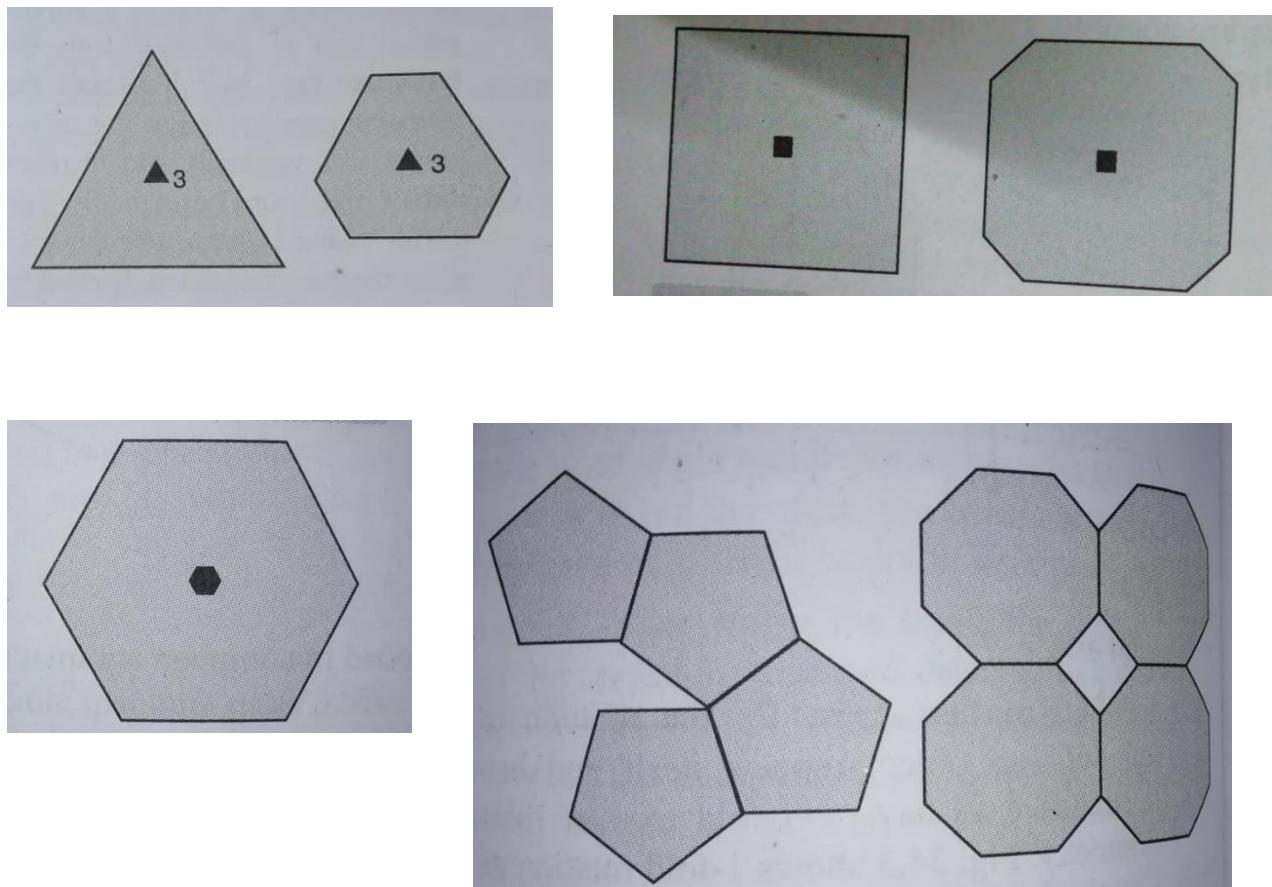
A lattice is said to possess the rotation symmetry if its rotation by an angle θ about an axis (or a point in a two-dimensional lattice) transforms the lattice to itself. Also, since the lattice always remains invariant by a rotation of 2π , the angle 2π must be an integral multiple of θ , i.e.,

$$n\theta = 2\pi$$

$$\text{or } \theta = 2\pi/n \quad (1.3)$$

The factor n takes integral values and is known as *multiplicity of rotation axis*.





5-fold and 8-fold Rotation Axis

the axis of rotation, the axis is said to have n -fold symmetry. However, because of the reticular structure of crystals, only 1-, 2-, 3-, 4- and 6-fold rotational symmetries (Fig. 1.14) are possible. They are known as symmetry elements corresponding to proper rotation, consequently, it means that a crystalline solid can not possess either 5-fold or any other rotational symmetry higher than 6-folds. They are being demonstrated in Fig. 1.14e, 1.14g and 1.14h.

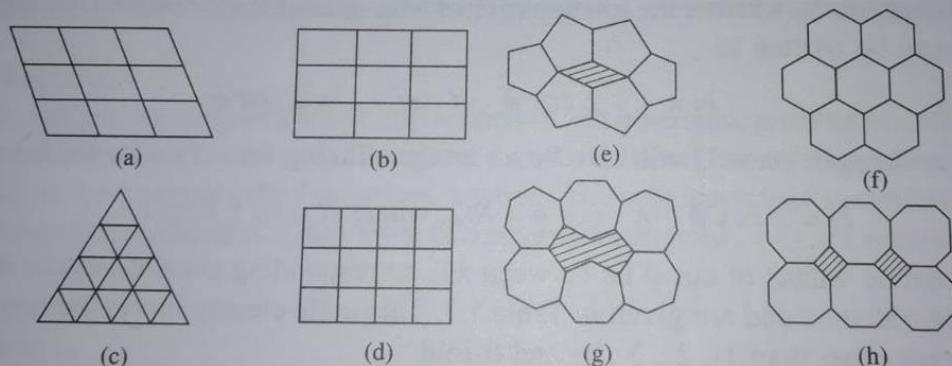


Fig. 1.14 Possible and non-existent symmetry axes

To show that Five-fold rotation is not compatible with lattice:

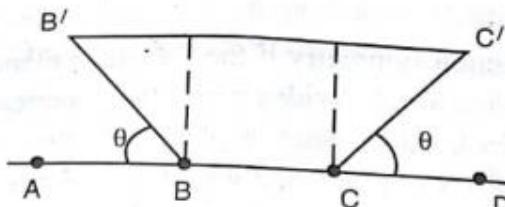


Fig. 1.6. Geometry used to prove that only 1, 2, 3, 4 and 6 - fold rotation axes are permissible.

B and C. Thus the points B' and C' must also be lattice points and should follow lattice translation symmetry. Hence B' C' must be some integral multiple of BC, i.e.,

$$B'C' = m(BC)$$

or

$$2T \cos \theta + T = mT$$

or

$$\cos \theta = (m - 1) / 2 \quad (1.4)$$

where m is an integer. Since $|\cos \theta| \leq 1$, the allowed values of m are 3, 2, 1, 0 and -1. These correspond to the allowed values of θ as 0° or 360° , 60° , 90° , 120° and 180° respectively. Hence from Eq. (1.3), the permissible values of n are 1, 6, 4, 3 and 2. Thus we conclude that 5-fold rotation is not permissible because it is not compatible with lattice translation symmetry. Similarly, other rotations, such as 7-fold rotation, are also not permissible.

$$\boxed{\cos \phi_n = \left(\frac{m-1}{2} \right) = \frac{N}{2}} \quad (4.1)$$

Table 4.2 Absence of five-fold rotation axis

| N | $\frac{N}{2}$ | $\cos \phi_n$ | ϕ_n | Possible fold of axis, $n = \left(\frac{360}{\phi_n} \right)^\circ$ |
|-----|---------------|---------------|-------------|--|
| -2 | -1 | -1 | 180° | 2 |
| -1 | -1/2 | -1/2 | 120° | 3 |
| 0 | 0 | 0 | 90° | 4 |
| +1 | +1/2 | +1/2 | 60° | 6 |
| +2 | +1 | +1 | 360° | 1 |

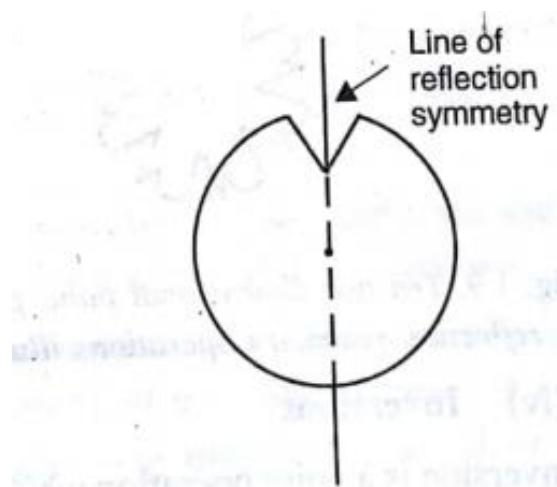
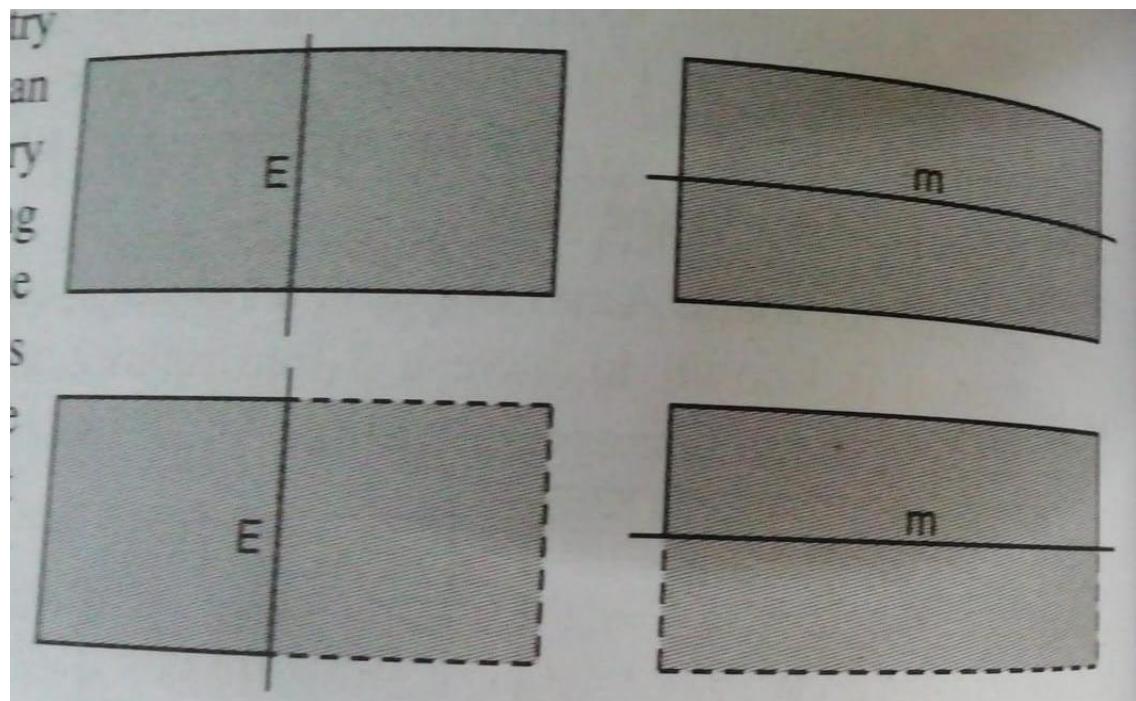


Fig. 1.8. *Reflection symmetry of a notched wheel about a line.*



(iii) Reflections

A lattice is said to possess reflection symmetry if there exists a plane (or a line in two dimensions) in the lattice which divides it into two identical halves which are mirror images of each other. Such a plane (or line) is represented by m . The reflection symmetry of a notched wheel is illustrated in Fig. 1.8. Considering the combinations of reflections with allowed rotations, we note that each allowed rotation axis can be associated with two possibilities : one is rotation with reflection and the other rotation without reflection. Since there are five allowed rotation axes, the possible number of such combinations is 10. These are designated as

$$1, 1m, 2, 2mm, 3, 3m, 4, 4mm, 6, 6mm$$

where the numerals represent the type of rotation axis, the first m represents a plane (or line) parallel to the rotation axis and the second m refers to another plane (or line) perpendicular to the rotation axis. These ten groups of symmetry operations are shown in Fig. 1.9.

