B.Sc. (Honours) Part-I
Paper-IA

Topic: Solid State- Crystal System & Miller Indices

UG
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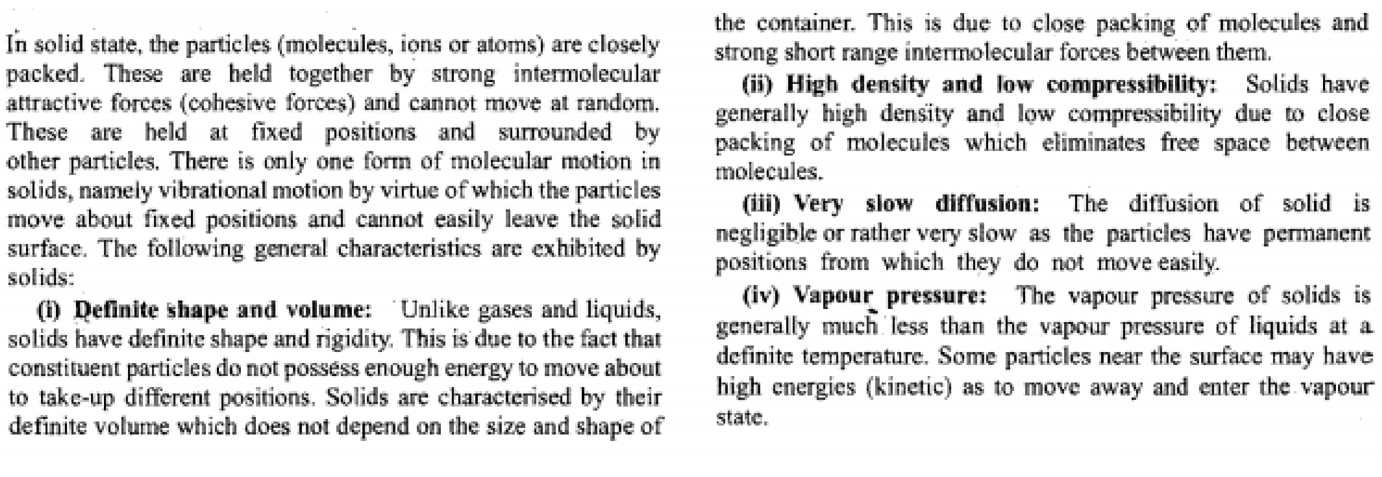
Solid state



In solid state, the particles (molecules, ions or atoms) are closely packed. These are held together by strong intermolecular attractive forces (cohesive forces) and cannot move at random. These are held at fixed positions and surrounded by other particles. There is only one form of molecular motion in solids, namely vibrational motion by virtue of which the particles move about fixed positions and cannot easily leave the solid surface. The following general characteristics are exhibited by solids:

(i) Definite shape and volume: Unlike gases and liquids, solids have definite shape and rigidity. This is due to the fact that constituent particles do not possess enough energy to move about to take-up different positions. Solids are characterised by their definite volume which does not depend on the size and shape of the container. This is due to close packing of molecules and strong short range intermolecular forces between them.

(ii) High density and low compressibility: Solids have generally high density and low compressibility due to close packing of molecules which eliminates free space between molecules.

(iii) Very slow diffusion: The diffusion of solid is negligible or rather very slow as the particles have permanent positions from which they do not move easily.

(iv) Vapour pressure: The vapour pressure of solids is generally much less than the vapour pressure of liquids at a definite temperature. Some particles near the surface may have high energies (kinetic) as to move away and enter the vapour state.

(v) Melting point: The temperature at which the solid and the liquid forms of a substance exist at equilibrium or both the forms have same vapour pressure, is called the **melting point.** On supplying heat energy, the particles acquire sufficient energy and move away from their fixed positions in space. This results in the formation of liquid state. The solids have definite melting points depending on the strength of binding energy. However, in some solids (amorphous solids)* the melting point is not sharp.

