CHAPTER
4

The Solid State

4.1 INTRODUCTION

In Chapter 2, the structure of a gas was simply described in terms of the chaotic motion of molecules which are separated from one another by distances larger than their own diameter. The volume actually occupied by the gas molecules is small in comparison to the volume of the container. In liquids, the motion of the molecules is still largely chaotic. However, the molar volume of a liquid is smaller than the molar volume of its vapour, a larger fraction of the space is occupied by the molecules in the liquid state. A less randomness in the space distribution of molecules and probably some partial and transient ordered arrangement may be expected for the liquid state. Ease of flow and generally low density in comparison to the corresponding solid indicates the irregular arrangement of molecules in the liquid and creates void space in its structure.

The constituents of crystalline solids, on the other hand, *are arranged spatially in a regular and repetitive manner yielding a completely ordered structure*. The highly ordered arrangement is always accompanied by a lowering of potential energy, so that energy is required to convert a solid into a liquid. The ordered arrangement usually has a smaller volume and low compressibility than the liquid.

Solids are usually classified as either *crystalline* or *amorphous*. The term solid is generally employed for substances which are crystalline in nature. In these crystalline solids, the constituents may be atoms, ions or molecules. The definite and ordered arrangement of the constituents extends over a large distance in the crystal and is called a *long-range order*. Crystalline solids such as sodium chloride, ice or sugar etc. possess a sharp melting point. Amorphous solids like glass, pitch, rubber, plastics etc. although possessing many characteristics of crystalline solids such as definite shape, rigidity and hardness, but are devoid of a regular internal structure and melt gradually over a range of temperature. For this reason, they are not considered as true solids but rather highly supercooled liquids.

An amorphous solid exhibits the same value of any property in all the directions and is said to be *isotropic*. For example, refractive index, thermal and electrical conductivities, coefficient of thermal expansion, solubility characteristics are independent of the direction along which they are measured. Crystalline solids (other than those belonging to the cubic class), on the other hand are, *anisotropic*. In these cases, the magnitude of the property depends on the direction along which it is measured. Isotropy arises due to the fact that the amorphous solids have the same arrangement in all the directions.

The size and shape of a crystal depends on the conditions under which crystallization takes place. The angle between any two faces is the inter-facial angle. The corresponding angles in different crystals of the same substance are the same. This is known as *the law of constancy of inter-facial angle*.

4.2 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

Symmetry is a peculiar regularity observed in arrangement of atoms, ions or molecules in a crystal. Crystals can be classified according to their symmetry aspects. This could help us to understand the molecular properties such as, dipole moment, optical activity and spectral characteristics. Before trying to classify molecules on the basis of symmetry, we must understand the terms, symmetry elements and symmetry operations.

Symmetry operation is the movement of an object which leaves the object looking the same. A symmetry operation brings the molecule into the equivalent or identical configuration. Consider a cardboard shaped like an equilateral triangle (Fig. 4.1). Label the three vertices of the triangle as 1, 2 and 3. If we rotate the cardboard through an angle 120° $\left(\frac{2\pi}{3}\right)$, an equilateral configuration (Fig. 4.1(*b*)) is obtained.

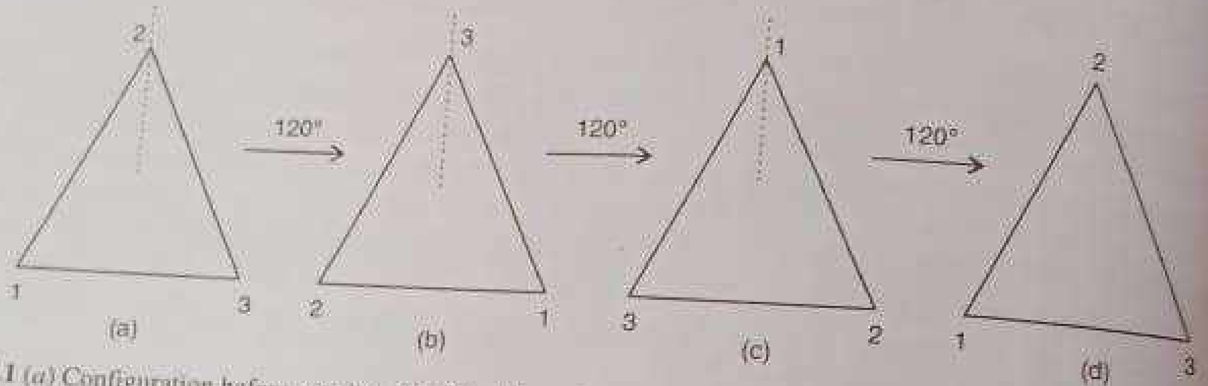


Fig. 4.1 (*a*) Configuration before rotation, the dotted line shows the axis of rotation in a direction perpendicular to the plane of the molecule; (*b*) and (*c*) equivalent configuration after anticlockwise rotation through $\left(\frac{2\pi}{3}\right)$ and $\left(\frac{4\pi}{3}\right)$ degree; (*d*) identical configuration of (*a*)

Further rotation through 120° ($2\pi/3$) will again give an equilateral configuration (*c*), whereas the rotation of (*a*) through 360° (2π) will result in an identical configuration (*d*). In the equivalent configuration, the positions of the atoms are the same as before applying symmetry operation. The rotation

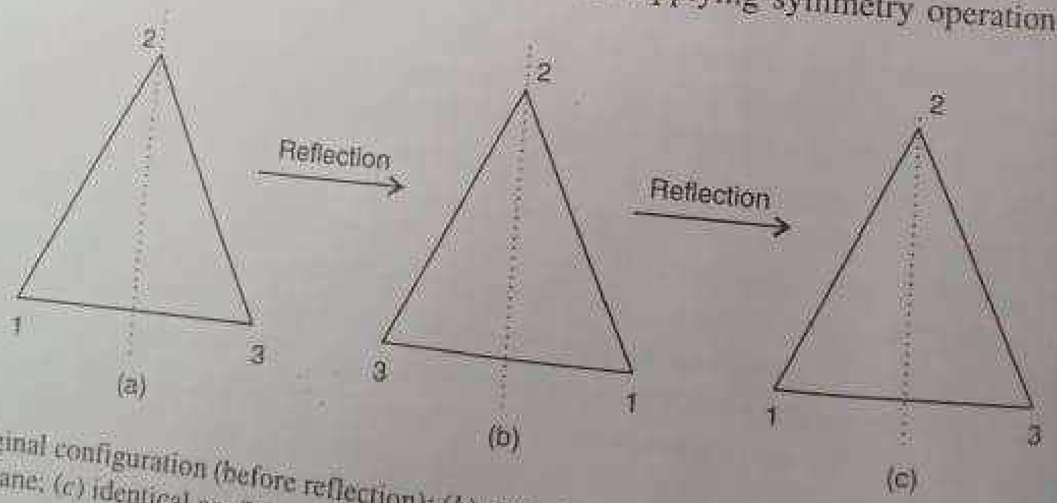


Fig. 4.2 (*a*) Original configuration (before reflection); (*b*) equivalent configuration resulting from reflection through a perpendicular plane; (*c*) identical configuration

through 120° (2p/3) once, twice and thrice can be denoted by C_3^1, C_3^2 and C_3^3. C_3 also represents three fold axis of symmetry.

Similarly, reflection across a plane passing through the vertex 2 of an equilateral triangle shaped molecule (the perpendicular plane is shown by dotted lines) results in equivalent configuration (Fig. 4.2).

Another reflection through this plane results in an identical configuration [Fig. 4.2(*c*)].

Table 4.1 lists the various symmetry operations, corresponding to each symmetry operation, there is a symmetry element. The symmetry element is a point, line, or plane with respect to which a symmetry operation is carried out.

Table 4.1 Symmetry Elements and Symmetry Operations

S.No.	*Symmetry element*	*Symmetry operation*
1.	Identity element (E)	Doing nothing to the object
2.	Proper axis of symmetry or n-fold axis of symmetry (C_n)	Rotation about the axis. Once or several time by an angle $\left(\frac{2\pi}{n}\right)$ or $\frac{360°}{n}$; *n* must be an integer
3.	Centre of symmetry (*i*)	Inversion of all atoms through the centre of symmetry
4.	Plane of symmetry (σ)	Reflection plane passing through the molecule
5.	Improper rotation axis of symmetry or rotation reflection axis (S_n)	Rotation about an axis by an angle $\left(\frac{2\pi}{n}\right)$ or $\frac{360°}{n}$, followed by reflection in a plane perpendicular to the axis of rotation

(1) **Identity:** It is denoted by *E* and is indistinguishable from itself if nothing is done on it. In other words, it leaves each point of the crystal unchanged when a rotation of 360° about any axis is performed. Every object possesses at least this type of symmetry.

(2) **Axis of symmetry:** An axis of symmetry is a line about which the crystal if rotated through an angle of 360°/*n* brings the molecule into a configuration indistinguishable from the original one. This rotation operation is denoted by C_n, where *n* is the order of rotation. The order of an axis is defined as

$$n = \frac{2\pi}{\text{Minimum angle of rotation for obtaining equivalent configuration}}$$

If the crystal is rotated in the counter-clockwise direction then the rotation is conventionally taken as positive. When a rotation about the axis by π leads to a result indistinguishable from the original one, two such equivalent arrangements will occur in a complete rotation, *i.e.*, through 2π, the axis is said to be a two-fold (diad) axis of symmetry (C_2). For example in water molecule, rotation about the axis by 180°(2π/2) leads to an equivalent configuration, *i.e.*, $n = \frac{360°}{180°} = 2$. Thus, water molecule has a two-fold axis of rotation (C_2). This is shown in Fig. 4.3.

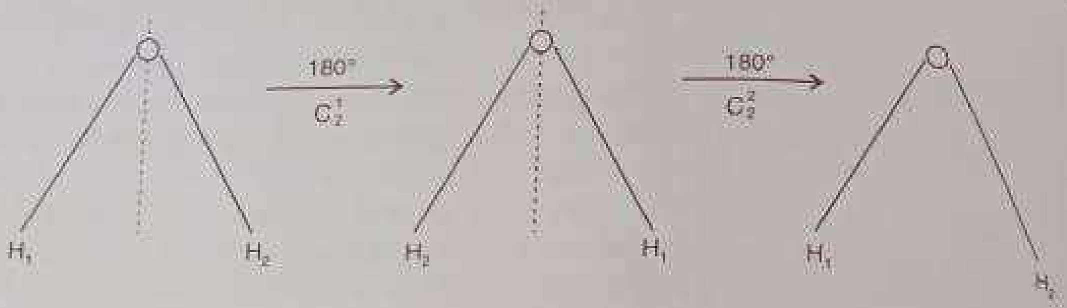
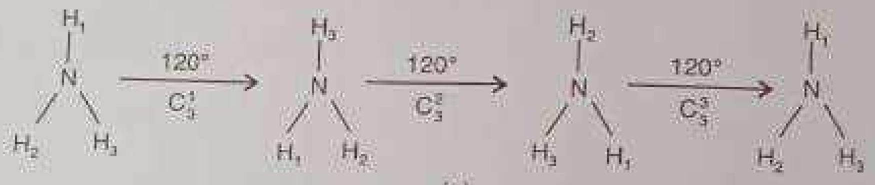


Fig. 4.3 The two-fold axis of symmetry (C_2) in water molecule

If the rotation through 120° $\left(\frac{2\pi}{3}\right)$ about its axis leads to an equivalent configuration, the axis is called a three-fold (triad) axis of symmetry (C_3). The ammonia molecule [Fig. 4.4(a)] has a three-fold axis of symmetry (C_3), passing through the nitrogen atom.

This is shown as follows.

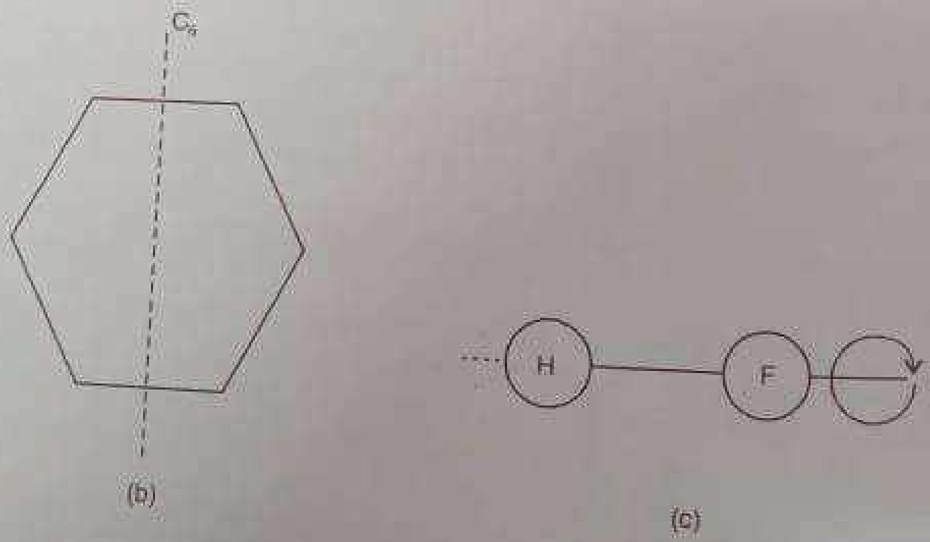


(a)

Fig. 4.4 (a) Axis of symmetry for ammonia molecule

The rotation through 120° (C_3^1) and 240° (C_3^2) results in equivalent configurations while 360° (C_3^3) leads to identical configuration. This three-fold axis of symmetry can be written as

$$C_3^1 C_3^2 = C_3^3 = E$$



(b)

(c)

Fig. 4.4 (b) Axis of symmetry for regular hexagon; (c) Hydrofluoric acid molecule

In case of a regular hexagon [Fig. 4.4(*b*)], it can be turned into the same configuration about a perpendicular axis passing through its centre; *i.e.*, the point of intersection of its diagonals. The hexagon comes into coincidence six times in a complete rotation. This is said to possess a six-fold axis (C_6) of symmetry. In general, an *n*-fold axis of symmetry (C_n) gives rise to $C_n^1, C_n^2, \ldots C_n^n$ operations and can be written as

$$C_n^n = E$$

where E is the identity operation. C_n^n means n times rotation about C_n axis.

If the rotation of $2\pi/3$, *i.e.*, by thirds of a complete revolution leads to the same result as the original one, the axis is called a three-fold (triad) axis of symmetry (C_3).

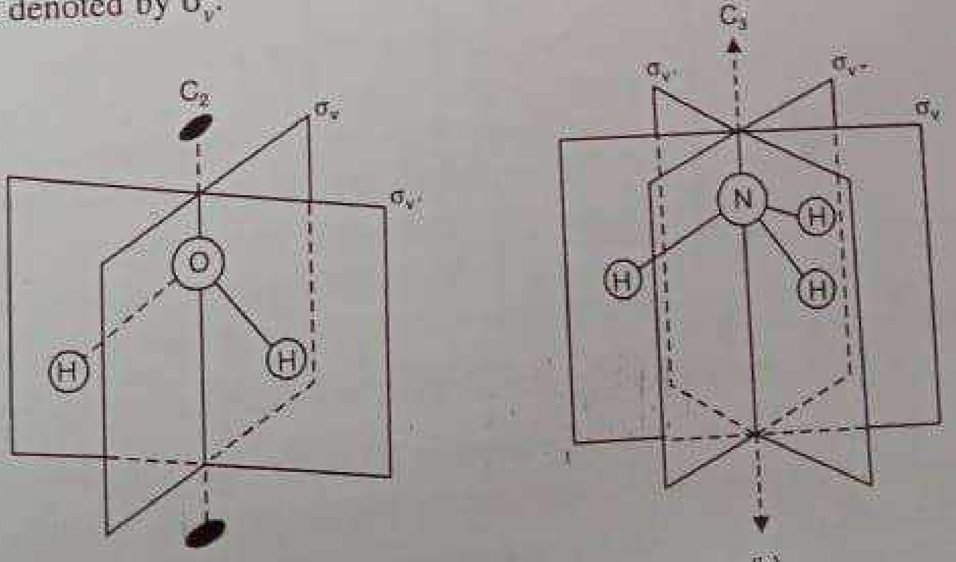
A linear molecule such as hydrofluoric acid [Fig. 4.4(*c*)] has C_∞ axis of symmetry because the rotation about the internuclear axis by any amount (∞ in numbers) would leave the molecule unchanged.

(3) **Centre of symmetry:** It is denoted by *i*. Centre of symmetry or inversion centre of a molecules is a point such that any line drawn through it intersects the surface of the crystal at equal distances in both the directions. To investigate the centre of symmetry, one changes coordinates (x, y, z) of each atom into $-x$, $-y$, $-z$, if a configuration indistinguishable from the original one is obtained, then the point of origin (0, 0, 0) is the centre of symmetry. A crystal can have only one centre of symmetry. If inversion process is applied twice, the original configuration is obtained, *i.e.*,

$$i.i = E$$

The successive application of *i* an even number of times produces the identity E. All homonuclear diatomic molecules (H_2, O_2, N_2 etc.) possess the centre of symmetry. Also CO_2, C_2H_4, C_6H_6, SF_6 and staggered confirmation of ethane possess centre of symmetry.

(4) **Plane of symmetry:** A molecule is said to possess a plane of symmetry if it can be divided by an imaginary plane into two parts such that one is the exact *mirror image* of the other. The plane of symmetry is usually designated by σ. When the mirror plane is perpendicular to the direction of the principal axis (axis of highest order), it is called the *horizontal mirror plane* and is denoted by σ_h. On the other hand, when a mirror plane contains the principal axis of symmetry, it is known as the *vertical mirror plane* and denoted by σ_v.



(a) (b)

Fig. 4.5 Planes of symmetry in the molecules of (*a*) water and (*b*) ammonia

Water molecule has two vertical planes of symmetry, σ_v and $\sigma_{v'}$, which are perpendicular to other [Fig. 4.5(*a*)]. One of these mirror planes $\sigma_{v'}$ contains the plane of the molecule and the oth perpendicular to it. In ammonia molecule, there are three vertical planes of symmetry, σ_v, $\sigma_{v'}$ and planes [Fig. 4.5(*b*)]. In Benzene all the six carbon atoms and six hydrogen atoms are in the horizon plane. This is perpendicular to the C_6 principal axis and hence has a C_6 axis and one σ_h and six planes. A linear molecule like hydrochloric acid has an infinite number of vertical mirror planes, all which include C_∞ rotation axis.

(5) **Improper rotation about an axis of improper rotation:** The improper rotation consists of rotation by $\left(\frac{2\pi}{n}\right)$ about an axis followed by reflection through a plane perpendicular to the ax (horizontal reflection). It is denoted by S_n. Thus, the improper rotation operator S_n is the product of tw operators.

$$S_n = \sigma C_n$$

This implies that two operations C_n and σ are applied successively.

An S_1 is equivalent to plane of symmetry (σ). It involves first rotation by 360° followed by reflec tion across the symmetry plane perpendicular to the axis of rotation. This can be simply represented as reflection across the mirror plane.

An S_2 is equivalent to a centre of symmetry. (*i*) It consists of a counter-clockwise rotation about axis through $\frac{2\pi}{2}$ or 180°, followed by reflection across a horizontal symmetry plane perpendicular this axis yield the original configuration. Similarly an S_3 axis has C_3 axis and a horizontal symmetry plane σ_h. Methane has three equivalent S_4 axis at right angles to each other (Fig. 4.6).