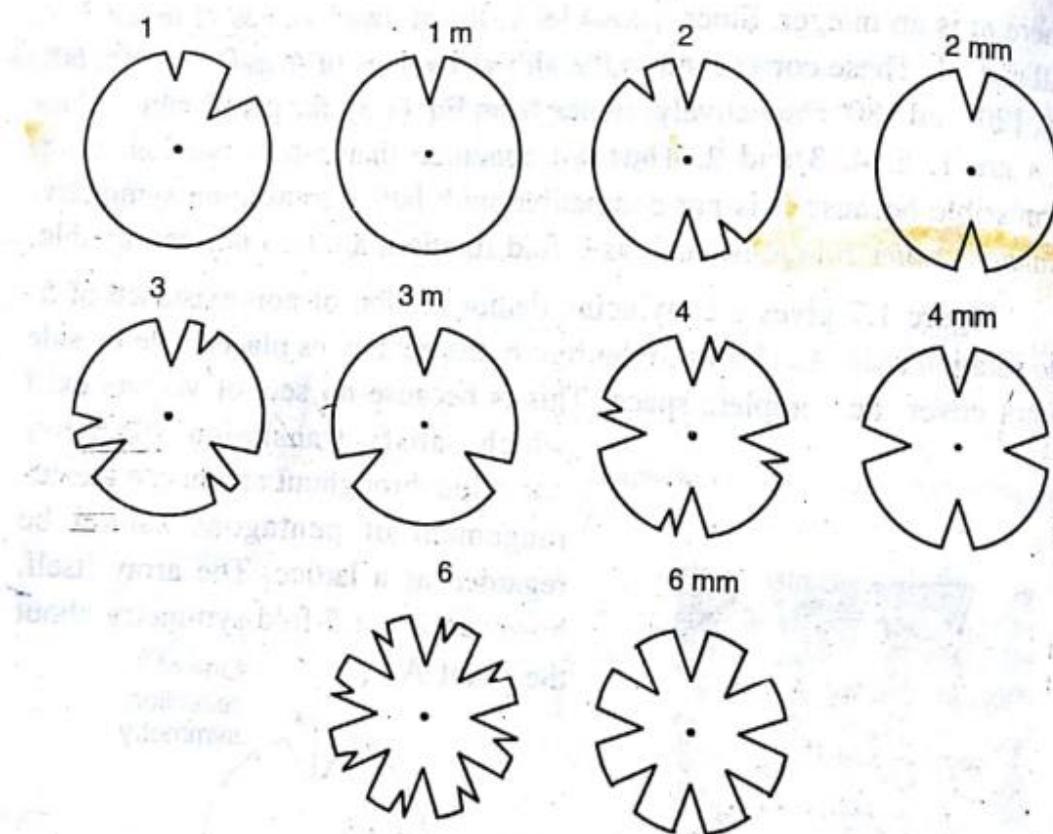


Fig. 1.9. Ten two-dimensional point groups consisting of rotation and reflection symmetry operations illustrated using notched wheels.

(iv) Inversion

(ii) Centre of symmetry

A simple cubic crystal has three pairs of parallel, opposite and identical faces. Hence such crystal is said to show a centre of symmetry, i.e. the body centre of the cubic crystals is a centre of symmetry (or inversion centre). See Figure 16.13.

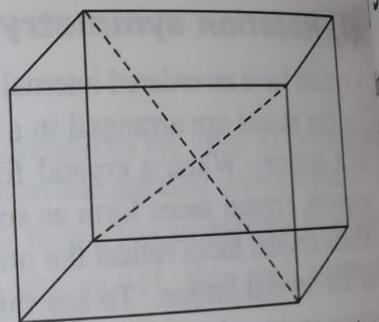


Figure 16.13 Centre of symmetry.

1.6 POINT GROUPS AND SPACE GROUPS

We have seen that there are mainly four types of symmetry operations, i.e., translation, rotation, reflection and inversion. The last three operations are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of space around a point. The group of such symmetry operations at a point is called a *point group*.

In two-dimensional space, rotation and reflection are the only point operations. As described earlier, their combinations yield 10 different point groups designated as 1, 1m, 2, 2mm, 3, 3m, 4, 4mm, 6, and 6mm which are shown in Fig. 1.9. In three-dimensional space, however, the situation is complicated due to the presence of additional point operations such as inversion. There are a total of 32 point groups in a three-dimensional lattice.

XIII. SPACE GROUPS

In a crystal, point group symmetry operations can also be combined with *translation symmetry elements*, provided they are compatible. Such combinations are called *space groups*. There are 230 space groups exhibited by crystals. The study of symmetry elements of the different crystals enables one to classify the crystals and their properties based on different symmetries.

The group of all the symmetry elements of a crystal structure is called *space group*. It determines the symmetry of a crystal structure as a whole. There are 17 and 230 distinct space groups possible in two and three dimensions respectively.

Crystallographic points, Directions, and planes:

where a, b and c are lattice constants in x, y and z directions
 p, q and r are integers.

If the lattice constants a, b and c are taken as **unit** axial lengths, $a = 1, b = 1$, and $c = 1$, and the co-ordinates of the lattice site will be (p, q, r) . These are the indices of the lattice site and are written with commas separating the numbers and enclosed in parenthesis.

As an example, the indices of atomic sites in the BCC cell are shown in Fig. 34.34. The atom positions for the eight corner atoms are $(0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,1), (1,1,0), (1,0,1)$, and $(0,1,1)$. The body cnetre atom in the cell has the coordinates $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. By convention,

the set of coordinates $(0,0,0)$ stands for the locations of all eight corners of cubic unit cell. Therefore, it is sufficient if the atom positions $(0,0,0)$ and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ are specified for the BCC cell.

The minimum number of coordinate sets necessary to specify the locations of all atoms in a unit cell are equal to the value of Z , the effective number atoms/cell.

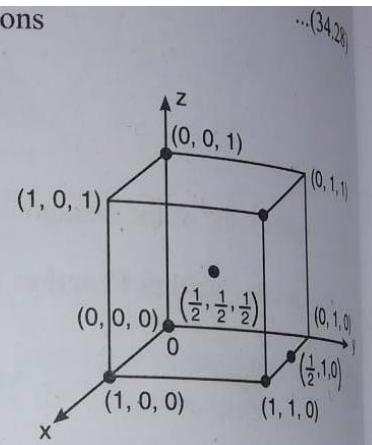
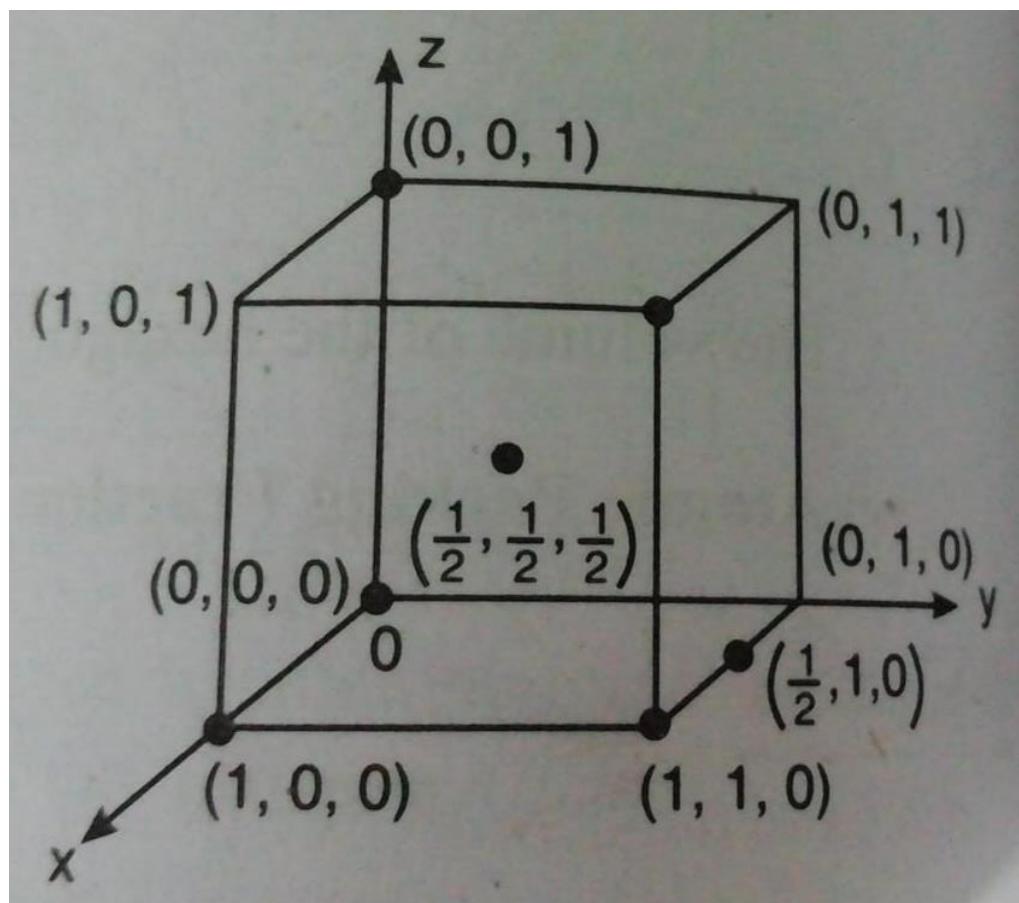


Fig. 34.34:

Rectangular right handed coordinate BCC lattice



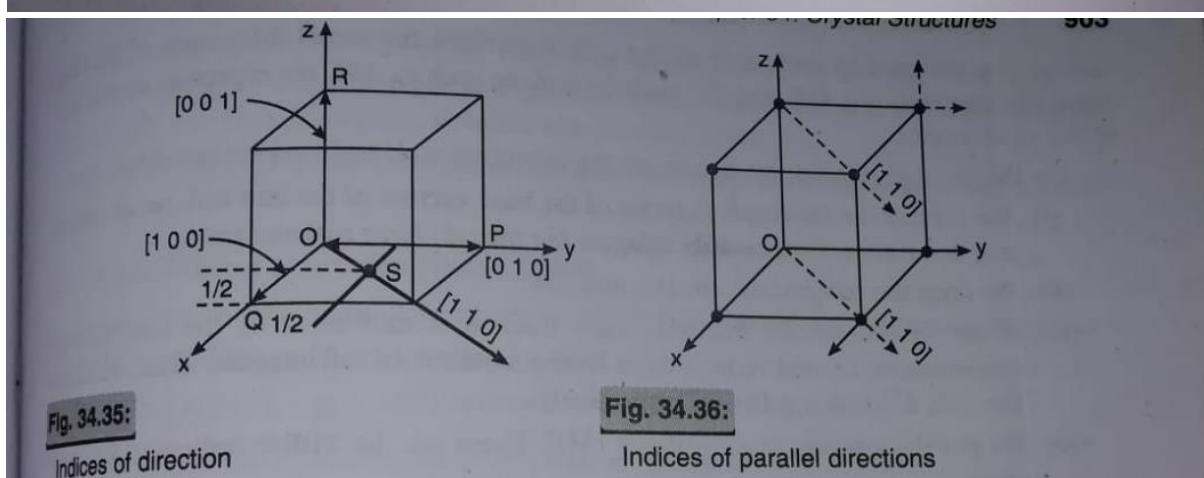
the indices of direction

The indices of direction are calculated by the following procedure.

- (i) First, find the coordinates of the lattice site nearest to the origin in a given direction.
- (ii) The coordinates are then divided by appropriate unit translations.
- (iii) If fractions are obtained, each of the fractions is multiplied by smallest common divisor.
- (iv) The integers obtained are the indices of direction written in square brackets, as $[p \ q \ r]$.

Thus, *the indices of direction in a crystal are the set of smallest integers, which have the same ratios as the components of a vector in the desired direction, referred to the axes.*

As an example let us consider a cubic cell shown in Fig. 34.35. Let the point 'O' be the origin. The point P is at the position $(0, b, 0)$. 'b' represents one unit distance. Therefore, the indices of the point P are $(0, 1, 0)$. The direction OP is given as $[0 \ 1 \ 0]$. On the other hand, the direction of PO is specified as $[0 \ \bar{1} \ 0]$. A bar on the number indicates a negative direction. Similarly, the directions OQ and OR are indicated as $[1 \ 0 \ 0]$ and $[0 \ 0 \ 1]$ respectively.



All the parallel directions have same direction indices and parallel directions are equivalent.

