

CHAPTER
3

*Supercooled liquid.
highly frozen below
freezing point without
slitfyring.
is glass*

SOLIDS

3.1.0 INTRODUCTION

Those substances which are rigid, hard, have definite shape and definite volume are called solids. They can retain their shape without being confined in a vessel.

There are two types of solids.

- (i) Amorphous solids
- (ii) Crystalline solids

(i) Amorphous solids:

"Those solids in which the constituent particles i.e., atoms, ions or molecules of the substances are not arranged in any regular fashion." They are not accepted as true solids.

For example, glass, pitch and the polymers of high molar masses are amorphous solids. They are also regarded as supercooled liquids of high viscosity.

(ii) Crystalline solids:

"Those solids in which the constituent particles like atoms, ions or molecules of the substance are arranged in definite geometric pattern within the solid are called crystalline solids." The substances like metals and many of the salts are crystalline in nature.

3.1.1 Space lattice:

"The regular arrangement of constituent particles i.e., atoms, ions and molecules of a crystalline substance in three dimensions is called space lattice."

The following diagram (1) shows the space lattice of a hypothetical crystalline substance.

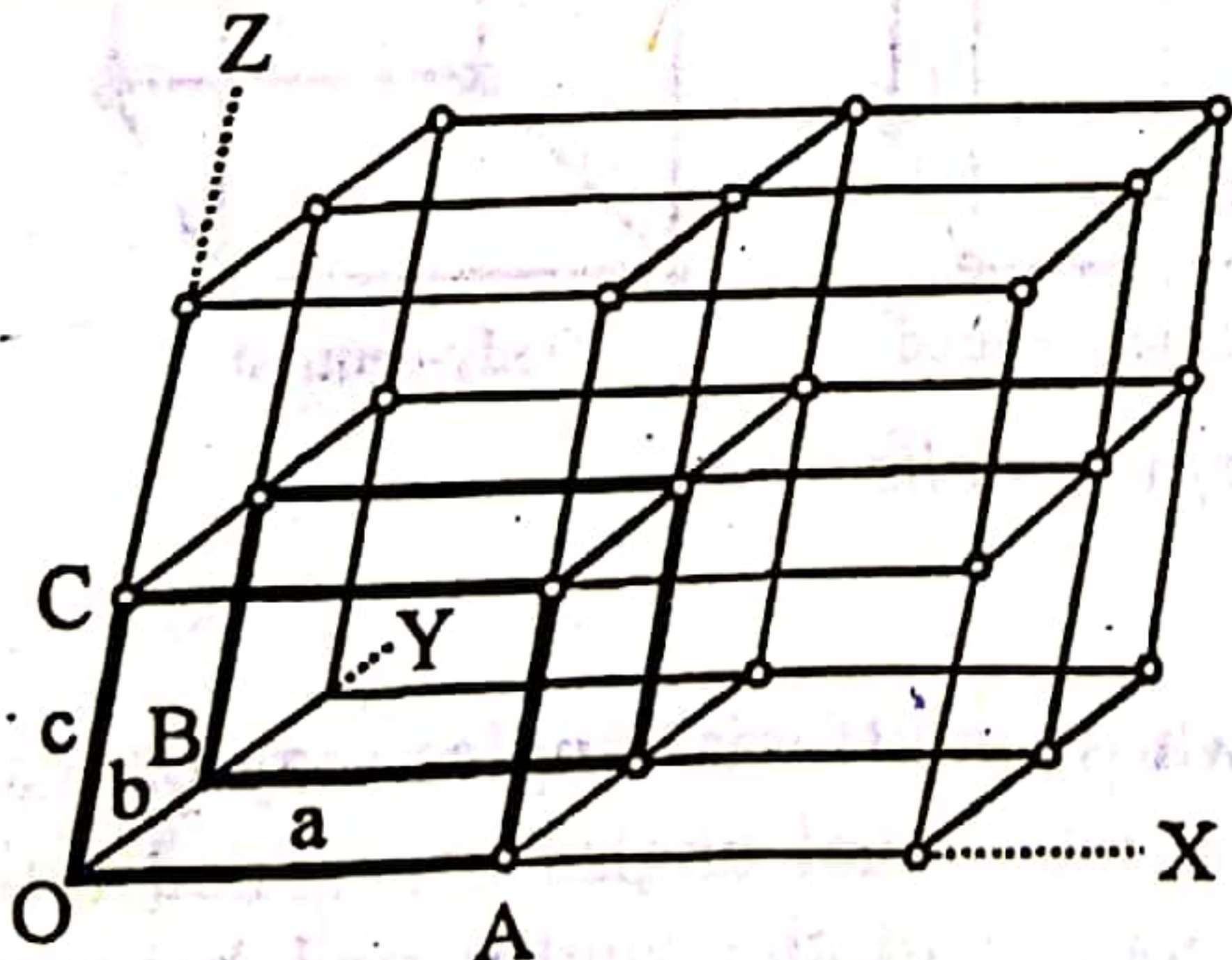


Fig. (1) Space lattice and lattice points

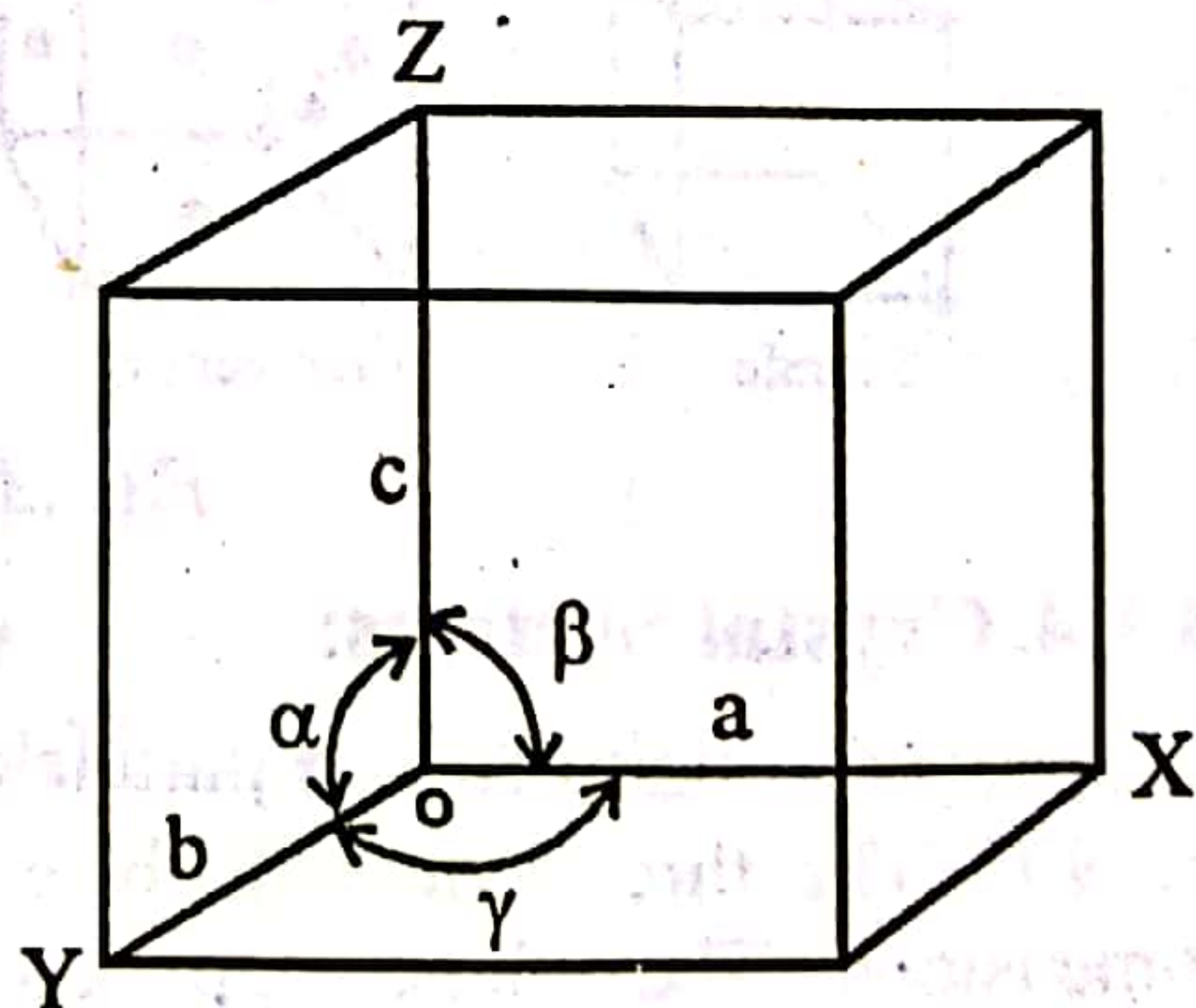


Fig. (2) Unit cell and unit cell dimensions

When we look at the crystal lattice, then we note that

- (i) Each lattice point has the same environment as that of any other point in the lattice.
- (ii) A constituent particle is to be represented by lattice point, irrespective of the fact and whether it contains the single atom or more than one atoms.

3.1.2 Unit cell:

When we picturize a crystal lattice as shown in the above diagram (1), then it is possible to select a group of lattice points. This group of lattice points repeated again and again is called the unit cell. The whole lattice can be generated by translation or stacking of these unit cells.

So, unit cell is a three dimensional group of lattice points which generate the whole lattice by translation or stacking. Fig. (2)

3.1.3 Types of unit cells:

Unit cell can be divided into four types.

- (i) **Simple unit cell:** This type of unit cell is produced, when the particles are present only at the corners of the unit cell.
- (ii) **Face centred unit cell:** When the particles are located at the centre of each face in addition to the corners, then it is called face centred unit cell.
- (iii) **End face centred unit cell:** When the particles are located at the centers of the end face in addition to the corners, then it gives end face centred unit cell.
- (iv) **Body centred unit cell:** When the particles are present at the centre of the cell in addition to the corners, then it is called body centred unit cell.

The following set of diagrams (3) show these four types of unit cell.

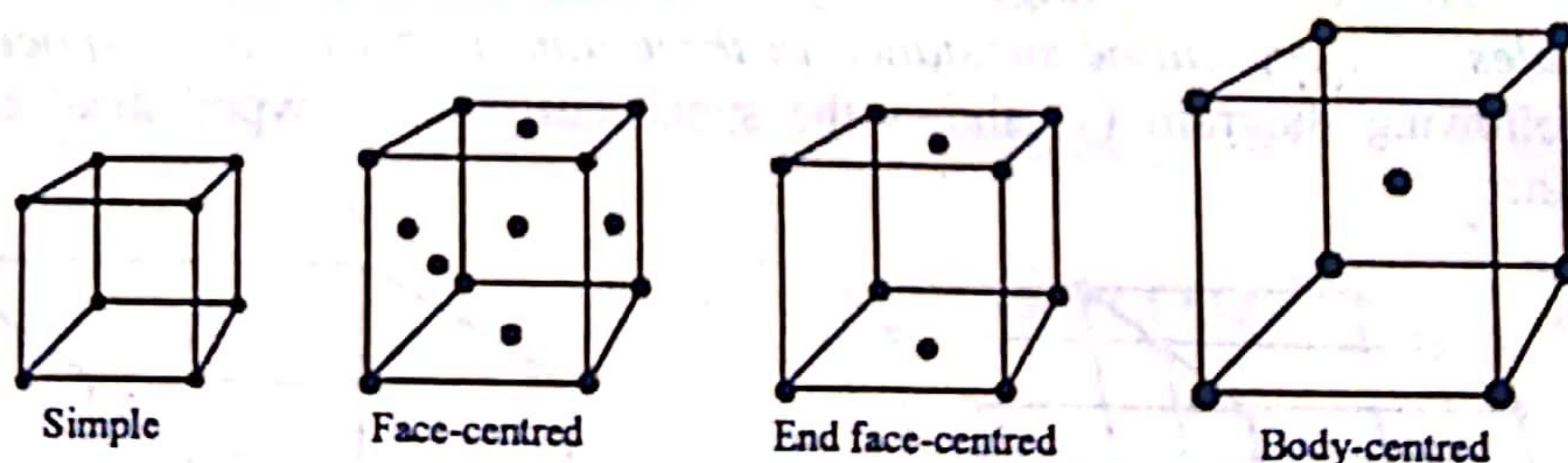


Fig. (3) Types of unit cells.

3.1.4. Crystal Systems:

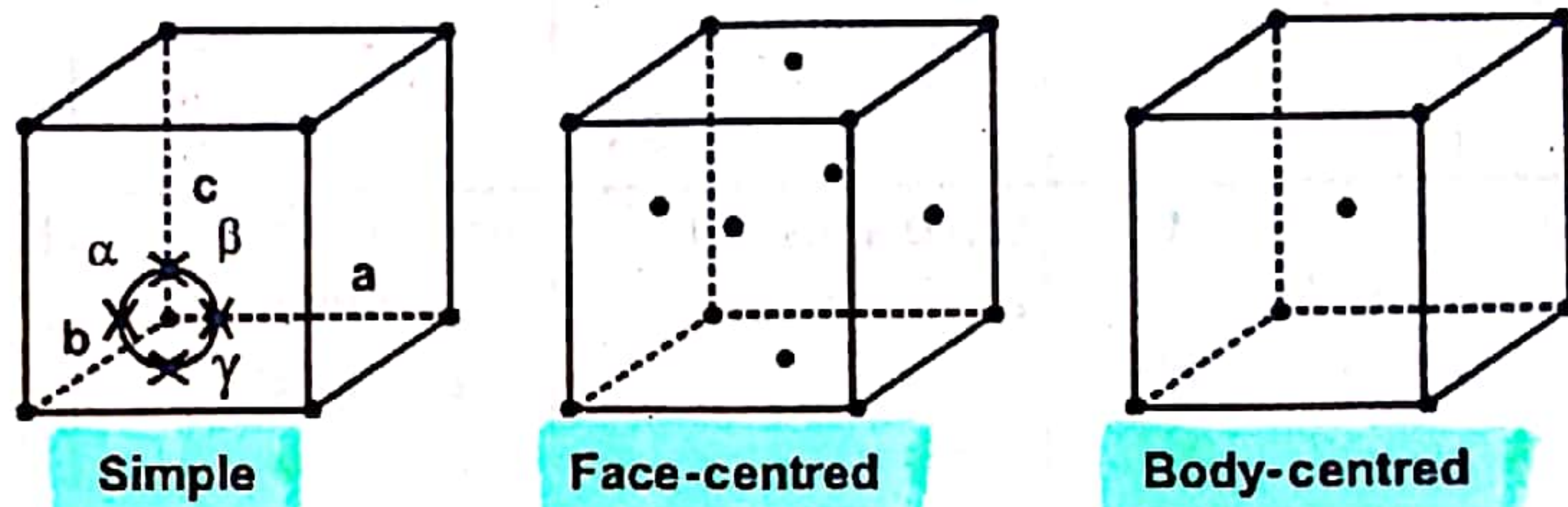
Each unit cell is a parallelepiped, whose interfacial angles may or may not be 90° . The three lengths a , b , c and three interfacial angles are called unit cell dimensions. The relationship between the values of the angles and between the lengths of the axes give us seven types of crystal systems as shown in the following Table (1).

Table (1): The seven crystal systems and fourteen Bravais lattices

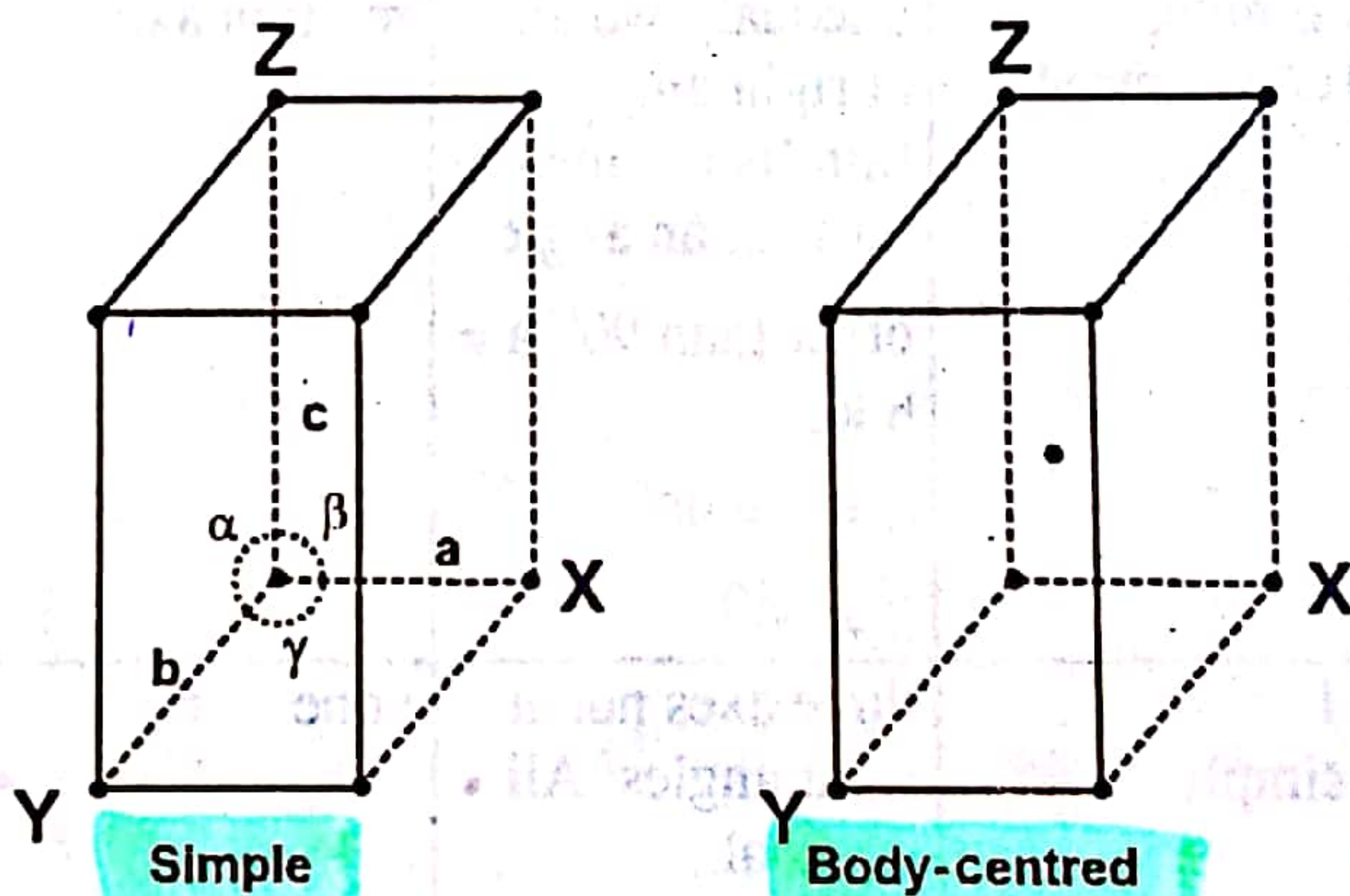
Systems	Bravais lattices	unit cell characteristics	characteristic symmetry elements	examples
Cubic	3 simple, body-centred, face-centred	three axes at right angles: all equal $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	four 3-fold rotation axes (along cubic diagonals)	NaCl, ZnS, FeS ₂ , KCl, Diamond, Au, Hg, Ag, Pb,
Tetragonal	2 simple, body-centred	three axes at right angles: two are equal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	one 4-fold rotation axis	SnO ₂ , TiO ₂ , Sn, KH ₂ PO ₄
Orthorhombic	4 simple, body-centred, face-centred, end-centred.	three axes at right angles: but all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	three mutually orthogonal 2-fold rotation axes	KNO ₃ , PbCO ₃ , BaSO ₄ , rhombic sulphur
Monoclinic	2 simple, end-centred	three axes, all unequal, two axes at right angles, third is inclined to these at an angle other than 90° $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	one 2-fold rotation axis	CaSO ₄ .2H ₂ O, Na ₂ SO ₄ .10H ₂ O, Na ₂ B ₄ O ₇ .10H ₂ O, monoclinic sulphur
Triclinic	1 simple	three axes not at right angles: All unequal. $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	none	CuSO ₄ .5H ₂ O, K ₂ Cr ₂ O ₇ , H ₃ BO ₃
Hexagonal	1 simple	two equal axes in one plane with included angle 120°; 3rd axis at rt. \angle to these; unequal $a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	one 3-fold rotation axis	ice, graphite, HgS, Mg, Zn, Cd
Rhombohedral or Trigonal	1 simple,	three equally inclined axes, not at rt. \angle ; All equal $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$	one 3-fold rotation axis	NaNO ₃ , Bi, Sb, As, ICl