4.13 FORMS OF SOLIDS

Solids are divided into two classes on the basis of haphazard and regular arrangement of the building constituents.

(i) Amorphous solids: The term 'amorphous' has been derived from a Greek word '*Omorphe*' meaning shapeless. In amorphous solids the arrangement of building constituents is not regular but haphazard. Although these solids possess some of the mechanical properties such as rigidity, incompressibility, refractive index, etc., but do not have characteristic shapes or geometrical forms. Amorphous solids in many respects resemble liquids which flow very slowly at room temperature and regarded as supercooled liquids in which the cohesive forces holding the molecules together are so great that the material is rigid but there is no regularity of the structure. Glass, rubber, plastics, etc., are some of the examples of amorphous solids.

Amorphous solids do not have sharp melting points. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt change from solid to liquid state.

Thus, amorphous substances are not true solids but can be regarded as intermediate between liquids and solids.

(ii) Crystalline solids: In crystalline solids, the building constituents arrange themselves in regular manner throughout the entire three-dimensional network. The ordered arrangement of building constituents (molecules, atoms or ions) extends over a large distance. Thus, crystalline solids have long range order. A crystalline solid consists of a large number of units, called crystals. **A crystal is defined as a solid figure which has a definite geometrical shape, with flat faces and sharp edges.**

A crystalline substance has a sharp melting point, *i.e.*, it changes abruptly into liquid state. Strictly speaking 'a solid state refers to crystalline state' or 'only a crystalline substance can be considered to be a true solid'.

4.14 ISOTROPY AND ANISOTROPY

The substances which show same properties in all directions are said to be isotropic and the substances exhibiting directional differences in properties are termed **anisotropic.**

Amorphous solids like liquids and gases are said to be isotropic as arrangement of building constituents is random and disordered. Hence, all directions are equal and therefore, properties are same in all the directions.

Crystalline solids are anisotropic. Magnitude of some of the physical properties of crystalline solids such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities, etc., is different in different directions, within the crystal. For example, in the crystal of silver iodide (AgI), the coefficient of thermal expansion is positive in one direction and negative in the other direction.

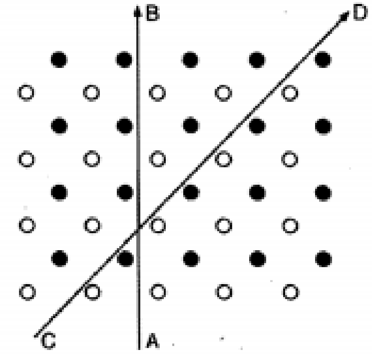


Fig. 4.21 Anisotropic behaviour of crystals

The phenomenon of anisotropy provides a strong evidence for the presence of ordered molecular arrangement in crystals. This can be explained with the help of Fig. 4.21 in which a simple two dimensional arrangement of two different kinds of atoms has been depicted. When a physical property is measured along the slanting line *CD*, it will be different from that measured in the direction of vertical line *AB*, as line *CD* contains alternate types of atoms while line *AB* contains one type of atoms only.

4.15 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids	Amorphous solids
1. They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.	They do not have any pattern of arrangement of atoms, ions or molecules and, thus, do not have any definite geometrical shape.
2. They have sharp melting points and change abruptly into liquids.	Amorphous solids do not have sharp melting points and do not change abruptly into liquids.
3. Crystalline solids are anisotropic. Some of their physical properties are different in different directions.	Amorphous solids are isotropic. Their physical properties are same in all directions.
4. These are considered as true solids.	These are considered pseudo-solids or supercooled liquids.
5. Crystalline solids are rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

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* Melting point of a solid depends on the structure of the solid. It is used for the identification of solids whether it is crystalline or amorphous.