$\langle pqr \rangle$ represents family of directions $[0 \ 1 \ 0], [0 \ 0 \ 1], [1 \ 0 \ 0], [0 \ \bar{1} \ 0], [0 \ 0 \ \bar{1}], [\bar{1} \ 0 \ 0]$. All of them are grouped as $\langle 1 \ 0 \ 0 \rangle$

Table 1.9 Angle between two crystal directions $[h_1k_1l_1]$ and $[h_2k_2l_2]$

| Crystal system | $\cos \phi$ |
|----------------|--|
| Cubic | $\frac{h_1h_2 + k_1k_2 + l_1l_2}{(h_1^2 + k_1^2 + l_1^2)^{1/2} (h_2^2 + k_2^2 + l_2^2)^{1/2}}$ |
| Tetragonal | $\frac{a^2(h_1h_2 + k_1k_2) + c^2(l_1l_2)}{\sqrt{\{a^2(h_1^2 + k_1^2) + c^2l_1^2\}\{a^2(h_2^2 + k_2^2) + c^2l_2^2\}}}$ |
| Orthorhombic | $\frac{a^2h_1h_2 + b^2k_1k_2 + c^2l_1l_2}{\sqrt{(a^2h_1^2 + b^2k_1^2 + c^2l_1^2)(a^2h_2^2 + b^2k_2^2 + c^2l_2^2)}}$ |
| Hexagonal | $\frac{h_1h_2 + k_1k_2 - \frac{1}{2}(h_1k_2 + k_1h_2) + \frac{c^2}{a^2}l_1l_2}{\sqrt{\left(h_1^2 + k_1^2 - h_1k_1 + \frac{c^2}{a^2}l_1^2\right)\left(h_2^2 + k_2^2 - h_2k_2 + \frac{c^2}{a^2}l_2^2\right)}}$ |

Miller Indices:

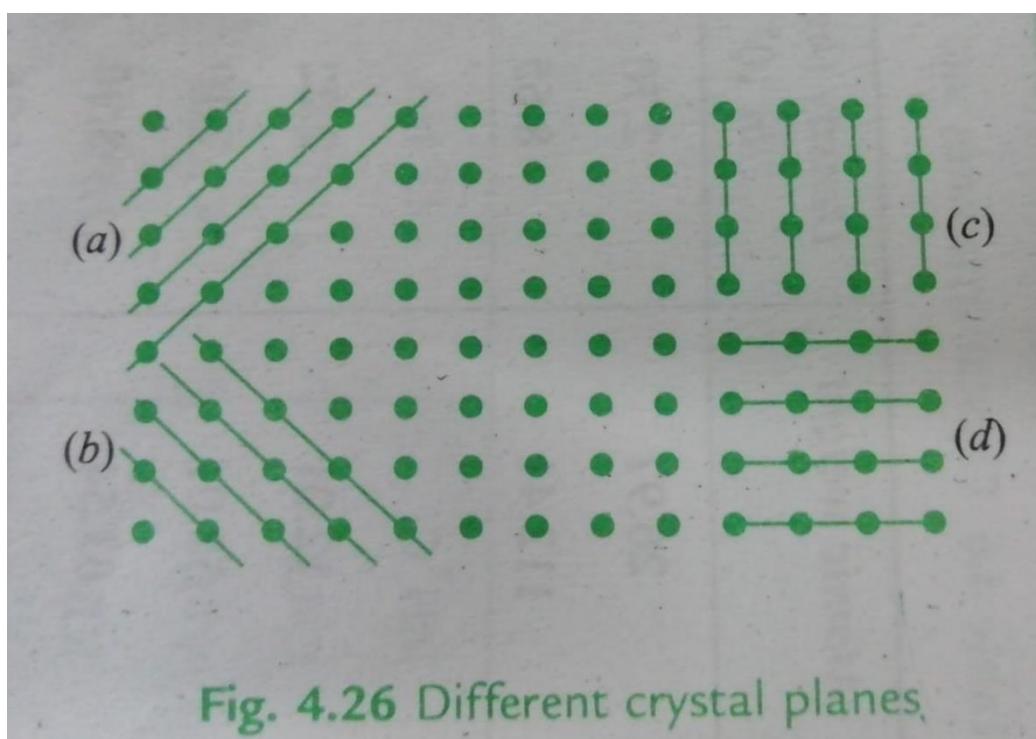


Fig. 4.26 Different crystal planes.

The crystal lattice may be regarded as made-up of an aggregate of a set of parallel equidistant planes, passing through the lattice points, which are known as *lattice planes*. For a given lattice, the lattice planes can be chosen in different ways as shown in Fig. 4.26. The problem is that how to designate these planes in a crystal. Miller evolved a method to designate a set of parallel planes in a crystal by three numbers $(h k l)$ known as *Miller indices*.

The scheme to represent the orientation of planes in a lattice was first introduced by Miller, a British crystallographer. The indices of planes are, therefore, known as the *Miller indices*. The steps involved to determine the Miller indices of a plane are as follows :

- (i) Find the intercepts of the plane on the crystallographic axes.
- (ii) Take reciprocals of these intercepts.
- (iii) Simplify to remove fractions, if any, and enclose the numbers obtained into parentheses.

In step (i), the intercepts are taken in terms of the lengths of fundamental vectors choosing one of the lattice points as the origin. If a plane is parallel to a certain axis, its intercept with that axis is taken as infinity. In

Simply,

- (i) Determine the intercepts of the plane on the three coordinate axes.
- (ii) Take the reciprocals of these intercepts
- (iii) Lastly convert these reciprocals into whole numbers by multiplying each reciprocal with their LCM to get the smallest whole number

The steps in the determination of *Miller indices* of a of parallel planes are illustrated with the aid of Fig. 4.27.

- (i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z).

| x | y | z |
|------|------|------|
| $2a$ | $3b$ | c |
| pa | qb | rc |

($p = 2, q = 3$ and $r = 1$)

Fig. 4.26 Different crystal planes

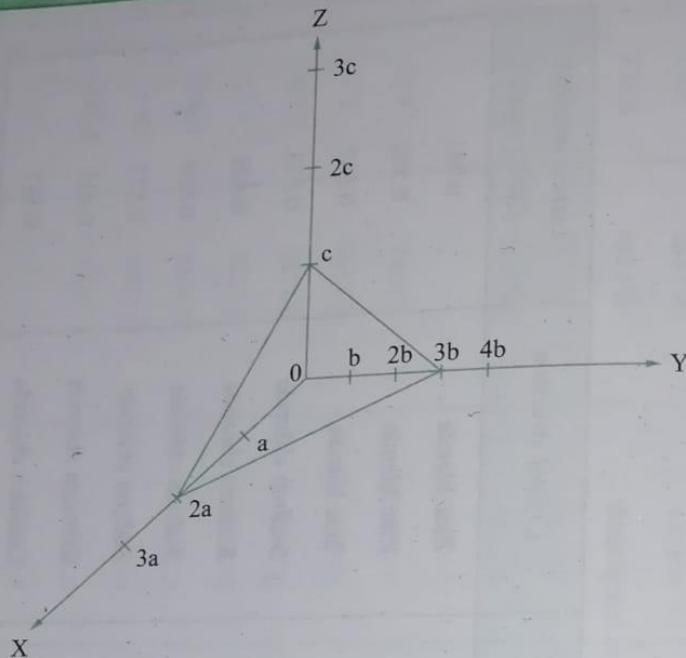


Fig. 4.27 Miller indices of planes

- (ii) Express the intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes.

i.e.,

$$\begin{array}{ccc} \frac{2a}{a} & \frac{3b}{b} & \frac{c}{c} \\ 2 & 3 & 1 \end{array}$$

- (iii) Determine the reciprocals of these numbers:

$$\begin{array}{ccc} \frac{1}{2} & \frac{1}{3} & \frac{1}{1} \end{array}$$

- (iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets:

| | | |
|------------------------|------------------------|--------------|
| $6 \times \frac{1}{2}$ | $6 \times \frac{1}{3}$ | 6×1 |
| (3) | (2) | (6) |

In general it is denoted by $(h k l)$. We also notice that:

$$\frac{1}{p} : \frac{1}{q} : \frac{1}{r} = h : k : l$$

$$\frac{1}{2} : \frac{1}{3} : \frac{1}{1} = 3 : 2 : 6$$

Thus, *Miller indices* may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

XIX. IMPORTANT FEATURES OF MILLER INDICES OF CRYSTAL PLANES

- (i) All the parallel equidistant planes have the same *Miller indices*. Thus the Miller indices define a set of parallel planes.
- (ii) A plane parallel to one of the coordinate axes has an intercept of infinity.
- (iii) If the *Miller indices* of two planes have the same ratio, i.e., (8 4 4) and (4 2 2) or (2 1 1), then the planes are parallel to each other.
- (iv) If $(h k l)$ are the *Miller indices* of a plane, then the plane cuts the axes into h , k and l equal segments respectively.

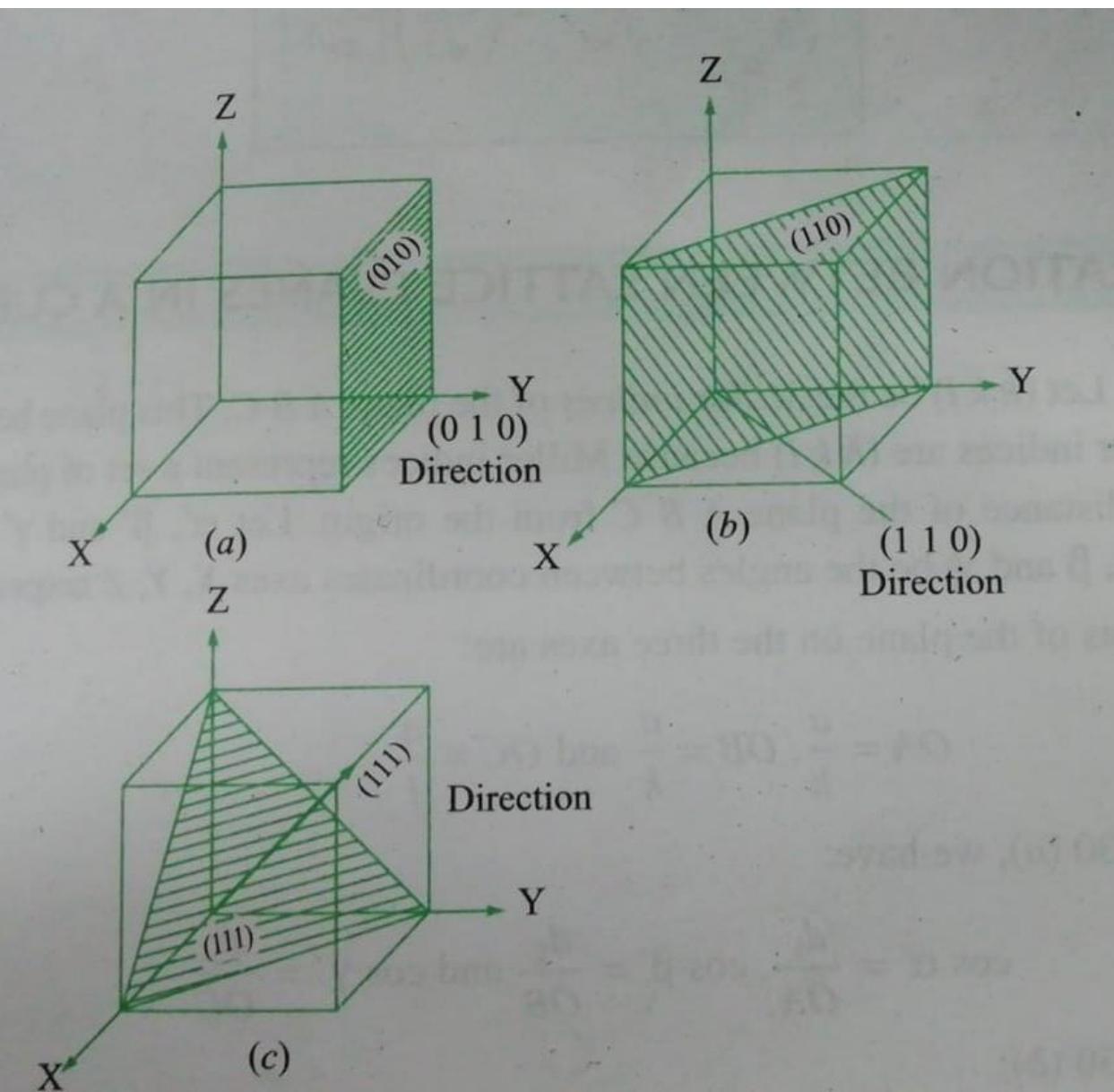
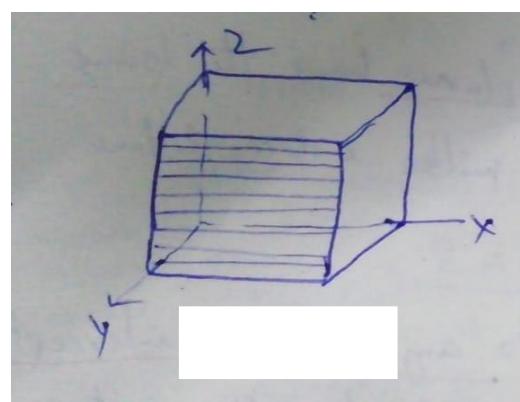
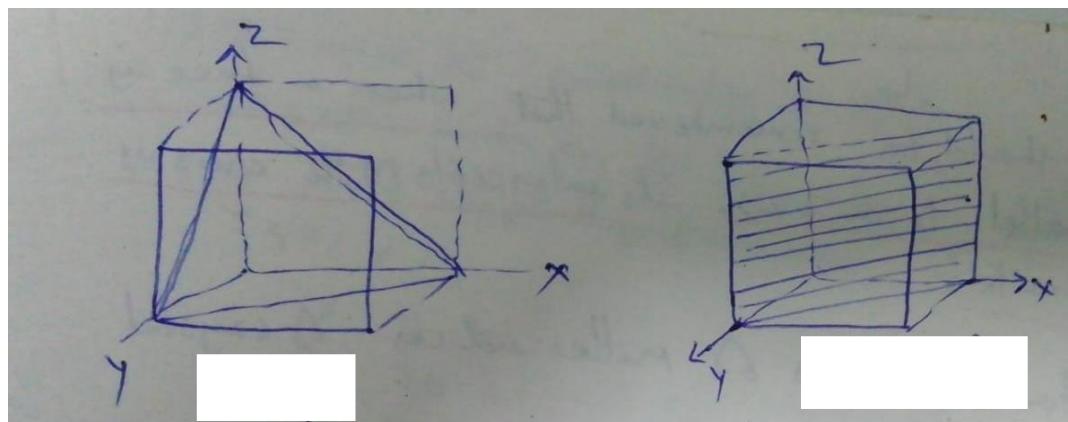
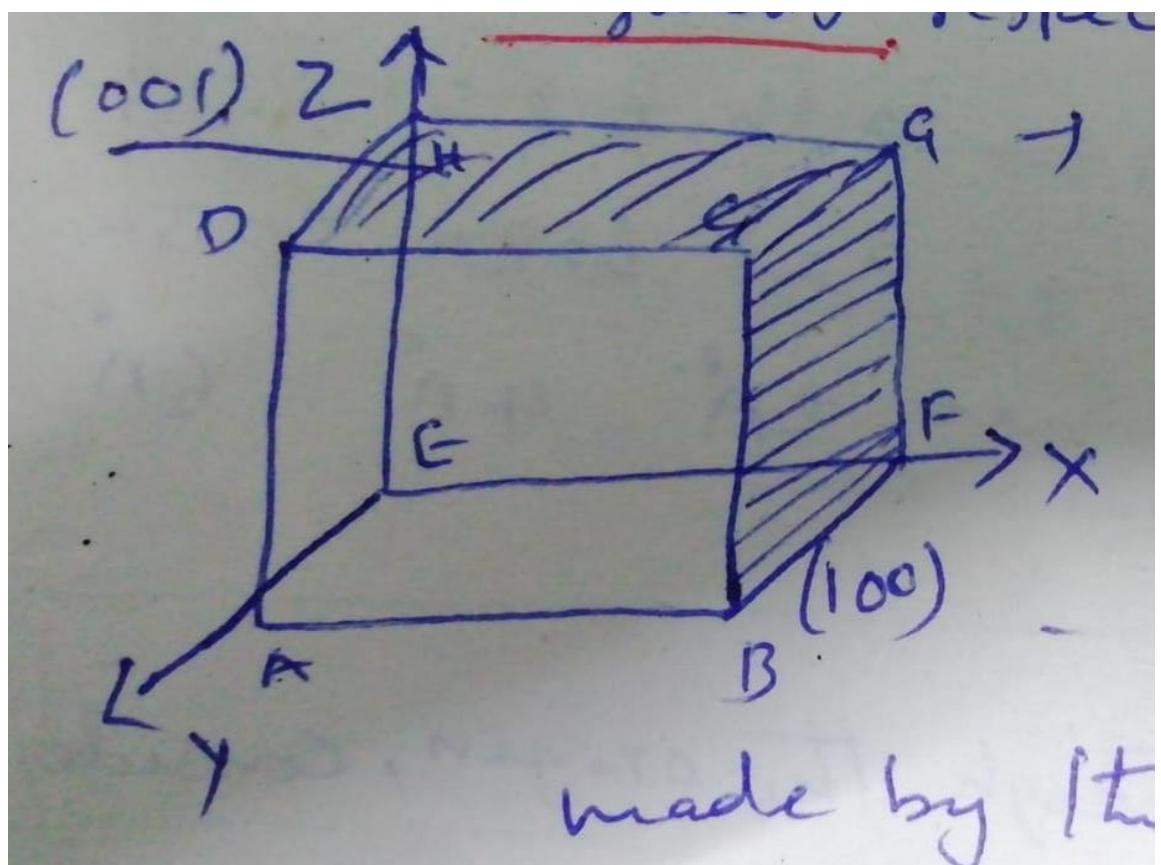