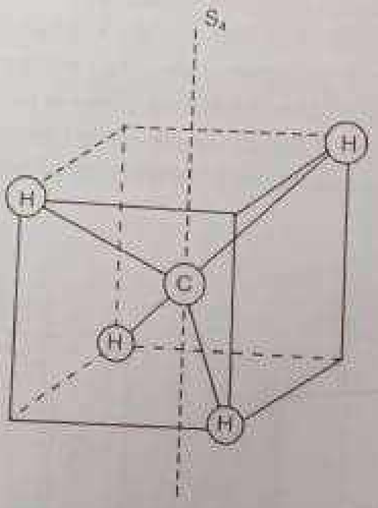


Fig. 4.6 Improper axis of rotation in methane

Problem 4.1: List out the symmetry elements present in (*a*) water—a nonlinear molecule, (*b*) boron trichloride—a planar triangular molecule, (*c*) ammonia—a trigonal pyramid with nitrogen at the vertex (*d*) benzene, and (*e*) a cube.

Solution: (*a*) *Water molecule:* Referring to Figs. 4.3 and 4.5 (*a*), it is clear that it has a two-fold axis of symmetry (C_2) and two vertical planes of symmetry (σ_v and $\sigma_{v'}$). There is no centre of symmetry (*b*) *Boron trichloride:* The molecule possesses a C_3 and three C_2 axes of symmetry; C_3 axis is perpendicular to the plane of the molecule while a C_2 axis contains a chlorine and boron atom and bisects the angle between the other two chlorine atoms [Fig. 4.6 (*a*)]. There are four planes of symmetry. Three of these lie along each of the C_2 axis and are normal to the plane of the molecule and the fourth one is coincident with the plane of the molecule. It is also perpendicular to the C_3 axis and is therefore the σ_h plane. The other three planes encompass it and are consequently σ_v planes. There is no centre of symmetry.

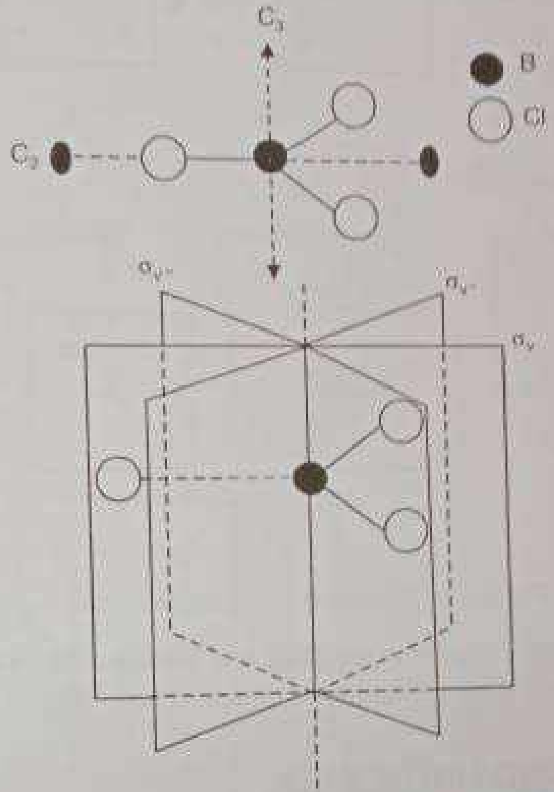


Fig. 4.6 (*a*) Symmetry elements in boron trichloride

(*c*) *Ammonia:* There is a C_3 axis of symmetry and three σ_v planes containing nitrogen and one hydrogen and bisecting the angle between the other two hydrogen atoms [Fig. 4.4(*a*)]. There is no centre of symmetry.

(*d*) *Benzene:* From Fig. 4.6 (*b*), the different symmetry elements are—one C_6 axis of symmetry and three C_2 symmetry axes which pass through the centre of the molecule and through two carbons and two hydrogens. There are three additional two-fold axes of symmetry (C_2') which pass through centre of the molecule and bisect the *C-C* bonds.

There is a σ_h plane and $3\sigma_v$ and $3\sigma_v'$ planes which bisect the angles formed by the C_2 and C_2' axes, respectively. There is a centre of symmetry.

(*e*) *A cube:* From Fig. 4.6 (*c*), the various symmetry elements are three C_4 axes of symmetry at right angles to each other, four C_3 axes of symmetry passing through the opposite corners of the cube and six C_2 axes of symmetry emerging from the opposite edges.

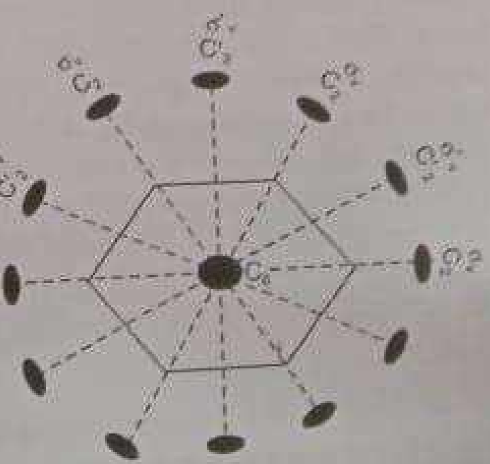


Fig. 4.6 (*b*) Symmetry elements in benzene

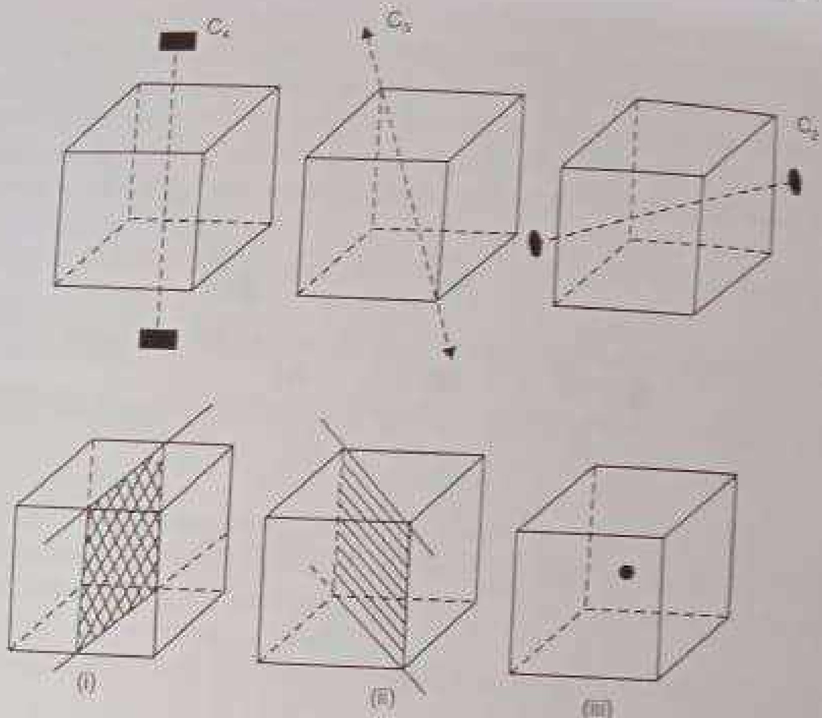


Fig. 4.6 (*c*) Symmetry elements in a cube

There are nine planes of symmetry, three are principal planes [Fig. 4.6*c* (*i*)] and six are diagonal planes [Fig. 4.6*c* (*ii*)] of symmetry. There is a centre of symmetry [Fig. 4.6*c* (*iii*)].

4.3 CRYSTAL LATTICE AND UNIT CELL

The idea of the lattice was developed from the internal regularity of the crystal structure. Lattice is defined as an arrangement of geometrical points in a definite pattern in space. *A highly ordered three-dimensional structure formed by atoms, molecules or ions is called a crystal lattice.* If the constituents of a crystal are denoted by points then a lattice may be regarded as an infinite set of points repeated regularly through space. A set of points repeated at a regular interval along a line is a one-dimension lattice. Thus, a line is the lattice for a one-dimensional pattern. This is shown in Fig. 4.7 (*a*). When a set of points are repeated regularly on a plane (along any two coordinate axes) it is called a *two-dimensional lattice*. This can be seen in Fig. 4.7 (*b*). The points in a two-dimensional plane can be arranged in five and only five different ways. If the two-dimensional lattice is extended in three-dimension, *i.e.*, the points are arranged in a regular, repeated manner along the three coordinate axes, it results in a three-dimensional lattice known as *space lattice or point lattice* [Fig. 4.7 (*c*)]. If the points in space lattice are replaced by the constituents of the crystal (atoms, molecules or ions), a crystal lattice is obtained. Thus, the parameters required to define the three types of lattices in their most general forms are given in Table 4.2.

If similar points are connected by s^ts of parallel lines along the three coordinate axes as shown in Fig. 4.7, the space lattice will be divid d into a large number of small symmetrical units. These basic units of the space lattice are known as the *unit cells***.** Thus, *a unit cell is the smallest fundamental* *building unit of crystal.* The unit cell is, therefore, the essential feature of the crystal structure. Any point placed in the unit cell must occupy the same relative position in every unit cell.

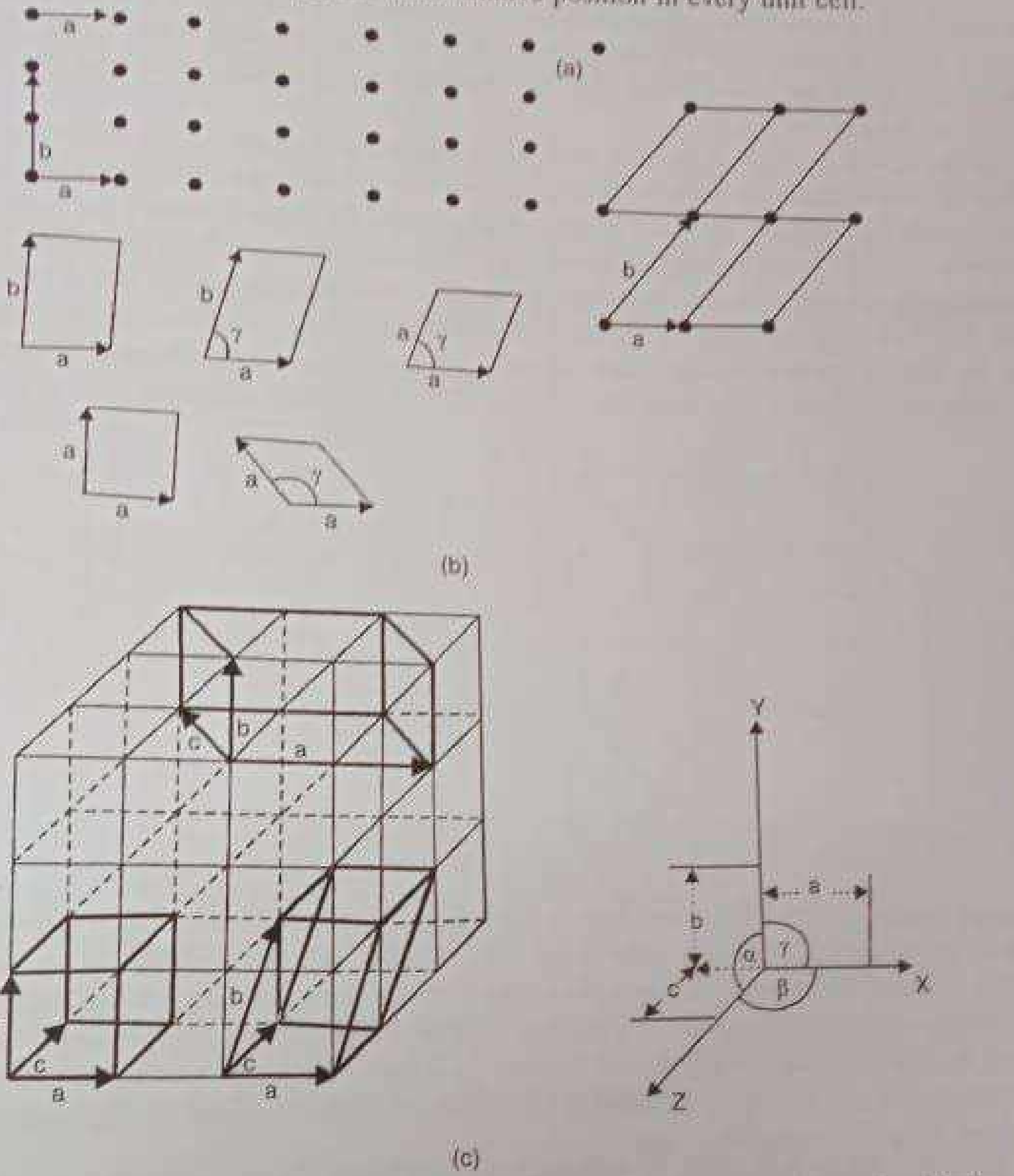


Fig. 4.7 (*a*) A one-dimensional lattice; (*b*) A two-dimensional lattice; (*c*) A three-dimensional lattice

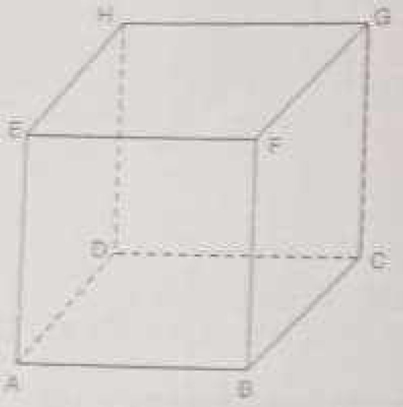
Table 4.2 Unit Cell Parameters in One, Two and Three-dimensional Lattices

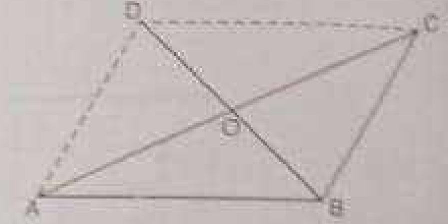
Lattice	*Lattice translation (repeated distance)*	*Interaxial angle*
One-dimensional	a	–
Two-dimensional	a, b	γ
Three-dimensional	a, b, c	γ, α, β

4.4 CRYSTAL SYSTEMS

The unit cell in a three-dimensional lattice is characterized by the lengths a, b and c and the angles α, β and γ, where α is the angle between b and c, β is the angle between a and c and γ between a and b respectively. These are known as the unit cell parameters. From these parameters a total of seven crystal lattices can be constructed.

Of the seven crystal systems, we are mainly interested in cubic system due to its simplicity and symmetry. Since a cube has all the sides equal, therefore, all the three lattice parameters ($a = b = c$) are same. A cube has six faces and each face has four corners. Each point where three faces of a cube meet is called a *corner*. A cube has eight corners. By joining the corners of a face diagonally, two face diagonals (AC and BD) are obtained. In a cube there are twelve face diagonals. The centre point of a face where two face diagonals meet is called a *face centre* (Point O). There are total six face centres in a cube. By joining any two corners which are not in the same face, a body diagonal is obtained. There are four body diagonals in a cube (AG, BH, FD and EC). All the body diagonals meet at the body centre.





Some crystal systems, may have one or more types of lattices depending on the number of lattice points. If there are lattice points only at the eight corners of a unit cell, this is known as *simple* or *primitive unit cell* (P). A cell that has eight lattice points at the corners and one at the body centre, it is called a *body-centered unit cell* (I). If a cell has eight lattice points at the corner and the six face centres is called as *face-centered cell* (F). A cell that has eight lattice points at the corners and two more at the centre of a pair of any two opposite faces is called an *end-centered cell* (C). The unit cells of the type F, C and I are called non-primitive cells.

Bravais showed that there are 14 different unit cells to account for the lattice points at the corners of the unit cell as well as those at the centres and on some of the faces. These 14 unit cells (Fig. 4.8 and Table 4.2) are known as the *Bravias lattices*.

The set or combination of symmetry elements associated with a point in a regular pattern is called a *point group*. In a two-dimensional lattice, there are 10 point groups. However, in a three-dimensional lattice, 32 *point groups* result from the various possible combinations of symmetry elements with each Bravais lattice. These symmetry operations do not include rotation-translation (screw axis) and reflection-translation (glide plane) operations. When these symmetry operations are included a total of 230 *space groups, i.e.*, a possible group of symmetry operations of infinite objects are obtained. A three-dimensional crystal must belong to any one of these space groups.

Table 4.3 lists the various crystal systems with their axial characteristics, the minimum symmetry elements necessary for each system and some typical examples of substances in the various systems.

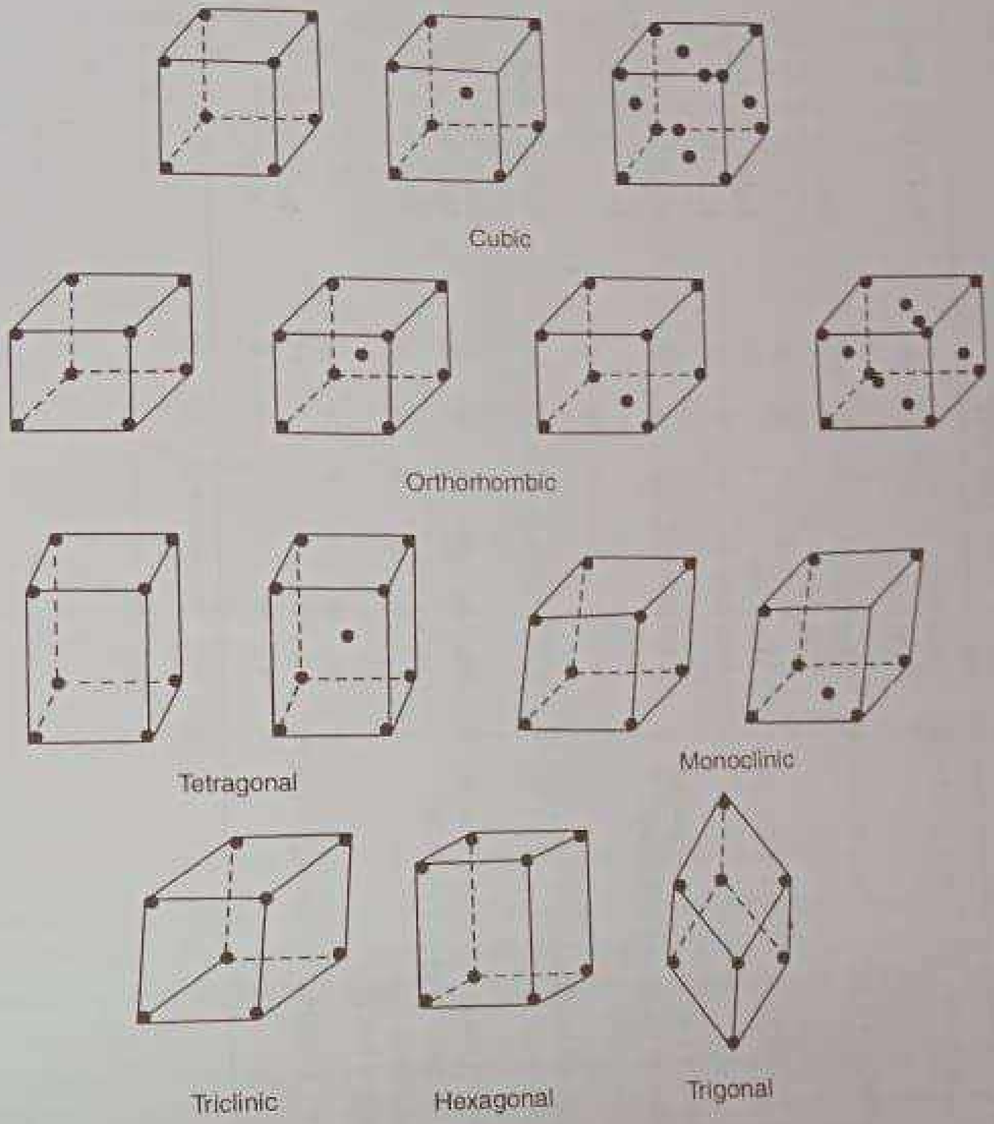


Fig. 4.8 The 14 Bravais lattices

4.5 LATTICE PLANES AND THEIR DESIGNATIONS

The points in a space lattice may be arranged in a large number of ways in a series of parallel and equidistant planes known as the *lattice planes*. In terms of these planes, it is convenient to describe a crystal lattice. The faces of a complete crystal are parallel to these planes containing the largest number of points. To illustrate this statement, consider a simple two-dimensional rectangular crystal lattice as shown in Fig. 4.9. The planes will appear as lines parallel to the z axis. A large number of planes with different orientations AA', BB', CC', DD' etc., are possible with each plane containing some of the lattice points.