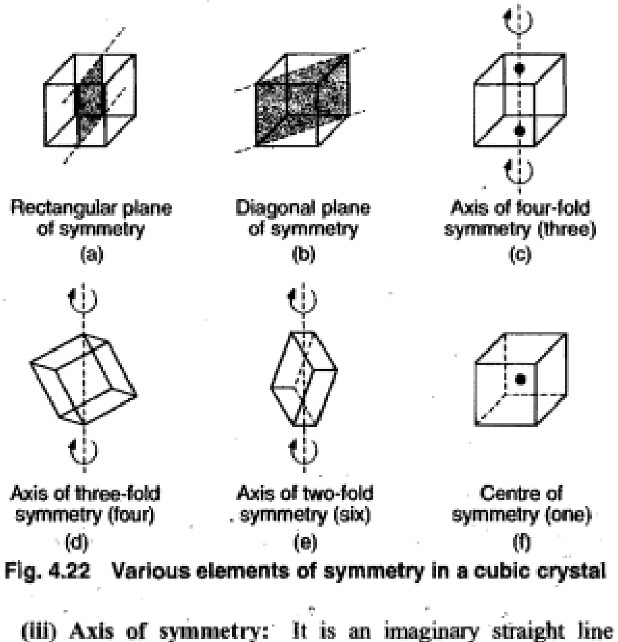
Crystalline solids	Amorphous solids
6. Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop. When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.	Amorphous solids do not have well defined planes. When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.
7. An important property of crystals is their symmetry. There are: (i) plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.	Amorphous solids do not have any symmetry.

4.16 TYPES OF SYMMETRY IN CRYSTALS

(i) Centre of symmetry: It is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry [Fig. 4.22 (f)].

(ii) Plane of symmetry: It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

A cubical crystal like NaCl possesses, in all, nine planes of symmetry; three rectangular planes of symmetry and six diagonal planes of symmetry. One plane of symmetry of each of the above is shown in Fig. 4.22 (a) and (b).



Rectangular plane of symmetry (a)

Diagonal plane of symmetry (b)

Axis of four-fold symmetry (three) (c)

Axis of three-fold symmetry (four) (d)

Axis of two-fold symmetry (six) (e)

Centre of symmetry (one) (f)

Fig. 4.22 Various elements of symmetry in a cubic crystal

(iii) Axis of symmetry: It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution. The axes of symmetry are called diad, triad, tetrad and hexad, respectively, if the original appearance is repeated twice (after an angle of 180°), thrice (after an angle of 120°), four times (after an angle of 90°) and six times (after an angle of 60°) in one rotation. These axes of symmetry are also called two-fold, three-fold, four-fold and six-fold, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle of $\frac{360°}{n}$, around an imaginary axis, the axis is called an n-fold axis.

In all, there are 13 axes of symmetry possessed by a cubical crystal like NaCl as shown in Fig. 4.22 (c), (d) and (e).

(iv) Elements of symmetry: The total number of planes, axes and centre of symmetry possessed by a crystal are termed as elements of symmetry. A cubic crystal possesses a total of 23 elements of symmetry.

Planes of symmetry $= (3 + 6) = 9$ [Fig. 4.22 (a) and (b)]

Axes of symmetry $= (3 + 4 + 6) = 13$ [Fig. 4.22 (c), (d) and (e)]

Centre of symmetry $= 1$ [Fig. 4.22 (f)]

Total number of symmetry elements = 23

4.17 SPACE LATTICE AND UNIT CELL

All crystals are polyhedra consisting of regularly repeating arrays of atoms, molecules or ions which are the structural units. A crystal is a homogeneous portion of a solid substance made of regular pattern of structural units bonded by plane surfaces making definite angles with each other. The geometrical form consisting only of a regular array of points in space is called a **lattice** or **space lattice** or it can be defined as an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space. Fig. 4.23 shows a space lattice. A space lattice can be subdivided into a number of small cells known as unit cells. It can be defined as the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance or it is the smallest block or geometrical figure from which entire crystal can be built up by its translational repetition in three-dimensions. A unit cell of a crystal possesses all the structural properties of the given crystal. For example, if a crystal is a cube, the unit cell must also have its atoms, molecules or ions arranged so as to give a cube.