3.2.0 BRAVAIS LATTICES

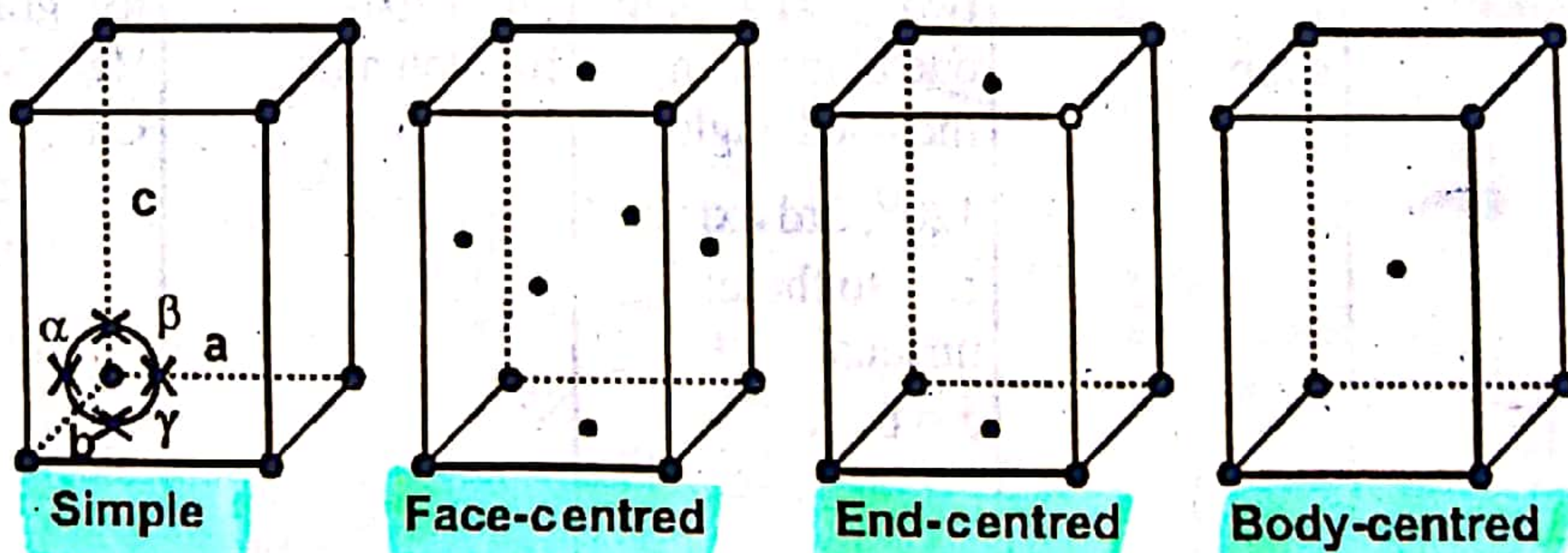
Bravais did the detailed study of internal structure of crystals and said that the points or the particles may be present not only at the corners of the unit cell, but at the centres of the faces within the body of the unit cell. This thing gives rise to different types of lattices corresponding to seven crystallographic systems. There are fourteen types of lattices, which are called Bravais lattices. The above table (1) shows that four crystal systems have more than one Bravais lattices while three crystal systems have only one Bravais lattice. The table (1) given above shows fourteen Bravais lattices. Now, look at their diagrams in Fig. (4).



$$1. \text{ Cubic } \left\{ \begin{array}{l} a = b = c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right.$$



$$2. \text{ Tetragonal } \left\{ \begin{array}{l} a = b \neq c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right.$$



$$3. \text{ Orthorhombic } \left\{ \begin{array}{l} a \neq b \neq c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right.$$

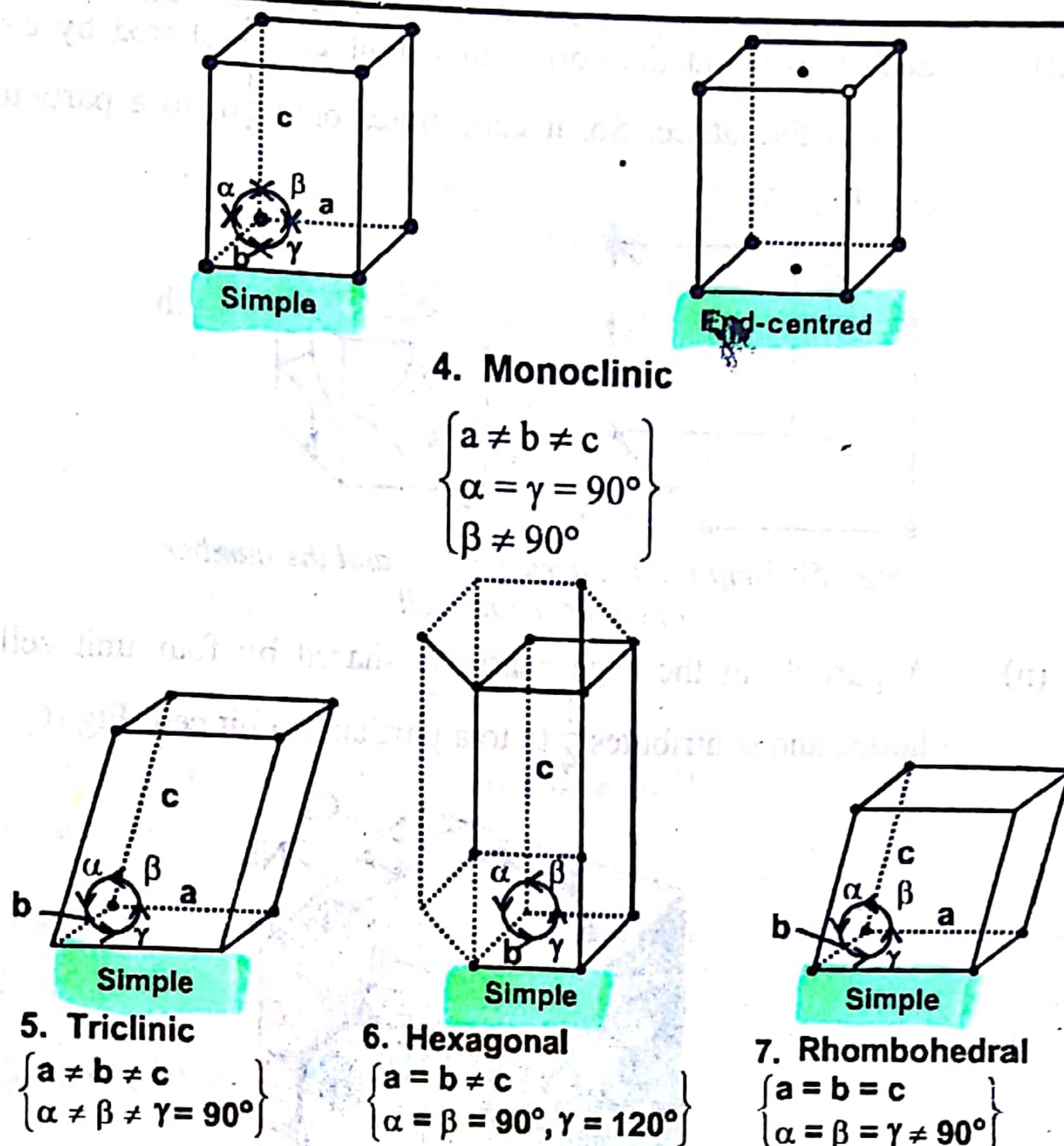


Fig. (4) Bravais lattices corresponding to seven crystallinographic systems.

3.2.1 Co-ordination Number:

Whenever we talk about the lattice points in crystal, then we mean that constituent particles are sitting at these points. These constituent particles may be represented by spheres which behave like hard spherical balls. This is suggested only to have the idea of packing of spheres more clear to human mind. The number of spheres which are in direct contact with a particular sphere is called co-ordination number of ionic solid. The co-ordination number of a particular ion is the number of oppositely charged ions surrounding that particular ion.

- (i) In the case of NaCl, the co-ordination number of Na^\oplus is 6 and that of Cl^\ominus is also 6.
- (ii) In the case of CsCl, the co-ordination number of both ions is 8.
- (iii) In the case of ZnS, CuCl, and HgS, the co-ordination number is 4.

3.2.2 Calculations of number of particles in a unit cell:

One should obey the following rules in order to calculate the number of particles in a unit cell.

- (i) Each particle at the corner of a unit cell is shared by eight unit cells in the lattice. So, it contributes only $\frac{1}{8}$ th to a particular unit cell. Fig. (5).

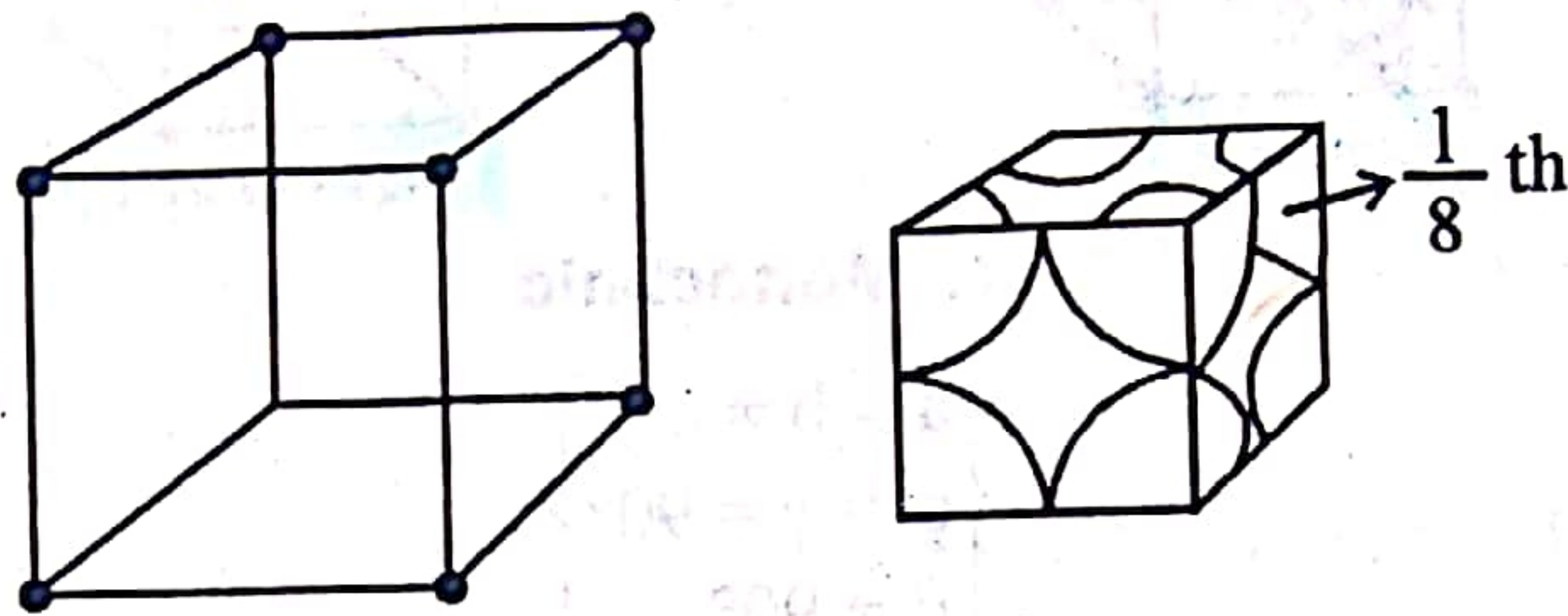


Fig. (5) Simple cubic arrangement and the number of atoms in unit cell.

- (ii) A particle at the edge centre is shared by four unit cells in the lattice and contributes $\frac{1}{4}$ th to a particular unit cell. Fig (6).

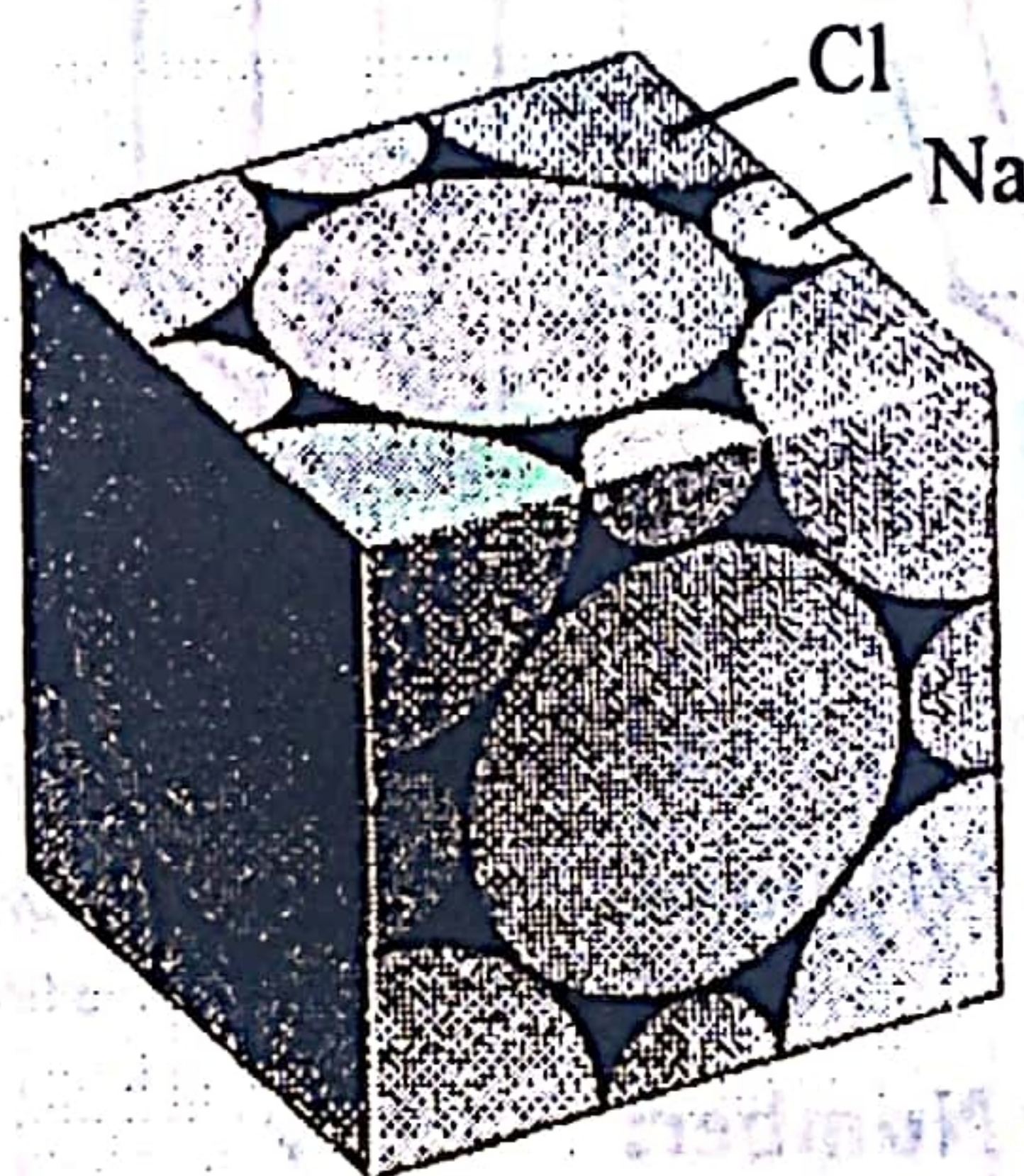
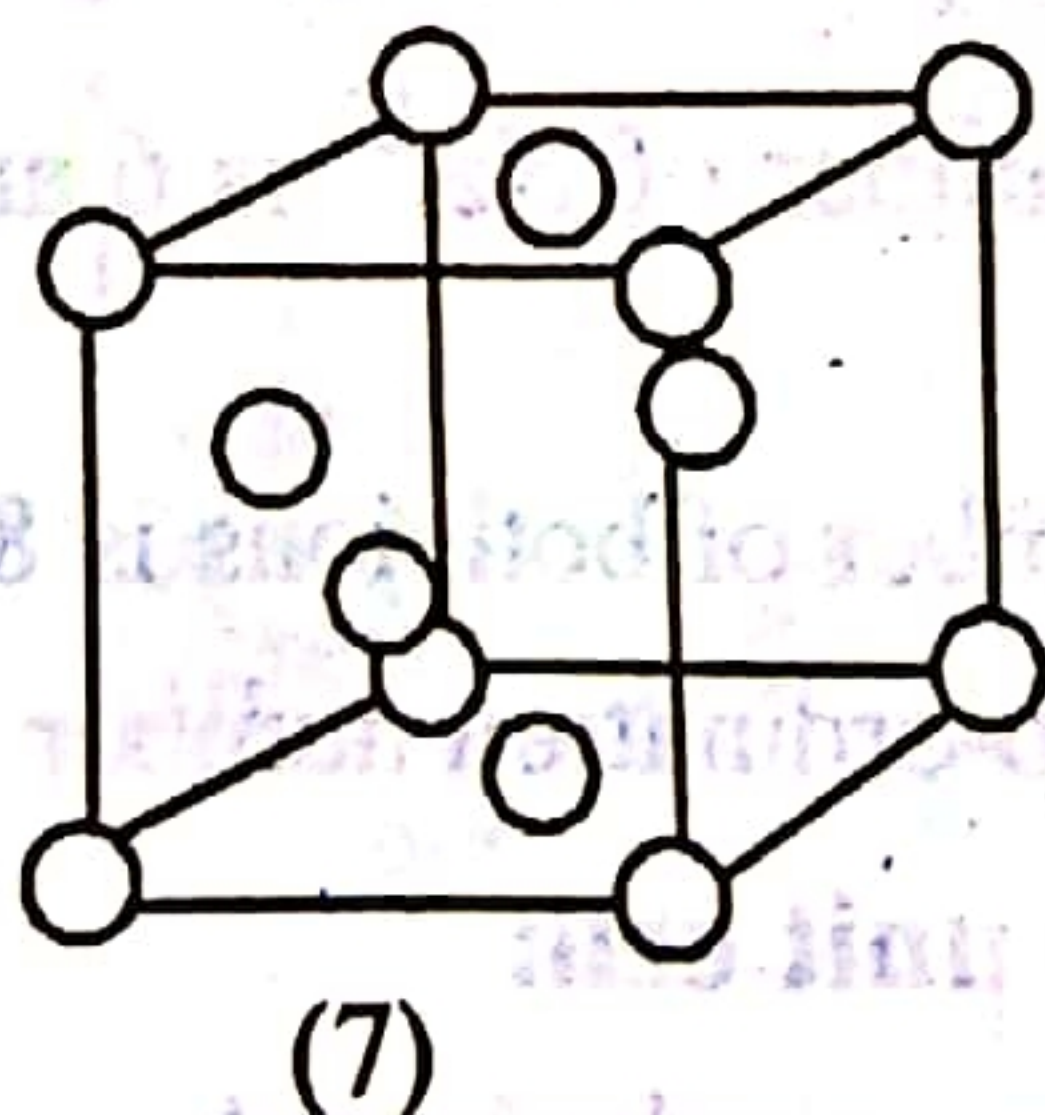


Fig. (6)

- (iii) A particle at the centre of the face of the unit cell is shared by two unit cells in the lattice and it contributes only half to a particular unit cell. Fig (7, 8).

