Solid state

Types of solids

There are two types of solids.

① crystalline solid ② amorphous solid.

[1] Crystalline solid : If ions, atoms or ~~m~~ and moles present in solid are arranged in definite geometric pattern, it is called crystalline solid.

eg: suger, NaCl

[2] Amorphous solid : If ions, atoms and mole present in solid are not arranged in any regular fashion, it is called amorphous solid.

eg: Glass, plastic.

Difference betn amorphous solid and crystalline solid :

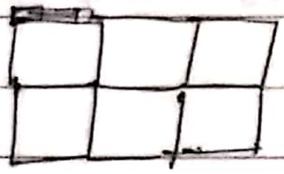
~~Amorphous~~ Crystalline solid	~~Crystalline~~ Amorphous solid
① The atoms or ions are arranged in a definite pattern.	① The atoms or ions are not arranged in a definite pattern.
② It having sharp melting point.	② It ~~ha~~ melts gradually over a range of temp
③ Properties like refractive index, electrical conductivity	③ properties like refractive index, electrical conducting

have different values in different dir^n called as anisotropy property shown by crystalline solid.

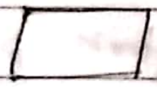
are identical in all dir^n called as isotropy property shown by amorphous solid.

Space lattice and Unit cell:

Space lattice: The regular arrangement of ions, atoms or mole, constituting the crystal in the three dimensional space within the crystal is called the space lattice.



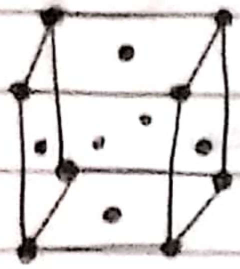
Unit cell:- The smallest portion of the complete space lattice, which when repeated over & again in different directions produces the complete space lattice is called unit cell.



Types of unit cell:

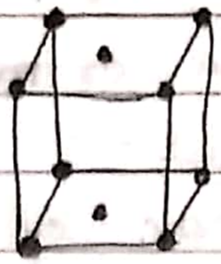
1. Simple unit cell: This type of unitcell is produced when the particles are present only at the corners of the unit cells.

[2] Face-centred unit cell: If the particles are located at the centre of each face in addition to the corners, face centred unit cell is produced.



[3] Body-centred unit cell: If the particles are present at the corners centres of the cell in addition to the corners, body centred unit cell is produced.

[4] End-face centred unit cell: If the particles are located at the centre of end faces, in addition to the corners, end face centred unit cell is produced.



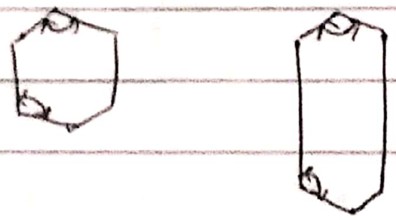
Laws of crystallography :

Three fundamental laws of crystallography are :

① The law of constancy of interfacial angles
② Law of symmetry
③ The law of rational indices .

[1] The law of constancy of interfacial angles :

The angles betn the corresponding faces called the interfacial angles of the crystals of a particular substance are always the same . This is called the law of constancy of interfacial angles .



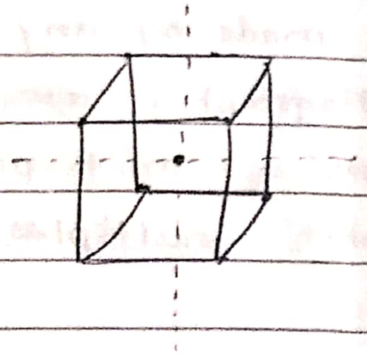
[2] law of symmetry : [Symmetry elements in crystals]

The symmetry element is a geometrical entity such as a plane, a line or point with respect to which one or more symmetry operation may be carried out .

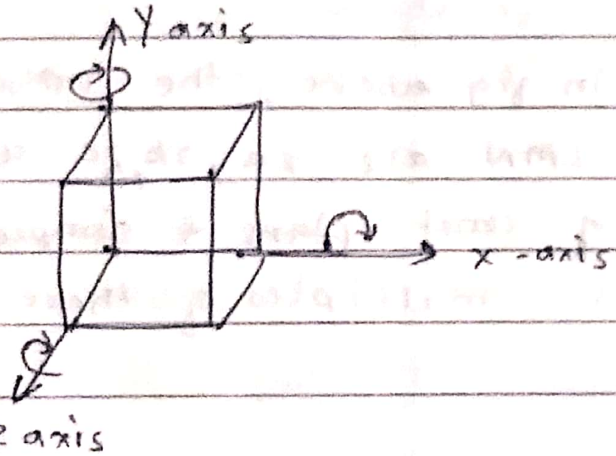
Different symmetry elements of a crystal are described as under :

[i] centre of symmetry :- It is defined as an imaginary point in the crystal such that any line passing thr' this point intersects the

crystal in equal two parts.