Fig. 4.28 Planes and directions in a cubic crystal



34.15.2 Sketching a lattice plane (hkl)

The intercepts made by a plane can be found if the Miller indices of the plane are known.

(i) Let the Miller indices of a plane be (hkl) .

(ii) A unit cell (for e.g. a cube) is drawn with three coordinate axes.

(iii) From the Miller indices, the reciprocals are obtained $\rightarrow \frac{1}{h}, \frac{1}{k}, \frac{1}{l}$

(iv) The intercepts are marked on the coordinate axes.

(v) The three non-planar points are joined and the plane is obtained.

Example: Draw a plane (321)

Step (i): A cube having *unit axial lengths* ($a = 1$) along the three coordinate axes is drawn as shown in Fig. 34.39.

Step (ii): The reciprocals of Miller indices are $p = \frac{1}{3}, q = \frac{1}{2}$ and $r = 1$.

Step (iii): The intercepts, $\frac{1}{3}, \frac{1}{2}$ and 1, are marked within the cube on x , y and z axes respectively.

Step (iv): A plane is drawn through the points and is shaded.

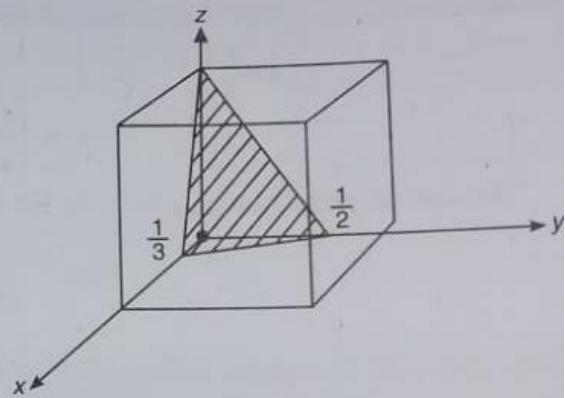
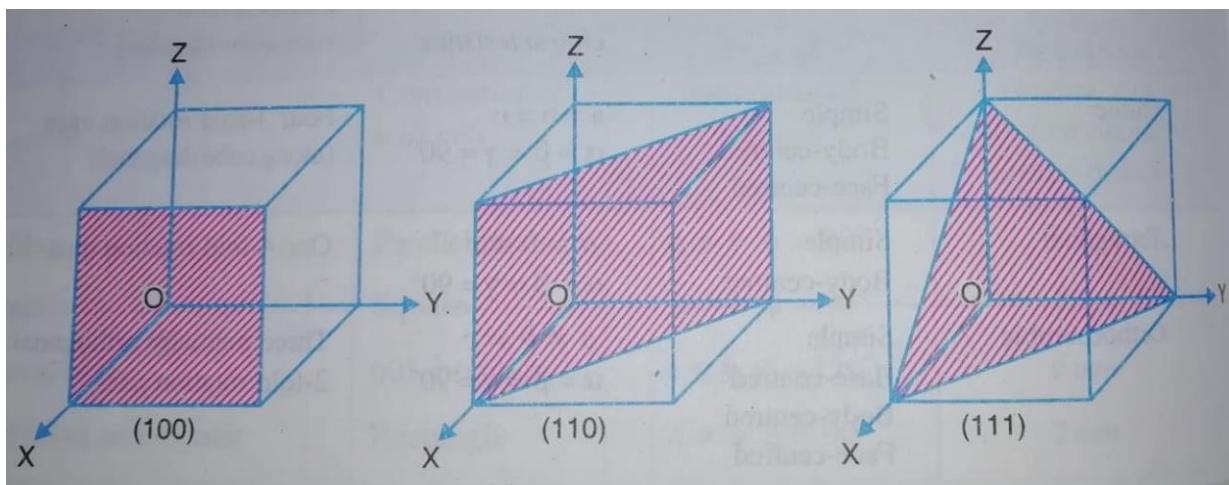


Fig. 34.39:

Sketching a lattice plane (321) plane



Example. In a crystal, a lattice plane cuts intercepts of $2a$, $3b$ and $6c$ along the axes, where a , b and c are primitive vectors of the unit cell. Determine the Miller indices of the given plane.

Sol. If the given plane cuts intercepts ra , sb , tc along the three axes, we have

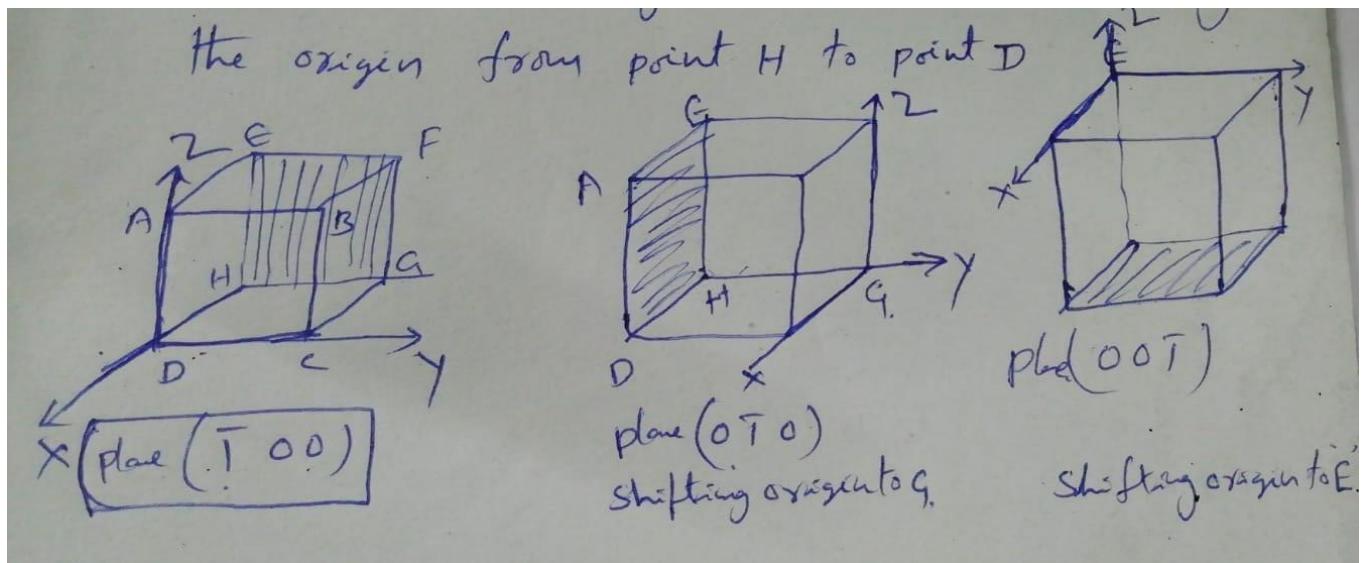
$$ra : sb : tc = 2a : 3b : 6c$$

where a , b and c are primitive vectors of the unit cell.

$$r : s : t = 2 : 3 : 6$$

$$\frac{1}{r} : \frac{1}{s} : \frac{1}{t} = \frac{1}{2} : \frac{1}{3} : \frac{1}{6} = 3 : 2 : 1$$

\therefore Miller indices of the plane are (321).



Negative integer values are indicated by placing a bar over the integer.

Interplanar spacing:

XXII. SEPARATION BETWEEN LATTICE PLANES IN A CUBIC CRYSTAL

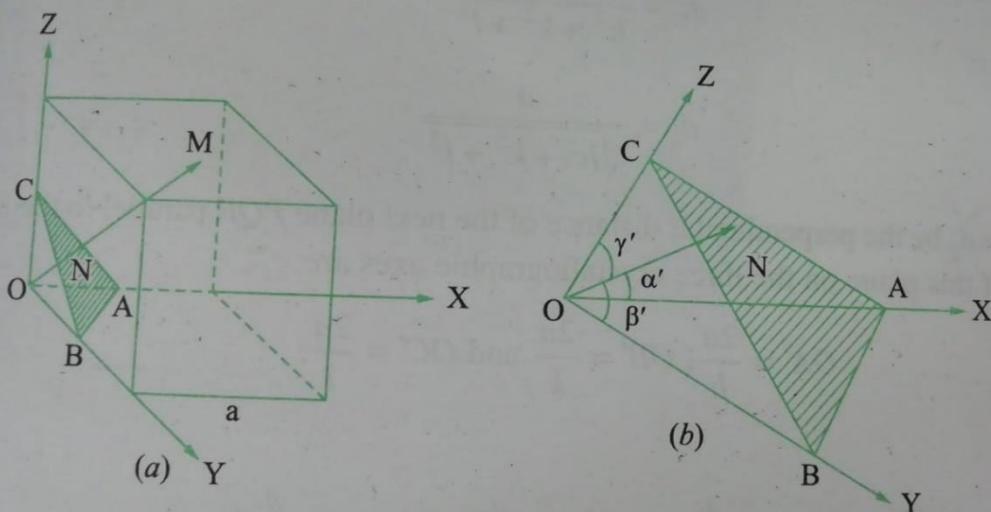
The cube edge is a . Let $(h k l)$ be the *Miller indices* of the plane $A B C$. This plane belongs to a family of planes whose Miller indices are $(h k l)$ because Miller indices represent a set of planes. Let $ON = d_1$ be the perpendicular distance of the plane $A B C$ from the origin. Let α' , β' and γ' (different from the interfacial angles α , β and γ) be the angles between coordinates axes X , Y , Z respectively and ON .