The lattice planes are designated in terms of their intercepts on x, y and z axes measured from an arbitrarily-chosen origin. For the set of parallel and equidistant planes AA' (Fig. 4.9), the first plane, makes intercepts of a and b on the x and y axes. Since it is parallel to the z axis, therefore, the intercept on the z axis is infinity. The ratio of the intercepts is $a{:}b{:}\infty$. The next plane makes the intercepts, $2a$, $2b$ and ∞. The ratio is again a simple multiple of a, b and ∞. Hence, this set of planes is designated as

Table 4.3 Crystal Systems, Bravais Lattices and Space Groups in Crystals

System	*Axial characteristic*	*Angles*	*Minimum symmetry*	*Number of space lattices*	*Number of space groups*	*Examples*
1. Cubic	Three axes at right angles; a = b = c	$\alpha = \beta = \gamma = 90°$	Four three fold axes	3	36	NaCl, KCl, CaF_2
2. Tetragonal	Three axes at right angles, only two of equal length; a = b ≠ c	$\alpha = \beta = \gamma = 90°$	One four fold axis	2	68	SnO_2, TiO_2
3. Orthorhombic	Three axes at right angles, but all of different length; a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	Three two fold axes	4	59	$BaSO_4$, KNO_3, K_2SO_4
4. Monoclinic	Three axes, all unequal, two axes at right angles, the third inclined to these at an angle other than 90°; a ≠ b ≠ c	$\alpha = \gamma = 90°$ $\beta \neq 90°$	One two fold axis	2	13	$CaSO_4 \cdot 2H_2O$ $Na_2SO_4 \cdot 10H_2O$
5. Triclinic	Three axes of unequal length, all inclined at angles other than 90°; a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90°$	None	1	2	$CuSO_4 \cdot 5H_2O$
6. Hexagonal	Two axes of equal length in one plane making an angle of 120° with each other and the third axis at right angles to these and of unequal length; a = b ≠ c	$\alpha = \beta = 90°$ $\gamma = 120°$	One six-fold axis	1	27	PbI_2, Mg, Zn, Cd
7. Rhombohedral	Three axes equal, inclined not at right angles; a = b = c	$\alpha = \beta = \gamma \neq 90°$	One three fold axis	1	25	Ice, graphite, Al_2O_3

$a:b:\infty$ planes. Now consider another set of planes BB′ (Fig. 4.9), in which the intercepts on the x, y and z axes are simple integral multiples of $3a$, $2b$ and ∞, respectively. These planes can be denoted as $3a:2b:\infty$ planes. Similarly, for the set of planes CC′ (Fig. 4.9) the intercepts on x axis are multiples of 'a' while the intercepts on y and z axes are infinity as the planes are parallel to these two axes. These planes can be represented as $a:\infty:\infty$ planes.

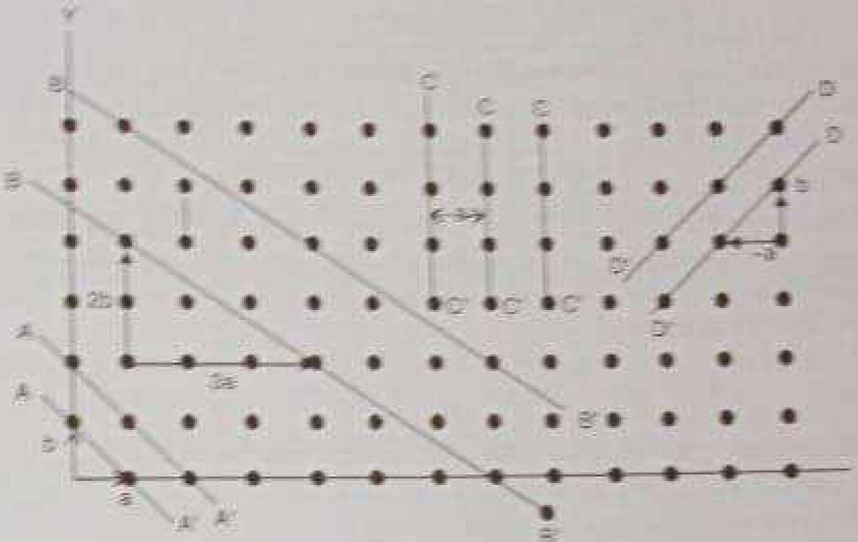


Fig. 4.9 End view of two-dimensional lattice planes

If one moves in the negative direction along an axis from the arbitrarily chosen point, the intercept is given a negative sign. For example, in the set of planes DD′ (Fig. 4.9), the intercepts on x axis in the negative direction are multiples of a while on y axis, these are multiples of b. These planes are referred to as $-a:b:\infty$ planes.

From the above discussions, we see that the intercepts of any plane along the three crystallographic axes are either equal to the ratio of the unit cell intercepts a, b, c or some integral multiples of them, *i.e.*, la, mb and nc where l, m and n are small whole numbers. This is known as *the law of rational indices.* The coefficients of a, b and c are known as the *Weiss indices* and characterize the given set of parallel and equidistant planes in the Weiss system of indexing the planes. The appearance of ∞ in the Weiss system is rather inconvenient and is avoided in the Miller system of indexing the lattice planes. The various steps involved in the inversion of Weiss indices into Miller indices are as follows:

(*i*) The reciprocals of the Weiss coefficients are taken.

(*ii*) The reciprocals are cleared of the fractions, if any.

(*iii*) These are then reduced to the smallest set of integers.

For examples, in the planes $a:b:\infty$, the reciprocals of Weiss indices are $\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty}$ and the Miller indices are written as (110). Similarly, for the set of planes $3a:2b:\infty$, the reciprocals of Weiss indices are $\frac{1}{3}, \frac{1}{2}, \frac{1}{\infty}$ and the Miller indices would be (230). The Miller indices for the set of planes $-a:b:\infty$ are $(\bar{1}10)$ where a bar sign above the number means a negative sign.

In general, the Miller indices of a plane can be expressed as (*hkl*) where *h*, *k* and *l* refer to the reciprocals of the intercepts expressed in units of the lattice distance, *i.e.*,

$$h = \frac{a}{\text{Intercepts of the plane along } x \text{ axis}}$$

$$k = \frac{b}{\text{Intercept of the plane along } y \text{ axis}}$$

and

$$l = \frac{c}{\text{Intercept of the plane along } z \text{ axis}}$$

It is clear that larger the value of a Miller index smaller will be the value of the intercept of the plane along the given axis and when it is zero (the intercept is infinity), the plane is parallel to that axis. Thus, *a* (222) plane has intercepts which are one-half of those of (111) planes. These sets of planes are, however, parallel to each other in space.

The Miller indices (*hkl*) of any plane gives the orientation of the plane in the crystal with reference to its three axes.

Problem 4.2: The planes in a crystalline solid intersect the crystal axes at (2*a*, *b*, *c*), (–*a*, *b*, *c*), (*a*, 2*b*, 3*c*), (3*a*, 2*b*, ∞) and (–*a*, *b*, ∞). Determine the Weiss and the Miller indices for these planes.

Solution: The unit cell intercepts are *a*, *b*, *c*

Intercepts	$2a$	b	c	$-a$	b	c	a	$2b$	$3c$	$3a$	$2b$	c	$-a$	b	∞
Weiss indices	2	1	1	–1	1	1	1	2	3	3	2	1	–1	1	∞
Reciprocal of Weiss indices	$\frac{1}{2}$	$\frac{1}{1}$	$\frac{1}{1}$	$-\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	1	$-\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{\infty}$
Clear fractions	1	2	2	–1	1	1	6	3	2	2	3	6	–1	1	0
Miller indices	(122)			$(\bar{1}11)$			(632)			(236)			$(\bar{1}10)$		

4.6 LATTICE PLANES IN CUBIC CRYSTALS

A cubic system is the simplest type of crystal system where the intercepts on the three axes are equal and all the angles are equal to 90°. In the primitive cubic lattice, the lattice points are present at each corner of the cube. The planes that can pass through the lattice points have Miller indices (100), (110) and (111) as shown in Fig. 4.10 (*a*). The (100) planes have intercepts only on these axis but are parallel to the *y* and *z* axes. The other planes (110) and (111) have intercepts on *x* and *y* axes and *x*, *y* and *z* axes respectively. The perpendicular distance between the adjacent planes is known as the interplanar spacing and is denoted by d_{hkl}. For (100) planes, the interplanar spacing

$$d_{100} = a$$

where *a* is side of the cube.

The spacing between (110) planes, d_{110} is one-half of the diagonal of he square base of the cube as shown in the Fig. 4.10 (*a*). Thus, $d_{110} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$. The spacings between (111) planes d_{111} can be calculated from the fact that two planes pass through the body diagonal of the cube dividing it into three equal parts. The body diagonal of the cube is given as $\left(\sqrt{2}a\right)^2+(a)^2=\sqrt{3}a$. Hence, $d_{111}=\frac{\sqrt{3}a}{3}=\frac{a}{\sqrt{3}}$.

The ratio of the inter-planar spacings, $d_{100}:d_{110}:d_{111}=a:\frac{a}{\sqrt{2}}:\frac{a}{\sqrt{3}}=1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}$

In the face-centered cubic (*fcc*) lattice, the points are present at the centre of each face in addition to those at the corners of the primitive cubic lattice. Hence, parallel planes can be drawn midway between (100) and (110) planes in the primitive cubic lattice [Fig. 4.10 (*b*)]. The Miller indices of these planes are (200) and (220) and the interplanar spacings are $d_{200}=\frac{a}{2}$ and $d_{220}=\frac{a}{2\sqrt{2}}$. Points on faces of the cube are contained in (111) planes of the simple cubic lattice and therefore no additional planes are required.

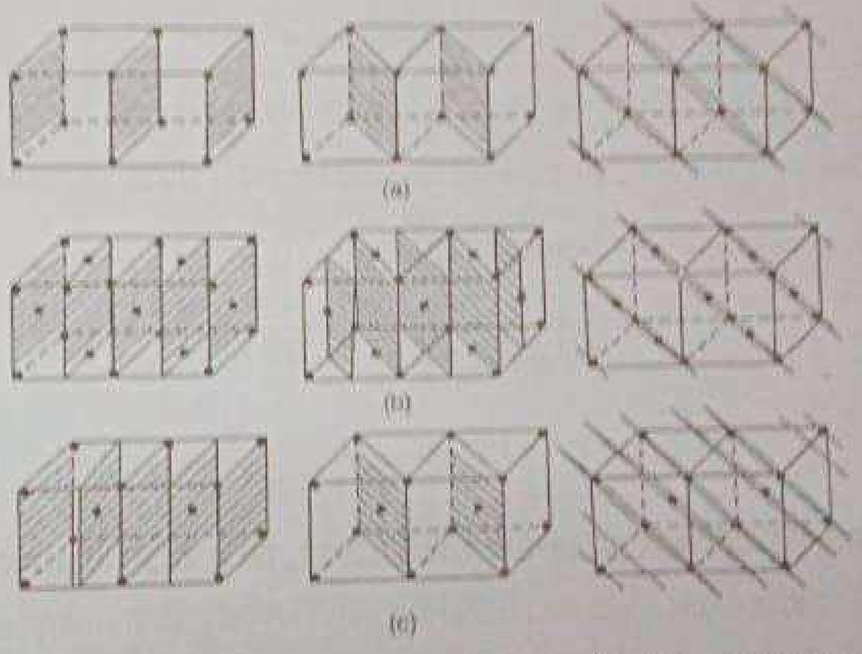


Fig. 4.10 Planes in the three types of cubic lattices (*a*) Planes in simple cubic lattice; (*b*) Planes in face centered cubic lattice; (*c*) Planes in body centered cubic lattice.

Finally in the body-centered cubic (*bcc*) lattice-additional points are present at the centre of each cubic lattice. As can be seen from the [Fig. 4.10 (*c*)], parallel planes with Miller indices (200) can be drawn midway between (100) planes; (222) planes can be drawn half-way between (111) planes in the simple cubic lattice. No additional plane is required in (110) planes as the body centered point is contained in this plane. The inter-planar spacings between d_{200} and d_{222} are

$$d_{200}=\frac{a}{2}$$

and

$$d_{222}=\frac{a}{2\sqrt{3}}$$

Table 4.4 gives the ratios of d_{hkl} for different cubic lattices.

Table 4.4 Ratios of d_{hkl} for Cubic Lattices

Simple cubic lattice	$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$
Face-centered cubic lattice	$d_{200} : d_{220} : d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 1.154$
Body-centered cubic lattice	$d_{200} : d_{110} : d_{222} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : 1.414 : 0.577$

In general, the interplanar spacing (d_{hkl}) between the planes hkl in a cubic lattice in given as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \text{...(4}$$

where a is the side of the cube.

Problem 4.3: Determine the interplanar spacing between the (221) planes of a cubic lattice of lengt 4.5Å (450 pm).

Solution: In a cubic lattice, the interplanar spacing d_{221} is given by

$$d_{221} = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}} = \frac{4.5}{(4 + 4 + 1)^{1/2}} \text{ Å}$$

$$= 1.5 \text{ Å} = 150 \text{ pm}$$

4.7 ASSIGNMENT OF ATOMS PER UNIT CELL IN A CUBIC LATTICE

In a primitive cubic lattice where atoms are present at the corners only, each atom at the corner is shared equally by eight other units cells. Hence the contribution of each atom to the unit cell is $\frac{1}{8}$ and the total number of atoms per unit cell is $8 \times \frac{1}{8} = 1$.

A face atom is shared equally between two unit cells and therefore a face atom contributes only $\frac{1}{2}$ to the unit cell. The number of atoms per unit cell in an *fcc* lattice is

contribution of 6 face atoms $= 6 \times \frac{1}{2} = 3$

contribution of 8 corner atom = $8 \times \frac{1}{8} = 1$

thus giving a total of 4 atoms per unit cell.

In a bcc lattice, the body-centered atom belongs exclusively to the unit cell. The total number of atoms per unit cell is two as shown below:

Contribution from corner atoms = $8 \times \frac{1}{8} = 1$

and from the body centre = 1

An edge atom is common to four unit cells and there are twelve edges of the unit cell. The contribution from each edge atom is therefore $\frac{1}{4}$ and the total from 12 edges is $12 \times \frac{1}{4} = 3$. The number of atoms per unit cell in such cases is therefore four (three from 12 edges and 1 from eight corners).

The summary of the above results is given in Table 4.5.

Table 4.5 Number of Atoms per Unit Cell in Cubic Lattices

Type of lattice	Location of atoms	Portion in the unit cell	Number of atoms in the unit cell
Primitive	Corner	$\frac{1}{8}$	1
Face centered	Face centre	$\frac{1}{2}$	4
Body centered	Body centre	1	2
Edge centered	Edge centre	$\frac{1}{4}$	4

Problem 4.4: In an fcc arrangement, the corner atoms are *A* type and those at the face centres are *B* type. What is the simplest formula of the compound?

Solution: Number of *A* type atoms in the unit cell = 1
Number of *B* type atoms in the unit cell = 3
Hence, the formula is AB_3

Problem 4.5: In an fcc lattice of *A* and *B*, *A* type atoms are present at the corners while *B* types are at face centres. If in each unit cell, one of the *A* type atom is missing from the corner, what is the simplest formula of the compound?

Solution: Number of atoms of *A* type in the unit cell = $\frac{7}{8}$
Number of atoms of *B* type in the unit cell = 3
Hence, the formula is $A_{7/8}B_3$ or A_7B_{24}

4.8 DIFFRACTION OF X-RAYS BY CRYSTALS

Ewall in 1911 showed that when light falls on an object which is of the same size as the wavelength radiation, it is diffracted. This fact is usually investigated by means of a diffraction grating which consists of a large number of fine, equidistant and parallel lines drawn on the metal or some other material. When monochromatic radiation falls on a diffraction grating, it is diffracted and a large number of images of different intensities are formed. If two diffracted waves are in the same phase, a constructive interference results and a series of bright spots would be observed on a screen placed on the path of the diffracted waves. On the other hand, if the waves are out of phase, a destructive interference would result and dark spots would be observed on the screen (Fig. 4.11). The condition for constructive interference is that the path difference for the two waves must be an integral multiple of wavelength.

X-rays are electromagnetic radiations of short wavelength of the order of 0.1 nm. The wavelength is comparable with the spacings of atoms in crystals. This led M. von Laue to suggest that crystals can act as three-dimensional diffraction grating to X-rays. This was confirmed experimentally by Friendrich and Knipping. They passed a beam of homogeneous X-ray through a crystal of zinc blende. The resulting radiation when allowed to fall on a photographic plate, a definite diffraction pattern was obtained.

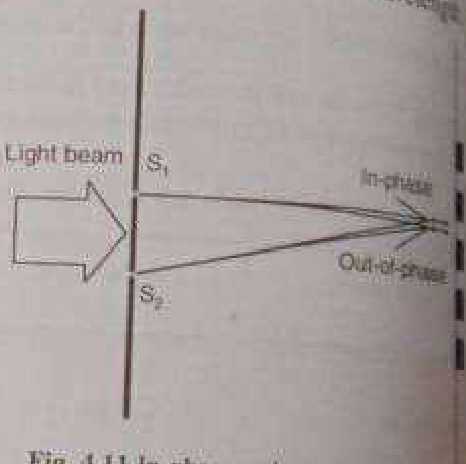


Fig. 4.11 In-phase and out-of-phase waves

If there are two waves starting from a common source, their phase difference will be directly proportional to their path difference. A pattern of this type is generally referred to as a Laue photograph or Laue pattern. From the Laue's pattern it is possible to arrive at the size, shape and the detailed information regarding the position of atoms in a crystal.

The important discovery that a crystal could behave as a three-dimensional diffraction grating to X-rays led W.H. Bragg and W.L. Bragg to use X-ray for the purpose of studying the internal structure of crystals.