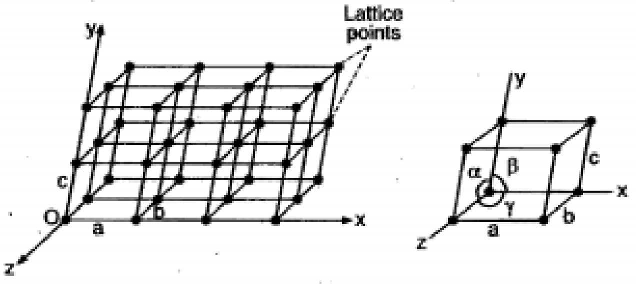


Fig. 4.23 Space lattice and unit cell

System	Edges	Angles	Maximum symmetry elements	Examples
1. Cubic $a = b = c,\ \alpha = \beta = \gamma = 90°$	All the three equal	All right angles	Nine planes, thirteen axes	NaCl, KCl, ZnS, diamond, alums
2. Orthorhombic $a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	All unequal	All right angles	Three planes, three axes	KNO_3, $BaSO_4$, K_2SO_4, rhombic sulphur.
3. Tetragonal $a = b \neq c,\ \alpha = \beta = \gamma = 90°$	Two equal	All right angles	Five planes, five axes	TiO_2, $PbWO_4$, SnO_2, NH_4Br
4. Monoclinic $a \neq b \neq c,\ \alpha = \gamma = 90°, \beta \neq 90°$	All unequal	Two right angles	One plane, one axis	Monoclinic sulphur, $KClO_3$, $CaSO_4 \cdot 2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$
5. Triclinic $a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$	All unequal	None right angles	No planes, no axis	$CuSO_4 \cdot 5H_2O$, H_3BO_3, $K_2Cr_2O_7$
6. Hexagonal $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Two equal	Angle between equal edges = 120°	Seven planes, seven axes	ZnO, CdS, HgS, SiC, AgI
7. Rhombohedral $a = b = c,\ \alpha = \beta = \gamma \neq 90°$	All three equal	All equal but none 90°	Seven planes, seven axes	$NaNO_3$, ICl, quartz ($CaCO_3$)

Each unit cell has three vectors a, b and c as shown in Fig. 4.23. The distances a, b and c are the lengths of the edges of the unit cell and angles α, β and γ are the angles between three imaginary axes OX, OY and OZ, respectively.

For example: For a crystal system, $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$:.

(a) tetragonal (b) hexagonal
(c) rhombohedral (d) monoclinic

[Ans. (c)]

[**Hint:** From the table $a = b = c$ for rhombohedral and cubic system both but $\alpha = \beta = \gamma \neq 90°$ for rhombohedral only.]

4.18 CRYSTAL SYSTEMS

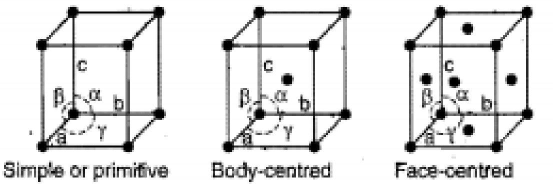
On the basis of geometrical considerations, theoretically there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems have been grouped together. In all, seven types of **basic** or **primitive unit cells** have been recognised among crystals. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral. These are shown in Fig. 4.24 and their characteristics are summarised in the following table.

All crystals do not have simple lattices. Some are more complex. Bravais pointed out that there can be 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven crystal systems are 14.

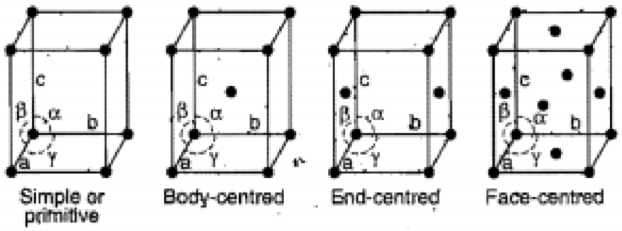
The crystals belonging to cubic system have three kinds of Bravais lattices. These are:

(i) ***Simple cubic lattice:*** There are points only at the corners of each unit.