The intercepts of the plane on the three axes are:

$$OA = \frac{a}{h}, OB = \frac{a}{k} \text{ and } OC = \frac{a}{l} \quad (4.4)$$

From Fig. 4.30 (a), we have:

$$\cos \alpha' = \frac{d_1}{OA}, \cos \beta' = \frac{d_1}{OB} \text{ and } \cos \gamma' = \frac{d_1}{OC} \quad (4.5)$$



Now, making use of the direction cosine, which states that

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad (13)$$

and substituting the values of $\cos \alpha$, $\cos \beta$, and $\cos \gamma$ in eq. 13, we obtain

$$\frac{d^2}{(a/h)^2} + \frac{d^2}{(b/k)^2} + \frac{d^2}{(c/l)^2} = 1$$

$$\left[\frac{d_1}{OA} \right]^2 + \left[\frac{d_1}{OB} \right]^2 + \left[\frac{d_1}{OC} \right]^2 = 1$$

$$\left[\frac{d_1 h}{a} \right]^2 + \left[\frac{d_1 k}{a} \right]^2 + \left[\frac{d_1 l}{a} \right]^2 = 1$$

$$\frac{d_1^2}{a^2} (h^2 + k^2 + l^2) = 1$$

$$d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Let $OM = d_2$ be the perpendicular distance of the next plane PQR parallel to the first plane ABC .
The intercepts of this plane on the three crystallographic axes are:

$$OA' = \frac{2a}{h}, OB' = \frac{2a}{k} \text{ and } OC' = \frac{2a}{l}$$

and

$$\cos \alpha' = \frac{d_2}{OA'}, \cos \beta' = \frac{d_2}{OB'}, \cos \gamma' = \frac{d_2}{OC'} \quad (4.8)$$

$$(OM)^2 = [d_2^2 \cos^2 \alpha' + d_2^2 \cos^2 \beta' + d_2^2 \cos^2 \gamma']$$

$$d_2^2 = d_2^2 [\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma']$$

$$\text{i.e., } \cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$$

Substituting this in equation (4.8), we get:

$$\left[\frac{d_2 h}{2a} \right]^2 + \left[\frac{d_2 k}{2a} \right]^2 + \left[\frac{d_2 l}{2a} \right]^2 = 1$$

$$\frac{d_2^2}{4a^2} (h^2 + k^2 + l^2) = 1$$

$$d_2^2 = \frac{4a^2}{h^2 + k^2 + l^2}$$

$$d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \quad (4.9)$$

Thus the interplanar spacing between two adjacent parallel planes of *Miller indices* $(h k l)$ in a cubic lattice is given by:

$$d = d_2 - d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

(4.10)

For convenience, the interplanar spacing

Table 1.10 Interplanar spacings of various crystal systems

| System | d_{hkl} |
|--------------|---|
| Cubic | $a(h^2 + k^2 + l^2)^{-1/2}$ |
| Tetragonal | $\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$ |
| Orthorhombic | $\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]^{-1/2}$ |
| Hexagonal | $\left[\frac{4/3(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$ |
| Rhombohedral | $\frac{a(1 + 2\cos 3\alpha - 3\cos^2 \alpha)^{1/2}}{[(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)]^{1/2}}$ |
| Monoclinic | $\left[\frac{h^2/a^2 + l^2/c^2 + (2hl \cos \beta)/ac}{\sin^2 \beta} + \frac{k^2}{b^2} \right]^{-1/2}$ |
| | $\left[\begin{array}{ ccc ccc ccc } \hline h/a & \cos \gamma & \cos \beta & 1 & h/a & \cos \beta & 1 & \cos \gamma & h/a \\ k/b & 1 & \cos \alpha & \cos \gamma & k/b & \cos \alpha & \cos \gamma & 1 & k/b \\ l/c & \cos \alpha & 1 & \cos \beta & l/c & 1 & \cos \beta & \cos \alpha & l/c \\ \hline \end{array} \right]^{-1/2}$ |
| Triclinic | $\left \begin{array}{ccc} 1 & \cos \gamma & \cos \beta \\ \cos \gamma & 1 & \cos \alpha \\ \cos \beta & \cos \alpha & 1 \end{array} \right ^{-1/2}$ |

Simple Crystal structures:

Definitions:

Some important crystal structure terms are defined below:

Coordination number (N): The coordination number is defined as the number of equidistant nearest neighbours that an atom has in the given structure. Greater is the coordination number, the more closely packed up will be the structure.

Nearest neighbour distance (2r): The distance between the centres of two nearest neighbouring atoms is called *nearest neighbour distance*. It will be $2r$ if r is the radius of the atom.

Atomic radius (r): Atomic radius is defined as half the distance between nearest neighbours in a crystalline solid without impurity.

Atomic packing factor: The fraction of the space occupied by atoms in a unit cell is known as *atomic packing factor (APF)*; or simply packing factor; i.e., it is the ratio of the volume of the atoms occupying the unit cell to the volume of the unit cell relating to that structure.

Simple Cubic:

cell is one. Thus sc is a primitive cell. In this structure the atoms touch each other along the edges. Hence the nearest neighbour distance is $2r = a$. We note the following features in an sc structure:

Coordination number, $N = 6$

Nearest neighbour distance, $2r = a$

Lattice constant, $a = 2r$

Number of atoms per unit cell; $n = \frac{1}{8} \times 8 = 1$

Number of lattice points = 1

Volume of all the atoms in a unit cell, $v = 1 \times \frac{4}{3}\pi r^3$

Volume of unit cell, $V = a^3 = (2r)^3$

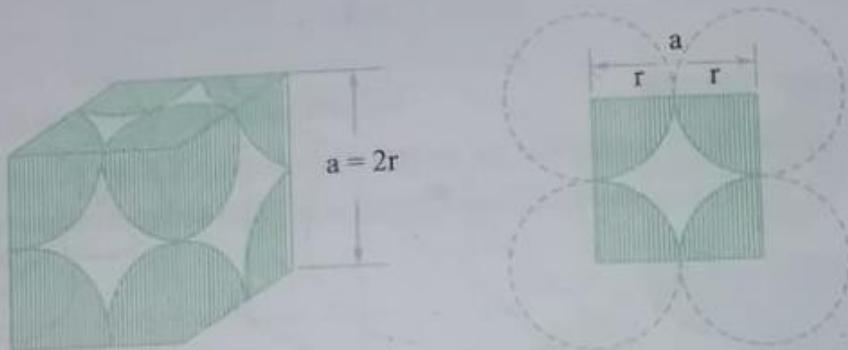


Fig. 4.16 Simple cubic structure

Hence the *packing factor* or *density of packing* of this structure is:

$$PF = \frac{v}{V} = \frac{\frac{4}{3}\pi r^3}{a^3}$$

$$PF = \left[\frac{4}{3} \right] \frac{(\pi r^3)}{8r^3} = \frac{\pi}{6} = 0.52 \text{ or } 52\%$$

Body Centred Cubic (bcc) structure:

entirely within the unit cell and is not shared by any surrounding unit cells. The number of atoms per cell in a bcc structure is $\frac{1}{8} \times 8 + 1 = 2$. The corner atoms do not touch each other, but each corner touches the body centre atom along the body diagonal. Hence, the coordination number of the structure is 8.

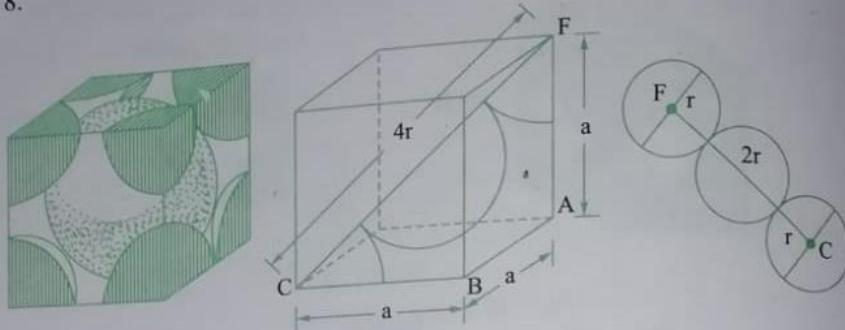


Fig. 4.17 Body centred cubic structure

The calculation of the lattice constant can be made with the help of Fig. 4.17.

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

$$(FC)^2 = (AC)^2 + (AF)^2$$

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

$$(4r)^2 = 3a^2$$

$$a^2 = \frac{(4r)^2}{3}$$

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

We shall now calculate the packing factor from the following data:

Coordination number, $N = 8$

$$\text{Nearest neighbour distance, } 2r = \frac{a\sqrt{3}}{2}$$

$$\text{Lattice constant, } a = \frac{4r}{\sqrt{3}}$$

$$\text{Number of atoms per unit cell, } n = \frac{1}{8} \times 8 + 1 = 2$$

$$\text{Volume of all the atoms in a unit cell, } v = 2 \times \frac{4}{3}\pi r^3$$

$$\text{Volume of unit cell, } V = a^3 = \frac{64r^3}{3 \times \sqrt{3}}$$

Therefore, atomic packing factor,

$$\begin{aligned} APF &= \frac{v}{V} = \frac{8}{3} \frac{\pi r^3 3\sqrt{3}}{64r^3} \\ &= \frac{\sqrt{3} \pi}{8} = 0.68 \text{ or } 68\% \end{aligned}$$

(iii) Face Centred Cubic (fcc) Structure

In the case of fcc lattice, there are eight atoms at the eight corners of the unit cell and six atoms at the centres of six faces. Considering the atom at the face centre as origin, it can be observed that this face is common to two unit cells and there are twelve points surrounding it situated at a distance equal to half the face diagonal of the unit cell. Thus, the coordination number of fcc lattice is twelve. The atoms touch each other along the face diagonal. Each corner atom is shared by 8 surrounding unit cells and each of the face centred atom is shared by 2 surrounding unit cells. Thus the total number of atoms

in fcc structure is $\left(\frac{1}{8} \times 8 + 6 \times \frac{1}{2}\right) = 4$. We thus note in fcc structure that:

Coordination number, $N = 12$

Lattice constant, $a = \frac{4r}{\sqrt{2}}$

Nearest neighbour distance, $2r = \frac{a\sqrt{2}}{2}$

Number of atoms per unit cell, $n = 4$

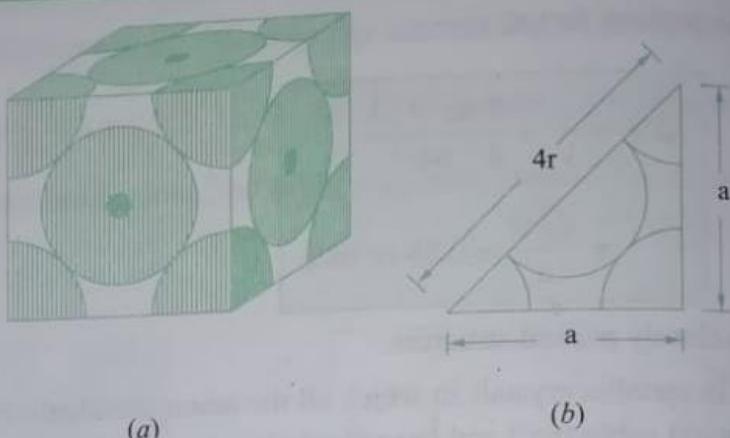


Fig. 4.19 Face centred cubic structure

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

$$\text{Volume of unit cell, } V = a^3 = \frac{64r^3}{2\sqrt{2}}$$

Atomic packing factor of fcc structure is thus calculated:

$$APF = v/V$$

$$\begin{aligned} APF &= \left(\frac{16}{3}\right) \frac{\pi r^3 2\sqrt{2}}{64r^3} = \frac{\sqrt{2}\pi}{6} \\ &= \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \end{aligned}$$

Copper, aluminium, lead and silver have this structure.