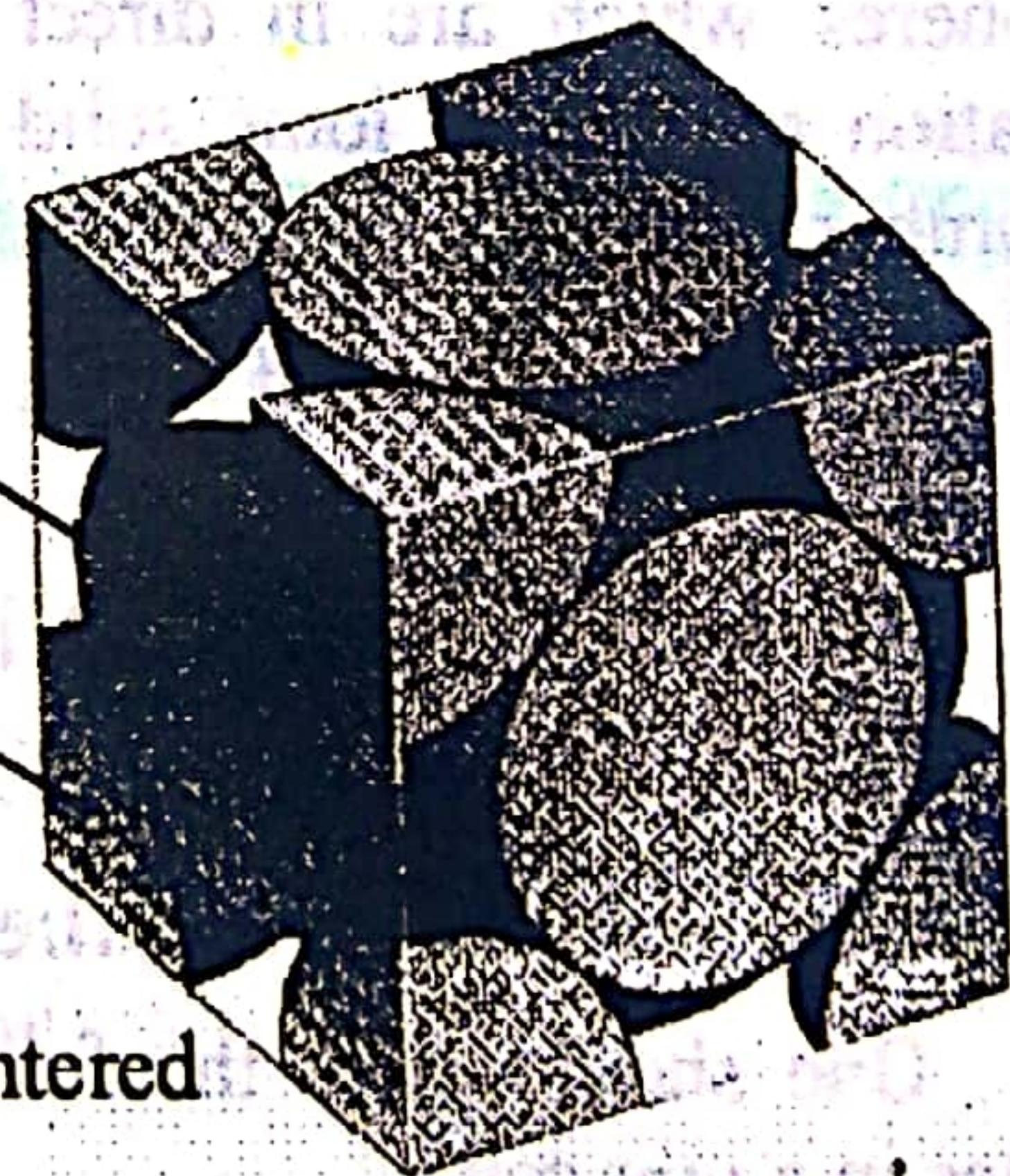


(7)

$\frac{1}{2}$ atom at
6 faces

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

Face-centered
cubic

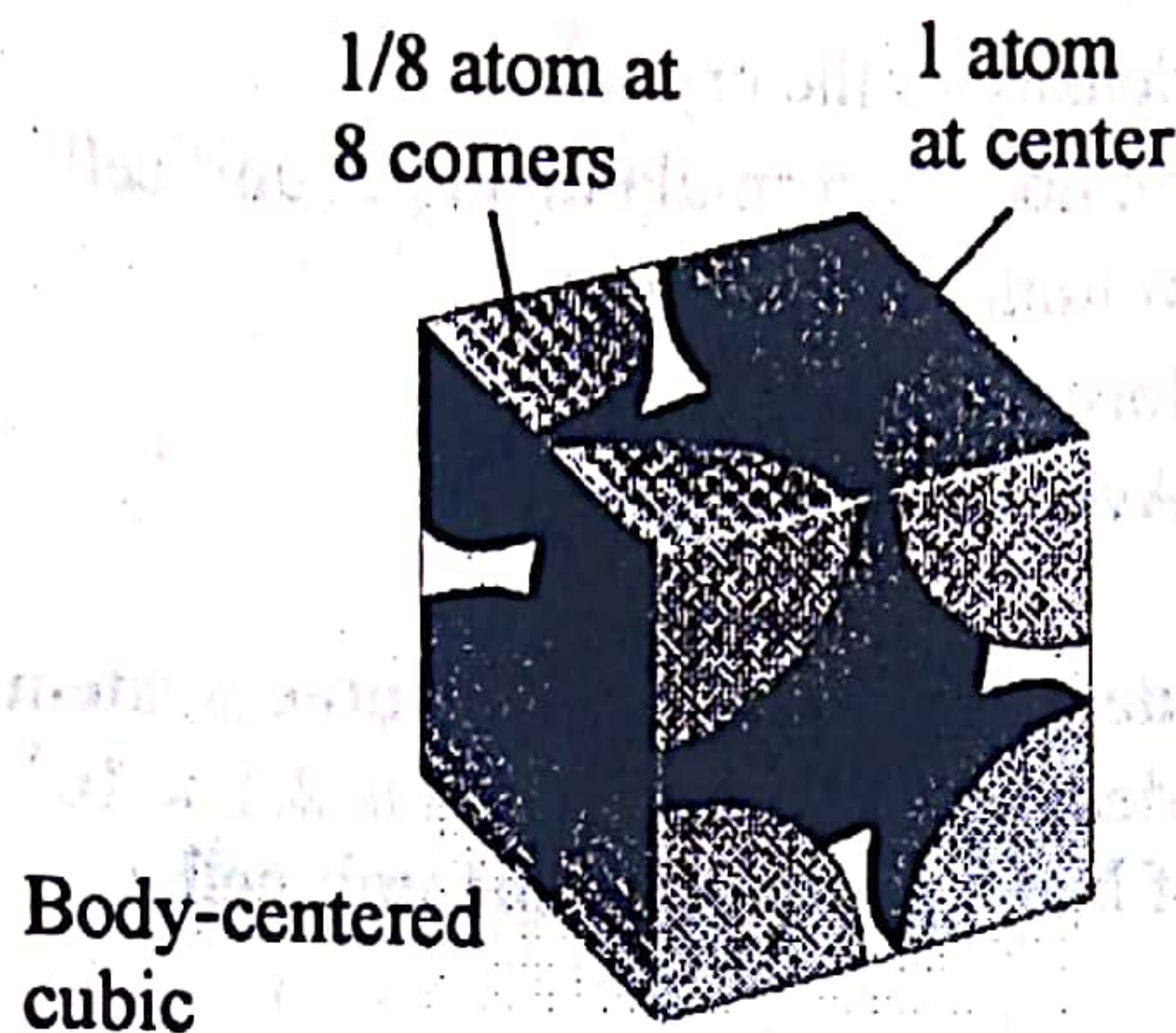


(8)

Fig. (7) Face-centred cubic arrangement.

Fig. 8 Atoms / unit cell = $\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$

- (iv) A particle at the body centre of a unit cell belongs only to the particular unit cell. Following diagrams (9) makes the ideas clear.



$$\text{Fig. (9) Atoms / unit cell} = \left(\frac{1}{8} \times 8 \right) + 1 = 2$$

3.2.3 Calculations of number of atoms in a unit cell:

(i) **Simple cubic:**

There are eight corners of the atom and each atom makes $\frac{1}{8}$ contribution to the unit cell. Hence, a simple or primitive cubic unit cell has only one atom in that,

$$8(\text{at corners}) \times \frac{1}{8} = 1 \text{ atom.}$$

(ii) **Body centred cubic:**

This unit cell has eight atoms at the corners and one at the centre of the body. Each corner atom makes $\frac{1}{8}$ contribution and the atom at the body centre belongs only to the particular unit cell. Hence, a body centred cubic cell has

$$8(\text{at the corners}) \times \frac{1}{8} + 1 (\text{at body centre}) \times 1 = 2 \text{ atoms}$$

(iii) **Face centred cubic:**

It has one atom at each corner and one atom at each face centre. Atom at this face centre is being shared by two unit cells and has the contribution of $\frac{1}{2}$ to a particular unit cell. Hence, a face centred cubic cell has

$$8(\text{at the corners}) \times \frac{1}{8} + 6(\text{at face centres}) \times \frac{1}{2} = 4 \text{ atoms}$$

Calculations of formula units in a unit cell:

The number of formula units of a ionic crystalline solid present in the unit cell of that substance can be mathematically calculated by the following expression. Actually, this equation relates the density of the crystal towards its molecular properties.

$$\rho = \frac{Z \times M}{N_A \times V}$$

where, ρ = density of the crystal

Z = number of formula units per unit cell

V = volume of unit cell

M = formula mass

N_A = Avogadro's number

EXAMPLE (1)

Sodium chloride crystallizes in the cubic system with edge length of cube as 5.65 \AA . The density of NaCl crystal is $2.1 \times 10^3 \text{ kg m}^{-3}$. Calculate the number of molecules of NaCl present in the unit cell.

SOLUTION:

Density, $\rho = 2.1 \times 10^3 \text{ kg m}^{-3}$

Molar mass, $M = 58.5 \times 10^{-3} \text{ kg mol}^{-1}$

$N_A = 0.6023 \times 10^{24}$

$V = (5.65 \times 10^{-10})^3 \text{ m}^3 = (5.65)^3 \times 10^{-30} \text{ m}^3$

$Z = ?$

On substituting the values in the equation,

$$Z = \frac{N_A \cdot V \cdot \rho}{M}$$

$$Z = \frac{6.023 \times 10^{23} \times (5.65)^3 \times 10^{-30} \times 2.1 \times 10^3}{58.5 \times 10^{-3}}$$

$$Z = \boxed{4} \quad \text{Ans.}$$

Calculation of Avogadro's number from crystal structure:

Let us solve the following numerical problem to understand calculations of Avogadro's number.

EXAMPLE (2)

Cesium chloride has a density of $3.97 \times 10^3 \text{ kg m}^{-3}$. It has body centred cubic lattice with 4.12 \AA as one edge, and having one CsCl molecule per unit cell. Calculate the value of Avogadro's number from this data.

SOLUTION:

$\rho = 3.97 \times 10^3 \text{ kg m}^{-3}$

$M = 158.5 \text{ g mol}^{-1} = 158.5 \times 10^{-3} \text{ kg mol}^{-1}$

$V = (4.12)^3 \times 10^{-30} \text{ m}^3$

$Z = 1$

$N_A = ?$

On substituting the values into following equation we get,

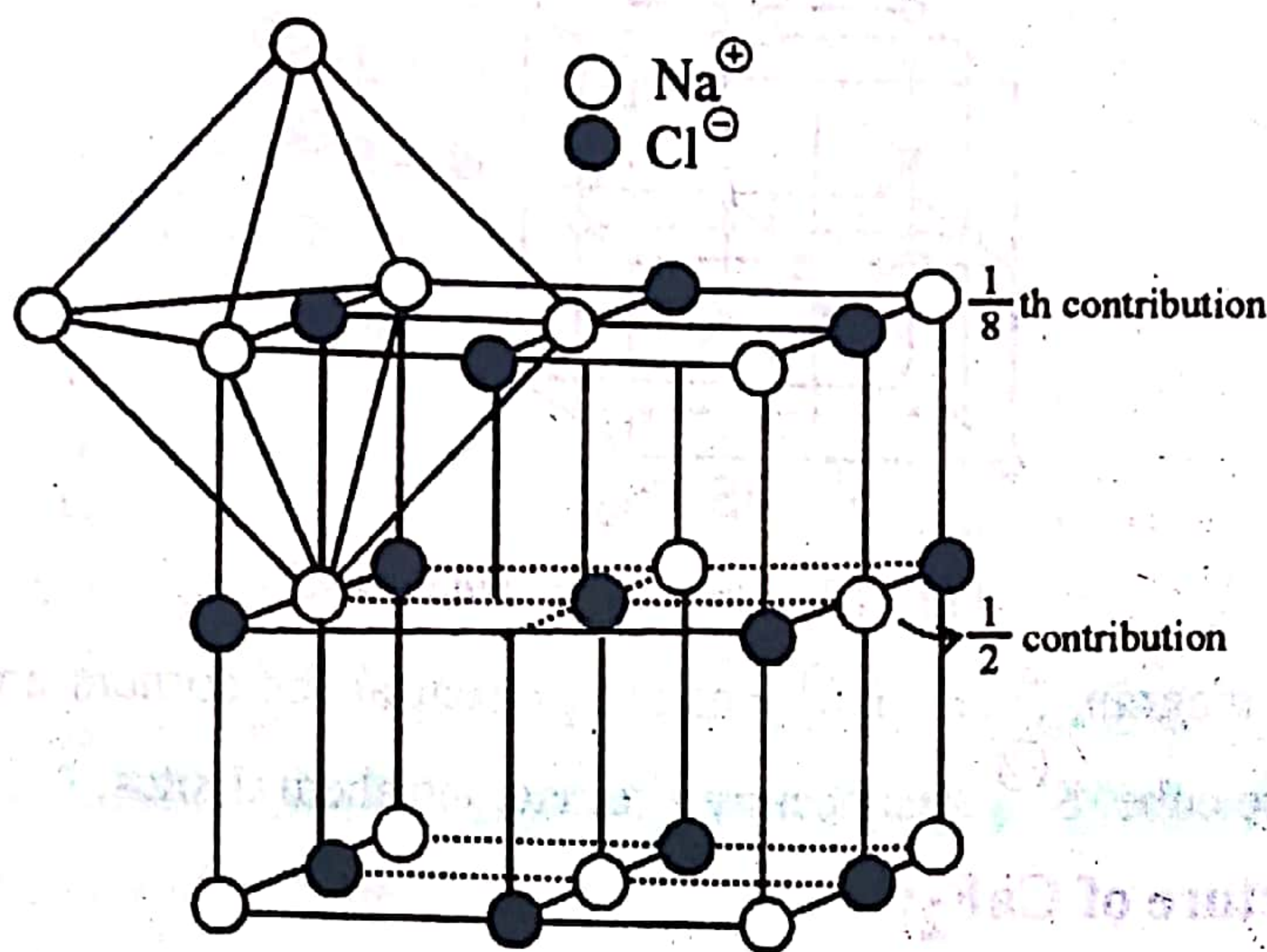
$$N_A = \frac{Z \cdot M}{\rho \cdot V}$$

$$N_A = \frac{1 \times 158.5 \times 10^{-3}}{3.97 \times 10^3 \times (4.12)^3 \times 10^{-30}}$$

$$= \boxed{6.023 \times 10^{23} \text{ molecules mol}^{-1}} \quad \text{Ans.}$$

3.2.4 Structure of NaCl:

It has face centred cubic lattice and each ion is surrounded by six oppositely charged ion. The co-ordination number of Na^{\oplus} and Cl^{\ominus} each is 6. There are four units of Na^{\oplus} and Cl^{\ominus} ions in a unit cell. The structure is shown in Fig. (10)



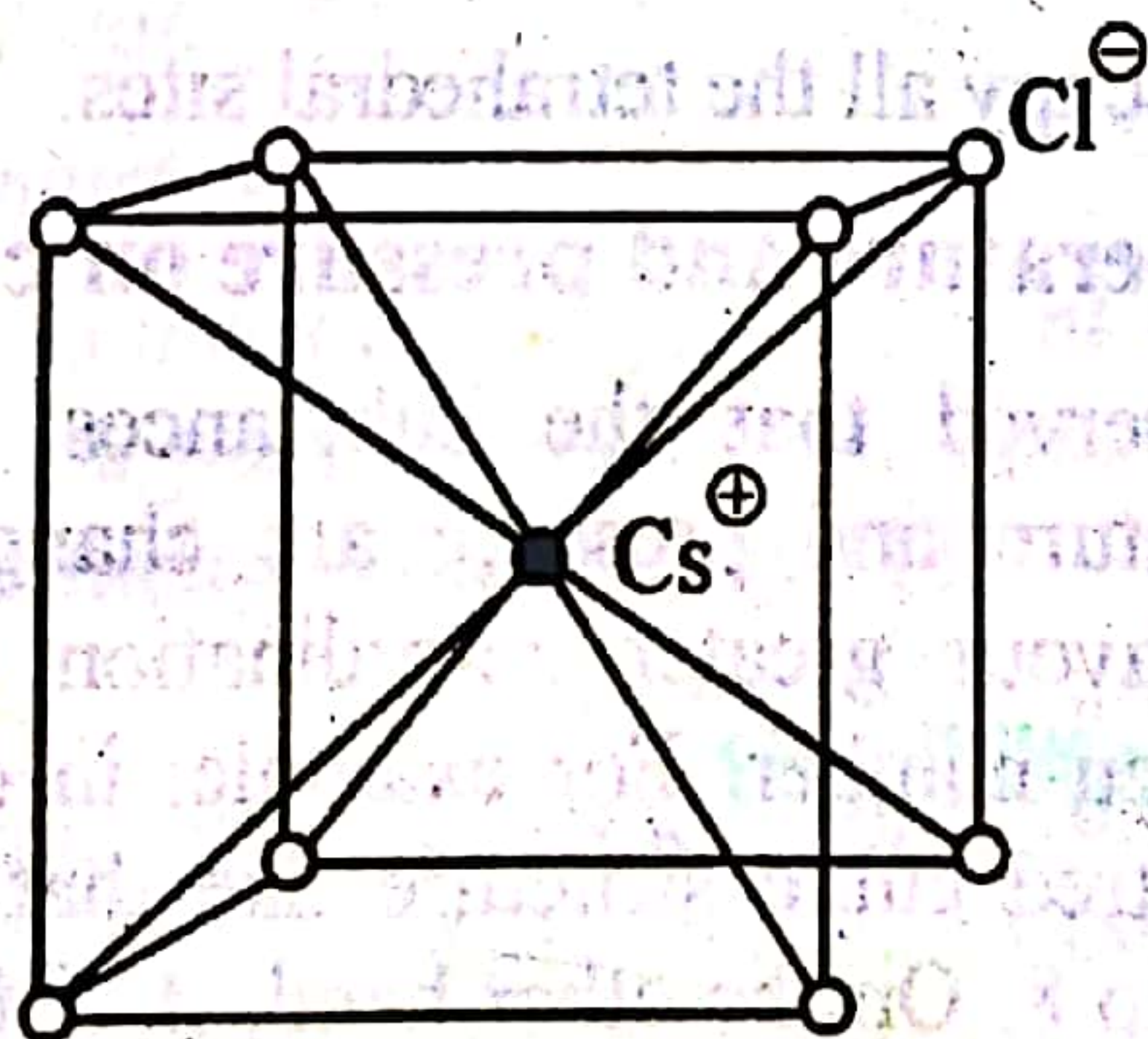
Coordination No
6

Fig. (10) Structure of unit cell of sodium chloride and contribution of each ion into the unit cell.

