UNIT - IV

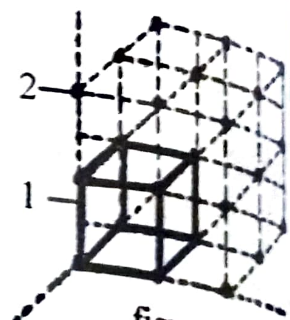
4.1. SOLID STATE

Matter can exist in the three states; solid, liquid and gaseous. In the solid state, the atoms, molecules or ions take up fixed positions and do not move. Solids are characterised by the orderly arrangement of atoms, molecules or ions. The essential characteristics of the solid state are rigidity, typical geometry (shape) and non compressibility. Solids are classified into two type:

i. Crystalline solids e.g. diamond, iodine, sugar, sodium chloride.
ii. Amorophous solids. e.g., rubber, plastics etc. Crystals possess regular arrangement of atoms, definite geometric structure and sharp melting points.

Typical Crystal Lattices :

The positions of atoms, molecules or ions in a crystal relative to one another in space are designated by points. Such a representation is called space or crystal lattice. *A crystal lattice* is an array of points showing how atoms, molecules or ions are arranged at different sites in three-dimensional space. The space lattice is made up of a large number of unit cells.



figure

1 – Uint cell
2 – Crystal lattice

Unit Cell :

A unit cell is the smallest and fundamental portion of crystal lattice; when a unit cell is repeated in three dimensions, it generates the crystal (or) A unit cell is the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance. The unit cell possesses the same geometric shape and the same symmetry properties of the crystal. The Crystal may be considered to consist of infinite number of unit cells.

Elements of Symmetry :

When a crystal is examined, the existence of various types of symmetry is revealed.

There are three essential elements of symmetry.

i) Centre of symmetry.

ii) Plane of symmetry.

iii) Axis symmetry.

Depending upon the arrangement of structural units, different crystals have different symmetries.

I) Centre of symmetry :

The centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions, i.e., meets equivalent points at equal distances on either side. A crystal can never have more than one centre of symmetry. (fig. a).

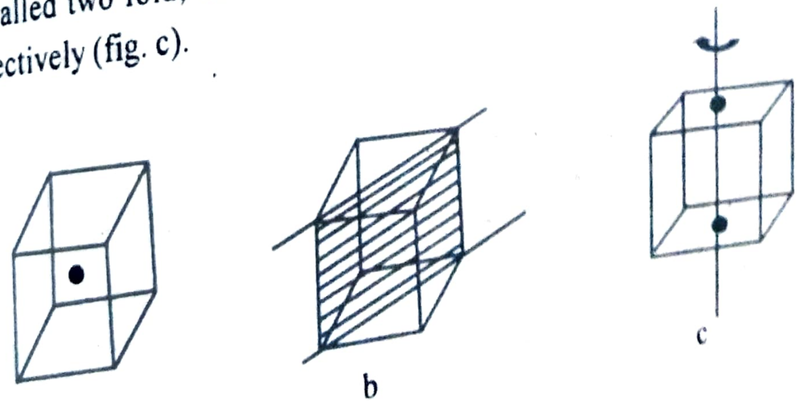
II) Plane of symmetry :

A plane of symmetry of crystal is an imaginary plane which divides the crystal into two halves (equal parts) so that one is the exact mirror image of the other (fig b).

III) Axis of symmetry :

An axis of symmetry is a line about which the crystal may be rotated such that it presents exactly the same appearance more than once in a complete revolution (i.e., through an angle of 360^0).

If the equivalent configurations occur twice, thrice, four times or six times (i.e., after the rotation of 180^0, 120^0, 90^0 or 60^0) the axes of rotation are called two fold, three fold, four fold and six fold axis of symmetry respectively (fig. c).



a b c

Symmetry elements of a cube :

There are 23 elements of symmetry in a simple cubic crystal. A cube has 2 types of planes of symmetry: three rectangular planes of symmetry and six diagonal planes of symmetry. There are 3 types of axes of symmetry: three four-fold axis of symmetry passing through the centres of opposite faces.

four three-fold axis passing through opposite corners and six two-fold axis passing through midpoints of opposite edged. The cube has a centre of symmetry. Thus a cube has the following elements of symmetry.

Axis of symmetry :		
Four-fold axis of symmetry	= 3	
Three-fold axis of symmetry	= 4	
Two-fold axis of symmetry	= 6	= 13
Plane of symmetry :		
Rectangular planes of symmetry	= 3	
Diagonal planes of symmetry	= 6	= 9
Centre of symmetry		= 1
Total number of elements of symmetry		23

Bragg Equation :

Bragg developed a simple equation to determine the structure of a crystal using X-rays. This equation in known as Bragg's equation or Bragg's law.