XVI. RELATION BETWEEN THE DENSITY OF CRYSTAL MATERIAL AND LATTICE CONSTANT IN A CUBIC LATTICE

Consider a cubic crystal of lattice constant a . Let the number of atoms per unit cell be n and ρ be the density of the crystal material. The atomic weight of the material is M_A . Let N_A be the Avogadro's number.

Thus $\left[\frac{M_A n}{\rho} \right] m^3$ of the material will contain N_A atoms. Hence n atoms in a unit cell will occupy

a volume $\left[\frac{M_A n}{\rho N_A} \right]$.

Thus,

$$a^3 = \frac{M_A n}{\rho N_A}; \text{ or } \rho = \frac{M_A n}{N_A a^3}; \text{ or } a = \left[\frac{M_A n}{N_A \rho} \right]^{1/3}$$

Crystal Structures:

NaCl:

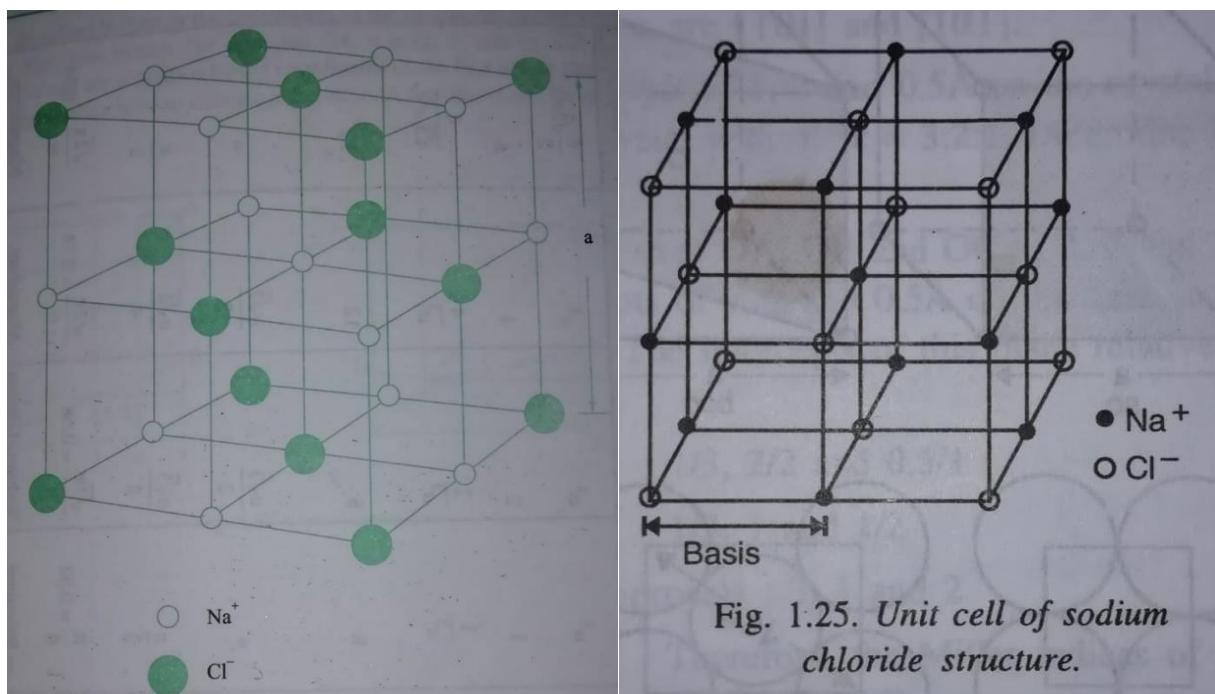
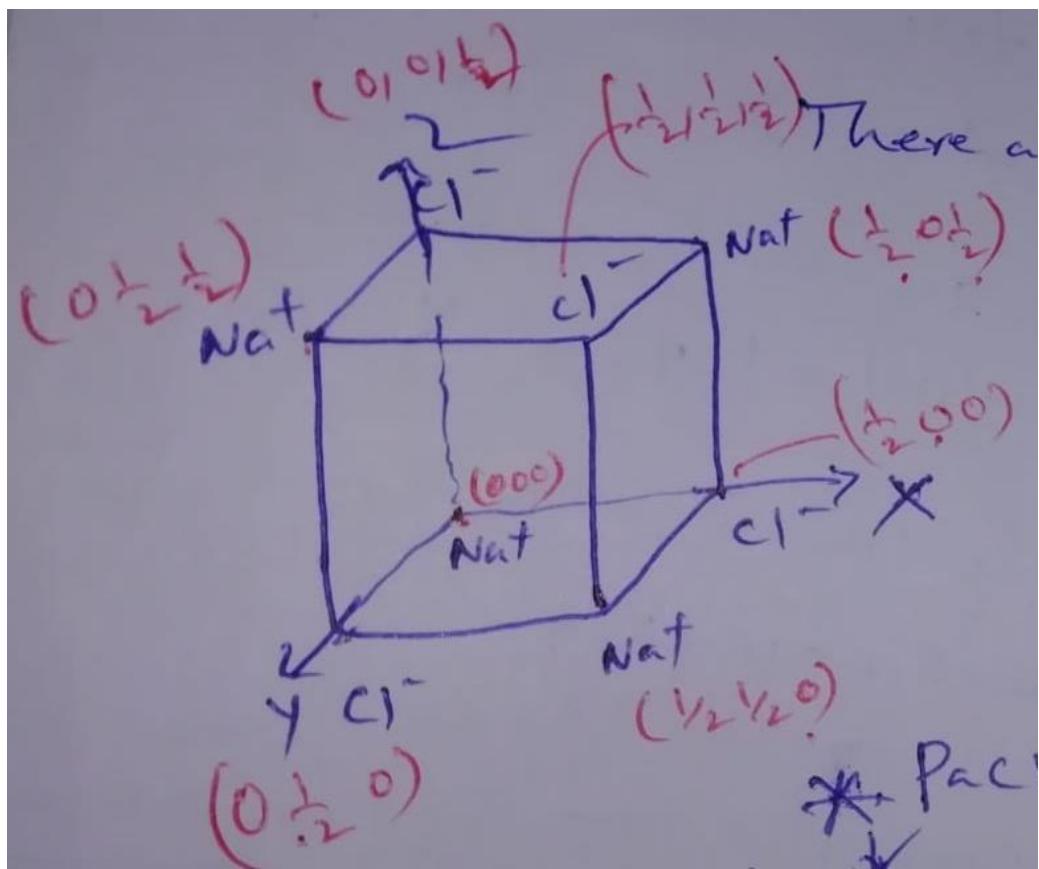


Fig. 1.25. Unit cell of sodium chloride structure.

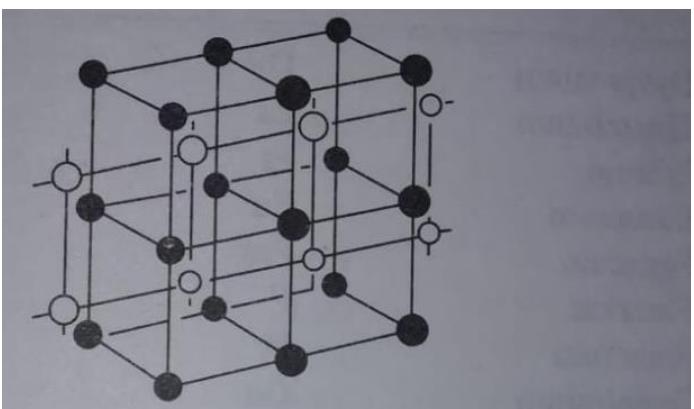
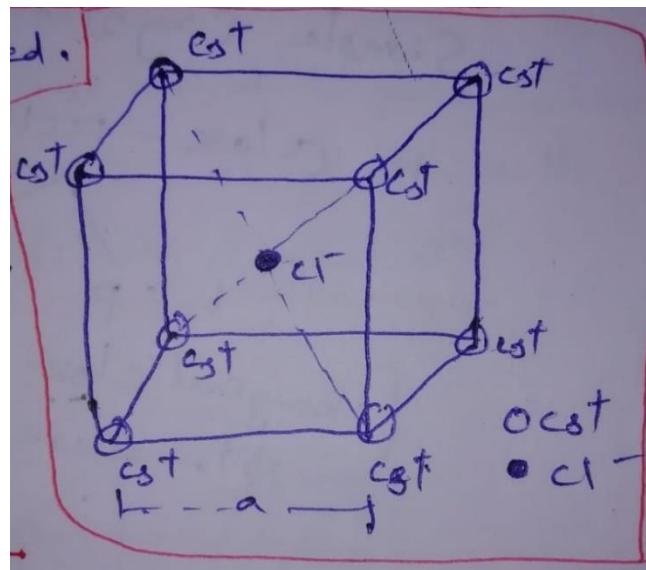
NaCl is an example of face centered cubic (FCC) Bravais lattice. Each cell has 8 corners and 8 cells meet at each corner. Thus, an ion at a corner of the cell is shared by 8 cells, i.e. only $1/8$ ion belongs to any one cell. Similarly, an ion at the center of a face of the cell is shared by 2 cells, i.e. only $1/2$ ion belongs to any one cell. Since a cell has 8 corners and 6 faces, it has $[(8 \times 1/8) + (6 \times 1/2)] = 4$ ions of one kind, and similarly 4 ions other kind.

Thus, there are 4 Na^+ - Cl^- ion pairs (molecules) per unit cell. The position coordinates of Na^+ and Cl^- are as follows.

| | | |
|--------------------------------|--|--|
| Na Cl | $0 \ 0 \ 0$ $\frac{1}{2} \ \frac{1}{2} \ 0$ $\frac{1}{2} \ 0 \ \frac{1}{2}$ $0 \ \frac{1}{2} \ \frac{1}{2}$ | $\frac{1}{2} \ \frac{1}{2} \ 0$ $0 \ 0 \ \frac{1}{2}$ $0 \ \frac{1}{2} \ 0$ $\frac{1}{2} \ 0 \ 0$ |
|--------------------------------|--|--|



CsCl:



The cesium chloride structure • and O represents two different ions which form interpenetrating simple cubic lattice

2.2 X-RAY DIFFRACTION

When an atomic electron is irradiated by a beam of monochromatic x-rays, it starts vibrating with a frequency equal to that of the incident beam. Since an accelerating charge emits radiations, the vibrating electrons present inside a crystal become sources of secondary radiations having the same frequency as the incident x-rays. These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiations is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another. The incident x-rays, however, have the same order of wavelength as that of the atomic dimensions; hence the radiations emitted by electrons are, in general, out of phase with one another. These radiations may, therefore, undergo constructive or destructive interference producing maxima or minima in certain directions.

In actual crystals, the problem is more complicated because of the presence of three-dimensional arrangement of atoms. The conditions for a crystal to diffract x-rays can be determined by using either *Bragg's treatment* or *Von Laue's treatment*.

VIII. BRAGG'S LAW

Consider a ray PA reflected at atom A in the direction AR from plane I and another ray QB reflected at another atom B in the direction BS. Now from the atom A, draw two perpendiculars AC and AD on QB and BS respectively. The two reflected rays will be in phase or out of phase depending on the path difference. When the path difference (CB + BD) is a whole wavelength (λ) or multiple of whole wavelength ($n\lambda$), then the two rays will reinforce each other and produce an intense spot. Thus condition of reinforcement is:

$$CB + BD = n\lambda$$

From Fig. (5.5), we have

$$CB = BD = d \sin \theta$$

where, θ is the angle between the incident ray and the planes of reflection (*glancing angle*). Therefore,

$$2d \sin \theta = n\lambda \quad (5.11)$$

where, d is the interplanar spacing of planes and $n = 1, 2, 3, \dots$ stands for first order, second order, third order, ... maxima respectively. Equation (5.11) is known as Bragg's law. Different directions in which intense reflections will be produced can be obtained by giving different values to θ , i.e.,

$$\text{for first maximum, } \sin \theta_1 = \frac{\lambda}{2d}$$

$$\text{for second maximum, } \sin \theta_2 = \frac{2\lambda}{2d}$$

$$\text{for third maximum, } \sin \theta_3 = \frac{3\lambda}{2d} \text{ and so on.}$$

It should be remembered that the intensity goes on decreasing as the order of spectrum increases.

Thus we see that when a beam of monochromatic X-rays falls on a crystal, each atom becomes a source of scattering radiations. It has already been mentioned that in a crystal there are certain planes which are particularly rich in atoms. The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. Generally, the *Bragg scattering* is regarded as *Bragg reflection*. Planes are in phase with each other, and hence they reinforce each other to produce maximum intensity. For other angles, the reflections from different planes are out of phase, and hence they reinforce to produce either zero intensity or extremely feeble intensity.