4.9 THE BRAGG EQUATION

Since a crystal may be regarded as consisting of a large numbers of parallel and equidistant atomic planes, Bragg considered that the diffraction effects observed for X-ray could be represented as reflection of X-ray by successive planes of atoms in the crystal. Thus, when X-rays are incident on a crystal face they penetrate into the crystal and are scattered by the atoms or ions. Consider a set of parallel and equidistant planes *AA*, *BB*, etc. in the crystal as shown in Fig. 4.12. These planes characterize the arrangement of the atoms or ions in the crystal. A parallel beam of monochromatic X-ray of wavelength λ strikes these planes at an angle of incidence θ. Some of the rays will be reflected by atoms from the upper layer *AA*, with angle of reflection being equal to the angle of incidence. Some of the rays will be absorbed and some will be reflected from the second layer *BB* and so on with the successive layers. When the rays reflected from the successive layers are in phase, constructive interference will occur and a bright diffraction spot would be obtained from these planes. The condition for the constructive interference is that the path difference between the reflected rays from successive planes must be an integral multiple of wavelength, λ. The condition for reinforcement can be obtained as follows.

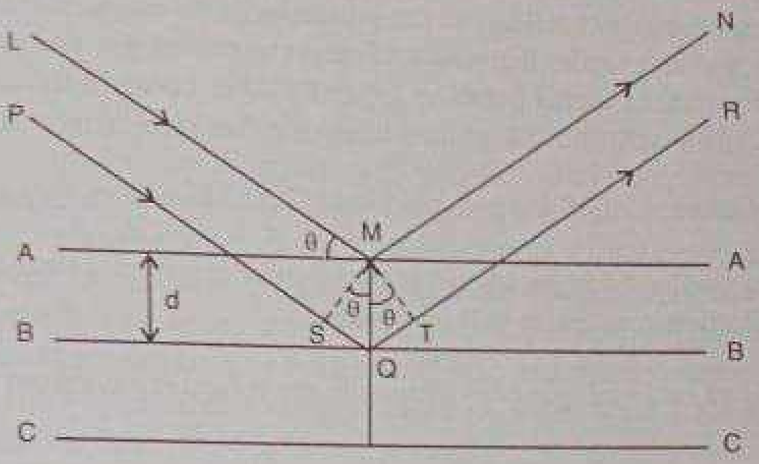


Fig. 4.12 X-ray reflection from equidistant planes

The path difference for *LMN* and *PQR* is equal to *SQ* + *QT*, where *MS* and *MT* are perpendiculars drawn from *M* to *PQ* and *QR*, respectively. If *d* is the interplanar spacing between the successive planes, then both SQ and QT are equal to *d* sinθ, since the angles *SMQ* and *QMT* are each equal to θ. The total path difference in thus 2*d* sinθ. For a reflection of maximum intensity, this quantity must be an integral number (*n*) of wavelength (λ), as stated above. Hence, the condition for maximum reflection is

$$n\lambda = 2\, d_{hkl} \sin\theta \qquad ...(4.2)$$

Equation 4.2 is known as the *Bragg equation* and gives the relationship between the interplanar spacing d_{hkl} and the angle at which the reflected radiation has maximum reflection for a given wavelength λ. The value of *n* gives the order of reflection. If $n = 1$, the order of reflection is one, if $n = 2$, the reflection is second order and so on. For a given value of *d* and λ, there may be a number of values of angle of incidence, θ_1, θ_2... corresponding to $n = 1, 2$...at which maximum reflection will occur. From eq. (4.2), it is clear that higher-order reflection will be obtained for larger values of θ. In case $\lambda >> 2d$, there is no solution for *n* and hence no diffraction would result. In other words, the light would pass through the crystal without diffraction by the planes. If $\lambda << d$, the rays are diffracted through small angles, and thus the Bragg equation does not indicate the intensities of the various diffracted rays. For higher intensities of diffracted rays, the angle of reflection should be small.

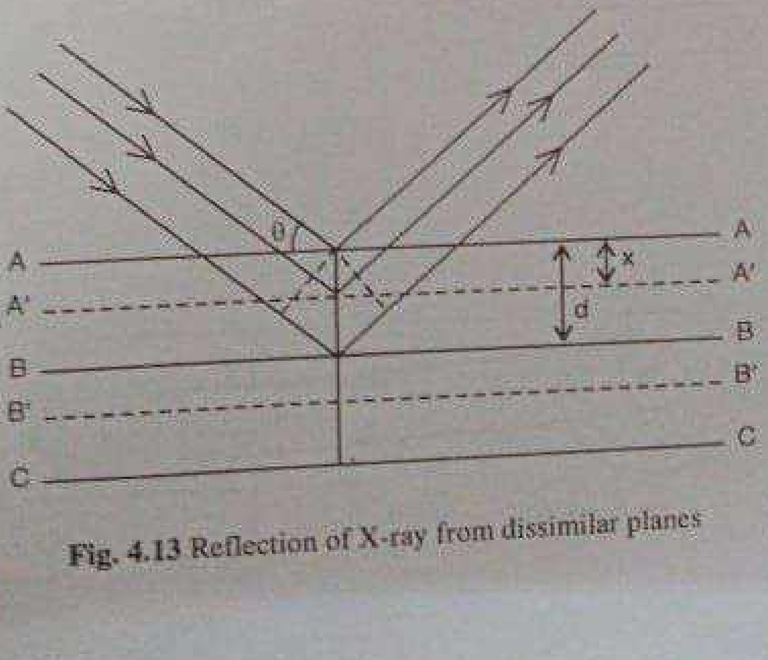


Fig. 4.13 Reflection of X-ray from dissimilar planes

The above treatment considers reflection from identical sets of planes. For reflection from tw different sets of planes, let us consider that one set is represented by *AA*, *BB*, etc. and another by *A'A'*, *B'B'* etc. (Fig. 4.13). If *x* is the distance between *AA* and *A'A'* or between *BB* and *B'B'* and $n\lambda$ the pa difference for the rays from *AA* and *BB* planes, then for the same angle of incidence θ, the pa difference for the rays from *A'A'*, *B'B'*, etc. planes is $\frac{xn\lambda}{d}$. If this is also an integral multiple of wavelength, then the rays reflected from *AA*, *BB* planes will be reinforced by the rays from *A'A'* or *B'B'* planes and a strong reflection maximum will be observed.

However, if $\frac{xn\lambda}{d}$ is an odd multiple of wavelength, the reflected rays from *AA* will be opposed by those from *A'A'*. If $x = d/2$ the path difference is $\frac{n\lambda}{2}$, it means odd order spectra will be missing; and if $x = \frac{d}{4}$, the path difference is $\frac{n\lambda}{4}$ indicating that second, sixth, tenth, etc. order spectra will also be weak.

4.10 EXPERIMENTAL METHODS OF CRYSTAL ANALYSIS

(*a*) **Bragg X-ray spectrometer:** It is evident from Bragg equation that if the angles of incidence θ are measured for the various orders of maximum reflection, the interplanar spacing *d* between the successive planes of a given type of crystal can be calculated, provided the wavelength λ of the X-ray is known. The reflection angle θ and the intensities of the reflected beams corresponding to these angles can be determined with a Bragg X-ray spectrometer shown in Fig. 4.14. The X-rays generated in X-ray tube are passed through a series of slits to give a sharp and monochromatic beam. The beam is then directed to strike the face of a crystal which is mounted on a graduated rotating table. The latter may be rotated to any desired angle of incidence. The rays reflected from the crystal are then allowed to pass through a detector known as an *ionizing chamber* filled with vapours of methyl bromide. The chamber is rotated

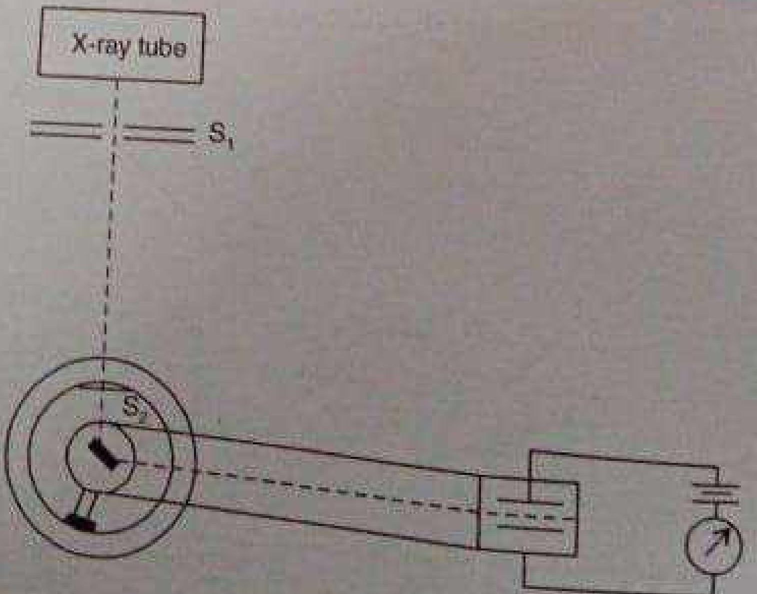


Fig. 4.14 Bragg X-ray spectrometer

coaxially with the crystal table. The crystal table and the chamber are so adjusted that when the crystal rotates through any angle, the chamber rotates at twice that angle so that the reflected rays always enter the chamber. The extent of ionization produced by the reflected beam is measured by the electrometer.

The value of incident angle θ is gradually increased by rotating the table. The intensities of the reflected X-rays for various angles are determined. Strong reflections are obtained from those planes which contain larger number of atoms and for those values of θ which satisfy the Bragg equation. The process is repeated for each plane of the crystal. The intensities of the reflected rays are plotted against twice the angle of incidence of the beam to the crystal and the lines are indexed.

(b) **The Powder Method:** This simple method for obtaining X-ray diffraction data was developed by Debye and Scherrer in 1916 and later by Hull in 1917. In this method instead of scattering X-rays from a single crystal, a finely-powdered sample is taken in a thin-walled glass capillary tube and is irradiated by a monochromatic beam of X-rays. In the powder, the crystal planes are randomly oriented in all possible directions. The sample is considered to be equivalent to a large number of single crystals

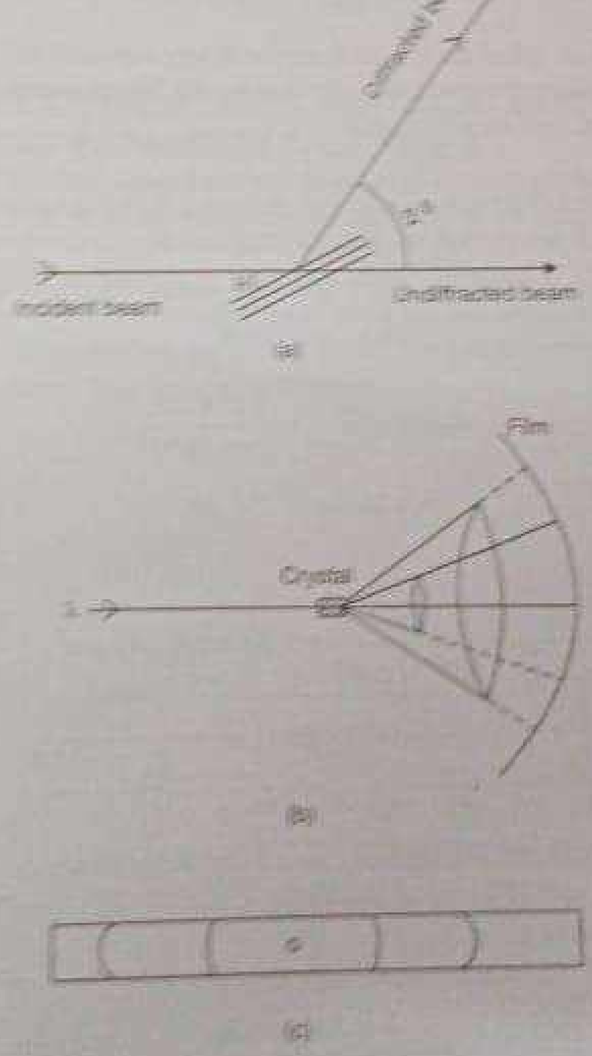


Fig. 4.15 Powder method (a) Angle between the diffracted and undiffracted beams; (b) Cone of diffracted beams; (c) Appearance of the photographic film

with all possible orientations. Out of these, some will be so oriented so as to satisfy the Bragg for a given set of planes. Another set of crystals will be oriented so that the Bragg condition is for another set of planes, and so on. Consider a set of parallel planes making an angle θ with incident beam of X-rays as shown in Fig. 4.15(*a*). The reflected ray from these planes will make angle of 2θ with the unreflected beam. When a given set of planes satisfying the Bragg rotated about the axis of the beam, the reflected ray will outline a cone of scattered radiation. The reflections may be recorded on a photographic film. If the strip of the film is curved into a cylinder then the different planes will intercept the film as curved or straight lines [Fig. 4.15(*c*)]. On a flat the observed pattern consists of a series of concentric circles.

After obtaining the powder pattern the lines are indexed. The distance x of each line from the central spot in measured, usually by halving the distance between the two reflections on either side of the centre. If r is the radius of the film, then its circumference $2\pi r$ corresponds to a scattering angle of 360°. Then

$$\frac{x}{2\pi r} = \frac{2\theta}{360}$$

Hence from this, one can calculate θ, and from the Bragg equation the interplanar spacing. The method is useful for crystal systems that have only one or two lattice parameters to be determined, cubic, tetragonal, hexagonal and rhombohedral.

Problem 4.6: A certain solid crystallizes in the body centered cubic lattice. First order X-ray (λ = 0.154 nm) reflection maximum from a set of (200) planes was observed at 16°6′. Calculate the edge length of the unit cell.

Solution: For a first order reflection, $n = 1$ and from Bragg equation, we have

$$\lambda = 2d_{200} \sin\theta$$

or

$$d_{200} = \frac{\lambda}{2\sin\theta} = \frac{0.154 \text{ nm}}{2\sin 16°6'}$$

$$= 0.28 \text{ nm} = 280 \text{ pm}$$

For a cubic lattice

or

$$d_{200} = \frac{a}{\sqrt{2^2+0+0}} = 0.28 \text{ nm} = 280 \text{ pm}$$

$$a = 2 \times 280 \text{ pm}$$

$$= 560 \text{ pm}$$

Problem 4.7: From (100), (110) and (111) planes first order reflection maxima for potassium chloride were observed with X-ray (λ = 0.154 nm) at the Bragg angle 11°27′, 16°30′ and 20°7′. Ascertain the crystal structure of potassium chloride.

Solution: For a first order reflection, we have

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

$$d_{hkl} = \frac{\lambda}{2\sin\theta}$$

For a given value of λ, d_{hkl} is therefore inversely proportional to $\sin\theta$. Hence,

$$d_{100} : d_{110} : d_{111} = \frac{1}{(\sin\theta)_{100}} : \frac{1}{(\sin\theta)_{110}} : \frac{1}{(\sin\theta)_{111}}$$

$$= \frac{1}{\sin 11°27'} : \frac{1}{\sin 16°30'} : \frac{1}{\sin 20°7'}$$

$$= \frac{1}{0.1986} : \frac{1}{0.2840} : \frac{1}{0.3440}$$

$$= 5.035 : 3.522 : 2.907$$

$$= 1.0 : 0.707 : 0.577$$

As the ratio corresponds to that for a simple cubic lattice hence potassium chloride belongs to a simple cubic lattice.

4.11 INDEXING OF LATTICE PLANES IN A CUBIC SYSTEM – STRUCTURE OF SODIUM AND POTASSIUM CHLORIDES

From external geometry, it is known that sodium and potassium chlorides belong to the cubic system. The experimental data can be used to investigate whether a cubic crystal is primitive, body centered, or face centered. For this purpose, intensity of the reflected X-ray beam is plotted against twice the angle of incidence (θ). A series of reflection maxima (Fig. 4.16) are obtained. The planes in the crystal responsible for producing these maxima are then indexed. The results are compared with those expected for these three types of lattices. This is done as follows:

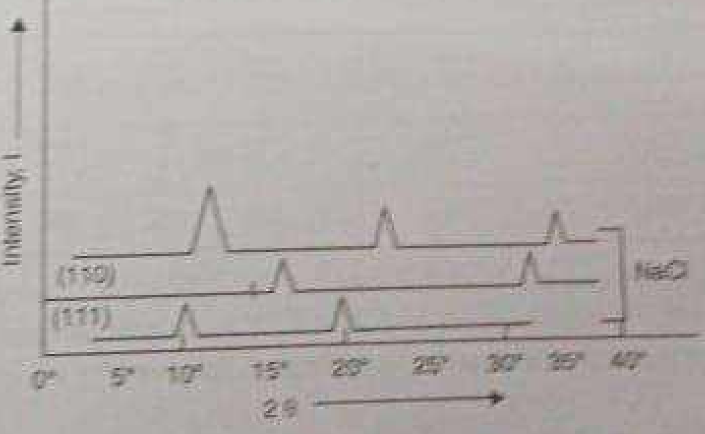


Fig. 4.16 Typical diffraction pattern; plot of I versus 2θ

For a cubic crystal, the interplanar spacing, d_{hkl} is given by

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

or

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

From the Bragg law we have

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

or

$$d_{hkl}^2 = \frac{\lambda^2}{4\sin^2\theta}$$

From Eq. (4.3) and (4.4), we obtain

$$\frac{\lambda^2}{4\sin^2\theta} = \frac{a^2}{h^2 + k^2 + l^2}$$

or

$$\sin^2\theta = \left(\frac{\lambda}{2a}\right)^2 \left(h^2 + k^2 + l^2\right) = K\left(h^2 + k^2 + l^2\right)$$

where

$$K = \frac{\lambda^2}{4a^2}$$

Equation 4.5 can be used to predict the diffraction patterns for the three types of cubic [illegible]. These are discussed below:

(1) **Primitive cubic lattice:** By assigning consecutive integral values (0, 1, 2...) to h, k and l, we can calculate a series of values of d_{hkl} and $\sin^2\theta$ from equations 4.3 and 4.5, respectively. These are listed in Table 4.6.

Table 4.6 Interplanar Distances and the Corresponding Expected Angles of Diffraction for a Primitive Cubic Lattice

hkl	100	110	111	200	210	211	220	300	310	311	222	[illegible]
d_{hkl}	a	$\frac{a}{\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$	$\frac{a}{\sqrt{5}}$	$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{3}$	$\frac{a}{\sqrt{10}}$	$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$	[illegible]
$\sin^2\theta$	K	2K	3K	4K	5K	6K	8K	9K	10K	11K	12K	[illegible]

It may be noted that $\sin^2\theta$ can not have the value of 7K, 15K, 23K... because there is no way [illegible] integers 7, 15, 23 can be written in the form $h^2 + k^2 + l^2$. Thus, a plot of intensity of reflected X-rays versus $\sin^2\theta$ yield a set of six lines which are equally spaced, followed by a gap and then another [illegible] of lines.

(2) **Body-centered lattice:** In the case of a body centered cubic crystal (Fig. 4.30), midway between (100) planes are (200) planes. X-rays reflected from (100) planes will be in phase and reinforce each other. However, the rays reflected from the planes lying midway between the (100) planes are opposed by half a wave-length and are exactly out of phase with those originating from (100) planes. If all the lattice atoms are identical or have equal scattering power, the observed intensity from (100) planes will be zero and a reflection maximum from (100) would be missing.