The other ionic compounds like NaBr, NaI, AgCl, MgO also have sodium chloride type structure.

3.2.5 Structure of CsCl:

It has body centred cubic structure. Eight corners of the cube are occupied by Cl^{\ominus} ions and centre is occupied by Cs^{\oplus} ion. When the lattice is completed, then we will observe that Cs^{\oplus} occupy the corner of a cube and Cl^{\ominus} is at the centre. Its co-ordination number is eight and the number of units of CsCl per unit cell is 1. One Cs^{\oplus} is surrounded by 8 Cl^{\ominus} ions and total contribution of 8 Cl^{\ominus} is one Cl^{\ominus} . It is clear from the following diagram Fig. (11). CsBr and ThCl also have the body centred cubic structures.



Complete lattice
 $\text{Cs}^{\oplus} \rightarrow @ \text{ centre}$
 $\text{Cl}^{\ominus} \rightarrow @ \text{ corner}$

When lattice complete
 $\text{Cs}^{\oplus} \rightarrow @ \text{ corner}$
 $\text{Cl}^{\ominus} \rightarrow @ \text{ centre}$

Fig. (11) Body centred which structure of cesium chloride.

3.2.6 Structure of zinc blend:

It has also face centred cubic structure. The co-ordination number of Zn^{+2} and S^{-2} is four. Every Zn^{+2} ion is surrounded by four S^{-2} ions and vice versa as shown in the following diagram. CuCl and HgS have also the same structures.

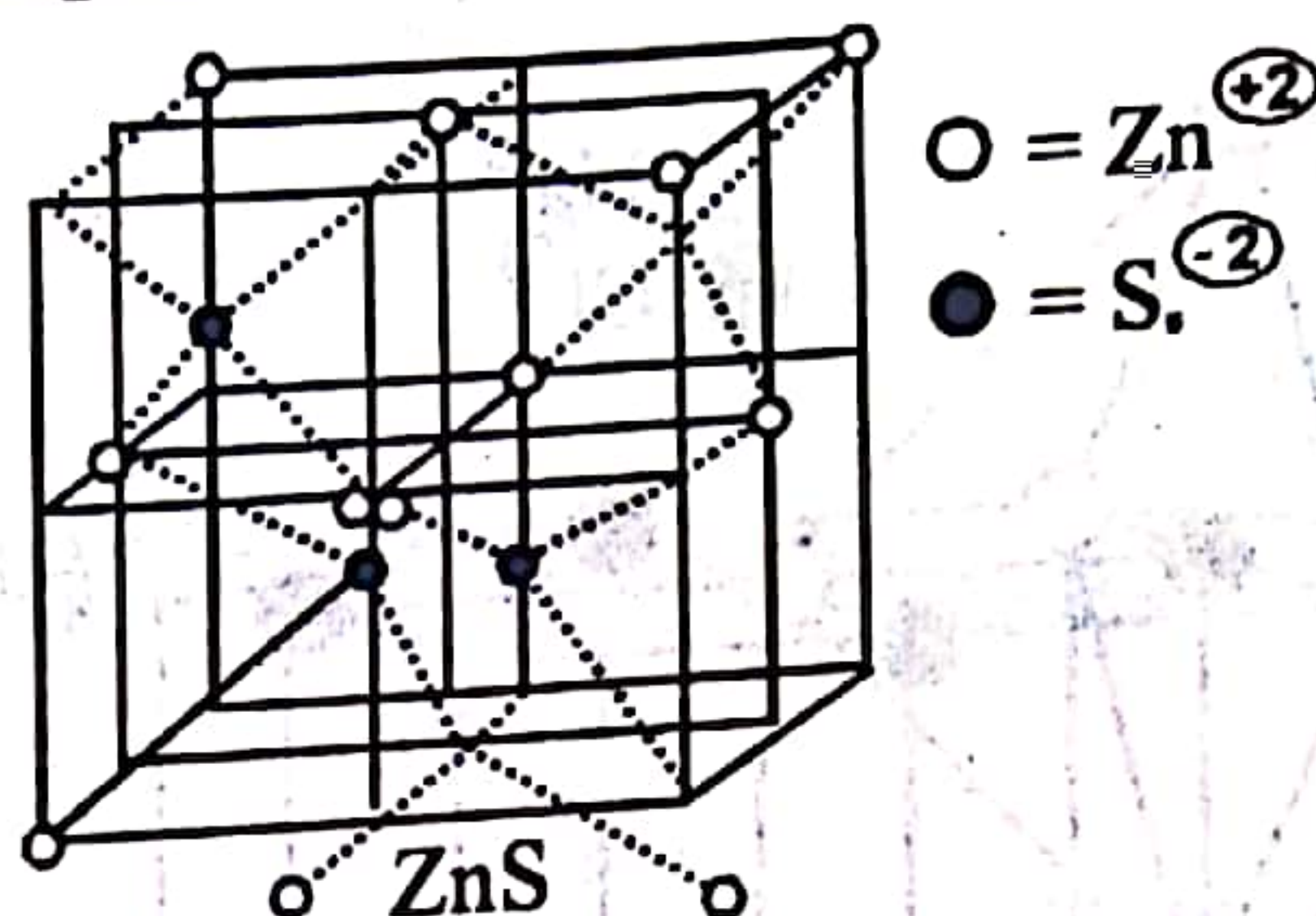


Fig. (12) Structure of zinc blend.

In the diagram (12), Zn^{+2} ions are present at the corners and the centre of each face of the cube. S^{-2} ions occupy alternate tetrahedral sites.

3.2.7 Structure of CaF_2 :

According to the following diagram (13) of CaF_2 , each F^- ion is surrounded by four Ca^{+2} ions and each Ca^{+2} ion is surrounded by eight F^- ions.

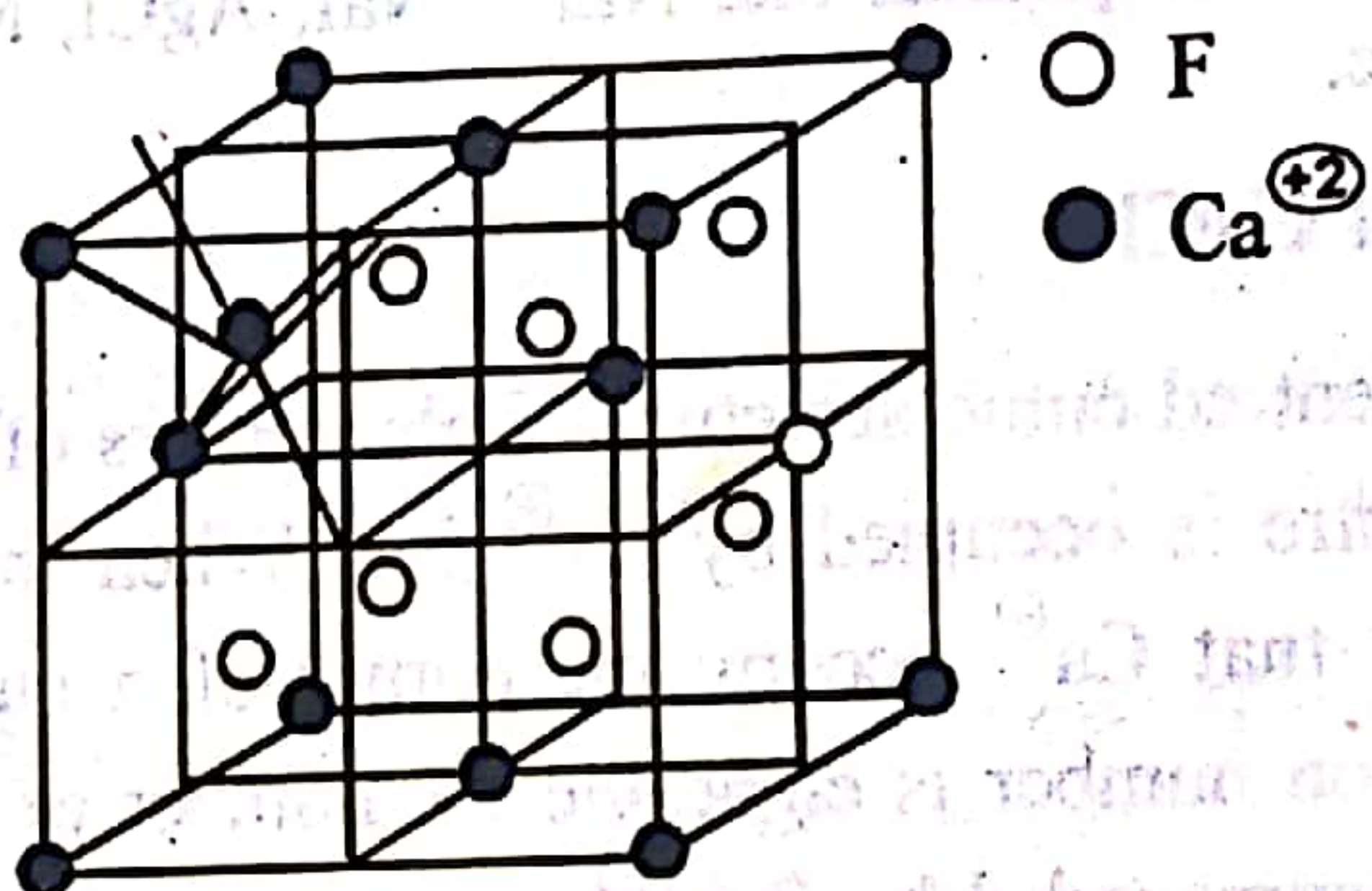


Fig. (13) Structure of CaF_2 .

F^- ions are present at all the corners and at the centre of each face of the cube and the Ca^{+2} ions occupy all the tetrahedral sites.

3.2.8 Effect of temperature and pressure on crystal lattice:

It has been observed that the substances undergo changes in their structures, when temperature and pressure are changed. When the pressure is increased, then it will favour greater co-ordination number. High temperature favours lower co-ordination number. For example, in case of NaCl high pressure converts it into body centred cubic structure like that of CsCl and co-ordination number increases from 6 to 8. On the other hand, if CsCl is heated to 760K, then it is converted to NaCl structure, whose co-ordination number is 6.

3.3.0 FUNDAMENTAL LAWS OF CRYSTALLOGRAPHY

"That branch of science which deals with the study of geometric properties and structures of crystals of crystalline substance is called crystallography." There are three fundamental laws of crystallography.

- (i) The law of constancy of interfacial angles.
- (ii) The law of symmetry.
- (iii) The law of rationality of indices.

(i) The law of constancy of interfacial angles:

The crystals are prepared by cooling a solution of the substance or by cooling the molten electrolyte. The size of the crystal depends upon the rate of the cooling. The size also depends upon the conditions under which the crystallization takes place. However, in spite of different sizes and shapes of crystal of the same substance, it is observed that the angle between the corresponding faces which are called interfacial angles of the crystal of a particular substance are always the same. The instrument which is used for the measurement of interfacial angles is called a goniometer.

(ii) The law of symmetry:

The informations about the crystal structure is present in the unit cell. Anyhow, there exists some symmetry in the unit cell which helps us in reaching the necessary information about the crystal structure. So, we should have a knowledge of symmetry operations which will throw some light on the arrangement of atoms in the unit cell and so give us the complete picture of crystal.

Symmetry Operation:

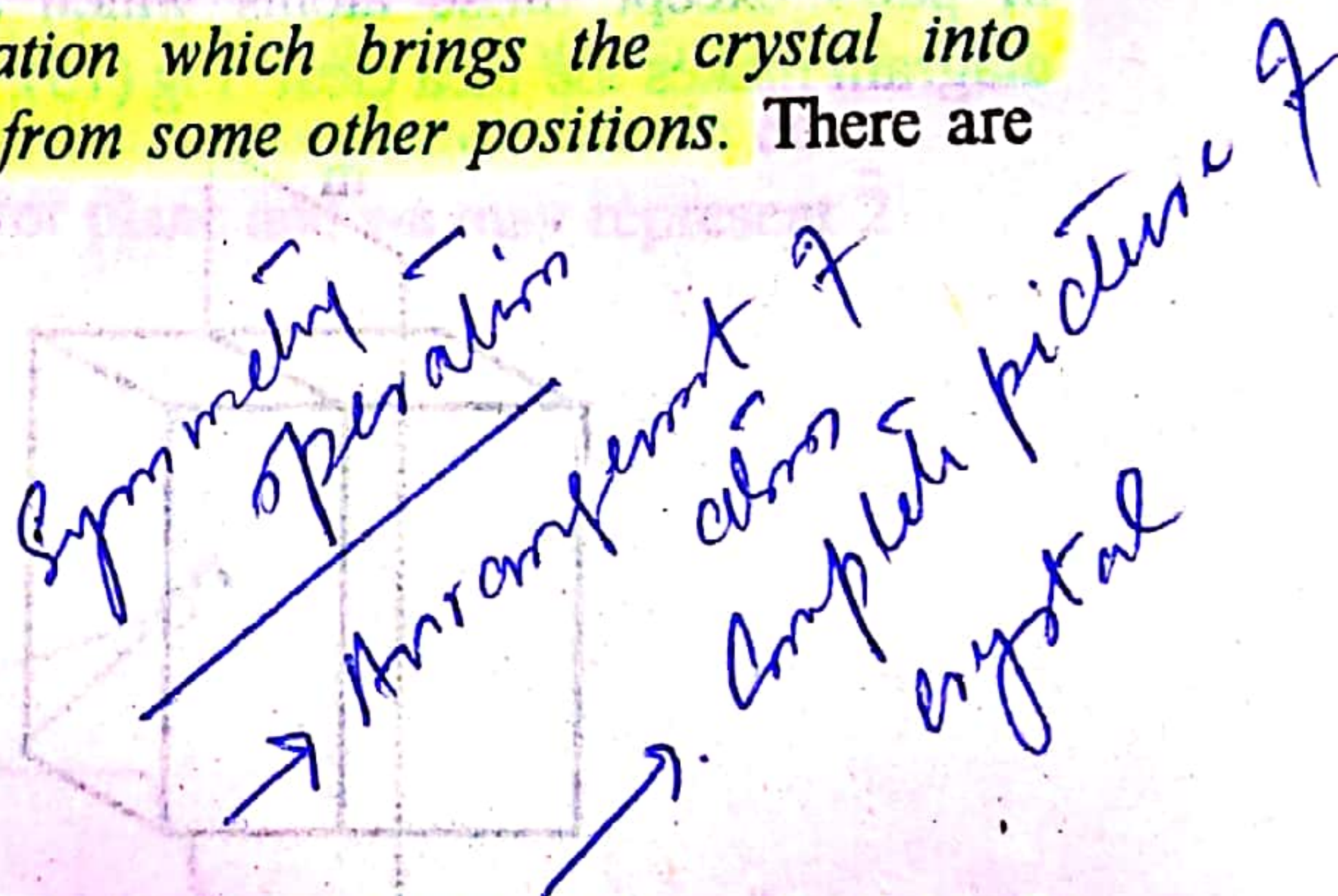
Symmetry operation is that operation which brings the crystal into identical position and is indistinguishable from some other positions. There are various types of symmetry operations.

- (a) Centre of symmetry
- (b) Plane of symmetry
- (c) Rotation axis of symmetry
- (d) Axis of rotation
- (e) Inversion axis

(a) Centre of symmetry:

Centre of symmetry is an imaginary point within the crystal such that any line passing through this point intersects the opposite face of the crystal at equal distance. Centre of symmetry is denoted by (T).

When we carry out this symmetry operation then a molecule having such a centre is transformed into itself. In other words, we can say that if a line is drawn from one atom through the centre and continued then it will meet a similar atom at the equal distance from the centre on opposite side. In order to understand it, consider the following diagram (14).



Interfacial angle

Goniometer
Angle measurement

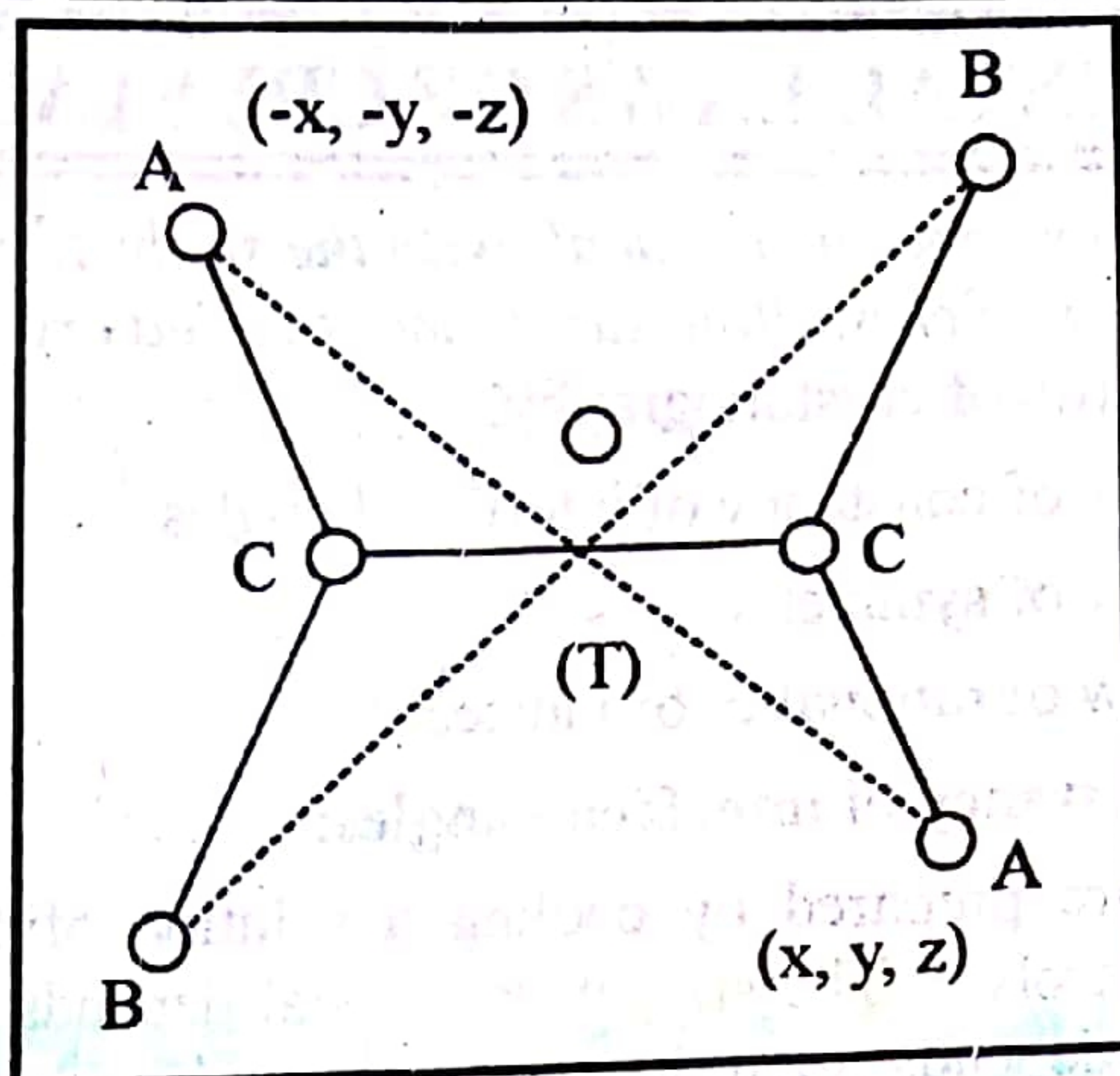


Fig. (14) Centre of symmetry as an element of symmetry.

The atom 'A' has the co-ordinates x, y and z , with respect to the centre of symmetry O , then the other atom 'A' has its co-ordinates $-x, -y$, and $-z$. It means that if we know the co-ordinates of one atom, then the co-ordinates of similar atom in the molecule can be guessed. In other words, we can say that the information which is required to describe the position of half of the molecule is sufficient to assign the position to the other half of the molecule by center of symmetry operation.