Bragg's equation/Law : $n\lambda = 2d \sin \theta$

Derivation :

Figure 1 shows a beam of X-rays falling on the crystal surface. Two successive atomic planes of the crystal are shown separated by a distance 'd'. Let the X-rays of wavelength λ strike the first plane at an angle θ. Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane if the extra distance travelled by them (CB+BD) is equal to integral number, n, of wavelengths. That is

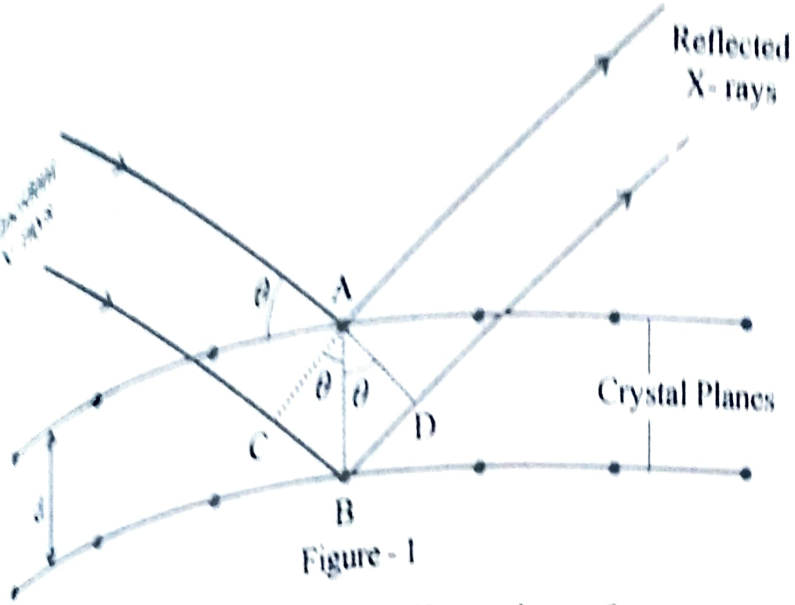


Figure - 1

Reflection of X -rays from two different planes of a crystal

$$n\lambda = CB + BD \qquad ...(1)$$

Geometry shows that

$$CB = BD = AB \sin\theta \qquad ....(2)$$

From (i) and (ii) it follows that

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

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

or

This is known as the **Bragg equation**. The reflection corresponding to n = 1 (for given series of planes) is called the **first order reflection** corresponding to n = 2 is the **second order reflection** and so on.

Bragg equation is used chiefly for determination of the spacing between the crystal planes 'd'. For X-rays of specific wave length λ, the angle θ can be measured with the help of Bragg X-ray spectrometer. The interplannar distance 'd' can then be calculated with the help of Bragg equation.

Miller Indices :

Let OX, OY and OZ be the crystallographic axes. Let ABC be a unit plane. The unit intercepts are a, b, and c. According to the law of rationality of indices of intercepts, the intercepts of any face as KLM on the same axis will be simple multiples of a,b, and c. From figure 2 the intercepts of the plane KLM on the three axis are 2a:2b:3c.

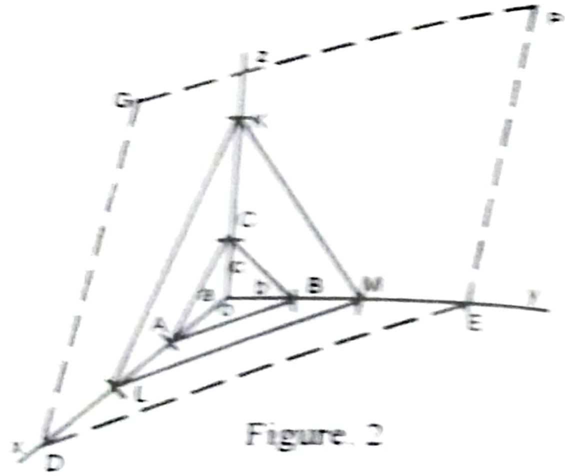


Figure. 2

Law :

The intercepts of any face of a crystal along the crystallographic axis are either equal to the intercepts (a,b,c) or some simple **multiples of them.**

The coefficients of a,b and c are known as **Weiss indices.** Weiss indices are not always whole numbers as in the given example. They may have fractional values as well as infinity. Therefore instead of Weiss indices. Miller indices have been introduced. To get the miller indices the reciprocals of the Weiss indices are taken. They are converted into whole numbers by multiplying them through out by the least common denominator.

Thus miller indices are the reciprocals of the coefficients of unit intercepts multiplied by their least common denominator.