The (200) and (110) planes however include all the atoms and hence produce sharp reflection maxima.

In case of (111) planes, no reflection maximum will be observed as midway between them are planes which destructively interfere with the reflections from (111) planes. The (222) planes will reinforce each other. It may be stated that for a body-centered cubic crystal, reflection from planes for which *$h + k + l$ is odd are not observed.* The observed diffraction lines at angles are given in table 4.7.

Table 4.7 Angles at which Diffraction Lines are Observed for a Body-centered Cubic Lattice

hkl	100	110	111	200	210	211	220	300 221	310	311	222	320
d_{hkl}	–	$\frac{a}{\sqrt{2}}$	–	$\frac{a}{2}$	–	$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$	–	$\frac{a}{\sqrt{10}}$	–	$\frac{a}{\sqrt{12}}$	–
$\sin^2\theta$	–	2K	–	4K	–	6K	8K	–	10K	–	12K	–

(3) **Face-centered lattice:** For a face-centered lattice,it may be seen (Fig. 4.10) that the reflection maxima from (100), (110) planes will be missing in the case of a face-centered cubic crystal. However, reflection maxima will be observed for rays from planes (200), (220), (111) etc. In fact, reflection maxima will be observed from planes for which *hkl* are **either all odd or all even.** The observed diffraction lines at angles are given in table 4.8.

Table 4.8 Angles at which Diffraction Lines are Observed for a Face-centered Cubic Lattice

hkl	100	110	111	200	210	211	220	221 300	210	311	222
d_{hkl}	–	–	$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$	–	–	$\frac{a}{2\sqrt{2}}$	–	–	$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$
$\sin^2\theta$	–	–	3K	4K	–	–	8K	–	–	11K	12K

Table 4.9 Calculated and Observed Diffraction Maxima for Cubic Crystals

	100	110	111	200	210	211		220	300	310	311
$h^2 + k^2 + l^2$	1	2	3	4	5	6	Missing	8	9	10	11
Primitive cubic	√	√	√	√	√	√		√	√	√	√
Body centred cubic	×	√	×	√	×	√		√	×	√	×
Face centred cubic	×	×	√	√	×	×		√	×	×	√
Potassium chloride	×	×	×	√	×	×		√	×	×	×
Sodium chloride	×	×	√	√	×	×		√	×	×	√

The calculated reflection maxima for the three types of cubic lattices and the observed reflection maxima obtained by comparing sin θ values are given in Table 4.9. The (✓) mark indicates that reflection maximum will be observed while the cross (×) shows the absence of reflection maximum.

It is found that sodium chloride belongs to the face-centered cubic lattice while potassium chloride has a simple cubic lattice. The reason why identical alkali halides such as sodium and potassium chlorides should differ in their crystal structure is due to the fact that both K^+ and Cl^- ions contain 18 electrons and thus have identical scattering powers. X-rays, therefore, do not distinguish these ions. On the other hand, in sodium chloride, the scattering power of Na^+ (having 10 electrons) is different from that of chloride ion (18 electrons).

The crystal lattice of sodium chloride is shown in Fig. 4.27. It consists of two interpenetrating face-centered cubic lattices of sodium and chloride ions. Each sodium ion is surrounded octahedrally by six chloride ions and each chloride ion in turn is surrounded octahedrally by six sodium ions. Thus, the chloride ion at the centre of the unit cell is surrounded by six equidistant sodium ions: four in the same plane one above and one below it. In this structure (100) or (110) planes contain equal number of both types of ions but (111) planes have either all sodium or chloride ions. The X-rays reflected from successive (111) planes containing sodium ions are destructively interfered by the rays from successive (111) planes containing chloride ions. Hence, the first order reflection from (111) planes will be comparatively weak in sodium chloride. In the case of potassium chloride reflection maximum from (111) planes would be missing as mid-way between (111) planes is another set of planes which would cause destructive interference.

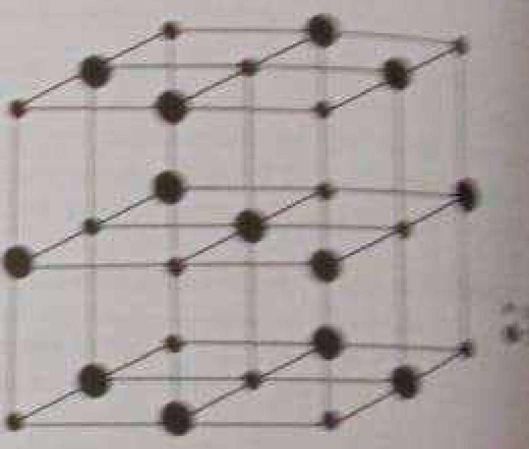


Fig. 4.27 Face-centred cubic lattice of sodium chloride

Caesium chloride structure: CsCl has a body-centered cubic structure in which each Cs^+ ion is surrounded by eight Cl^- ions which is turn is surrounded by eight Cs^+ ions (Fig. 4.28).

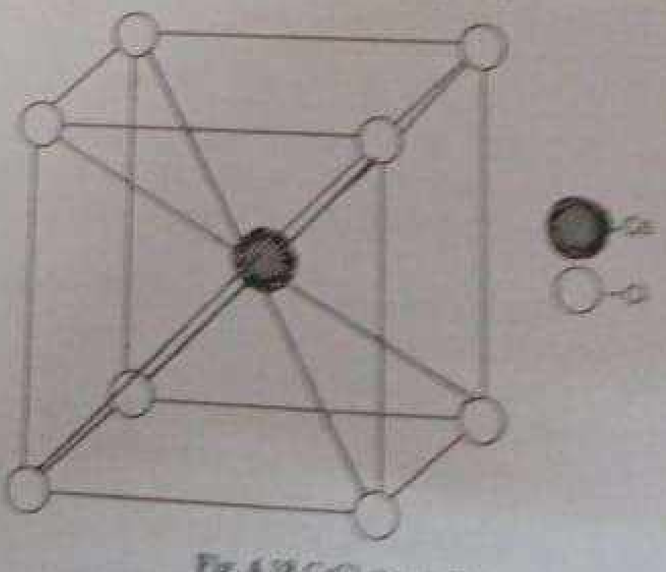


Fig. 4.28 CsCl structure

Problem 4.8: An X-ray (λ = 0.1785 nm or 178.5 pm) powder photograph of a cubic crystalline solid was taken. Reflection maxima were observed at the following Bragg angles: 18.5°, 27.0°, 33.7°, 40.0°, 45.9° and 51.9°. Index the planes and indicate the type of the cubic lattice. Calculate the unit cell dimension, *a*.

Solution: For a cubic lattice we have, $\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2)$

θ	18.5	27.0	33.7	40.0	45.9	51.9
$\sin\theta$	0.3173	0.4540	0.5534	0.6428	0.7181	0.7869
$\sin^2\theta$	0.1007	0.2062	0.3062	0.4132	0.5157	0.6193

Dividing by the common factor 0.0515, we get the values of $h^2+k^2+l^2$ which are approximately as

2 4 6 8 10 12

These correspond to *hkl* values of (110), (200), (211), (220), (310) and (222). The sum of *h*, *k* and *l* values is even in each case showing that the unit cell belongs to the body-centered cubic arrangement.

The larger Bragg angles can be measured more accurately than the smaller one, so a more accurate value for θ is 51.9°; the value of $\frac{\lambda^2}{4a^2}$ may be found by dividing $\sin^2\theta$ by 12

$$\frac{\lambda^2}{4a^2} = \frac{0.6193}{12}$$

Hence,

$$a^2 = \frac{(0.1785\text{ nm})^2}{4 \times 0.6193}$$

$$= 0.3928\text{ nm}$$

$$= 392.8\text{ pm}$$

4.12 DENSITY FROM CUBIC LATTICE DIMENSION

The density of the crystal can be measured accurately from experiments and it can be compared calculated for its structure. The density based on the structure can be calculated from the mass contained in a unit cell and its volume. If *a* is the edge length of the unit cell, then its volume is a^3.

The mass of an atom of substance is obtained by dividing the mass of one mole atom (*M*) by Avogadro constant, N_A *i.e.*

$$\text{Mass of an atom} = \frac{M}{N_A}$$

The density of the crystal $d = \frac{Mz}{N_A a^3}$

where *z* is the number of atoms per unit cubic cell.

(*i*) For a simple (primitive) cubic cell, atoms are present at the corners of the cube. There are eight corners of a cube and thus eight atoms are present at these corners. Therefore, the number of atoms associated with a single primitive unit cell is $8 \times \frac{1}{8} = 1$. Therefore the density of a primitive cubic cell is $\frac{M}{N_A a^3}$.

(*ii*) In a body-centered cubic unit cell (bcc), there are atoms at the eight corners and one atom in the centre of the cube. Therefore, the number of atoms per unit cell are $\left[\left(8 \times \frac{1}{8}\right) + 1\right] = 2$. Thus, the density of a body-centered cubic cell $= \frac{2M}{N_A a^3}$.

(*iii*) In a face-centered cubic cell (*fcc*), besides eight atoms at the corners, there are six atoms at the centres of six faces. Each of these atoms is shared between two such unit cells. Therefore, the net atoms per unit cell is $\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$. Hence, the density of an *fcc* cell $= \frac{4M}{N_A a^3}$

Problem 4.9: Copper crystallizes in the *fcc* pattern. From X-ray diffraction the edge length of the unit cell has been found to be 0.360 nm (360 pm). If the density of copper is 8.94×10^3 kg m^{-3}, calculate the value of N_A.

Solution: The lattice is *fcc*, hence the number of atoms per unit cell is 4. The edge length of the unit cell is 0.360 nm and its volume is

$$...(360 \times 10^{-12} \text{m})^3 = 4.66 \times 10^{-29} \text{m}^3$$

Now mass of 4 copper atoms is

$$\frac{4 \times 63.54}{N_A} \times 10^{-3} \text{ kg mol}^{-1}$$

$$\text{Hence, the density } = \frac{4 \times 63.54 \times 10^{-3} \text{kg mol}^{-1}}{N_A \times 4.66 \times 10^{-29} \text{m}^3}$$

$$\text{But the density is} \qquad 8.94 \times 10^3 \text{kg m}^{-3}$$

Therefore,

$$8.94 \times 10^3 \text{ kg m}^{-3} = \frac{4 \times 63.54 \times 10^{-3}}{N_A \times 4.66 \times 10^{-29}} \text{kg mol}^{-1}\text{m}^{-3}$$

or

$$N_A = \frac{4 \times 63.54 \times 10^{23}}{8.94 \times 4.666} \text{mol}^{-1}$$

$$= 6.095 \times 10^{23} \text{ mol}^{-1}$$

Problem 4.10: Silver crystallizes in the cubic lattice. The density is found to be 10.7 g cm^{-3}. If the unit cell length is 0.406 nm, calculate the number of atoms per unit cell. Suggest the unit cell type.

Solution: If z is the number of atoms of silver per unit cell, then the density is given by

$$\frac{z \times 108 \times 10^{-3}\,\text{kg mol}^{-1}}{\left(6.023 \times 10^{23}\,\text{mol}^{-1}\right)\left(406 \times 10^{-12}\,\text{m}\right)^3}$$

and it is equal to 10.7×10^3 kg m^{-3}.

Hence $$z = \frac{\left(10.7 \times 10^3\,\text{kg m}^{-3}\right)\left(6.023 \times 10^{23}\,\text{mol}^{-1}\right)\left(4.06 \times 10^{-10}\,\text{m}\right)^3}{\left(108 \times 10^{-3}\,\text{mol}^{-1}\right)}$$

$$= 4.024$$

The number of atoms per unit cell is 4. The lattice is therefore an *fcc* type.

Problem 4.11: A certain solid X (at. mass 27) crystallizes in the *fcc* arrangement. if the density of X is 27 g cm^{-3}. What is the unit cell length?

Solution: There are four atoms of X in the unit cell and the mass of these atoms is given by

$$\frac{4 \times 27}{N_A}\,\text{g}$$

If a is the unit cell length, then the volume of the unit cell is a^3 and its density is

$$\frac{4 \times 27}{N_A a^3}\,\text{g cm}^{-3}$$

But the density as given is 2.7 g cm^{-3}, hence

$$\frac{4 \times 27}{N_A a^3} = 2.7$$

or $$a^3 = \frac{27 \times 4}{2.7\,N_A}$$

or $$a = \left(\frac{27 \times 4}{2.7 \times 6.023 \times 10^{23}}\right)^{1/3}\text{cm}$$

$$= 4.049 \times 10^{-8}\,\text{cm}$$

$$= 4.049 \times 10^{-10}\,\text{m} = 404.9\ \text{pm}$$

Problem 4.12: A closed-packed structure of uniform spheres has a cubic unit cell with side 0.8 nm. What is the radius of the spherical molecule?

Solution: The unit cell has an *fcc* structure. Here the spheres are touching each other along the face diagonal. If f is the radius of the sphere and a the side of the unit cell, then

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

$$r = \frac{a}{2\sqrt{2}} = \frac{0.8\ \text{nm}}{2\sqrt{2}} = 0.2828\ \text{nm} = 282.8\ \text{pm}$$

4.13 CLOSEST PACKING

In crystals, the atoms, ions or molecules are arranged in a regular way in three-dimensional space. The arrangement has minimum energy and hence maximum stability. For maximum stability, a constituent in the aggregate must be surrounded by the maximum number of neighbours. For maximum number of contacts, each constituent of the crystal must by packed as closely as possible. However, if the constituents are spheres of the uniform size, then the problem reduces to arranging the uniform spheres in three-dimensional space. In a two-dimensional plane, the closest arrangement being that in which each sphere is in contact with six other spheres (Fig. 4.19). Let us denote this layer of spheres by *A*. To obtain the closest packing in space, the spheres are placed over the layer *A* in a regular manner. There are six vacant sites or triangular pockets around any sphere in layer *A*. In Fig. 4.19 around a sphere *X* these sites are labelled as 1, 2, 3, 4, 5 and 6. We can place only three spheres touching each other in alternate vacant sites, e.g., either in 1, 3 and 5 or in 2, 4 and 6. Suppose the second layer is constructed by placing the spheres in the vacant sites labelled as 1, 3 and 5 then the sites marked 2, 4 and 6 are left unoccupied. Let us denote the second layer of spheres by *B*. The second layer again has two types of vacant sites. Around any atom in the second layer (Fig. 4.19), one set of vacant sites lies just above the vacant sites 2, 4 and 6 of the first layer and the other set lies above the centres of the spheres of the first layer. Thus, after the second layer is complete, there are two different ways of placing the spheres in the third layer. If the spheres in the third layer are placed in the vacant sites which are above the centres of the spheres

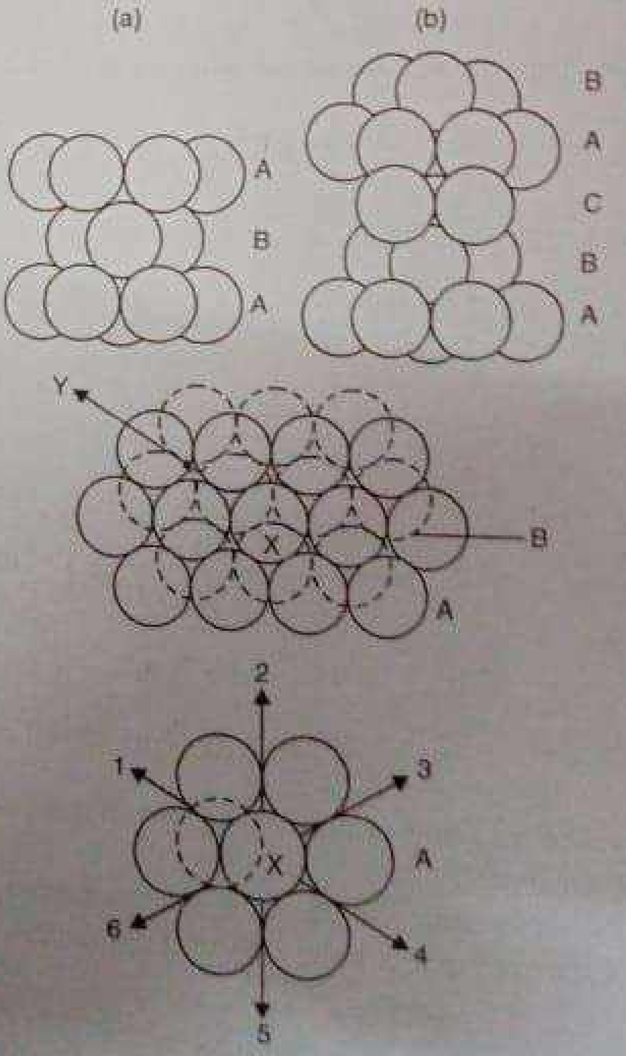


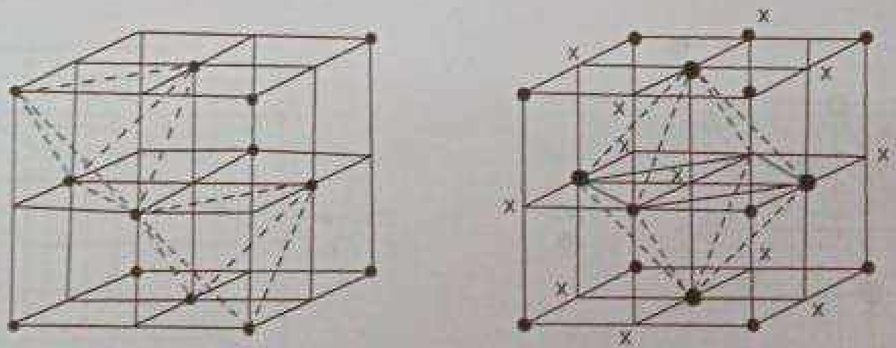
Fig. 4.19 Close-packed structures (*a*) Hexagonal closest packing; (*b*) Cubical closest packing

of the first layer, then the third layer repeats the arrangement of the first layer and we have only two types of layers, viz., *ABAB*......etc. This is called *a hexagonal closest packing, hcp* [Fig. 4.19(*a*)]. On the other hand, if the spheres are placed in the vacant sites above 2, 4 and 6, a new arrangement (*C*) of the spheres is produced [Fig. 4.19(*b*)]. The entire arrangement is now of the type *ABCABC*......etc., and is referred to as *a cubical closest packing, ccp or face-centered cubical closest packing, fcc.*

The number of nearest neighbours (known as the *coordination number*) in each arrangement is twelve: six in the same layer, three in the layer above and three in the layer below it.

In the *fcc* structure, there are two types of vacant sites or holes: *tetrahedral and octahedral*. A tetrahedral hole is surrounded by four spheres while an octahedral hole is the empty space surrounded by six spheres. These vacant sites can accommodate other smaller atoms or molecules giving rise to a variety of different structures.

In an *fcc* structure, there are eight tetrahedral holes per unit cell as shown in Fig. 4.20 (*a*). The number of octahedral holes in the unit cell of the *fcc* structure is four as can be deduced from the following considerations. In Fig. 4.20(*b*), each (X) mark represent a vacant site and there are twelve such vacant sites at the edges of unit cubic lattice. The vacancy at an edge is common to four unit cells and hence the number of such vacant sites per unit cell is $\frac{12}{4} = 3$. In addition to these vacancies, there is one octahedral hole at the centre of the unit cell. Thus, the total number of octahedral holes per unit cell is four.