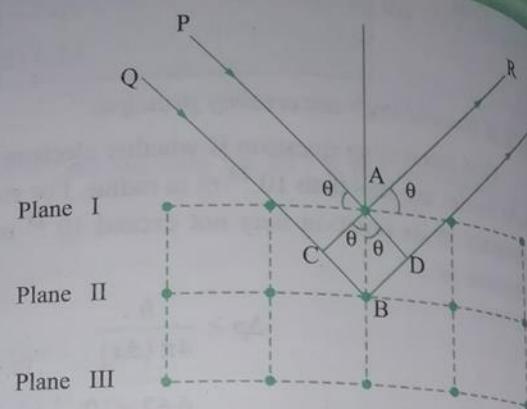
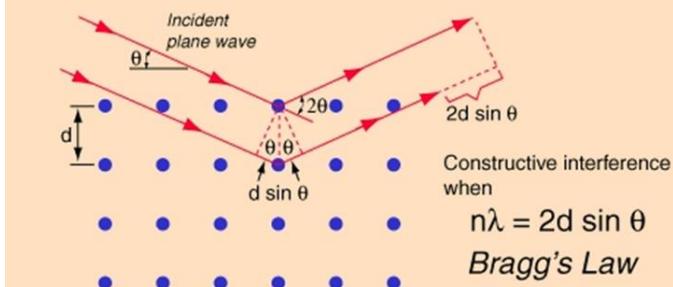


Fig. 5.5 Reflection of X-rays from lattice planes in a crystal

Bragg's Law



XII. CORRECTION FOR BRAGG'S EQUATION

Let us consider the surface layer of a crystal on which an X-ray of wavelength λ (in air) is incident. Suppose θ is the glancing angle, and we take the layer immediately below the surface, the glancing angle at that layer will not be θ but θ' .

The Bragg's law for the reflection at that layer is:

$$n\lambda' = 2d \sin \theta' \quad (5.14)$$

where, λ' is the wavelength in the crystal.

The refractive index μ can be written as:

$$\mu = \frac{\sin i}{\sin r} = \frac{\cos \theta}{\cos \theta'} = \frac{\lambda}{\lambda'} \quad (5.15)$$

or

$$\lambda' = \frac{\lambda}{\mu}$$

Substituting this in the above equation (5.14), we get:

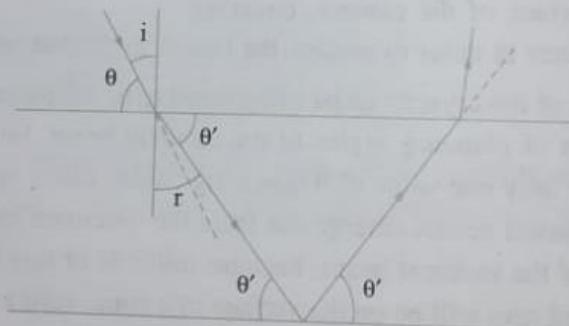


Fig. 5.8 Refraction of X-rays on layers of a crystal

Source: Solid state Physics From S.O. Pillai

$$\begin{aligned}
 n \frac{\lambda}{\mu} &= 2d [1 - \cos^2 \theta']^{1/2} \\
 n\lambda &= 2d \mu [1 - \cos^2 \theta']^{1/2} \\
 &= 2d [\mu^2 - \mu^2 \cos^2 \theta']^{1/2} \\
 &= 2d [\mu^2 - \cos^2 \theta]^{1/2} \\
 &= 2d [\mu^2 - (1 - \sin^2 \theta)]^{1/2} \\
 &= 2d [\mu^2 - 1 + \sin^2 \theta]^{1/2} \\
 &= 2d \sin \theta \left[1 - \frac{(1 - \mu^2)}{\sin^2 \theta} \right]^{1/2}
 \end{aligned}$$

The value of $(1 + \mu)$ is approximately 2 as is μ nearly 1.

Thus

$$n\lambda = 2d \sin \theta \left[1 - \frac{1}{2} \times 2 \frac{(1 - \mu)}{\sin^2 \theta} \right]$$

$$= 2d \sin \theta \left[1 - \frac{(1 - \mu)}{\sin^2 \theta} \right]$$

Let

$$\delta = (1 - \mu)$$

$$n\lambda = 2d \sin \theta \left[1 - \frac{\delta}{\sin^2 \theta} \right] \quad (5.16)$$

We know,

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

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4d^2}$$

Substituting this in equation (5.16), we get:

$$n\lambda = 2d \sin \theta \left[1 - \frac{4\delta d^2}{n^2 \lambda^2} \right] \quad (5.17)$$

Hence, equation (5.17) is *modified Bragg's equation*. The correction term $\frac{4d^2 \delta}{n^2 \lambda^2}$ decrease as n increases for a given value of λ . Thus, Bragg's ordinary equation $n\lambda = 2d \sin \theta$ holds good for high values of n .

X. POWDER CRYSTAL METHOD

The Laue's and Bragg's techniques for the investigation of crystal structures can be applied only if single crystals of reasonable size are available. But in general, large crystals, without fault are difficult to obtain. Therefore, Debye-Scherrer adopted a different technique. The specimen was taken in the form of a well powdered sample of the crystal in a thin glass capsule. The experimental arrangement is shown in Fig. 5.7(a).

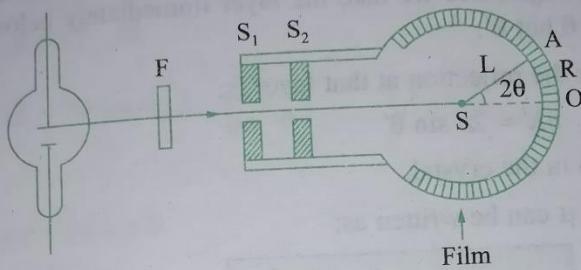


Fig. 5.7(a) Powdered crystal spectrometer

A narrow beam of these monochromatic X-rays suitably collimated by two lead slits S_1 and S_2 , falls on the powdered specimen S . The specimen is suspended vertically on the axis of a cylindrical camera. The photographic film is mounted round the inner surface of the camera, covering nearly the whole circumference in order to receive the beams diffracted up to 180° .

The powder specimen of the crystal can be imaginatively considered to be a collection of randomly oriented tiny crystals, presenting all values of glancing angles to the incident beam. For a given wavelength and given value of d , there can be only one value of θ (glancing angle) which satisfies the equation $2d \sin \theta = n\lambda$, where, $n = 1$. Such reflected beams emerge out from the specimen in all directions inclined at an angle 2θ with the direction of the incident beam, because millions of tiny crystals in the specimen are randomly oriented. The reflected rays will be on the surface of a cone, vertex at the specimen, base on the photographic film and having a semi-vertical angle 2θ . The traces obtained on the photographic film will be as in Fig. 5.7(b).

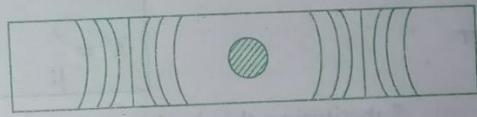
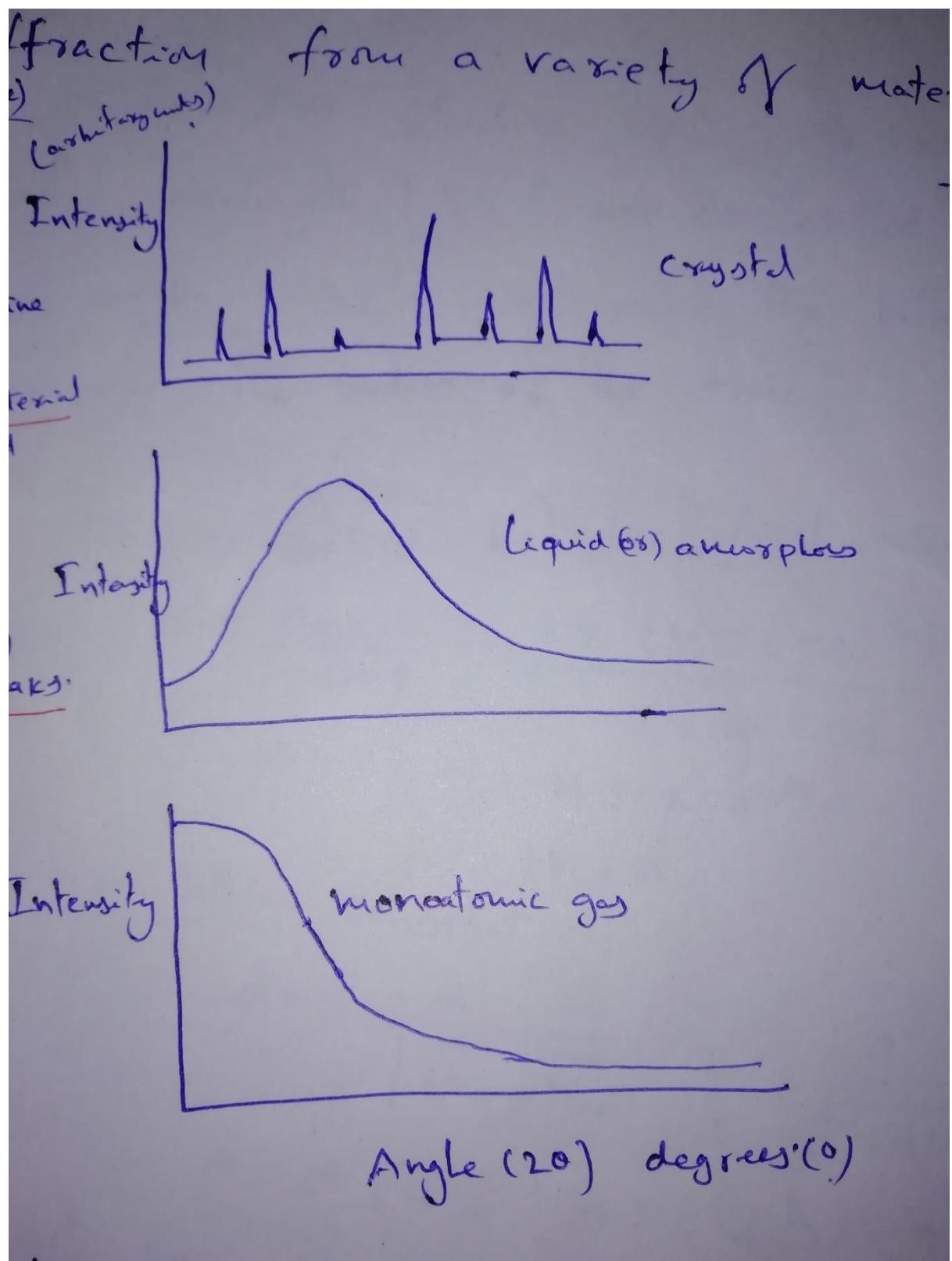


Fig. 5.7(b) Developed film

Let L be the radius of the cylindrical camera. The direct beam strikes the film at O . Suppose a spectrum with glancing angle θ is found at A which is at a distance R from O . Then $\theta = \frac{R}{2L}$. Using the value θ in the Bragg's equation and knowing the value of λ , d (spacing of the plane involved) can be calculated. The powder method has been employed in the study of microcrystalline substance like metals, alloys, carbon, fluorescent powders and other forms where single crystals are not available.

XRD for amorphous and crystalline material



2.3.1 The Laue's Method

An experimental arrangement used to produce *Laue's patterns* is shown in Fig. 2.5. It consists of a flat plate camera which contains a collimator with a fine hole to obtain a very fine beam of x-rays. The sample is placed on a goniometer which can be rotated to change the orientation of the single crystal. Two flat photographic films are used, one for receiving the transmitted diffracted beam and the other for receiving the reflected diffracted beam for back reflection experiments. Such experiments are performed particularly when there is excessive absorption of x-rays in the crystal.

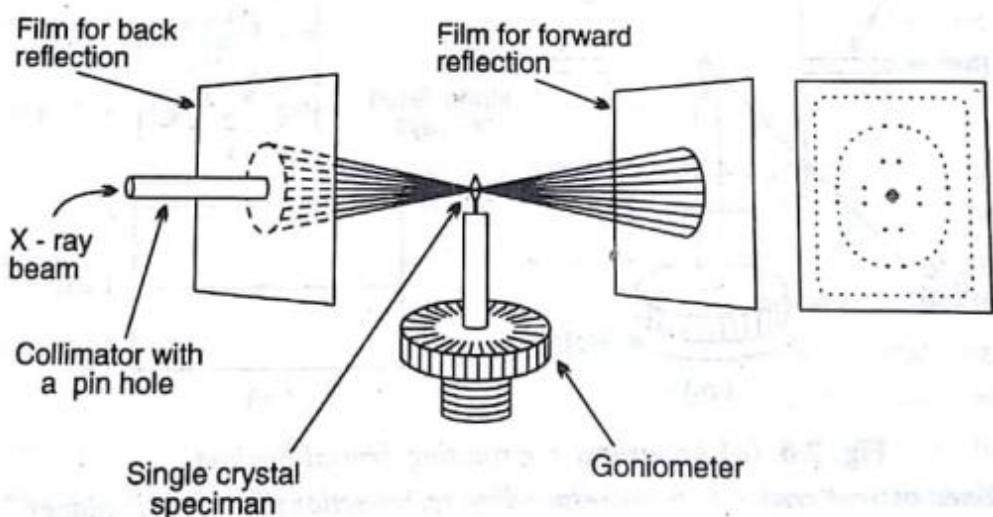


Fig. 2.5. A flat plate camera used in Laue's diffraction method.