(b) **Plane of symmetry:**

"Plane of symmetry is an imaginary plane which divides the body of the crystal into two halves in such a way that each half is exactly the mirror image of other half." Those crystals which have this plane of symmetry have all the atoms in pairs except those atoms which are on the plane of symmetry. Following diagram makes the idea clear. Fig (15).

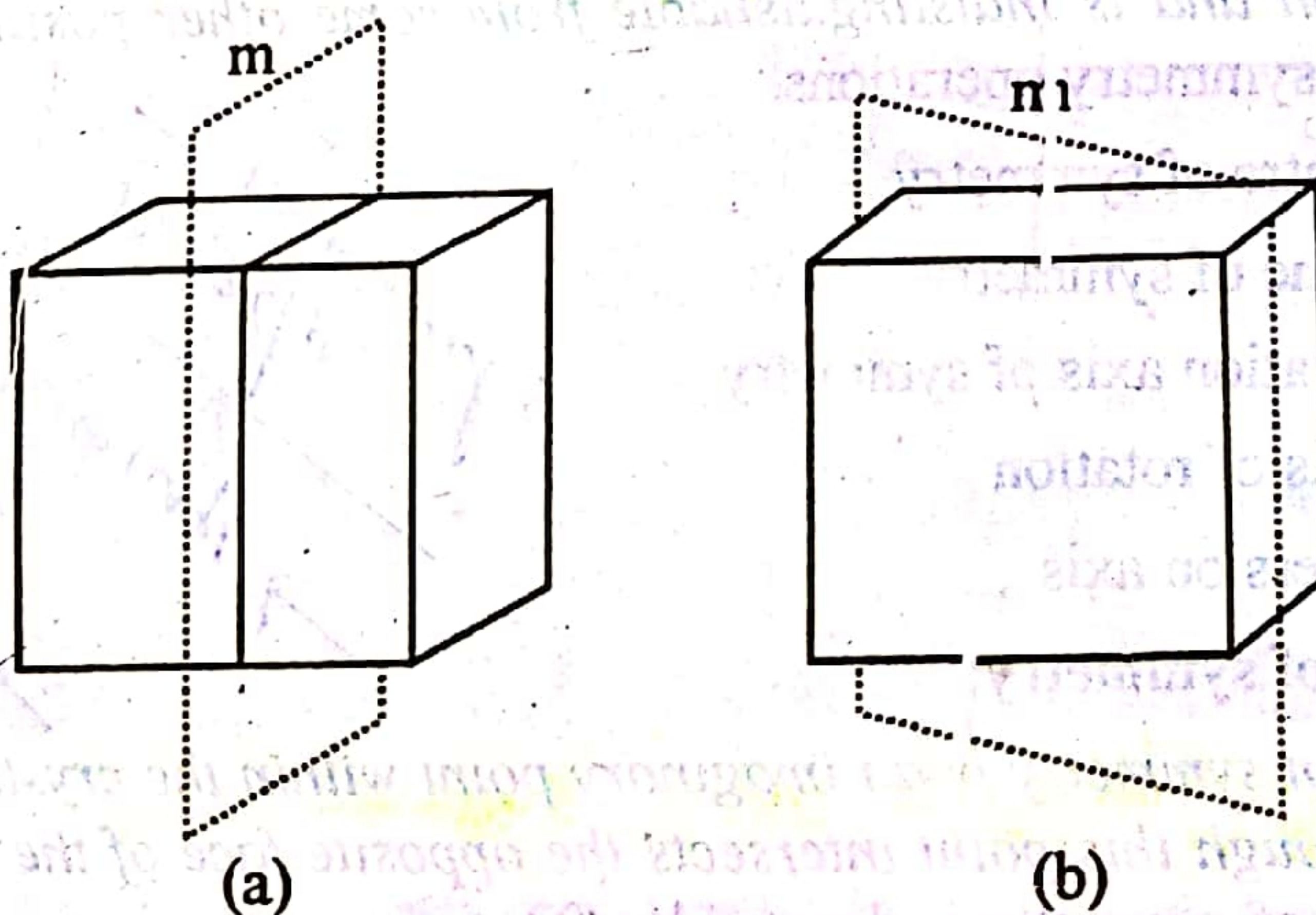


Fig. (15) Planes of symmetry in a cube.

(c) **Rotation axis of symmetry:**

"The rotation axis of symmetry is an imaginary line about which the crystal may be rotated, so that it shows exactly the same appearance more than once." It shown in the following diagram (16). Once in the course of complete

rotation the axis may be a three-fold rotation. It means that in a complete revolution by 360° , the same type of the face is repeated three times that is after each 120° . There are no 5-fold, 7-fold or 8-fold axis of rotation. The reason is that it is impossible to fill all the space with figures of 5, 7, and 8-fold symmetry.

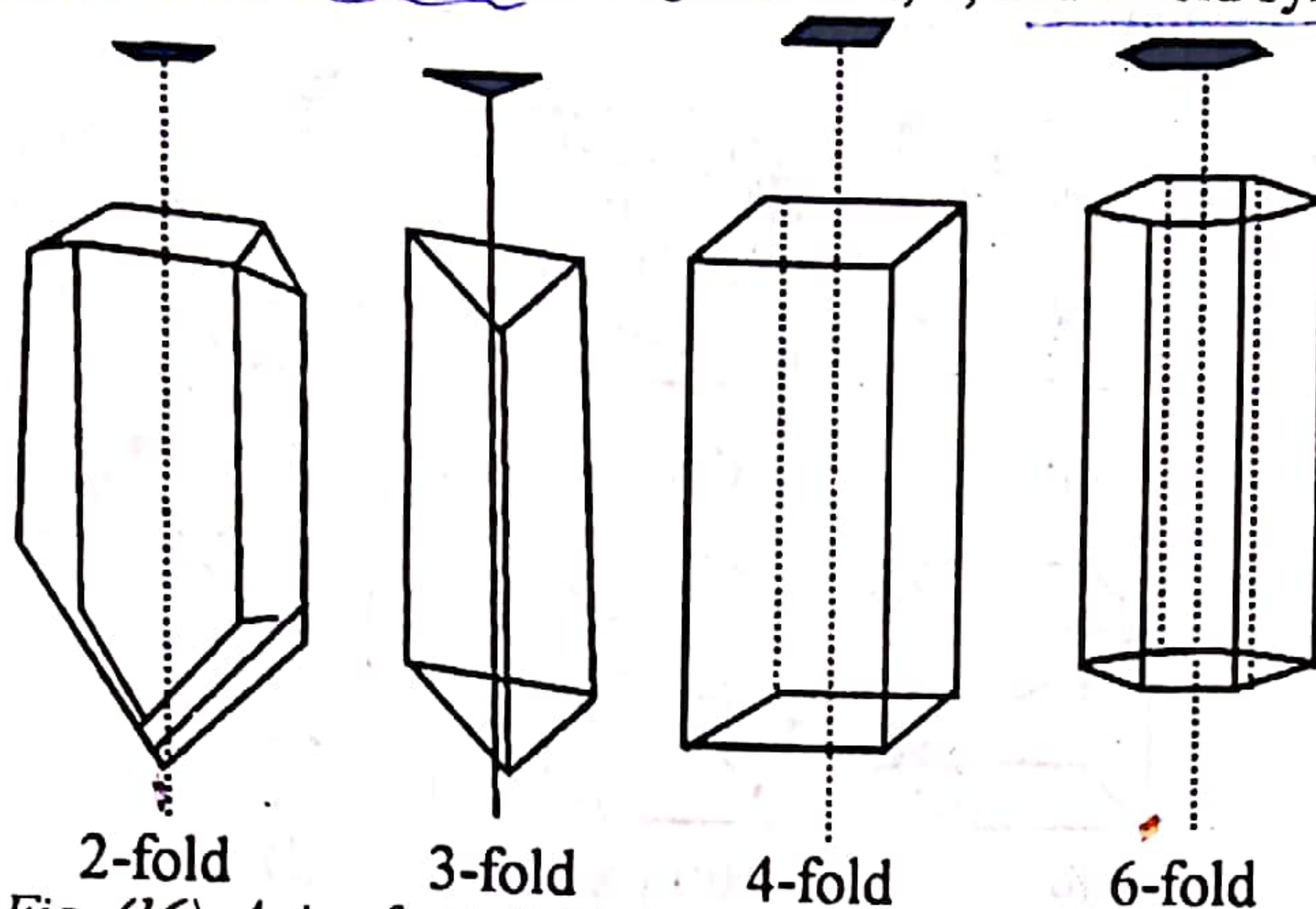


Fig. (16) Axis of rotation as one of the symmetry element.

(d) **Axis of rotation:**

When the rotation of a molecule or a crystal about n -fold axis of proper rotation is followed by reflection through a plane perpendicular to the axis, then this axis is called n -fold rotation reflection axis. The new configuration obtained is not congruent but is enantiomorphous.

(e) **Inversion axis:**

Inversion axis involves an n -fold rotation followed by inversion through a center of symmetry, where $\bar{n} = \bar{1}, \bar{2}, \bar{3}, \bar{4}, \dots$ etc. A molecule is said to possess $\bar{2}$ axis, if a rotation of 180° is followed by inversion through a center of symmetry. Let us consider a point 'A' in the following diagram (17). It is transformed by symmetry operation $\bar{2}$ to 'A''. The point 'A' is related to 'A'' as its mirror image, in a plane perpendicular to the axis and passing through the origin of inversion. In other words the affect of $\bar{2}$ axis is the same as that mirror plane and we may represent $\bar{2}$ axes by m , (mirror plane).

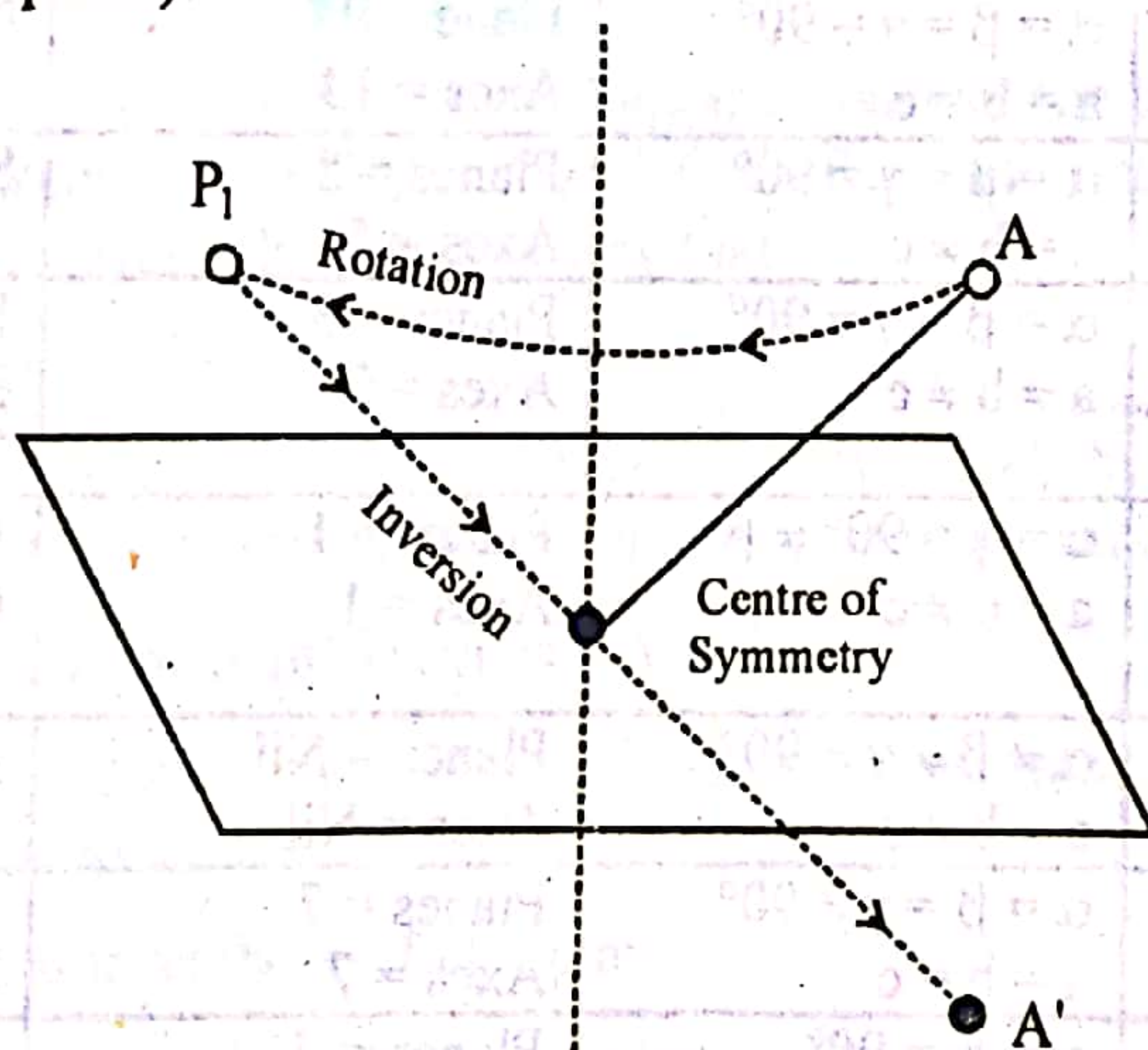


Fig. (17) Equivalence of $\bar{2}$ axis and mirror plane m .

3.3.1 Laws of symmetry in a crystal:

The crystal of a particular substance always possesses the same elements of symmetry. A cubic crystal always possesses 23 different elements of symmetry.

The following set of six diagrams (18) for a cubic crystal show that there are 23 elements of symmetry overall.

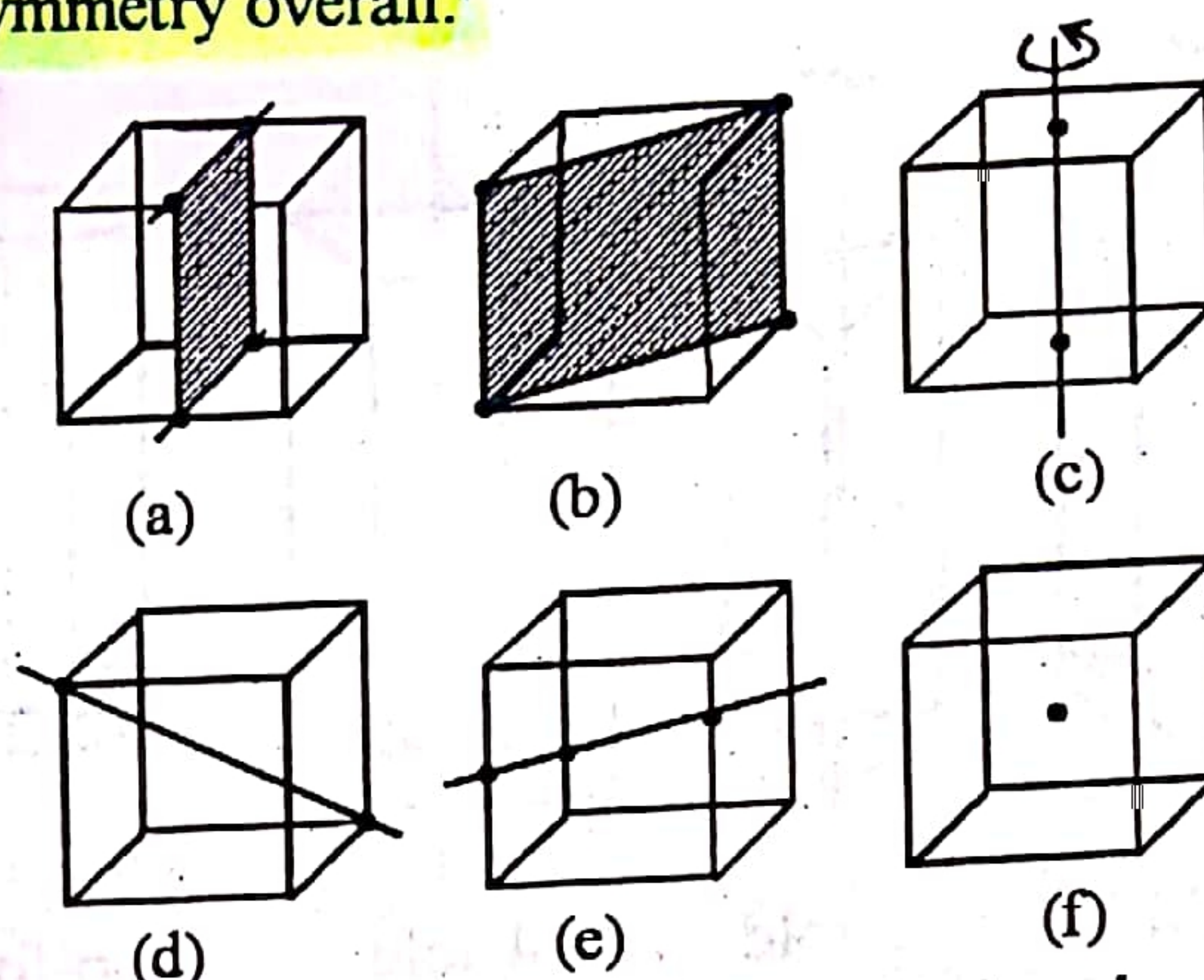


Fig. (18) Elements of symmetry of a cube.

The calculations are as follows.

$$\left. \begin{array}{l} \text{(a) Rectangular planes of symmetry} = 3 \\ \text{(b) Diagonal plane of symmetry} = 6 \end{array} \right\} = 9$$

$$\left. \begin{array}{l} \text{(c) Four-fold axes of symmetry} = 3 \\ \text{(d) Three-fold axes of symmetry} = 4 \end{array} \right\} = 13$$

$$\left. \begin{array}{l} \text{(e) Two-fold axes of symmetry} = 6 \\ \text{(f) Centre of symmetry (located at the centre of gravity of cube)} = 1 \end{array} \right\} = 23$$

Total elements of symmetry of a cube = 23

In the similar way, the maximum elements of symmetry for seven crystal graphic systems are shown in the following table (2).

Table (2) Related information regarding crystallographic systems

System	Axial characteristics	Maximum symmetry	Examples
1. Cubic	$\alpha = \beta = \gamma = 90^\circ$ $a = b = c$	Plane = 9 Axes = 13	NaCl, KCl Alums, Diamond
2. Tetragonal	$\alpha = \beta = \gamma = 90^\circ$ $a = b \neq c$	Planes = 5 Axes = 5	Sn, SnO ₂ , TiO ₂
3. Orthorhombic or Rhombic	$\alpha = \beta = \gamma = 90^\circ$ $a \neq b \neq c$	Planes = 3 Axes = 3	KNO ₃ , K ₂ SO ₄ , BaSO ₄ , PbCO ₃ Rhombic sulphur
4. Monoclinic	$\alpha = \gamma = 90^\circ \neq \beta$ $a \neq b \neq c$	Planes = 1 Axes = 1	Na ₂ SO ₄ · 10H ₂ O CaSO ₄ · 2H ₂ O Monoclinic sulphur
5. Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$ $a \neq b \neq c$	Planes = Nil Axes = Nil	CuSO ₄ · 5H ₂ O K ₂ Cr ₂ O ₇
6. Rhombohedral or Trigonal	$\alpha = \beta = \gamma \neq 90^\circ$ $a = b = c$	Planes = 7 Axes = 7	NaNO ₃ , ICl, As, Sb, Bi
7. Hexagonal	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ $a = b \neq c$	Planes = 7 Axes = 7	HgS, Ice, Graphite, Mg, Zn, Cd

3.3.2 Crystallographic axis and axial ratio:

Now at this stage, the relative positions of the atoms, ions or molecules are to be located in crystal. For this purpose, three suitable axes are chosen which meet at a point O. These axes can be selected in a number of ways depending upon the symmetry of the crystal. One of the best choice is the edges between those lines which are parallel to the edges between the principle faces. Look at the following diagram of a cubic crystal Fig. (19) and Fig. (20). We have chosen three lines mutually at right angles to each other. These three lines are called crystallographic axes.