(a) (b)

Fig. 4.20 (*a*) Tetrahedral holes and (*b*) octahedral holes in an *fcc* structure

Another less-packed arrangement of spheres is the body-centered cubic arrangement (Fig. 4.21) in which each sphere has eight nearest neighbours: four in the same plane, two above and two below it in the adjacent layers. Since the coordination number in *fcc* or *hcp* structures is greater than that in the *bcc* structures, the latter are therefore less denser.

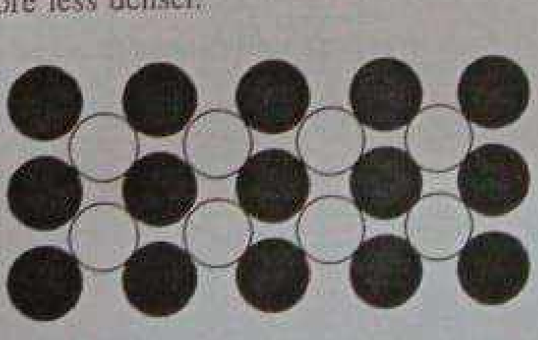


Fig. 4.21 Body centered cubical close-packed structure

4.14 PACKING IN IONIC SOLIDS

The packing of spheres in ionic solids involves cations and anions. If the cations and anions
but opposite charges, then a stable electrically neutral structure requires that the number of
surrounding an anion should be equal to the number of anions surrounding a cation. An
neutral structure with twelve coordination number is not possible with ions of the same size. A
closely-packed stable structure of like charged ions in a *bcc* arrangement in which the ion at the
centre is surrounded by eight oppositely charged ions at the corners of the cube. This the structure
caesium chloride, the coordination number of each ion is 8.

Sodium chloride has an *fcc* structure (Fig. 4.17) and may be considered as a face-centered arrangement of Cl^- ions in which the Na^+ ions occupy the octahedral sites resulting in a 6-6 coordination number.

Zinc blende (ZnS) structure may be regarded as an *fcc* arrangement of S^{2-} ions in which half of the
tetrahedral holes are alternatively occupied by the Zn^{2+} ions. Each Zn^{2+} ion [Fig. 4.22(*a*)] is surrounded
by four S^{2-} ions at the corner of a tetrahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+}
tetrahedrally giving 4-4 coordination number.

In fluorite (CaF_2), calcium ions have the *fcc* arrangement [Fig. 4.22(*b*)] where all the tetrahedral
holes are occupied by F^- ions. Each F^- ion is tetrahedrally coordinated to four Ca^{2+} ions and each Ca^{2+}
ion is surrounded by eight F^- ions at the corners of a cube. This gives a cation:anion ratio of 1:2
8-4 coordination number.

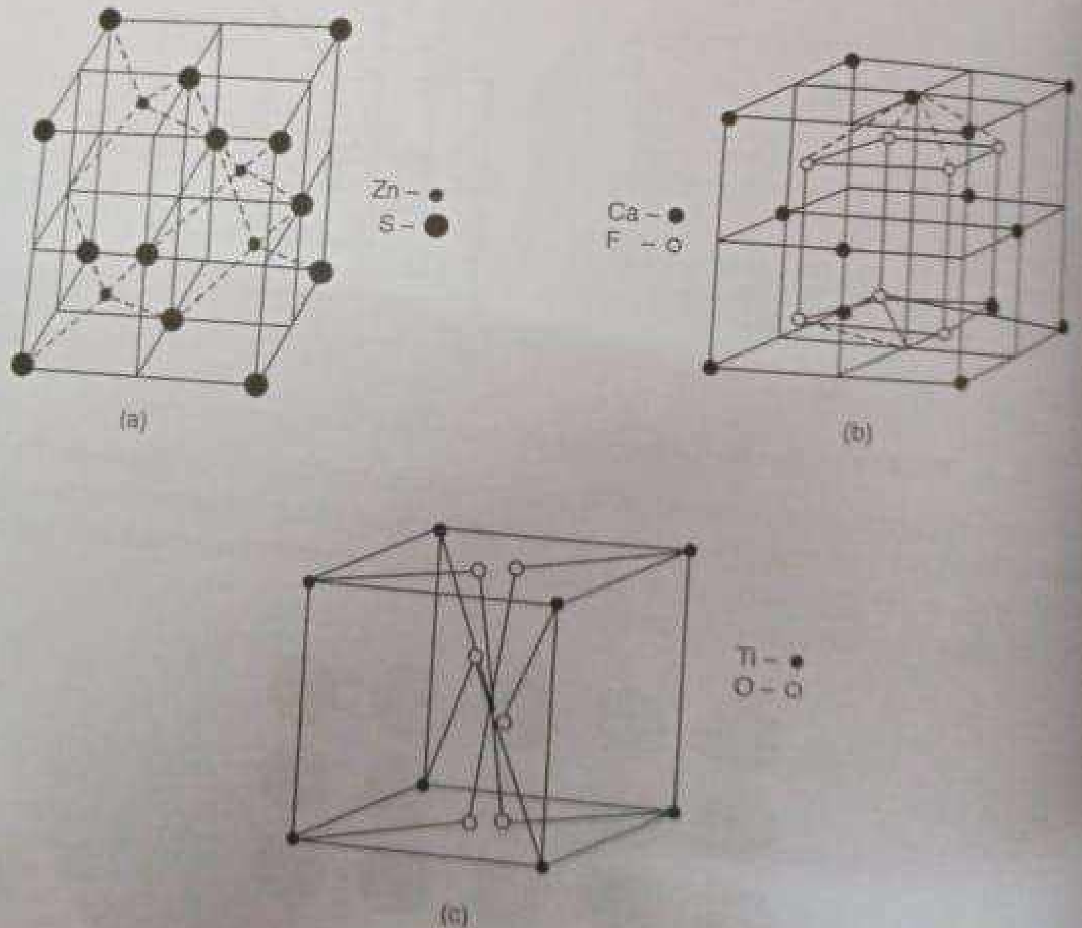


Fig. 4.22 Unit cells in (*a*) zinc blende; (*b*) fluorite and (*c*) rutile

Rutile (TiO_2) [Fig. 4.22(*c*)], on the other hand, has a 6-3 coordination number. Hence, each Ti^{4+} ion is octahedrally coordinated to O^{2-} while each O^{2-} is surrounded by three Ti^{4+} ions at the corners of a triangle.

4.15 EFFECT OF ION SIZE ON CRYSTAL STRUCTURE—RADIUS RATIO

In close-packed arrangements of like charged ions, the oppositely-charged ions touch one another. The difference in the crystal structure depends on the size of the ions. Larger the size of a given ion, greater will be the number of oppositely-charged ions which can be packed around it. The geometrical requirement for a given structure in terms of the size of the two ions is expressed by *radius ratio* which is defined as

$$R = \frac{r_s}{r_l} \qquad \text{...(4.7)}$$

where r_s and r_l are the radii of the smaller (usually a cation) and the larger ions (anion), respectively. Let us calculate the radius ratio for 3, 4, 6 and 8 coordinate structures.

Radius ratio for three coordinate structures: A three coordinate structure gives rise to an equilateral triangular arrangement as shown in Fig. 4.23.

The perpendicular distance *CD* is given by

$$\frac{r_l}{\sqrt{3}}$$

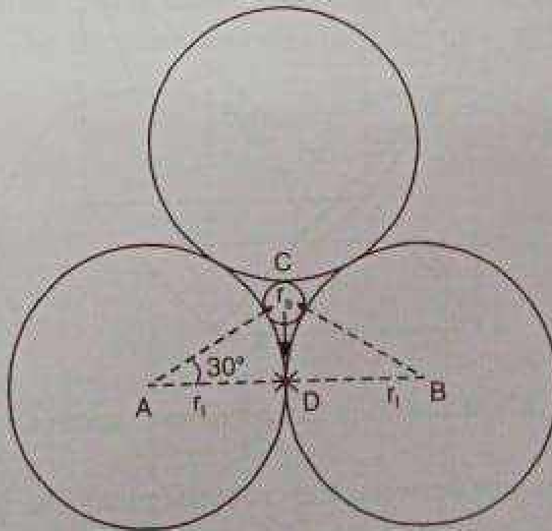


Fig. 4.23 Ions in a three coordinate structure

Since ACD is a right angled triangle, hence

$$AC^2 = AD^2 + CD^2$$

$$(r_l + r_s)^2 = (r_l)^2 + \frac{r_l^2}{3}$$

$$r_l^2 + 2r_l r_s + r_s^2 = r_l^2 + \frac{r_l^2}{3}$$

$$3\left(\frac{r_s}{r_l}\right)^2 + 6\left(\frac{r_s}{r_l}\right) - 1 = 0$$

$$\frac{r_s}{r_l} = \frac{-6 \pm \sqrt{36+12}}{6} = \frac{2\sqrt{3}}{3} - 1 = 0.155$$

If the ratio falls below this value, then the large ions can no longer touch the central small ion so this arrangement becomes unstable. If r_s increases, the larger ions are no longer in contact with each other, and when the ratio approaches a value of 0.225 it is possible to accommodate four larger ions around the central ion at the vertices of a regular tetrahedron.

Radius ratio for four coordinate structures: A tetrahedral arrangement can be drawn with a cube as shown in Fig. 4.24. The anions 1 and 3 (or 1 and 2, 2 and 4, 2 and 3, etc.) will touch each other and lie on the face-diagonal, the length of which is $\sqrt{2}a$. Thus,

$$r_l + r_s = \sqrt{2}a$$

or

$$r_l = \frac{a}{\sqrt{2}}$$

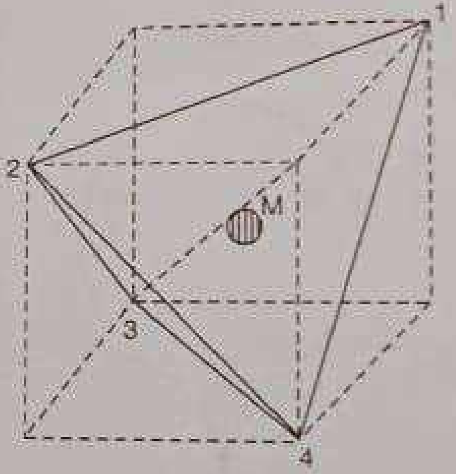


Fig. 4.24 Ions in four coordinate structure

The central cation M will be just between the cross diagonal, the length of which is $\sqrt{3}a$. Thus

$$2(r_l + r_s) = \sqrt{3}a$$

or

$$r_l + r_s = \frac{\sqrt{3}}{2}a$$

Dividing the above equation by r_l, we get

$$1 + \frac{r_s}{r_l} = \left(\frac{\sqrt{3}}{2}a\right)\left(\frac{\sqrt{2}}{a}\right)$$

$$= \sqrt{\frac{3}{2}} = \frac{1.73}{1.41}$$

or

$$\frac{r_s}{r_l} = \frac{1.73}{1.41} - 1$$

$$= 0.225$$

Radius ratio for six coordinate structures: In these structures, the ions are in contact along the face diagonal of a cube. Fig. 4.25 shows a view of the square planar cross section of an octahedron. From the geometry, it is clear that

$$(2r_l)^2 + (2r_l)^2 = \left[2(r_s + r_l)\right]^2$$

$$4r_l^2 + 4r_l^2 = 4r_s^2 + 4r_l^2 + 8r_l r_s$$

$$\left(\frac{r_s}{r_l}\right)^2 + 2\left(\frac{r_s}{r_l}\right) - 1 = 0$$

$$\frac{r_s}{r_l} = \frac{-2 \pm \sqrt{8}}{2} = 0.414$$

This is the lowest value of the radius ratio in which six larger ions could be arranged octahedrally about the central smaller ion. The structure becomes unstable as r_s decreases or r_l increases.

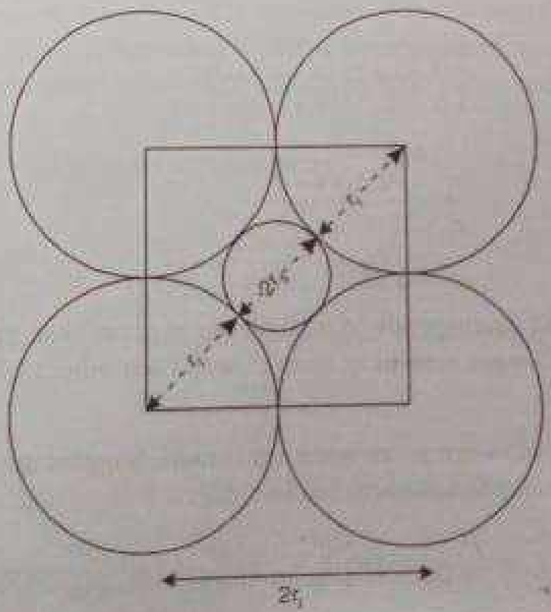


Fig. 4.25 Ions on the face of a unit cell

Radius ratio for eight coordinate structures: In an eight coordinate structure, oppositely-charged ions are touching each other along the body diagonal of the cube (Fig. 4.26), while the ions with

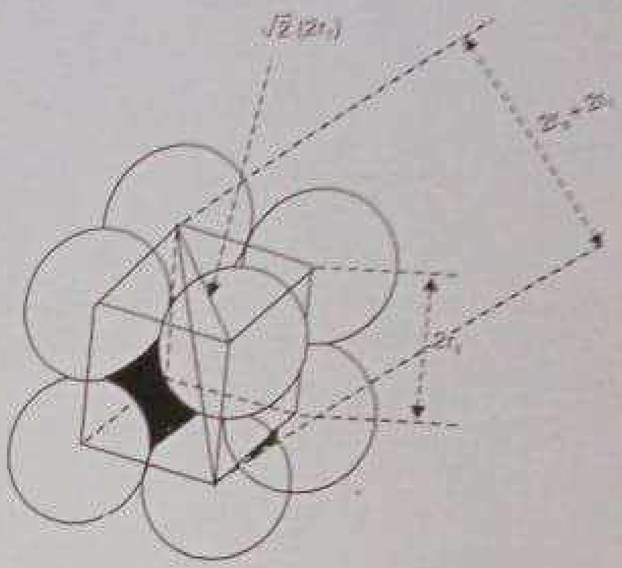


Fig. 4.26 Ions in *bcc* structure

radius r_l are in contact with each other along the sides of the cube. The body diagonal has a length of $2r_l + 2r_s$ and the face diagonal being $2\sqrt{2}r_l$. For a cube, the body diagonal is given by

...(Body diagonal)^2 = (Face diagonal)^2 + (Side of the cube)^2

$$(2r_s + 2r_l)^2 = \left(2\sqrt{2}r_l\right)^2 + (2r_l)^2$$

$$\left(\frac{r_s}{r_l}\right)^2 + 2\left(\frac{r_s}{r_l}\right) - 2 = 0$$

$$\frac{r_s}{r_l} = \frac{-2 \pm \sqrt{4-8}}{2}$$

$$= 0.732.$$

Thus, the value of 0.732 corresponds to a stable eight coordinate structure. If r_s decreases a increases, eight ions can no longer remain in contact with each other and an unstable structure would result.

Problem 4.13: In the table below are given some ionic radii. Suggest the most probable structures for (*i*) KBr, (*ii*) CsBr, (*iii*) MgO, (*iv*) SrS, and (*v*) MgSe.

Ions	K^+	Cs^+	Mg^{2+}	Sr^{2+}	Br^-	O^{2-}	S^{2-}	Se^{2-}
Ionic radii Å	1.33	1.69	0.66	1.12	1.96	1.40	1.84	1.98

Solution: (*i*) The radius ratio for KBr is given as

$$\frac{r_{K^+}}{r_{Br^-}} = \frac{1.33}{1.96} = 0.678$$

The ratio is less than 0.73 therefore KBr has an *fcc* lattice.
(*ii*) For CsBr, the radius ratio is

$$\frac{r_{Cs^+}}{r_{Br^-}} = \frac{1.69}{1.96} = 0.863$$

The lattice is thus *bcc*.
(*iii*) For MgO,

$$\frac{r_{Mg^{2+}}}{r_{O^{2-}}} = \frac{0.66}{1.40} = 0.472$$

The lattice is an *fcc*.
(*iv*) For SrS,

$$\frac{r_{Sr^{2+}}}{r_{S^{2-}}} = \frac{1.12}{1.84} = 0.609$$

It corresponds to an *fcc* lattice.
(*v*) For MgSe,

$$\frac{r_{Mg^{2+}}}{r_{Se^{2-}}} = \frac{0.66}{1.98} = 0.333$$

The ratio corresponds to a tetrahedral structure.

Problem 4.14: An ionic compound AB has Na^+Cl^- structure. If the radius of A^+ ion is 414 pm then (*a*) what is the ideal radius of B^- ion? (*b*) If the radius of A^+ ion decreases and becomes equal to 30 pm, then what type of structure AB would have? What would be the co-ordination number of A^+ ion?

Solution: (*a*) For Na^+ Cl^- structure the radius ratio, $\frac{r_+}{r_-} = 0.414$

Therefore,
$$r_{B^-} = \frac{r_+}{0.414} = \frac{414 \text{ pm}}{0.414} = 100 \text{ pm}$$

(*b*) If the radius of A^+ ion is 30 pm, then the radius ratio would become

$$\frac{r_+}{r_-} = \frac{30}{100} = 0.3$$

and AB would have zinc sulphide type of structure and the co-ordination number of A^+ ion would be 4.

4.16 VOID OR EMPTY SPACE IN CUBIC LATTICES

In the preceding section it has been shown that uniform spheres can be packed in a number of ways, namely, a primitive unit cell, *fcc* (or *hcp*) and *bcc*. In these close-packed structures, some space is always left unoccupied. This is known as the *void or empty space*. In the closest-packed structures, *fcc* or *hcp*, the void space would be less in comparison to a *bcc* or a primitive unit cell. Let us calculate the fraction of the total volume occupied by the spheres in these lattices.

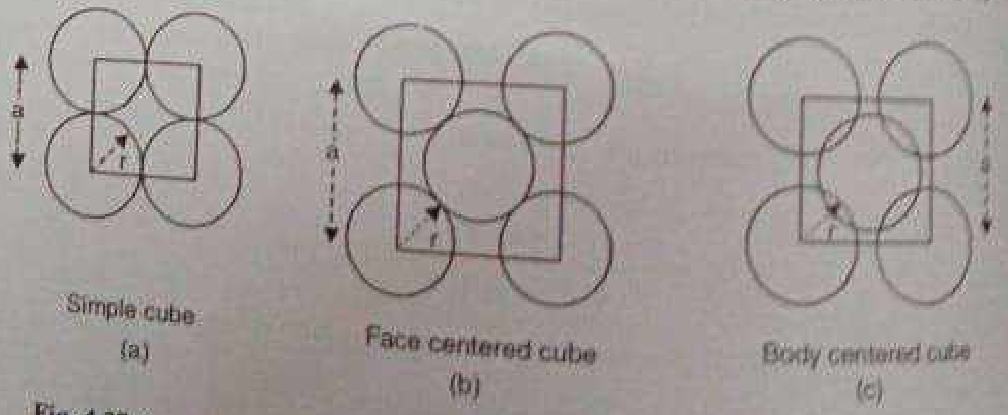
(*a*) **Primitive cubic lattice:** In a primitive unit cell of length a, the spheres are present only at the corners of the cube. Each corner atom is shared by eight other unit cells. Hence, the contribution of a sphere at the corner of the cube is 1/8, and the total number of spheres per unit cell is $8 \times \frac{1}{8}$ In a primitive unit cube, the spheres are touching each other along the side of the unit cell [Fig. 4.27 The distance between the centres of the two spheres is a, and the radius of the sphere is $a/2$. The volume of the sphere is $\frac{4}{3}\pi\left(\frac{a}{2}\right)^3$. The volume of the unit cell is a^3, and there is only one sphere in the unit

Therefore, the fraction of the total volume occupied by the sphere is

$$\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = 0.523 \text{ or } 52.3\%$$

It is clear that the void space is 47.7%.