Initially, a single crystal specimen having dimensions of the order of $1\text{mm} \times 1\text{mm} \times 1\text{mm}$ is held stationary in the path of white x-rays having wavelengths ranging from 0.2 to 2\AA . Since the crystal contains a number of sets of parallel atomic planes with different interplanar spacings, diffraction is possible for certain values of λ and d which satisfy the Bragg's condition. Thus diffraction spots are produced on the photographic films as shown in Fig. 2.5. The crystal can be rotated with the help of goniometer to change its orientation with respect to the incident beam. By doing so, the diffraction condition may be satisfied for a new set of atomic planes and hence a different type of pattern may be obtained on the photographic film. The symmetry of the crystal is, however, reflected in each pattern.

The Laue's method is mostly used to determine the crystal symmetry. For example, if a crystal having four-fold axial symmetry is oriented so that its axis is parallel to the beam, the resulting Laue's pattern also exhibits the four-fold symmetry. The symmetry of the pattern helps to determine the shape of the unit cell. It is, however, not practicable to determine the structure of

2.3.2 Rotating Crystal Method

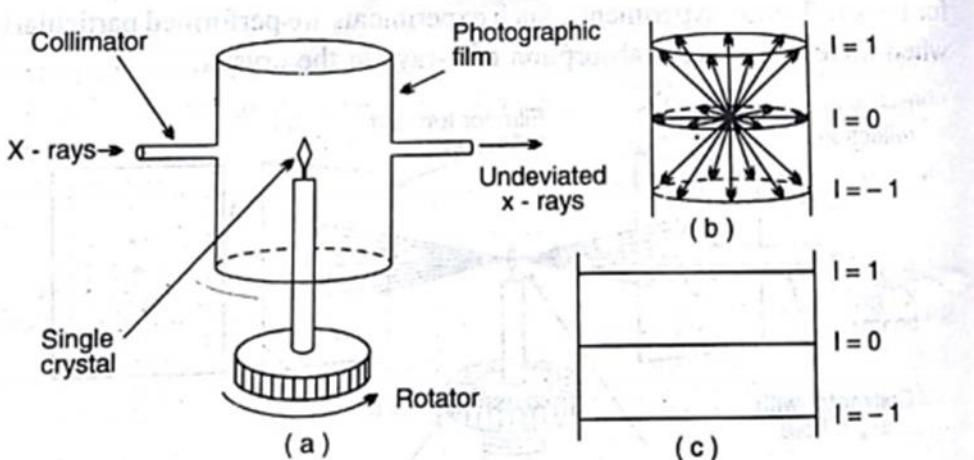


Fig. 2.6. (a) Apparatus for rotating crystal method
 (b) Cones of scattered x-rays corresponding to reflections from (hkl) planes.
 (c) Layer lines produced after flattening the photographic film.

In this method, a monochromatic beam of x-rays is incident on a single crystal mounted on a rotating spindle such that one of its crystallographic axes coincides with the axis of rotation which is kept perpendicular to the direction of the incident beam. The single crystal having dimensions of the order of 1mm is positioned at the centre of a cylindrical holder concentric with the rotating spindle as shown in Fig. 2.6. A photographic film is attached at the inner circular surface of the cylinder.

The diffraction takes place from those planes which satisfy the Bragg's law for a particular angle of rotation. The planes parallel to the axis of rotation diffract the incident rays in a horizontal plane. However, reflections cannot be observed for those planes which always contain the incident beam. The planes inclined to the rotation axis produce reflections above or below the horizontal plane depending upon the angle of inclination. The horizontal lines produced by diffraction spots on the photographic film are called *layer lines*. If the crystal is positioned such that its c-axis coincides with the axis of rotation, all the planes with Miller indices of the type $(hk0)$ will produce the central layer line. Likewise, the planes having Miller indices of the type $(hk1)$ and $(hk\bar{1})$ will produce the layer lines above and below the central line respectively, and so on. These layer lines are shown in Fig. 2.6c. The vertical spacing between the layer lines depends on the distance between the lattice points along the c-axis. Hence the distance c can be measured from the photographic film. Similarly, one can determine the translation vectors a and b on mounting the crystal along a and b axes respectively. Thus the dimensions of the unit cell can be easily determined.

2.4 RECIPROCAL LATTICE

As described earlier, the diffraction of x-rays occurs from various sets of parallel planes having different orientations (slopes) and interplanar spacings. In certain situations involving the presence of a number of sets of parallel planes with different orientations, it becomes difficult to visualize all such planes because of their two-dimensional nature. The problem was simplified by P.P. Ewald by developing a new type of lattice known as the *reciprocal lattice*. The idea underlying the development was that each set of parallel planes could be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing. Thus the direction of each normal represents the orientation of the corresponding set of parallel planes and its length is proportional to the reciprocal of the interplanar spacing.

The normals are drawn with reference to an arbitrary origin and points are marked at their ends. These points form a regular arrangement which is called a reciprocal lattice. Obviously, each point in a reciprocal lattice is a representative point of a particular parallel set of planes and it becomes easier to deal with such points than with sets of planes.

A reciprocal lattice to a direct lattice is constructed using the following procedure :

- (a) Take origin at some arbitrary point and draw normals to every set of parallel planes of the direct lattice.
- (b) Take length of each normal equal to the reciprocal of the interplanar spacing for the corresponding set of planes. The terminal points of these normals form the reciprocal lattice.

Consider, for example, a unit cell of monoclinic crystal in which $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$ and $\beta > 90^\circ$ as shown in Fig. 2.8. For simplicity, we orient the unit cell in such a way that the **b**-axis is perpendicular to the plane of the paper; hence **a** and **c**-axes lie in the plane of the paper as shown in Fig. 2.9.

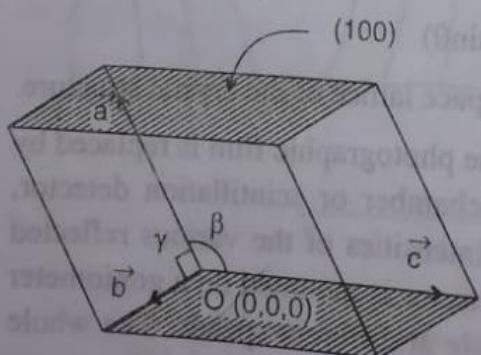


Fig. 2.8. Unit cell of a monoclinic crystal.

Consider planes of the type $(h0l)$ which are parallel to **b**-axis, i.e., perpendicular to the plane of the paper. Hence normal to these planes lie in the plane of the paper. The planes $(h0l)$, being perpendicular to the plane of the paper, are represented by lines. Thus the line (101) in fact means the plane (101) , and so on. Taking the point of intersection of the three axes as the origin, normals are drawn to the

planes ($h0l$) and their lengths are taken to be $1/d_{h0l}$ where d_{h0l} is the interplanar spacing for the planes ($h0l$). For example, since the planes (200) have half the interplanar spacing as compared to the plane (100), the reciprocal lattice point (200) is twice as far away as point (100) from the origin. If normals to all the (hkl) planes are drawn, a three-dimensional reciprocal lattice is obtained.

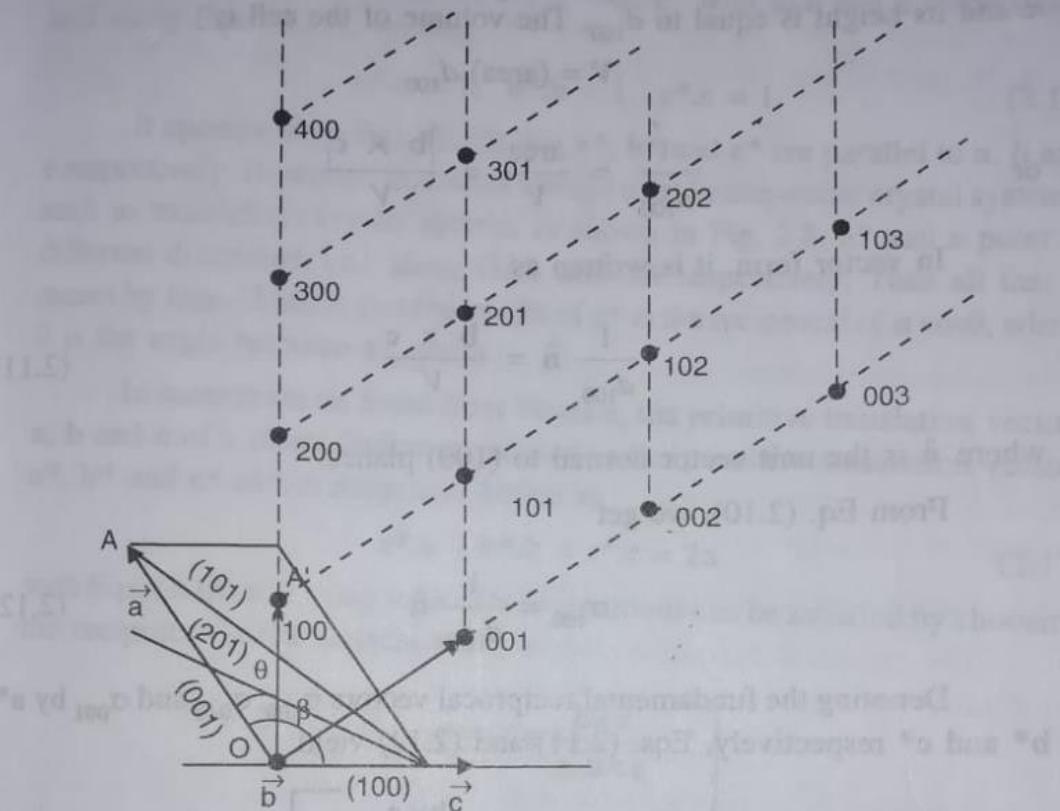


Fig. 2.9. Two-dimensional reciprocal lattice to a monoclinic lattice.

The b-axis is perpendicular to the plane of the paper.

2.4.1 Reciprocal Lattice Vectors

A *reciprocal lattice vector*, σ_{hkl} , is defined as a vector having magnitude equal to the reciprocal of the interplanar spacing d_{hkl} and direction coinciding with normal to the (hkl) planes. Thus, we have

$$\sigma_{hkl} = \frac{1}{d_{hkl}} \cdot \hat{\mathbf{n}} \quad (2.1)$$

where $\hat{\mathbf{n}}$ is the unit vector normal to the (hkl) planes. In fact, a vector drawn from the origin to any point in the reciprocal lattice is a reciprocal lattice vector.

A reciprocal lattice to a direct lattice is constructed using the following procedure:-

(or)

The general rules for constructing the reciprocal lattice:-

- (a) Take origin at some arbitrary point in the direct lattice.
 - (b) From its common origin, draw normals to each and every set of parallel planes in the direct lattice.
 - (c) Fix (or) Take length of each normal equal to the reciprocal of interplanar spacing (d_{hkl}) of the set of parallel planes (hkl).
 - (d) put a point at the end of each normal and the terminal points of these normals form the reciprocal lattice.
- The collection of all these points in space is the reciprocal lattice space.

Vector algebraic discussion: (or) Reciprocal Lattice vectors:-

Relationship b/w σ_{hkl} and Crystallographic Axes:-

Relation b/w fundamental reciprocal vectors and primitive translation vectors of direct lattice.

- A reciprocal lattice vector, σ_{hkl} is defined as a vector having magnitude equal to the reciprocal of the interplanar spacing d_{hkl} and direction coinciding with normal to the (hkl) planes. Then we have $\sigma_{hkl} = \frac{1}{d_{hkl}} \hat{n}$ — (i) where \hat{n} is the unit vector normal to the (hkl) planes.

Consider a direct crystal lattice, whose unit cell is defined by vectors a , b and c . for example, face triclinic system

$$(a+b+c \neq \alpha + \beta + \gamma \neq 90^\circ)$$

$a, b, c \rightarrow$ primitive translation vectors of the direct lattice
real or unit vectors