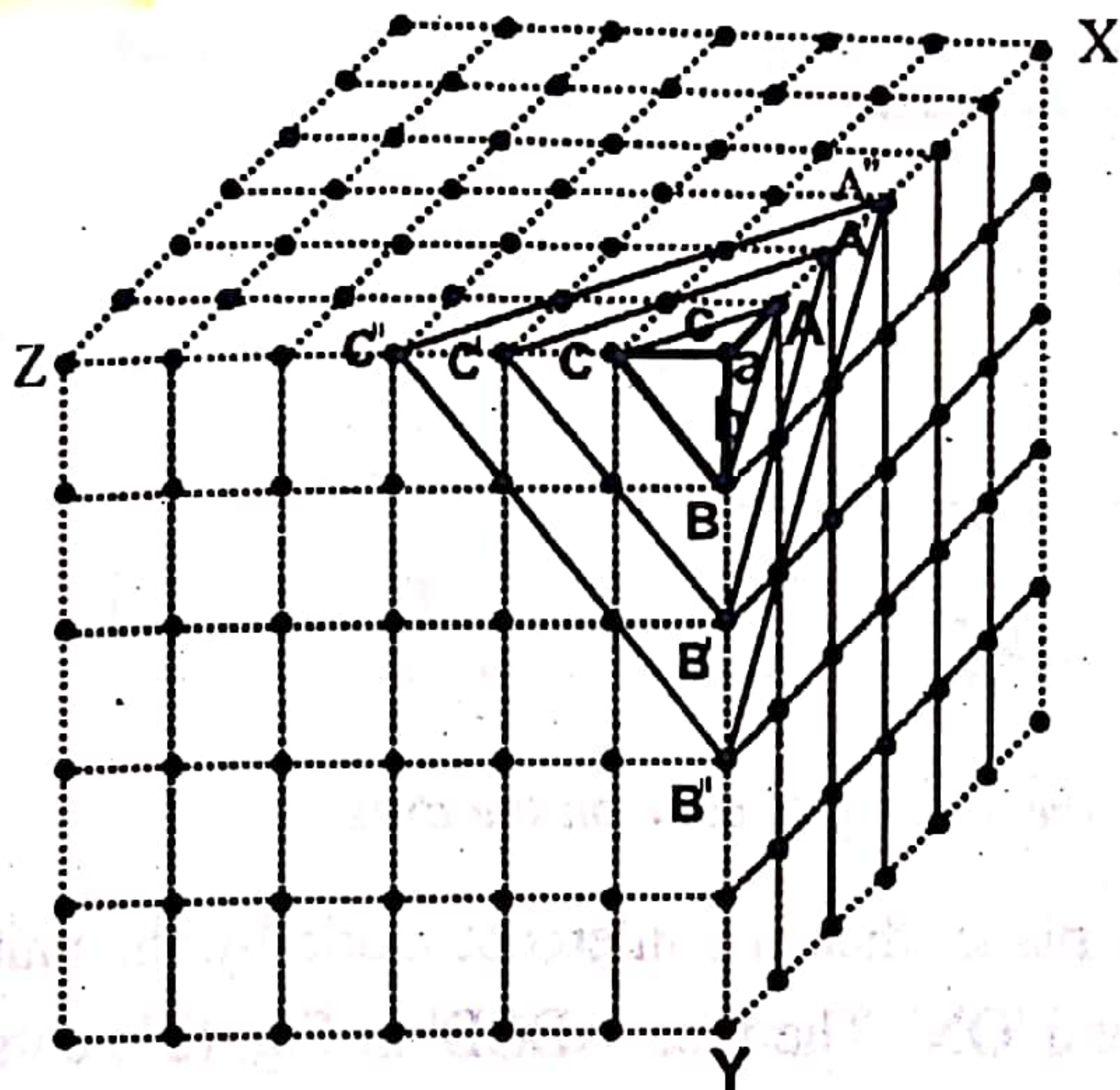


Fig. (19) Sets of planes drawn in the crystal.

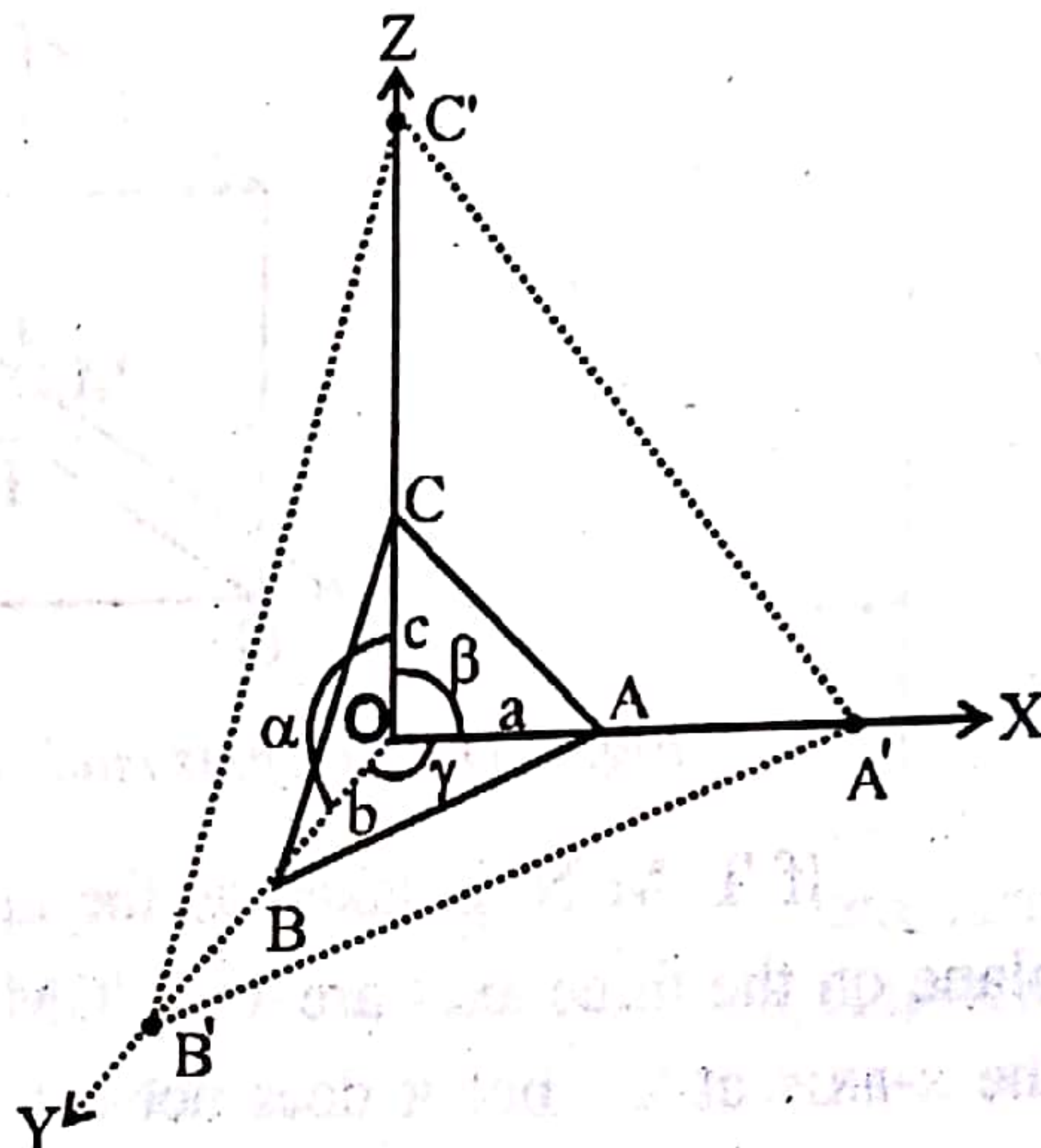


Fig. (20) Crystallographic axes and axial ratio.

a, b, c , are the intercepts and the respective angles in front of them are α , β , and γ .

Axial ratio:

Keeping in view the above diagram, consider the unit plane 'A B C'. Three axis are represented by 'OX', 'OY' and 'OZ'. The unit plane 'A B C' cuts these axis at 'A', 'B', 'C' respectively in such a way that

$$OA = a, OB = b, OC = c$$

This ratio of 'a', 'b', 'c' is called axial ratio. So, the axial ratio is the ratio of the intercepts made by the unit plane on the crystallographic axes.

3.3.3 Law of rational indices:

The intercepts which are made by any face of the crystal on the crystallographic axes, are

- (i) Same as those of unit plane.
- (ii) Simple whole number multiple of unit plane.
- (iii) One or two intercepts may be infinity.

In other order to understand it, consider the diagram (20) and take into account the intercepts made by the face, 'A' B' C''. These lengths are '2a', '2b', '2c'. These are simple whole number multiples of unit plane 'a', 'b', 'c'.

In order to explain it take into account the cubic structure as in Fig. (21). The origin 'O' of the crystallographic axes lies at the centre of the symmetry. The axes OX, OY and OZ are parallel to the edges. The axes OX, cuts the face ABCD at the point 'L'. Other cutting points are 'M' and 'N'.

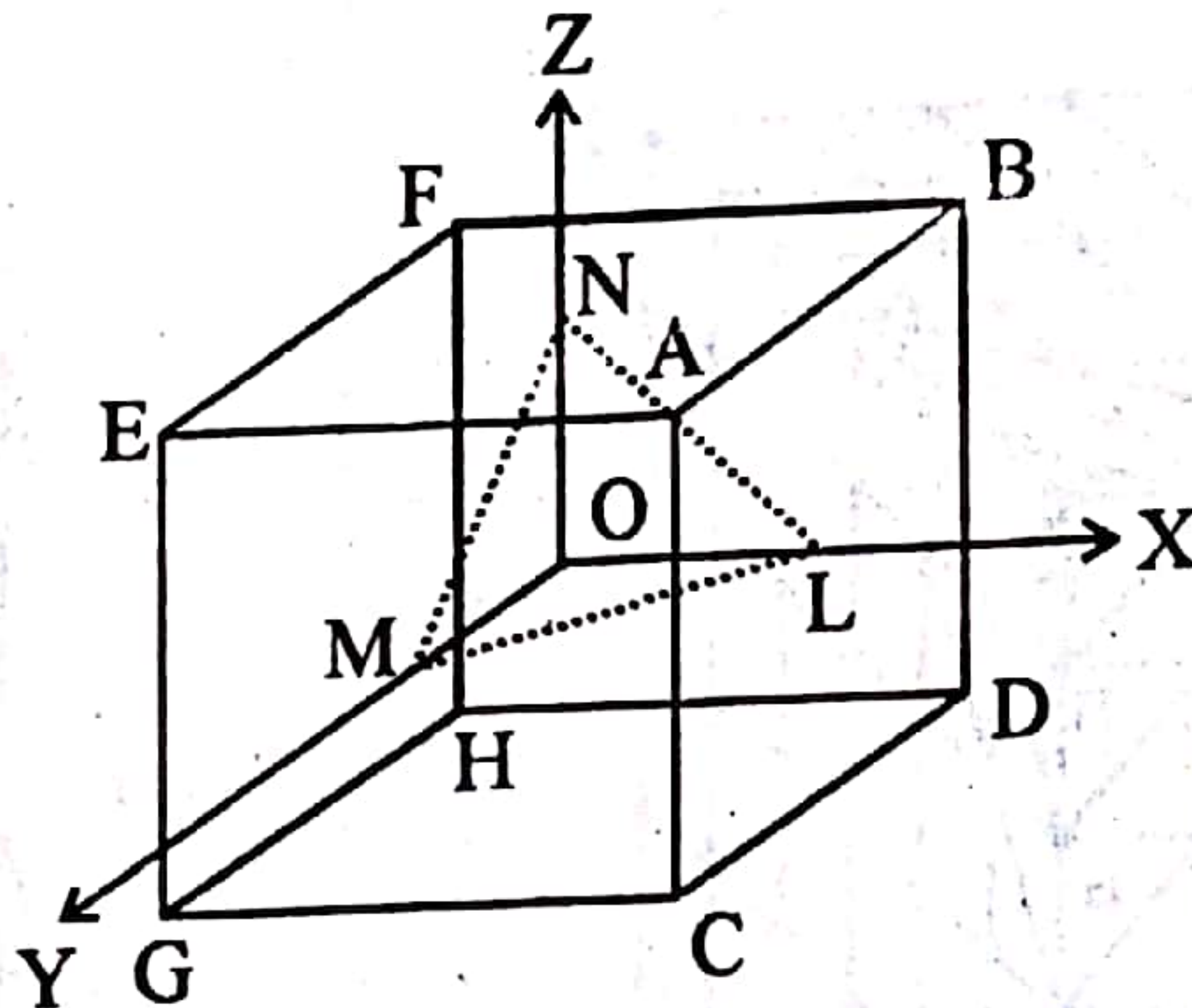


Fig. (21) Intercepts made by the faces of a cube on the axes.

If 'L M N' is taken as the unit plane, then the intercept made by the unit plane on the three axes are 'OL', 'OM' and 'ON'. The face 'ABCD' in Fig. (21) cuts the x-axis at 'L', but it does not cut the y-axis and z-axis at all, because they are parallel to 'ABCD'. We can say that the intercepts made by the face 'ABCD' on 'y' and z-axis are infinity.

In order to define other planes 'A'B'C'D'' with respect to the unit plane 'ABCD', the intercepts OA', OB' and OC' are multiples of these intercepts of the planes in the crystal and are given by $ma : nb : pc$. The 'm', 'n', 'p' are either integral whole numbers including infinity or fraction of whole numbers.

$$ma : nb : pc = d : e : f$$

This conclusion was made by Hauy and known as law of rational intercepts. The co-efficients of a, b, c, which are m, n, p are called Weiss indices.

3.3.4 Miller Indices:

Weiss indices were used by scientists to index the crystal faces, but Weiss indices are no longer used in crystallography. They have been replaced by Miller indices i.e., h, k, l. These are reciprocals of Weiss indices and they are in the ratio of whole number. They can be reduced to whole number by multiplication with a least common denominator. In order to have a relationship between Weiss and Miller indices following table (3) will help us.

Table (3). Weiss indices and corresponding Miller indices.

Weiss Indices			Reciprocal of Weiss Indices			Miller Indices		
m	n	p	$\frac{1}{m} = h, \frac{1}{n} = k, \frac{1}{p} = l$			h	k	l
1	1	1	1	1	1	1	1	1
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	2	3	4	2	3	4
2	4	∞	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{\infty}$	2	1	0
3	1	∞	$\frac{1}{3}$	$\frac{1}{1}$	$\frac{1}{\infty}$	1	3	0
$\bar{2}$	3	1	$\frac{1}{2}$	$\frac{1}{3}$	1	$\bar{3}$	2	6
$\bar{2}$	$\bar{4}$	1	$\frac{1}{2}$	$\frac{1}{4}$	1	$\bar{2}$	$\bar{1}$	4

The above table (3) shows that some of the values of Miller indices are having a bar upon them. In order to understand it, look at the following diagram (22) for positive and negative values of Miller indices. There are three axes as AA', BB' and CC'.

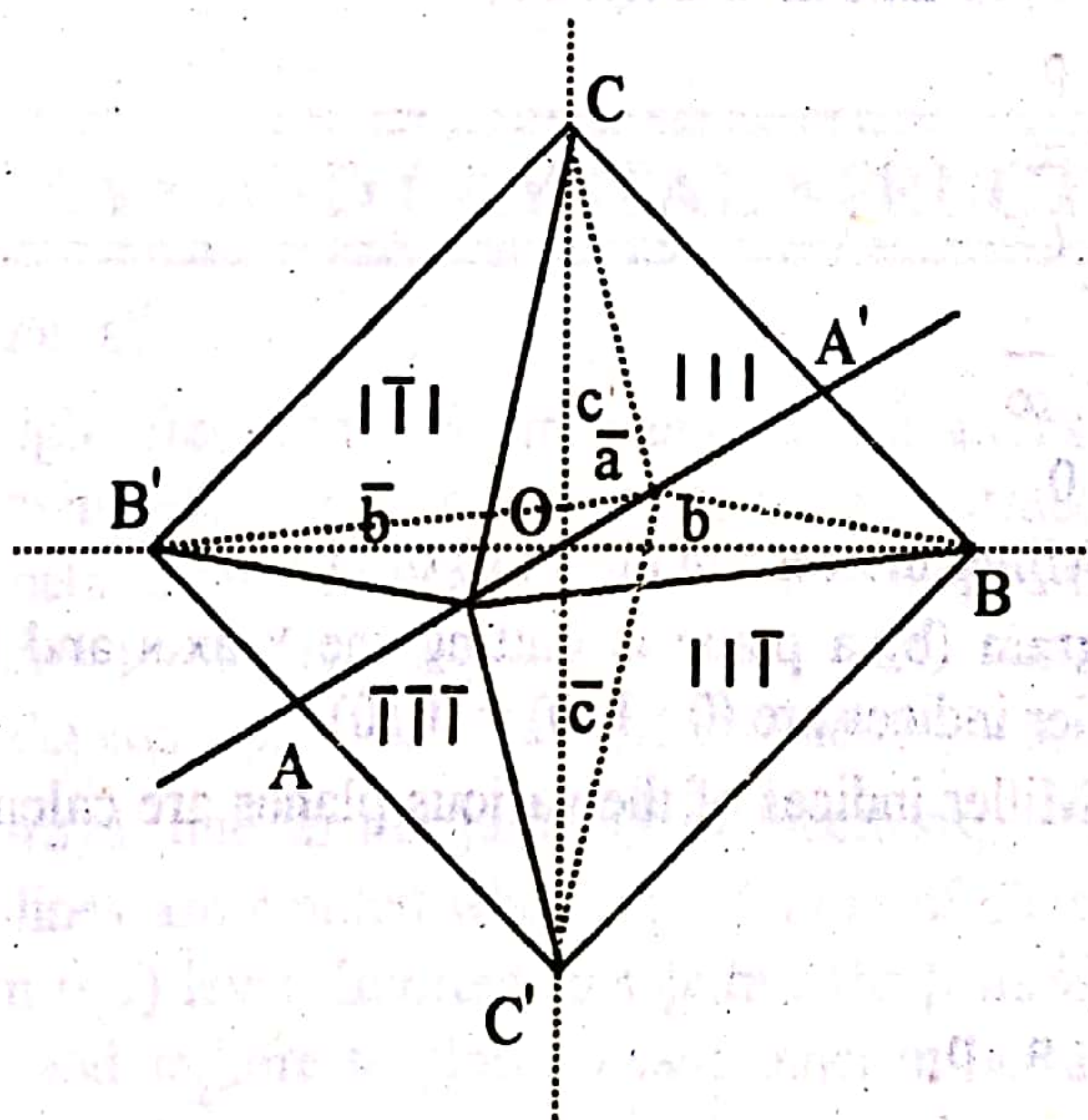


Fig. (22) Positive and negative values of Miller indices.

They are intersecting at the point O. The intercept on these axes towards the front, right and upwards are regarded as positive. The intercepts towards the back, left and downward are taken as negative. These negative intercepts are indicated by a bar over the number.

3.3.5 Diagrammatic representation of Miller indices of a cubic system:

In the following set of diagrams (23), the origin is taken at the lower left front corner of each cubic crystal. The direction of the axis of each cube are taken along the edges.