In figure for the plane KLM the Weiss indices of the planes are 2,2 and 3. The reciprocals are 1/2, 1/2, and 1/3. Multiplying them by least common denominator i.e., 6 we get 3, 3 and 2. Thus the miller indices for the plane KLM are 3:3:2. The plane is designated as (332) plane. In general the planes are termed (hkl) planes. Here for the KLM plane in figure, h=3, k=3 and l=2. The h, k and l and are the miller indices.

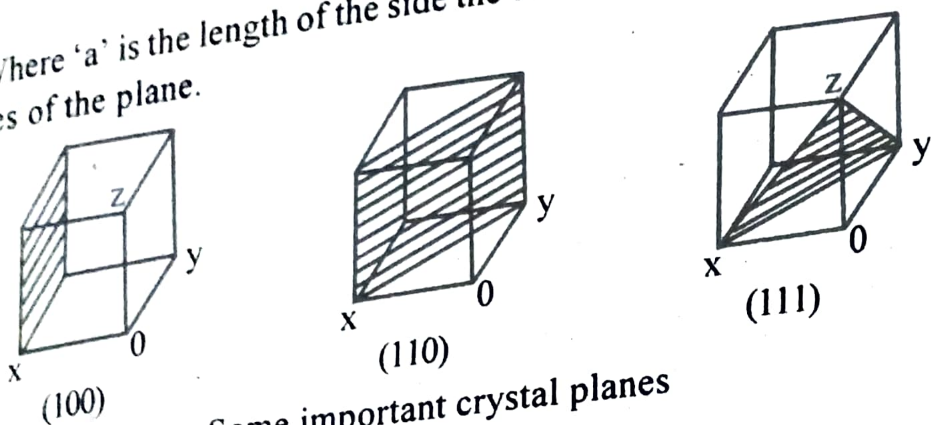
For the plane ABC in the Figure 2, the Weiss indices are l, l and l and the miller indices are also 1, l and 1. Therefore the plane ABC is called (111) plane.

For the plane DEFG in Figure 2 the Weiss indices are 3,3 and ∞. Therefore the miller indices are 3,3 and 0. Therefore the plane DEFG is known as the (330) plane.

The distances between the parallel plane in a crystal are designated at d_{hkl}. For a cubic lattice.

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

Where 'a' is the length of the side the cube and h, k and l are the miller indices of the plane.



Some important crystal planes

Crystal systems :

All crystals belong to one of the following seven crystal systems: Cubic, Hexagonal, Tetragonal, Orthorthombic, Monoclinic, Triclinic and Rhombohedral.

Cubic systems :

The cubic system is the chief among the seven basic crystal systems. Crystals belonging to this system are built upon three equal axis at right angles to one other. There are three types of lattices depending upon the shape of the unit cells.

i) Simple cube (sc):

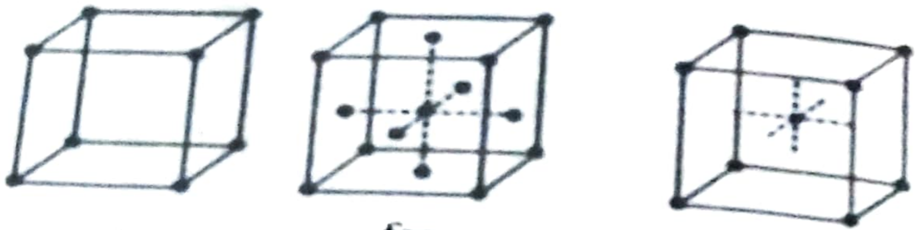
(Simple cubic lattice) : This type of unit cell contains an atom (or particle) in each corner of the cube. Each atom is surrounded by 6 nearest neighbours. Example : Potassium chloride.(figure - a)

ii) Face centred cube (fcc) :

There is a particle at the centre of each face of the cube in addition to one at each of the eight corners. Each atom in fcc lattice is surrounded by 12 nearest neighbours. Example: sodium chloride, diamond, aluminium, silver.(figure - b)

iii) Body centred cube (bcc) :

In addition to the eight particles at the corners of the cube, there is one particle atom at the centre. Each atom in bcc lattice is surrounded by 8 nearest neighbours. Example: Calcium chloride, tungsten, iron (figure ...



sc a   fcc b   bcc c

Solved University problem:

1. What are the miller indices of planes in a crystal which make following intercepts on x,y and z axis respectively.

Solution :

i. $\frac{a}{2}$, b $\frac{-c}{3}$;   ii. $\frac{-a}{3}$, b, $\frac{c}{2}$

i) The Weiss indices of the planes are 1/2, 1 and 1/3. The reciprocals are 2,1, -3.

The Miller indices for the planed are 2,1 and -3 (Here least common denominator is 1.)

ii) The Weiss indices of the planes 1/3, 1 and 1/2

The reciprocals are - 3, 1 and 2.

The miller indices for this plane are - 3, 1 and 2.

2. How do the spacin...