(*b*) **Face centered cubic lattice:** In an *fcc* structure, there are spheres at the centres of each face in addition to those at the corners. A face sphere is common to two unit cells, therefore the contribution of the spheres from the faces is $6 \times \frac{1}{2} = 3$. The contribution from the spheres at the corners of the unit cell is $8 \times \frac{1}{8} = 1$. The total number of spheres per unit cell in an *fcc* structure is, therefore, 4. In fcc arrangement the spheres are touching each other along the face diagonal [Fig. 4.27 (*b*)].



Simple cube
(a)

Face centered cube
(b)

Body centered cube
(c)

Fig. 4.27 Arrangement of spheres in cubic lattices (*a*) simple, (*b*) *fcc*, and (*c*) *bcc*

The face diagonal is given by $\sqrt{2}\,a$, and the distance between centres of any two nearest spheres would be $\frac{a}{\sqrt{2}}$.

The radius of the sphere $= \frac{a}{2\sqrt{2}}$.

The volume of the sphere of radius $\frac{a}{2\sqrt{2}}$ is $\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3$

Since there are four atoms per unit cell, therefore the volume occupied by four spheres

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

Hence, the fraction of the total volume occupied by the spheres of the unit cell is

$$\frac{4\times\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}=\frac{\sqrt{2}}{6}\pi=0.74 \text{ or } 74\%$$

So, we notice that in the closest-packed structure only 74% of the space is actually occupied by the spheres. It means that 26% is the void space.

(*c*) **Body-centered cubic lattice:** In a body-centered arrangement, the sphere present at the centre of the unit cell exclusively belongs to it. In addition to this the contribution of the spheres from the corners to the unit cell is $8\times\frac{1}{8}=1$. Therefore, the total number of spheres per unit cell of a *bcc* lattice is 2. In this arrangement, the spheres are touching each other along the body diagonal [Fig. 4.27(*c*)] which is given by

$$(\text{Body diagonal})^2=(\text{Face diagonal})^2+(\text{Side of the unit cell})^2$$

$$=\left(\sqrt{2}a\right)^2+a^2$$

$$=3a^2$$

Body diagonal $=\sqrt{3}\,a$

The distance between the centres of two nearest spheres would be $\frac{\sqrt{3}}{2}a$.

The radius of the sphere would be $\frac{\sqrt{3}a}{4}$

The volume of a sphere $=\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3$

As there are two spheres per unit cell, therefore the volume occupied by these spheres

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

Hence, the fraction of the total volume occupied by the spheres $= \dfrac{2\times\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3}{a^3}$

$$= \frac{\sqrt{3}}{8}\pi = 0.68 = 68\%$$

Evidently, the body-centered cubic lattice is less closely packed than the *hcp* or *fcc* lattice as 32% is the void space.

4.17 TYPES OF CRYSTALS

A number of different types of bonding forces operate in the crystals to hold them together. Properties of the crystals depend on the nature of these binding forces. Based on this, it is possible to classify them into four categories.

(*a*) **Ionic crystals:** In ionic crystals like sodium chloride, the structural units are held in position by electrostatic forces between the oppositely charged ions. This leads to a regular three-dimensional structure. Due to these electrostatic forces, the ionic crystals usually have high lattice energy. The ionic bond is spherically symmetrical and has no direction. The number of nearest neighbours surrounding a given ion in a crystal is known as the co-ordination number of the ion. The co-ordination numbers commonly encountered in ionic crystals are 4, 6 and 8. In a 4 co-ordinated structure, the arrangement is tetrahedral with the anions at the corners and cation at the centre. In 6 co-ordination number, an octahedral arrangement with the anions at the corners of the octahedral and a cation at the centre. For 8 co-ordination number, the arrangement is like a body-centered cube with cation at the centre and anions at the corners. Ionic crystals are brittle, have very little elasticity and can not be easily bent. The melting points of ionic crystals are usually high. Their solutions in polar solvents conduct electricity.

(*b*) **Covalent crystals:** A covalent crystal results from the overlapping of valence orbitals between the atoms. When extended in three-dimension, it leads to a variety of crystal structures depending on the number of electrons available for bonding. Structure of diamond is an example of this type. There is a tetrahedral arrangement (sp^3 hybridization) and every carbon atom is covalently bonded to four equidistant carbon atoms [Fig. 4.28(*a*)]. The crystal is therefore a three-dimensional molecule without any limit on its extension giving rise to a giant molecule, a polymer of carbon. The structure may be looked as an *fcc* lattice of carbon atoms where alternate four out of eight tetrahedral holes are occupied by carbon atoms. The bonds in diamond are similar to the C—C bonds in the saturated hydrocarbons such as ethane. The C—C bond distance is 1.54 Å (0.154 nm). Since the bonding orbitals are fully occupied, the crystal is an insulator. The hardness of diamond is probably due to the strength of the bonds and their uniformity in all the directions throughout the crystal.

Silicon carbide, silver iodide and zinc sulphide also form crystals of the diamond type and the bonding is essentially covalent in character.

In graphite, each carbon atom is bonded to three other carbon atoms through sp^2 hybridization forming the hexagonal network sheets like those in benzene rings. The structure is shown in Fig. 4.28(*b*). The π electrons are mobile contributing to electrical conductivity in the direction parallel to the sheets. The distance between the atoms is 1.42 Å (0.142 nm). The layers are held by weak van der **Waals forces**. The distance between the adjacent layers is 3.35 Å (0.335 nm). Weak binding between the layers results the graphite crystals slipper and flaky conferring on graphite its valuable lubricating property. The crystals are strong and hard and have high melting points. The covalent compounds have low melting points and boiling points. Hence, the covalent compounds are often gases liquids or soft solids.

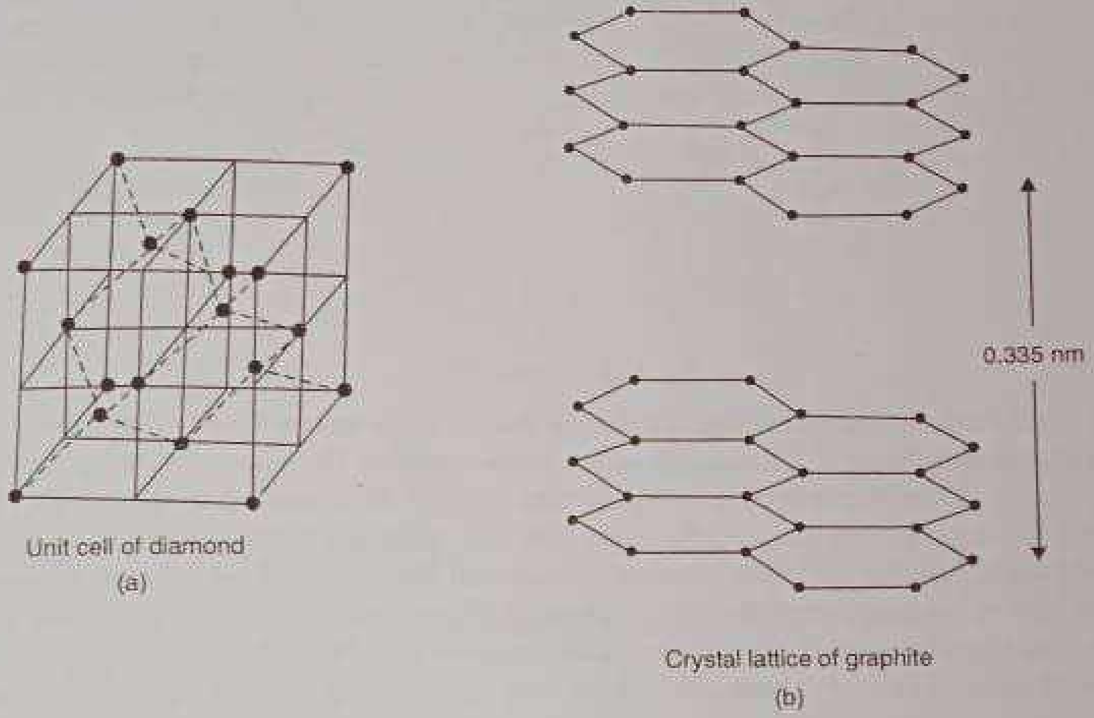

Unit cell of diamond
(a)
Crystal lattice of graphite
(b)

Fig. 4.28 (*a*) Diamond lattice; (*b*) Graphite lattice

(*c*) **Molecular crystals:** These crystals have short range forces that attract all discrete species like atoms, molecules or ions to each other. They arise from dipole-induced dipole and dispersion forces and are relatively weak but sufficiently strong to hold the species (usually molecules) together in liquids and solids. Crystals held by these forces, are called *molecular crystals*. Crystals of nitrogen, carbon tetrachloride, benzene etc., are examples of molecular crystals. In these crystals, the molecules tend to pack as closely as their size and shape allow. Because of weak forces in molecular crystals they possess comparatively low melting points and are soft.

(*d*) **Hydrogen bonding:** Such crystals are held together by the sharing of protons between electronegative atoms. Many inorganic and organic acids, salt hydrates, water, glycols and ice are examples of crystals where hydrogen bonds are involved. In ice, each oxygen is tetrahedrally surrounded by four hydrogens. Two are covalently bonded to it. The other two, one from each of the two neighbouring molecules, are held by hydrogen bonds (Fig. 4.29). The bond lengths of these bonds is more than twice that of OH bonds in water molecule. Each water molecule is then bonded to four other water molecules giving a very strong structure with large numbers of hydrogen bonds. Strong orientation of hydrogen atoms towards oxygen atoms causes less efficient packing in the crystal and thus gives rise to open structure which is less denser than the liquid water. Hydrogen bonds are comparatively weak but play an important role in the structures of proteins, polypeptides, etc.

(*e*) **Metallic crystals:** Atoms with fewer and loosely-held electrons form metallic crystals. Each metal atom forms covalent bonds with its nearest neighbour through the overlap of valence orbitals. The

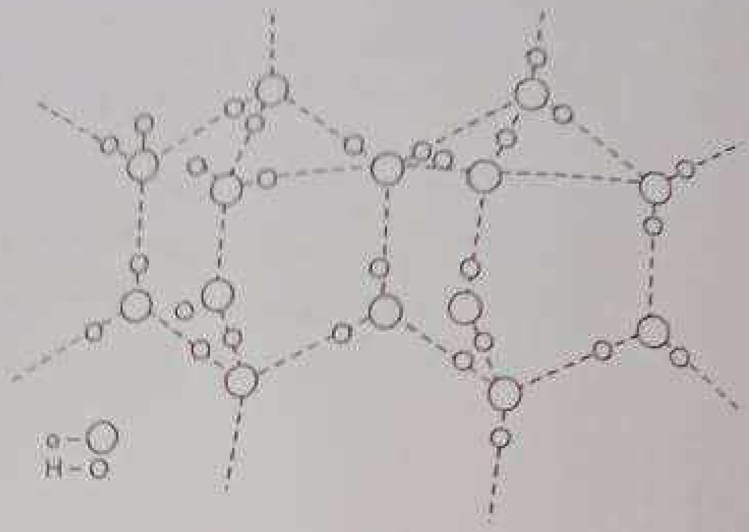


Fig. 4.29 Structure of ice

bonds are highly delocalized in the metal structure and resonate among alternate positions between each atom and its neighbour. The resonance enhances the stability. The vacant orbitals permit a ready flow of electrons under the influence of an applied electric field leading to their high electrical conductivity. The high reflectance arises due to the ease with which the free electrons can be accelerated by high frequency radiation and then reradiate virtually all the energy of the incident radiation they absorb. This type of bonding gives metals their characteristic properties like lustre, opaque and malleable nature. It is observed that there is a gradual transition between metallic and non-metallic properties. As the number of valence electrons increases and are held more tightly there is a transition to covalent properties.

4.18 DEFECTS IN CRYSTALS

A crystal with perfect lattice is very rare and they usually suffer from imperfection or defects of various kinds. The defect may be at a point or along a line or over a surface. The defects may modify the physical and chemical properties of the crystals.

Two types of defects may be observed in stoichiometric compounds, called *Schottky* and *Frenkel defects* respectively. Crystals have a perfectly ordered arrangement at absolute zero. As the temperature increases, the amount of thermal vibrations of ions in their lattice sites increases. If the vibration of a particular ion becomes large enough, it may jump out of its lattice site. This constitute a point defect. At higher temperatures, the chances of lattice sites to be unoccupied are greater.

Schottky defects: A Schottky defect consists of a pair of holes in the crystal lattice. One cation and one anion (pair-wise) are absent (Fig. 4.30). This type of defect occurs mainly in highly ionic

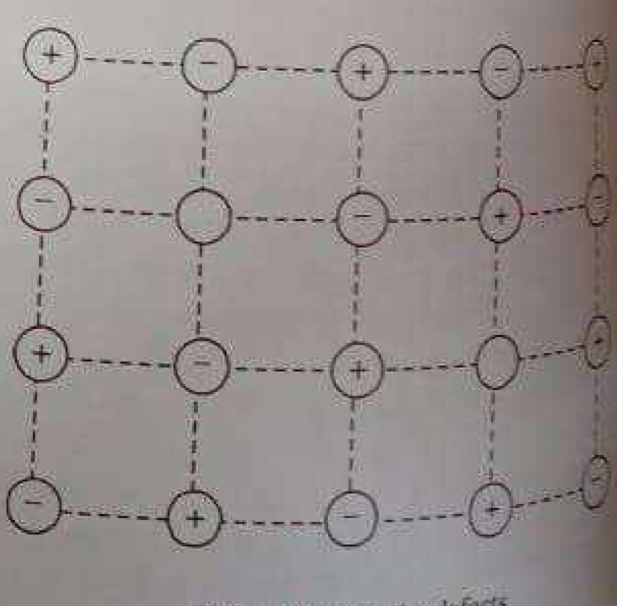


Fig. 4.30 Schottky defects

compounds where the cations and anions are of a smaller size, e.g., NaCl, KCl, CsCl and KBr etc. (coordination number usually 8 or 6). Crystals with Schottky defects have holes from both positive and negative ions. Schottky defects leads to a lowering of the density of the crystal.

Frenkel defects: It arises when a cation leaves its normal lattice site and occupies an interstitial position (Fig. 4.31). Metal ions are generally smaller than the ions and therefore it is easier to squeeze cation (+) into alternative interstitial positions. This type of defect is generally observed when there is a large size difference between the cation and anion, e.g., ZnS, AgCl, AgBr, AgI etc. Crystals with Frankel defects have only one type of hole. Frankel defects donot change the density of the crystal.

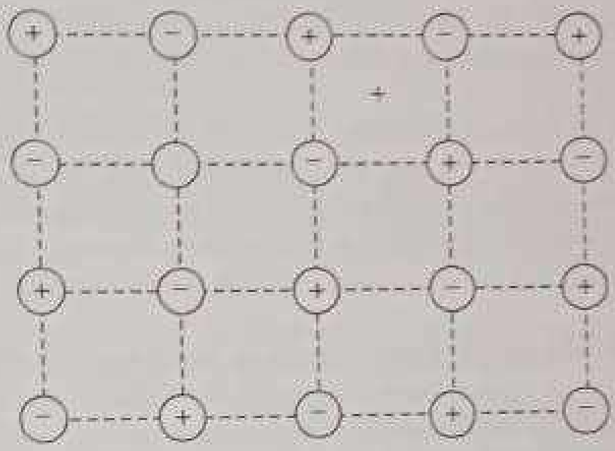


Fig. 4.31 Frenkel defects

Metal excess: This may occur in two ways.

F-centres (Colour Centres)

An anion may be absent from its lattice site, leaving a hole which is occupied by an electron, thereby maintaining the electrical balance (Fig. 4.32(*a*)). This is rather similar to a Schottky defect but only with one hole rather than a pair. This type of defect is formed by crystals which would be expected to from Schottky defects. When compounds like NaCl, KCl, LiH etc. are heated with excess of their constituent metal vapours, or treated with high energy radiation, they become deficient in the anions

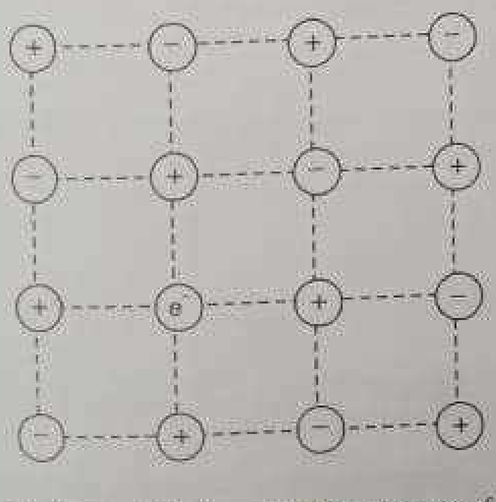


Fig. 4.32 (*a*) Metal excess defect because of absence of anions

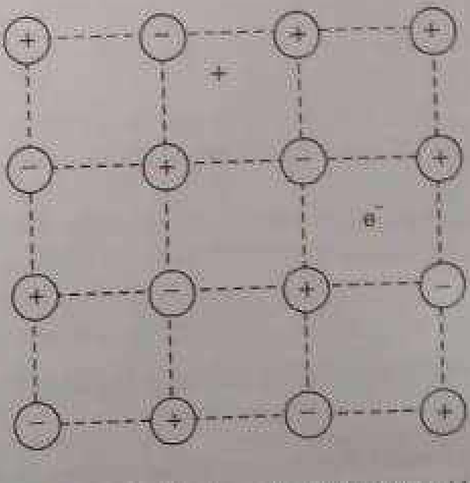


Fig. 4.32 (*b*) Metal excess defects caused by interstitial cations

and their formulae may be represented by $AX_{1-\delta}$ where δ is a small fraction. The non-stoichiometric form of NaCl is yellow, non-stoichiometric form of KCl is blue-lilac in colour.

The crystal lattice has vacant anion sites which are occupied by electrons. Anion sites occupied by electrons in this way are called *colour centres*. These colour centres are associated with the colour of the compound. More the colour centres present greater will be the intensity of colour. Solids containing colour centres are paramagnetic because the electrons occupying the vacant sites are unpaired.

Interstitial ions and electrons: Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice and electrical neutrality is maintained by the inclusion of interstitial electron (Fig. 4.32(*b*)). Their composition may be represented by the formula $A_{1+\delta}X$. This type of defect is rather like a Frankel defect in that ions occupy interstitial position, but there are no holes, and there are also interstitial electrons. This type of defect is generally observed in ZnO, Fe_2O_3, CdO etc.