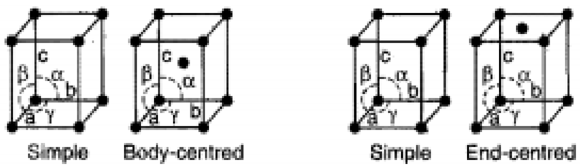
(ii) ***Face-centred cubic lattice:*** There are points at the corners as well as at the centre of each of the six faces of the cube.



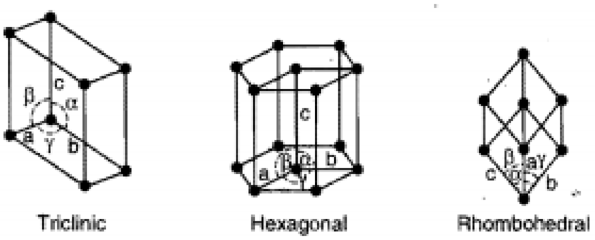
(a) Cubic space lattices



(b) Orthorhombic space lattices



(c) Tetragonal and monoclinic space lattices



(d) Triclinic, hexagonal and rhombohedral space lattices

Fig. 4.24 Bravais lattices

(iii) *Body-centred cubic lattice:* There are points at the corners as well as in the body-centre of each cube.

The number of Bravais space lattices in a given system is listed in the following table and shown in Fig. 4.24.

Crystal system	No. of space lattices	Lattice type
1. Cubic	3	Simple, face-centred and body-centred.
2. Orthorhombic	4	Rectangular and body-centred rectangular prism; rhombic and body-centred rhombic prism.
3. Tetragonal	2	Simple and body-centred tetragonal prism.
4. Monoclinic	2	Monoclinic parallelopiped, monoclinic face-centred parallelopiped.
5. Triclinic	1	Triclinic parallelopiped.
6. Hexagonal	1	Hexagonal prism.
7. Rhombohedral	1	Rhombohedron.

In various unit cells, there are three kinds of lattice points: points located at the corners, points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corner and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

(i) A point that lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one-eighth of each such point lies within the given unit cell.

(ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.

(iii) A face-centred point is shared by two unit cells and only one half of it is present in a given unit cell.

(iv) A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

Type of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-centre	1/2
Body-centre	1

Total number of constituent units per unit cell

$$= \frac{1}{8} \times \text{occupied corners} + \frac{1}{4} \times \text{occupied edge-centres}$$

$$+ \frac{1}{2} \times \text{occupied face-centres} + \text{occupied body-centre}.$$

Determination of Number of Constituent units per unit cell:

Let edge length of cube = a cm

Density of substance = d g cm^{-3}

Volume of unit cell = a^3 cm^3

Mass of unit cell = volume × density = $(a^3 \times d)$ g

$$\text{Number of mol per unit cell} = \frac{a^3 \times d}{M};$$

where, M = molar mass

Number of molecules per unit cell = Number of mole × Avogadro's number

$$Z = \frac{a^3 \times d}{M} \times N = \frac{a^3 \times d \times N}{M}$$

Calculation of number of constituent units in hexagonal unit cell

(i) Constituent units at each corner of unit cell is common among six unit cells hence contribute 1/6th to each unit cell.

(ii) Constituent unit at edge is common to three unit cells hence contribute 1/3rd to each unit cell.

(iii) Constituent units present at the body centre is considered in single unit cell.

(iv) Constituent unit at face centre is common between two unit cells hence contribute 1/2 to each unit cell.