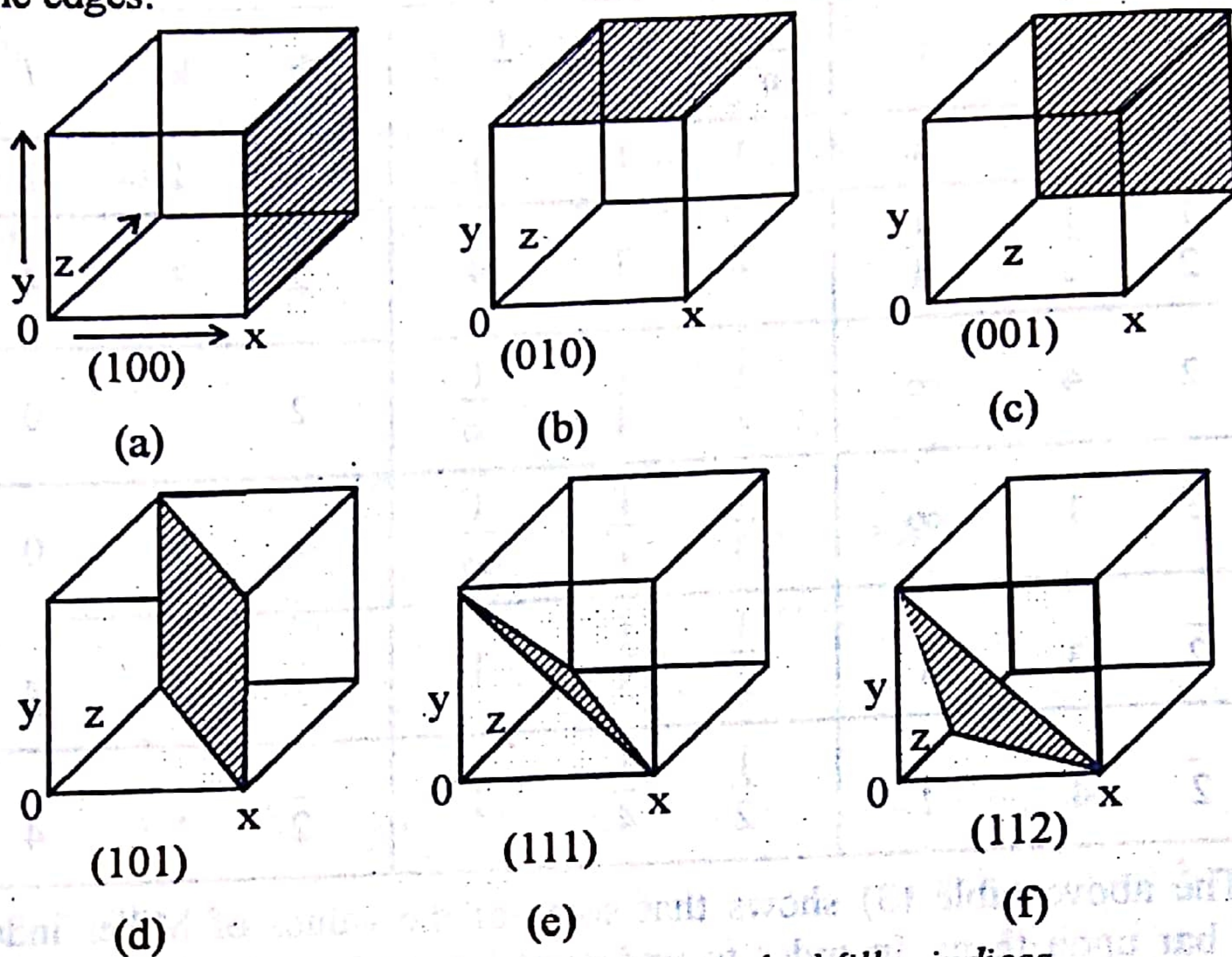


Fig. (23) Designation of planes by Miller indices.

In diagram (a), the plane cuts x-axis at unit distance and is parallel to y and z-axis. It cuts the y and z-axis at infinity. So,

$$m : n : p$$

$$1 : \infty : \infty$$

$$\text{So, } h : k : l$$

$$\frac{1}{1} : \frac{1}{\infty} : \frac{1}{\infty}$$

$$1 : 0 : 0$$

Hence, its Miller indices are $(1 : 0 : 0)$ or (100)

In the diagram (b) a plane is cutting the Y-axis and is parallel to x and z-plane. So, its Miller indices are $(0 : 1 : 0) = (010)$

Similarly, Miller indices of the various planes are calculated along with the diagram.

Diagram (c)

$$\text{As, } m : n : p$$

$$\infty : \infty : 1$$

$$\text{So, } h : k : l$$

$$\frac{1}{\infty} : \frac{1}{\infty} : \frac{1}{1}$$

$$0 : 0 : 1 = (001)$$

Diagram (d)

$$m : n : p$$

$$1 : \infty : 1$$

So, $h : k : l$

$$\frac{1}{1} : \frac{1}{\infty} : \frac{1}{1}$$

$$1 : 0 : 1 = (101)$$

Diagram (e)

$$m : n : p$$

$$1 : 1 : 1$$

$$h : k : l$$

$$\frac{1}{1} : \frac{1}{1} : \frac{1}{1}$$

$$1 : 1 : 1 = (111)$$

Diagram (f)

$$m : n : p$$

$$1 : 1 : \frac{1}{2}$$

So, $h : k : l$

$$\frac{1}{1} : \frac{1}{1} : \frac{2}{1}$$

$$1 : 1 : 2 = (112)$$

3.4.0 X-RAYS AND CRYSTAL STRUCTURE

3.4.1 What are X-rays?

X-rays are high frequency electromagnetic radiations and they are produced when fast moving electrons are allowed to hit the surface of a metal. The inner electrons of the metal atom especially from $n = 1$ are disturbed. The photons of light are emitted, due to the jumping of electrons. The wavelengths and the energies of the x-rays depend upon the nature of the metal. Actually, ' α_1 ' and ' α_2 ' are the lines of the x-rays, due to the jumping of electrons, from L ($n = 2$) to K ($n = 1$) level, and β -lines are emitted when the jumping of electrons takes place from M ($n = 3$) to K ($n = 1$) level. In order to separate the β -lines from the α -line, ' β ' filters are used. ' α_1 ' and ' α_2 ' are so close to each other in wavelengths that they are thought to be monochromatic. Their resolution is difficult and they can be used for the crystal study jointly.

Following table (4) helps to understand the x-rays from various metals, their wavelengths and the β -filters. β -filters can separate the wavelengths of lower wavelengths, so that α -lines may be used in x-rays crystallography.

Table (4) Wavelength of x-rays of the various metals and filters.

Metal Target	Line	Wave length in A°	β Filter	Thickness of the filter in mm
Cr	$K\alpha_1$	2.289	V	0.016
	$K\alpha_2$	2.293		
	$K\beta$	2.085		
Co	$K\alpha_1$	1.789	Fe	0.018
	$K\alpha_2$	1.973		
	$K\beta$	1.621		
Cu	$K\alpha_1$	1.540	Ni	0.021
	$K\alpha_2$	1.544		
	$K\beta$	1.392		
Mo	$K\alpha_1$	0.709	Zr	0.108
	$K\alpha_2$	0.713		
	$K\beta$	0.632		

3.4.2 Diffraction of x-rays:

X-ray tube provides electromagnetic radiations with wavelengths of about atomic dimensions. In most of the cases we can think that a typical atom might behave like a hard sphere of about 2A° diameter. The characteristic x-rays which are obtained from copper may be used for x-ray crystallography. The wavelength of such rays are 1.5418A° . When these x-rays are passed through a crystal, they are diffracted. They form an interference pattern like that of visible light, which is diffracted by grating. The spacing in the gratings are comparable to its wavelength.

x-rays are electromagnetic radiations. Electric and magnetic fields are propagating perpendicular to each other. They are also perpendicular to the direction of propagation. The scattering of x-rays is due to the reason that the interaction between the electrical field of x-rays takes place with the negatively charged electrons in the crystal structure. This scattering power of an atom is proportional to the atomic number or the number of the electrons of the atom. The crystal acts as three dimensional diffraction grating towards x-rays. So, a diffraction pattern is obtained when x-rays pass through the crystal.

3.4.3 Bragg's equation:

Bragg has given a simple account of diffraction from a three dimensional crystal structure. The complex phenomenon of x-ray diffraction is reduced theoretically to simple geometrical problems looking as if we are studying the reflection of x-rays from crystal planes.

Let us consider a crystal having three planes '11' '22' and '33'. These planes are successive. A beam of X-rays of wavelength ' λ ' is incident on these planes at an angle ' θ '. A part of the beam 'BC' is reflected from the point 'B'. On the other hands, some rays like 'A'B'C'' penetrate into crystal and are reflected by the

atoms present in the lower planes '22' and '33''. The diagram is as follows. Fig. (24).

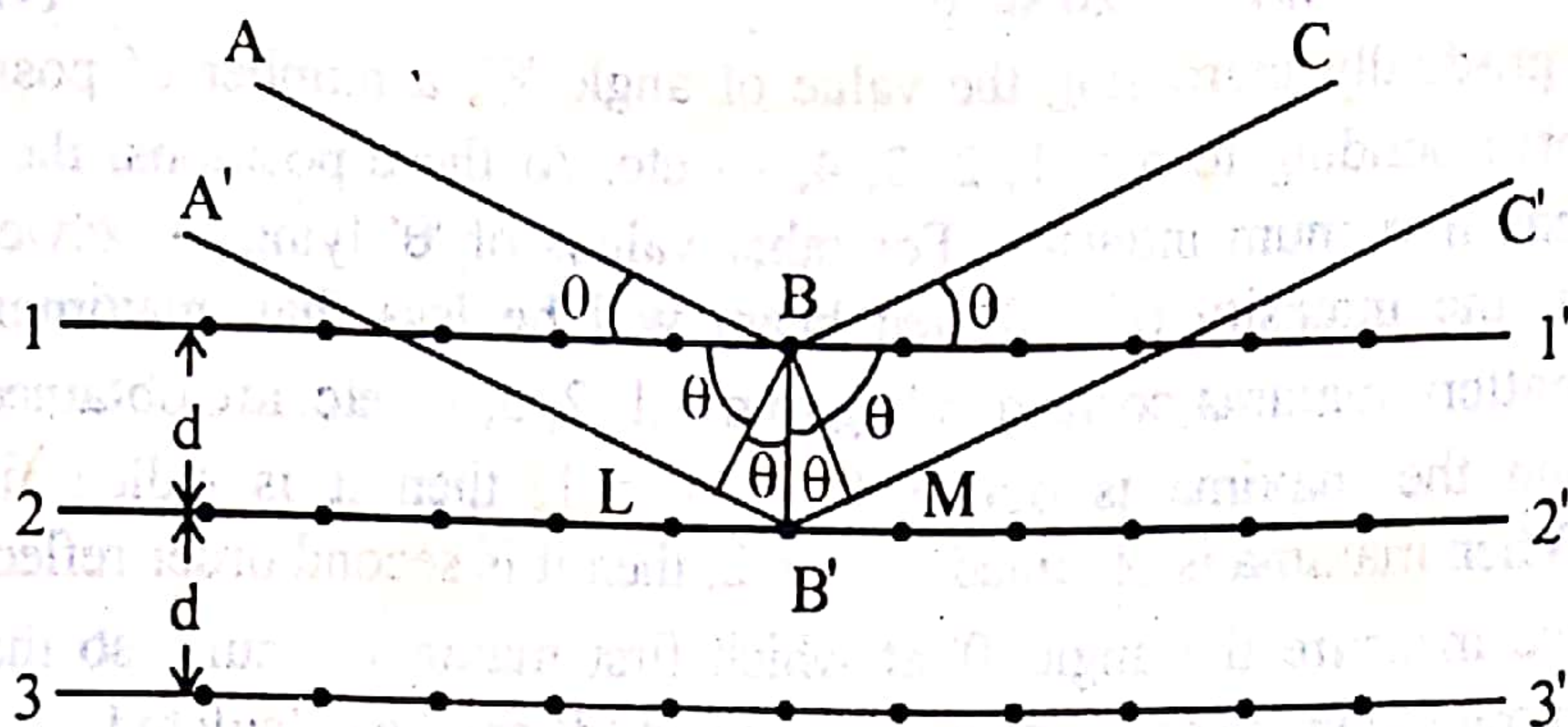


Fig. (24) The condition of reflection by a crystal lattice.

The ray A' B' C' has to travel a longer distance in order to emerge out of crystal. 'BL' and 'BM' are the perpendiculars on A'B'C' ray. The reflected beams 'BC' and 'B'C'' undergo interference with each other. If these reflected rays are in phase then they reinforce each other and the intensity of the reflected ray is maximum. When we say that rays are in phase with each other, then it means that the crest falls over the crest and trough over the trough.

If the reflected rays are out of phase, then the intensity of reflected beam is very low. When a photographic plate is placed to receive the reflected rays, then the diffraction pattern is obtained.

It is clear that, the reflected rays 'BC' and 'B'C'' can do the constructive interference, if the path difference (LB' + MB') is the integral multiple of wavelength of X-rays.

From the right angled triangle, 'LBB'', the length 'LB'' is perpendicular and 'BB'' is hypotenuse

So, $\frac{LB'}{BB'} = \sin \theta$

$LB = BB' \sin \theta$

From the right angled triangle MBB', the length MB' is perpendicular and BB' is hypotenuse.

So, $\frac{MB'}{BB'} = \sin \theta$

Hence, $MB' = BB' \sin \theta$

$BB' = d$ (inter planar distance)

$MB' = d \sin \theta$

Path difference,

$LB' + B'M = d \sin \theta + d \sin \theta$

Path difference = $2 d \sin \theta$

The path difference is integral multiple of wavelength. Let that integral multiple is 'n'. So,

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

By gradually increasing the value of angle ' θ ', a number of positions are observed corresponding to $n = 1, 2, 3, 4, \dots$ etc. At these positions, the reflected beam will have maximum intensity. For other values of ' θ ' lying in between, those values of n , the intensity of reflected beam will be less than maximum. So, a diffraction pattern maxima corresponding to $n = 1, 2, 3, \dots$ etc. are obtained.

When the maxima is obtained for $n = 1$, then it is called first order reflection. When maxima is obtained for $n = 2$, then it is second order reflection.

If we measure the angle ' θ ' at which first maxima occurs, so that $n = 1$, then if we know the value of ' λ ' of the x-rays and ' d ' can be calculated.

If the crystal is of known dimensions, then wavelength of unknown x-rays can be calculated.

EXAMPLE (3)

The x-rays of wavelength 2.29×10^{-10} m are diffracted from a crystal. The first order reflection happens at $27^\circ 8'$. Calculate the interplanar distance of crystal.

SOLUTION:

Data:

$$\lambda = 2.29 \times 10^{-10} \text{ m}$$

$$\theta = 27^\circ 8'$$

According to Bragg's equation

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

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

Putting values

$$d = \frac{1 \times 2.29 \times 10^{-10} \text{ m}}{2 \sin (27^\circ 8')}$$

$$d = \frac{2.29 \times 10^{-10} \text{ m}}{2 \times 0.466}$$

$$d = 2.45 \times 10^{-10} \text{ m} = \boxed{2.45 \text{ \AA}} \quad \text{Ans.}$$

EXAMPLE (4)

A crystal has a interplaner distance of 2.04 \AA and wavelength of x-rays used is 1.54×10^{-10} m. Calculate the angle of reflection.

SOLUTION:

Data:

$$d = 2.04 \times 10^{-10} \text{ m}$$

$$n = 1$$

$$\lambda = 1.54 \times 10^{-10} \text{ m}$$

$$\theta = ?$$

From Bragg's equation

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

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

By putting the values

$$\sin \theta = \frac{1 \times 1.54 \times 10^{-10}}{2 \times 2.04 \times 10^{-10}}$$

$$\sin \theta = 0.3774$$

$$\theta = \sin^{-1}(0.3774)$$

$$\theta = \boxed{27^\circ 17'}$$

Ans.

3.4.4 Bragg's method of x-ray analysis:

Bragg invented a x-ray spectrometer which is shown in the following diagram (25).

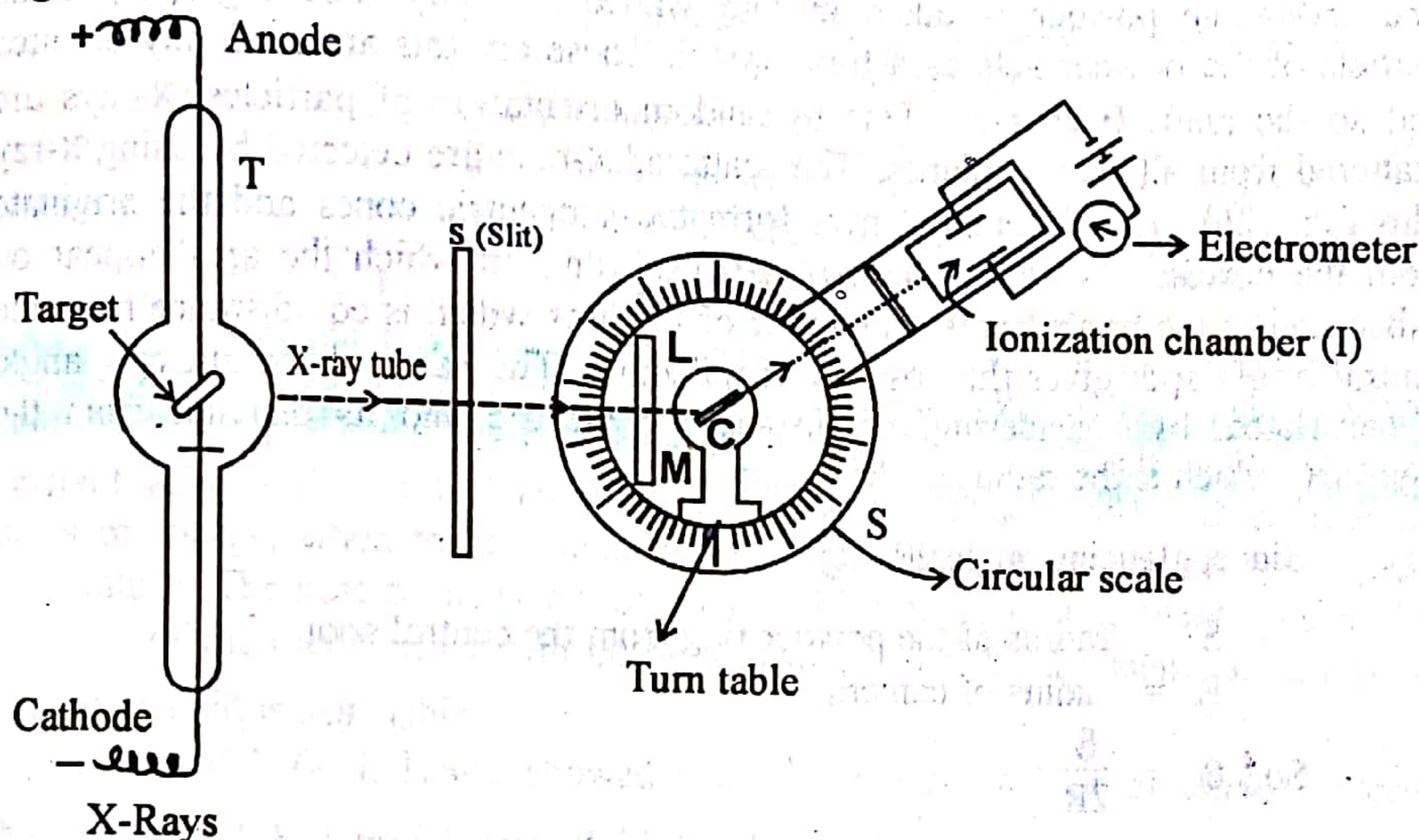


Fig. (25) X-ray spectrometer.