Crystals with this type of defect contain free electrons and if these migrate they conduct electric current. The amount of current carried is very small compared with that in metals, fused salts or salts in aqueous solutions, and these defect materials are called *semiconductors*. Since the mechanism is normal electron conduction and they are called *n-type semiconductors*.

Metal deficiency: Metal deficient compounds may have general formula $A_{i-\delta}X$. It can occur in two ways.

(*i*) **Positive ion absent:** If a cation is absent from its lattice site, the charges can be balanced by an adjacent metal ion having an extra positive charge (Fig. 4.33(*a*)). Crystals with metal deficiency defects are semiconductors. Thus on the whole there is an excess of anion and the lattice remains deficient of cations. Considering FeO crystal, we notice some Fe^{3+} ions in the defective crystals in addition to Fe^{2+} ions. Some other compounds that show this defect are FeS, NiO etc. Suppose a lattice contains A^+ and A^{2+} metal ions. If an electron 'hops' from A^+ ion to the positive centre (A^{2+}), then A^+ becomes a new positive centre. There has been an apparent movement of A^{2+} ion. With a series of similar hops, an electron may be transferred in one direction across the structure. At the same time the positive hole migrates in the opposite direction across the structure. This is called *positive hole*, or p-type semiconduction.

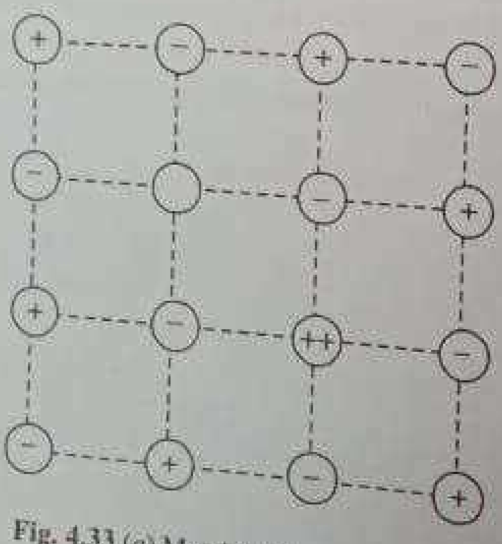


Fig. 4.33 (*a*) Metal deficiency caused by missing positive ion

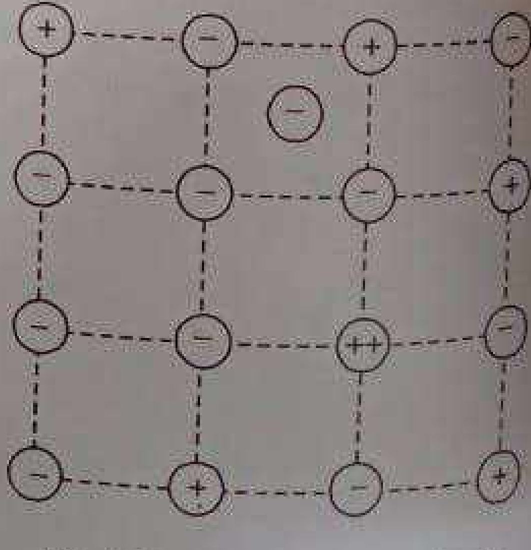


Fig. 4.33 (*b*) Metal deficiency due to interstitial anion

(*ii*) **Defect due to interstitial anion:** In this type of defect an anion is trapped in between the lattice sites. This extra negative ion is in the interstitial position and of an extra charge on an adjacent metal ion (Fig. 4.33(*b*)). In crystals possessing this defect, the anions are relatively small when compared to the size of cation, thus allowing the anion to find a place in the interstitial site.

EXERCISES

1. Explain, giving reasons, the following:
   (*i*) Solids are essentially incompressible whereas gases are easily compressed.
   (*ii*) Diffusion in solids is slower than in liquids.
   (*iii*) Density of a solid is generally greater than its liquid.
   (*iv*) Covalent crystals are hard while molecular crystals are soft.
   (*v*) Attractive forces in metals are non directional.
   (*vi*) Metals are malleable (easily flattened into sheets) are ductile.
   (*vii*) A long range order exists in crystals.
   (*viii*) Centre of symmetry can be represented by rotation inversion axis.
   (*ix*) Crystalline solids are anisotropic while amorphous solids are isotropic.
   (*x*) Solids with *ccp* structures are more dense than those with *bcc* structures.

2. Explain why it is not possible
   (*i*) to deduce the position of hydrogen atoms from X-ray diffraction studies,
   (*ii*) to use too large or too small crystals in the Debye-Scherrer method,
   (*iii*) to distinguish K^+ ions from Cl^- ions by X-ray diffraction studies,
   (*iv*) to replace X-ray by UV of 10 nm wavelength in the diffraction studies of crystals,
   (*v*) to use polychromatic X-rays in the debye-Scherrer powder method.

3. State which of the following statements are true and which are false:
   (*i*) All crystalline solids are isotropic.
   (*ii*) Tetrahedral methane molecule has a centre of symmetry and a four fold axis of symmetry.
   (*iii*) Amorphous solids are supper cooled liquids with high viscosity.
   (*iv*) In crystals short range order exists.
   (*v*) Unit cell is the smallest building unit in the crystals.
   (*vi*) Every object possesses an identity element.
   (*vii*) There are five and only five possible lattices in a two-dimensional plane.
   (*viii*) *n* in the Bragg's equation can have any value—positive or negative integer or fraction.
   (*ix*) In the closest packed structure, 26% of the space is vacant.
   (*x*) The number of atoms per unit cell in an *fcc* structure is 4 while in a *bcc* structure it is 2.

   Ans. True: (*iii*), (*v*), (*vi*), (*vii*), (ix), (*x*).
   False: (*i*), (*ii*), (*iv*), (*viii*).

4. What types of crystals would be expected to be (*i*) the hardest, (*ii*) the softest, (*iii*) the highest melting, (*iv*) the lowest melting, (*v*) good conductors of heat and electricity, (*vi*) having directional lattice forces, (*vii*) having non directional lattice forces.

   Ans. (*i*) Covalent, (*ii*) molecular, (*iii*) covalent, (*iv*) molecular, (*v*) metallic, (*vi*) ionic and metallic, (*vii*) covalent and molecular.

5. What types of crystals are given by (*i*) diamond, (*ii*) KCl, (*iii*) Au, (*iv*) anthracence and (*v*) H_2O?

   Ans. (*i*) Covalent, (*ii*) ionic, (*iii*) metallic, (*iv*) and (*v*) molecular.

6. LiBr, NaBr, KBr, RbBr all have the same crystal structure. However, X-ray analysis indicates that RbBr is a simple cubic while all others are face centered. Explain.

   Ans. Rb^+ and Br^- ions have the same number of electrons.

7. $SnCl_4$ is a colourless liquid (b. pt. 114°C and m. pt.–33°C) while $SnCl_2$ is a white solid melting at 246°C. What type of solid (ionic, covalent, etc.) is most likely to be formed when $SnCl_2$ solidifies? **Ans.** Ionic.

8. In the table below are given unit cell parameters. Identify the crystal system in each case.

	a (*nm*)	*b* (*nm*)	*c* (*nm*)	α	β	γ
(*i*)	5	5	5	90°	90°	90°
(*ii*)	6.5	6.5	10.5	90°	90°	90°
(*iii*)	7	7	7	96°	96°	96°
(*iv*)	6	6	5	90°	90°	120°

Ans. (*i*) Cubic, (*ii*) tetragonal, (*iii*) rhombohedral, (*iv*) hexagonal

9. Sketch the following crystal structures:
   (*i*) Diamond—tetrahedral covalent lattice
   (*ii*) NaCl—face centered cubic lattice
   (*iii*) CsCl—body centered cubic lattice

10. Suppose you have a face centered cubic arrangement of A and B atoms where A atoms are at the corners of the unit cell and B atoms at the face centres. (*a*) What is the formula of the compound? (*b*) What would be the simplest formula if (*i*) one of the A atoms were missing from a corner in each unit cell and (*ii*) two A atoms were missing from two corners?
Ans. (*a*) AB_3, (*b*) (*i*) A_7B_{24}, (*ii*) AB

11. A certain compound of X and Y (both monovalent ions) crystallizes in the *bcc* lattice with X at the corners and Y at the body centre. (*a*) What is the formula of the compound? (*b*) If one of the X atoms from a corner be replaced by Z (also a monovalent ion) what would be the simplest formula of the resulting compound?
Ans. (*a*) XY, (*b*) ZXY

12. What is meant by symmetry operations and symmetry elements? Explain the following symmetry elements: (*i*) Proper and improper rotation axes, (*ii*) mirror plane, and (*iii*) centre of symmetry.

13. (*i*) List out the symmetry elements is (*a*) H_2O, (*b*) NH_3, (*c*) C_2H_4, (*d*) CH_4, (*e*) letter 'M', and (*f*) football, (*ii*) Which of the following molecules have a centre of symmetry?
(*i*) C_6H_6, (*ii*) SF_6, (*iii*) CO_2, (*iv*) C_2H_4, (*v*) NH_3.
Ans. (*i*): (*a*) C_3, σ_v, $\sigma_{v'}$, E, (*b*) C_3, $3\sigma_{v'}$, E, (*c*) $3C_2$, σ_v, $\sigma_{v'}$, σ_h, i, E
(*d*) $4C_3$, E, S_4; (*e*) C_2, σ_v, $\sigma_{v'}$, E, (*f*) $C\infty$, ∞C_2, $\infty\sigma_v$, σ_h, i, E

14. How many unit cells are possible in a planar lattice? Sketch a two-dimensional lattice of closest packed identical spheres indicating a suitable unit cell.

15. What are the seven crystal systems? What parameters are used to describe a particular system? Write down the characteristics of each system. Name the Bravais lattices of each class.

16. What is the law of rational indices? How are the rational indices arrived at for a crystal plane. The Weiss indices of some crystal planes are (*i*) a:b:∞c, (*ii*) a:b:c, (*iii*) a:∞b:c, (*iv*) a:2b:2c, (*v*) a:–b:∞c, (*vi*) $\frac{a}{2}:\frac{2}{3}b:\infty c$, (*vii*) $\frac{2a}{3}:2b:\frac{1c}{3}$. What are the corresponding Miller indices of these planes?
Ans. (*i*) (110), (*ii*) (111), (*iii*) (101), (*iv*) (211), (*v*) $(1\bar{1}0)$, (*vi*) (430), (*vii*) (316)

17. Prepare sketches showing the planes that have Miller indices (011), (111), (222), (010), $(1\bar{1}0)$ and (200)

18. (*a*) Derive the Bragg's equation, $n\lambda = 2d \sin\theta$ and show that it can be written as $\lambda = d_{hkl} \sin\theta$. What is the physical significance of *n* in this equation? Under what conditions reflection of X-rays from dissimilar planes can give rise to reflection maxima?
(*b*) On what factors does the intensity of reflected X-ray beams depend?

(*c*) Explain why one should employ monochromatic X-rays in studying the reflections from the faces of crystals?

19. Define the following terms:
(*i*) Unit cell (primitive and non-primitive), (*ii*) space lattice, (*iii*) lattice planes, (*iv*) law of rational indices, (*v*) interfacial angle, (*vi*) space and point groups, (*vii*) centre and planes of symmetry.

20. (*a*) Prove that the interplanar spacing (d_{hkl}) in a cubic system is given by

$$d_{hkl} = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}}$$

where a is edge length of the cube.

(*b*) Calculate the interplanar spacing (d_{hkl}) for a cubic system between the following sets of planes: (*i*) (100), (*ii*) (200), (*iii*) (110), (*iv*) (220), (*v*) (111), (*vi*) (222). Assume 'a to be the edge length of the cube.

Ans. (*i*) $d_{100} = a$, (*ii*) $d_{200} = \frac{a}{2}$, (*iii*) $\frac{a}{\sqrt{2}}$, (*iv*) $\frac{a}{2\sqrt{2}}$, (*v*) $\frac{a}{\sqrt{3}}$, (*vi*) $\frac{a}{2\sqrt{3}}$.

21. What are the three types of cubic crystals? How are they distinguished from each other? Calculate the number of atoms per unit cell in each case.

22. Illustrate, with the help of diagrams, the following planes with Miller indice (*i*) (100), (110) and (111) in a simple cube, (*ii*) (200), (220) and (111) in a face centered cubic, and (*iii*) (200), (100) and (222) in a body centered cubic cell.

23. CsCl has a body centered cubic lattice. How many Cs^+ and Cl^- ions are there in the unit cell?
Ans. $Cs^+ = 1$, $Cl^- = 1$.

24. NaCl has an *fcc* structure. How many Na^+ and Cl^- ions are there in the unit cell?
Ans. $Na^+ = 4$, $Cl^- = 4$.

25. NaCl has a face-centered cubic lattice. What is the coordination number of (*a*) the sodium (*b*) the chlorine? (*c*) What are the individual lattice structures of sodium and chlorine in sodium chloride? (*d*) Calculate the number of Na^+ and Cl^- ions is the unit cell of sodium chloride.
Ans. (*a*) 6, (*b*) (*c*) face-centered, (*d*) 4 Na^+ ions and 4 Cl^- ions.

26. (*a*) Calculate the number of atoms per unit cell of (*i*) a simple cube, (*ii*) face centered cube, (*iii*) body centered cube, (*iv*) an edge centered cube, (*v*) face centered tetragonal and (*vi*) simple orthorhomic.
Ans. (*i*) 1, (*ii*) 4, (*iii*) 2, (*iv*) 4, (*v*) 4, (*vi*) 1.

(*b*) A hexagonal cell contains three unit cells. (*i*) How many atoms are there in the hexagonal cell? How many atoms are there in the unit cell?
Ans. (*i*) 6, (*ii*) 2.

27. What is understood by the closest packing of identical spheres? What is meant by the stacking sequences ABAB... and ABC ABC...? How do these structures differ from each other? Can we have a pattern like ABC ACB AB AC...? Show that number of octahedral holes per unit atom in an *fcc* structure is one and in a *bcc* structure it is 1.5. How many tetrahedral holes per unit atom are there in an *fcc* structure?
Ans. 2 holes per atom.

28. Show that the maximum proportion of available volume which may be filled by hard spheres in various structures is (*i*) simple cube $= \frac{\pi}{6} = 0.52$, (*ii*) body centered cube $= \frac{\pi\sqrt{3}}{8} = 0.68$, (*iii*) face centered cube $= \frac{\pi\sqrt{2}}{6} = 0.74$, (*iv*) hexagonal closest packed structure $= \frac{\pi\sqrt{2}}{6} = 0.74$, (*v*) diamond $= \frac{\pi\sqrt{3}}{6} = 0.34$. What is the percentage of void space in each case?
Ans. (*i*) 48%, (*ii*) 32%, (*iii*) & (*iv*) 26%, (*v*) 66%.

29. (*a*) What is the radius ratio? What is its significance? Calculate the limiting radius ratio of cation (smaller) to that of anion (larger) in the following arrangements:

(i) Triangular, (ii) face centered cubic structures, (iii) body centered cubic arrangements.

(c) Account for the fact that LiCl, KCl, RbCl have face centered cubic structures while CsCl has a b centered cubic structure.

30. Three uni-univalent ionic crystal, AX, AY and AZ are composed of ions having the following radii (arbi units):

A^+	X^-	Y^-	Z^-
1.0	1.0	2.0	3.0

Assuming that ions are hard spheres, predict (a) whether each crystal will have the sodium chloride or caesium chloride structure; explain. (b) Calculate the volume of the unit cell in each case.

Ans. (a) AX will have CsCl structure, AY, and AZ will have NaCl struct

(b) AX = 12.3 AY = 216, AZ = 60

31. Describe the crystal structure of zinc blende. What is the cation to anion ratio in this structure? What g metric arrangement of cations is there about each anion?

32. Calculate the interplanar spacings that correspond to reflections at $\theta = 20°$, $27.4°$, and $35.8°$ by X-rays wavelength 0.141 nm. Assume $n = 1$. **Ans.** 0.206 nm, 0.153 nm and 0.121 n

33. Silver has an atomic radius of 0.144 nm. What would be the density of silver if it were to crystallize in t following structures: (a) simple cubic, (b) body centered cubic, (c) face centered cubic, (d) If the density silver is 10.6×10^3 kg m^{-3}, which of these correspond to the correct structure?

Ans. (a) 7.5×10^3 kg m^{-3}, (b) 9.7×10^3 kg m^{-3} (c) 10.6×10^3 kg m^{-3}, (d) fc

34. CsCl forms a simple cubic lattice in which there are Cs^+ ions at the corners of the unit cell and Cl^- ions at th centre of the unit cell. The cation/anion contact occurs along the body diagonal of the unit cell. The length unit cells is 0.4123 nm and the radius of the Cl^- ion is 0.81 nm. Calculate the radius of the Cs^+ ion.

Ans. 0.176 n

35. Copper (at. mass 63.54 and density 8.936 g cm^{-3}) crystallizes is the *fcc* pattern. If the edge length of the un cell is 0.3615 nm, calculate the Avogadro constant.

Ans. 6.02×10

36. Metal X (at. mass 55.8) crystallizes in body centered cubic pattern. The unit cell dimension is 0.286 nm. (How many atoms are there per unit cell? (ii) What is the number of nearest neighbours? (iii) What is the volume of the unit cell? (iv) Determine the density of the metal?

Ans. (i) 2, (ii) 8, (iii) 2.34×10^{-2} nm^3 = 2.34×10^{-23} cm^3, (iv) 7.91×10^3 kg m^{-3}

37. KF crystallizes in the NaCl type structure. If the radius of K^+ ion is 0.132 nm and F^- ion is 0.135 nm, wha is the shortest K-F distance? (ii) What is the edge length of the unit cell? (iii) What is the closest K-K distance? (iv) What is the volume of the unit cell?

Ans. (i) 0.267 nm, (ii) 0.534 nm, (iii) 0.378 nm (iv) 1.52×10^{-22} cm^3

38. The observed densities of NaF, AgCl and CsI are respectively 2.79, 5.56 and 4.51 g cm^{-3} while the corresponding theoretical densities are 2.84, 5.57 and 4.53 g cm^{-3}. Calculate the percentage of unoccupied sites in the crystal lattices of these compounds.

Ans. 2%, 0.2%, 0.4%

39. NaF and KF form crystals having the same cubic lattice. The strongest X-ray reflection occurs from crystal surfaces (200) at angles 8° 47′ and 7° 40′. Calculate the ratio of the molar volumes of both the crystalline fluorides.

Ans. 1 : 1.5

40. Copper has a face-centered cubic lattice with a unit cell edge length of 0.361 nm. What is the size of the largest atom which could fit into (i) octahedral holes and (ii) tetrahedral holes of this lattice without disturbing the lattice?

Ans. (i) 0.053 nm, (ii) 0.029 nm

41. KCl has a simple cubic lattice with K^+ and Cl^- ions taken as identical and the (100) plane spacings as 0.3152 nm. At what angle would first and second order reflections from (100) and (110) planes be observed if X-rays of wavelength 0.1537 nm are used?

Ans. First order: 14°7′ for (100) planes, 20°10′ for (110) planes;
Second order: 29°12′ for (100) planes, 48°36′ for (110) planes