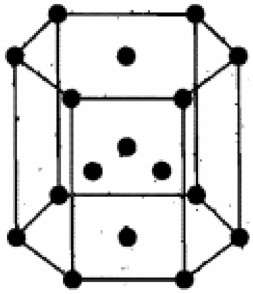


Fig. 4.25 Hexagonal unit cell

In the hexagonal unit cell (Fig 4.25), 12 corners, 2 face centres and 3 constituent units within the unit cells are occupied, hence effective number of constituent units present in the unit cell may be calculated as

$$z = \frac{1}{6} \times \begin{matrix}\text{occupied}\\ \text{corners}\end{matrix} + \frac{1}{2} \times \begin{matrix}\text{occupied}\\ \text{face clutres}\end{matrix} + \begin{matrix}\text{Central}\\ \text{constituent units}\end{matrix}$$

$$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3$$

$$= 6$$

4.19 DESIGNATION OF PLANES IN CRYSTALS—MILLER INDICES

Planes in crystals are described by a set of integers (h, k and ℓ) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts a, b and c along x, y and z-axes, respectively (Fig. 4.26). Then, the intercepts of the unknown plane are given with respect to a, b and c of the parametral plane.

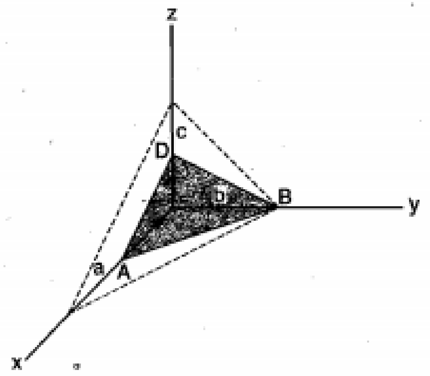


Fig. 4.26 Parametral (intercepts *a*, *b*, *c* along *x*, *y* and *z*-axes)

Thus, the Miller indices are:

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

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

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

Consider the shaded plane *ABD* in Fig. 4.26. The intercepts of the shaded plane along *X*, *Y* and *Z*-axes are $a/2$, b and $c/2$, respectively. Thus,

$$h = \frac{a}{a/2} = 2;$$

$$k = \frac{b}{b} = 1;$$

$$l = \frac{c}{c/2} = 2$$

The plane is, therefore, designed as (212) plane.

Note: (i) If a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller indices will be zero.

(ii) While defining Miller indices for orthogonal crystal, *X*, *Y* and *Z*-axes are considered crystallographic axes.

Some of the important planes of cubic crystals are shown in Fig. 4.27.

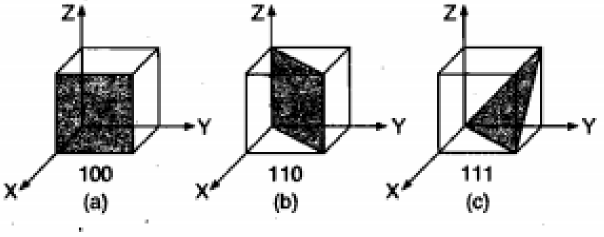


Fig. 4.27 Miller indices of planes in cubic lattice

In (a) intercepts are	1	∞	∞
So, Miller indices are	1	0	0
The plane is designated (100)			
In (b) intercepts are	1	1	∞
So, Miller indices are	1	1	0
The plane is designated (110)			
In (c) intercepts are	1	1	1
So, Miller indices are	1	1	1
The plane is designated (111)			

The distances between the parallel planes in crystals are designated as d_{hkl}. For different cubic lattices these interplanar spacings are given by the general formula,

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

where, *a* is the length of the cube side while *h*, *k* and *l* are the Miller indices of the plane.

The spacings of the three planes (100), (110) and (111) of simple cubic lattice can be calculated.

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

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

The ratio is,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Similarly, $d_{(\text{hkl})}$ ratios for face-centred cubic and body-centred cubic can be calculated. For face-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154$$

For body-centred cubic,

$$\begin{aligned} d_{(100)} : d_{(110)} : d_{(111)} &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \\ &= 1 : \sqrt{2} : \frac{1}{\sqrt{3}} \\ &= 1 : 1.414 : 0.577 \end{aligned}$$

4.20 CRYSTALLOGRAPHY AND X-RAY DIFFRACTION

Crystallography is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances. Geometric crystallography is concerned with the external spatial arrangement of crystal planes and geometric shapes of crystals.