X-ray spectrometer is consisted of an X-ray tube 'T'. The x-rays are converted to monochromatic x-rays by passing through a screen. Monochromatic x-rays are passed through a slit (s) to get a fine beam. This fine beam is allowed to fall on the face of a crystal 'C', which is mounted on a turn table. The turn table can be moved over a circular scale 'S'. The beam is reflected from the surface of crystal 'C' and is sent to the ionization chamber I. This ionization chamber can also be moved on a circular scale independent of the turn table. The chamber contains easily ionizable gas as SO_2 . The ionization of this gas is directly proportional to the intensity of the reflected beam of x-rays. When the crystal faces are rotated by rotating the turn table, the direction of the reflected beam changes. For this purpose the ionization chamber is also to be rotated through double the angle ' θ ', through which the crystal faces are rotated. This practice will help us to measure the values of an angle ' θ ', corresponding to first, second and third maxima.

3.4.5 Structure of NaCl:

For the face of NaCl crystal having Miller indices (100) The value of θ is 5.9° , for $n = 1$ $\sin(5.9^\circ) = 0.103$, so when we substitute this value in Bragg's equation.

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

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times \lambda}{2 \times 0.103} = 4.85\lambda.$$

If we know the wavelengths X-rays used, then 'd' can be determined. However, if 'd' of NaCl is known to us then wavelength of unknown X-rays can be calculated.

4.6 Powder method:

This method finds its name because the crystalline substance whose analysis is to be done is taken in the form of powder. This method was advanced by Debye and Sherrer in 1916. A source of monochromatic x-rays is managed. A fine crystalline powder is taken in thin walled capillary tube Fig. (26). Each particle of the powder acts as a tiny crystal. These crystals are randomly oriented and so the angle θ changes. Due to random orientation of particles, X-rays are scattered from all sets of planes. The scattered X-rays are detected by using X-ray film Fig. (26). The different X-rays form the concentric cones and the originate from the powder. There is a narrow strip of film, on which the arcs appear on either side of the bright spots. Each pair of the arcs which is equidistance from the central bright spot gives the position of reflection. The value of the glancing angle is calculated, by considering the distance of the arc and its distance from the capillary, which is the radius of the arc.

$$\text{Since, glancing angle } 2\theta = \frac{S}{R}$$

S = radius of the powder ring from the central spot

R = radius of camera

$$\text{So, } \theta = \frac{S}{2R}$$

' θ ' which is obtained in radians and can be converted into degrees.

$$\theta(\text{in radian}) = \theta \times \frac{180}{\pi} \text{ degrees} = \theta \times 57.296$$

By using the Bragg's equation as, $2d \sin \theta = n\lambda$, and knowing the value of ' λ ' and ' θ '; 'd' can be calculated.

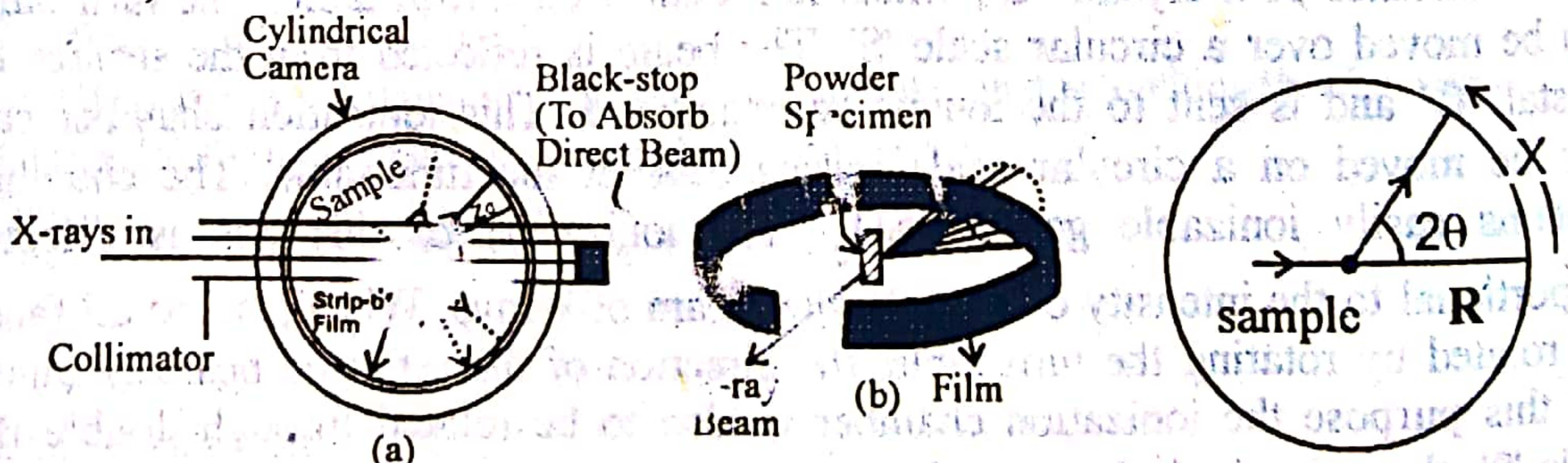


Fig. (26) The powder method of crystal structure.

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Laue's method:

The x-rays from x-ray tube are collimated into a beam by a lead shield having a hole in it. The crystal is placed in path of the x-ray beam. Each atom in the plane scatters the X-rays and its impression is obtained on the photographic plate. The values of ' θ ' is fixed and the wavelength of x-ray is changed. The photographic plate is developed. The spots of different sizes and intensities are obtained. The arrangement is shown in the following diagram. Fig (27)

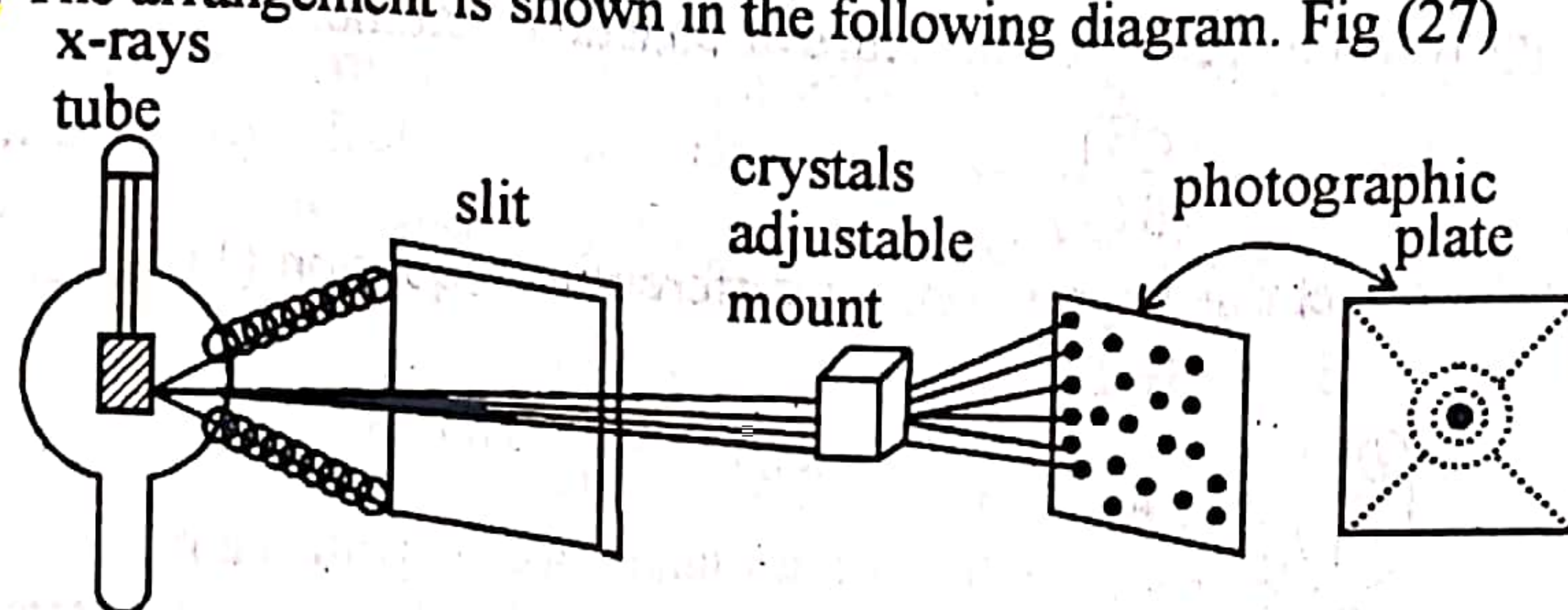


Fig. (27) The Laue's method of crystal analysis by x-rays.

The spots which are produced on the photographic plate represent the scattering part of the original beam through various characteristic angles. The arrangement of this part depends upon the nature of the crystal.

3.5.0 HEAT CAPACITIES OF SOLIDS

In 1819 Dulong and Petit, who discovered that the heat capacities of the solid elements particularly the metals measured at room temperature have the constant values of $26 \text{ J K}^{-1} \text{ mol}^{-1}$. It means that one mole of metal absorbs 26 joules of energy, when the temperature is increased by 1K, in the range of room temperature. The heat capacity of solid should be measured at constant volume. So it is ' C_V ' of the metal which will be discussed, but not ' C_P ' because the change in volume of solid is negligible.

In 1907, G.N. Lewis showed that ' C_V ' values of solid elements are very close to $24.9 \text{ J K}^{-1} \text{ mol}^{-1}$ around 25°C . Some of the elements at 25°C have the following values of heat capacities. Table (5).

Table (5). C_V value of metals at 25°C

Metal	$C_V(\text{J k}^{-1} \text{ mol}^{-1})$
Sb	24.7
Ag	24.7
Fe	24.7
Bi	26.0
Pd	26.7

Reasons:

Law of equipartition of energy can explain the constant heat capacity of solid elements. Each degree of freedom contributes ' $\frac{1}{2} RT$ ' kinetic energy to

1 mole of monoatomic substance. In solids, there are vibrational motions in three independent directions.

On the average, for a vibrational motion, there is an equal amount of potential energy as well. So, total energy is $\frac{3}{2}RT + \frac{3}{2}RT = 3RT$ (1)

According to the fundamental definition of ' C_V ' it is the rate of change of internal energy with respect to temperature at constant volume.

$$\text{So, } C_V = \left(\frac{\partial E}{\partial T} \right)_V \text{ (2)}$$

In order to get this expression, we differentiate equation (1)

$$E = 3RT$$

$$\left(\frac{\partial E}{\partial T} \right) = 3R$$

$$\text{So, } C_V = 3R \text{ (3)}$$

Putting the value of ' R ' as $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

$$C_V = 3 \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

3.5.1 Heat capacities and temperature:

In order to understand the effect of temperature on heat capacities of solid, look at the following graph in Fig (28).

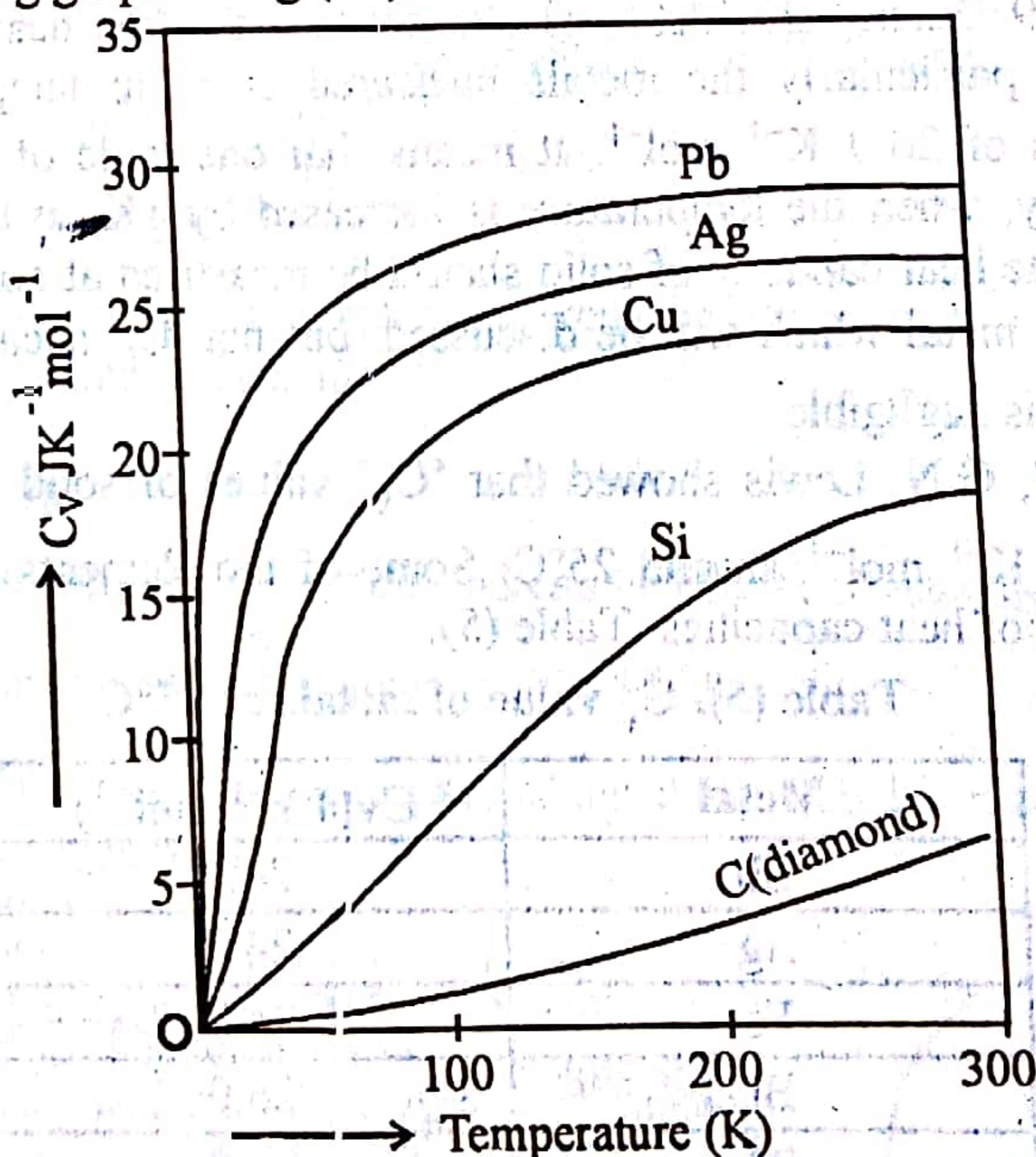


Fig. (28). Variation of heat capacity with temperature.

The graph shows that heat capacities are zero at zero kelvin. The heat capacities increase for Cu, Ag and Pb very rapidly with the increase of temperature. When the temperature is close to the room temperature then values of heat capacities become $25 \text{ J K}^{-1} \text{ mol}^{-1}$.

Carbon and silicon show the exceptional behaviour. They increase their heat capacities very slowly. One of the allotropic forms of carbon i.e., diamond attains this value above 1300°C.

3.5.2 Einstein's explanation of heat capacities:

According to Einstein, the atoms which make a crystal are not at rest, but they vibrate about their equilibrium position even at absolute zero. Every substance has a characteristic vibrational frequency. He says that the vibrating system absorbs the energy only in quanta and the absorption does not take place continuously. Einstein has related the value of ' C_V ' of solid elements with the temperature ' T ' and vibrational frequency ' ν ' of the bond. The equation is as follows,

$$C_V = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

According to this equation the value of ' C_V ' approaches to zero at very low temperature i.e., 0K. When the temperature is high, then the term $h\nu/kT$ is small in comparison with unity. The value of C_V will approach asymptotically to the value of $3R$.

For the elements like Cu, Ag, and Pb, $h\nu/kT$ is sufficiently small at ordinary temperature and heat capacities can become $25 \text{ J K}^{-1} \text{ mol}^{-1}$.

The vibrational frequency of the diamond is very high due to its very strong bonds and very high temperature is required to attain the value of $25 \text{ J K}^{-1} \text{ mol}^{-1}$.

3.5.3 Modification of Einstein's theory:

In 1912, Debye's modified Einstein's theory. He says that all the particles of a crystal do not vibrate with same frequency. They vibrate with any frequency between the limits of zero and maximum possible frequency called γ_m . So, we use the term ' $h\gamma_m/kT$ '. Following diagram (29) shows the Debye's plot for aluminum metal. The dotted line is according to Einstein's theory which is away from the actual results.

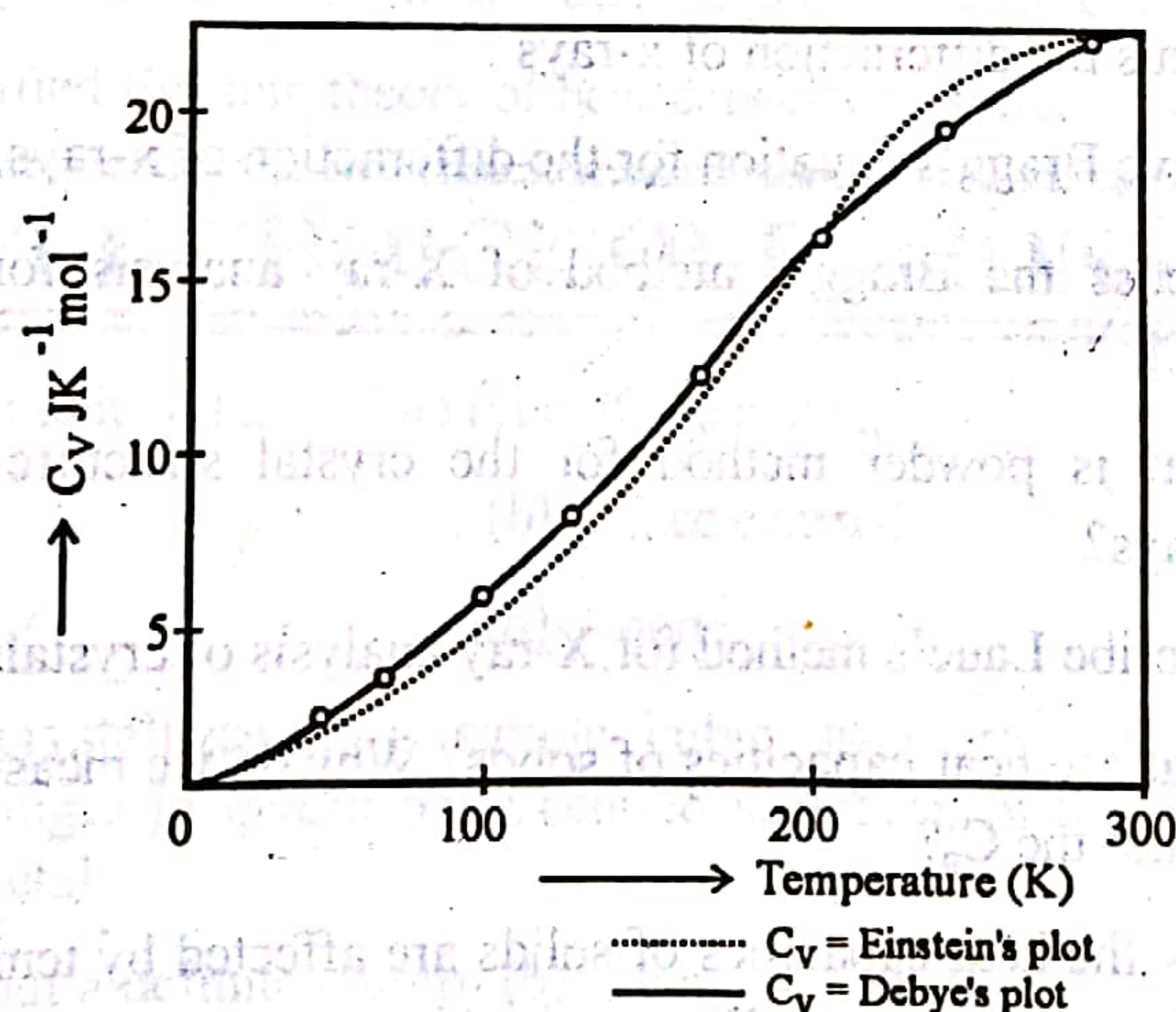


Fig. (29). Comparison of plots of Einstein and Debye between C_V and temperature in K.