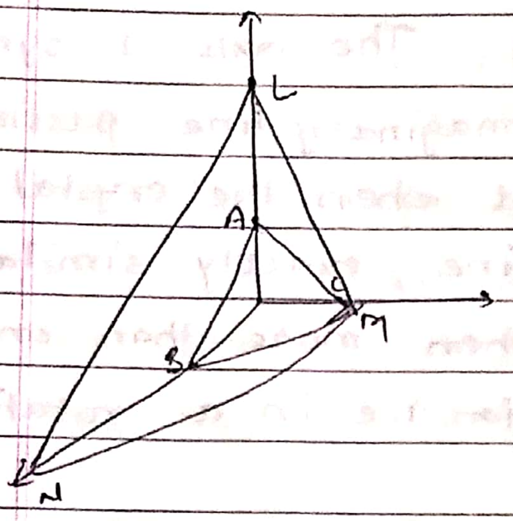
ii) Axis of symmetry: The axis of symmetry is defined as the imaginary line passing thr the crystal such that when the crystal is rotated about this line, exactly similar appearance occurs when more than once in one complete revolution i.e in a rotation th 360°.



iii) Plane of symmetry: It is defined as an imaginary plane passing thr, the crystal such that it ~~de~~ divides the crystal into two pa in such a way that one part is ~~mi~~ mirror image of the other.

13 The law of rational indices:

The intercepts made by any face of the crystal on the crystallographic axes are either same as intercepts of unit plane or simple whole number multiples of those of the unit plane.



For example, in fig above, the intercepts made by face LMN are 2a, 2b, 3c which are intercept of ~~unit plane & simple~~ whole number multiples of those of unit plane.

Weiss indices:

If a face makes intercepts na, n'b & n''c on the crystallographic axes, the face may be represented by (n, n', n''). The no. n, n', n'' thus used to represent a face are called Weiss indices.

Miller indices: It is defined as the reciprocals of the coeffi of the intercepts, expressed as

Integers.

① A crystal plane has intercepts on the three axes of crystal in the ratio of 3 : 2 : 1. What are the Miller indices of the plane ?

→

The reciprocal of the ratio of intercepts are

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

Multiplying by no. 6

2 : 3 : 6

The Miller indices of the plane are 236

② The intercepts made by the face LMN are 2a, 3b, 3c. What are the Miller indices of the plane ?

→

The reciprocal of the intercepts are

$\frac{1}{2}, \frac{1}{3}, \frac{1}{3}$

Multiplying by no. 6

3, 2, 2

The face is represented as (3 2 2)

③ The weiss indices of a planes are $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ What are the Miller indices ?

→

Miller indices are reciprocals of weiss indices

$1/\frac{1}{2}\quad 1/\frac{1}{2}\quad 1/\frac{1}{2}$

2 2 2

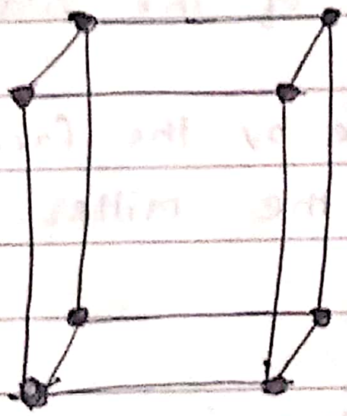
Miller indices will be (2 2 2)

Cubic lattice and types of cubic lattice

The crystals belonging to the cubic system have three kinds of lattices depending upon the shape of the unit cell. These are:

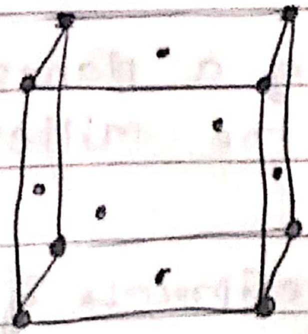
1. The simple cubic lattice (P) :-

The simple cubic lattice in which there are points only at the corners of each unit cell.

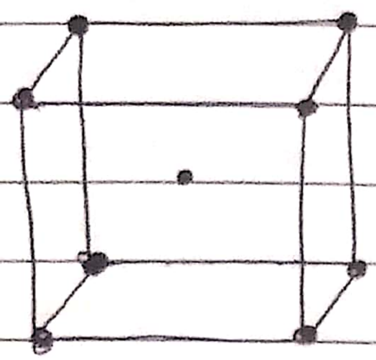


2 The ~~phase~~ face centred cubic lattice (F):-

The face centred cubic lattice in which there are points at the corners as well as at the ~~corners~~ centre of each of the six faces of the cube.



3. The body - centred cubic lattice (I): The body centred cubic lattice (I) in which there are points at the corners as well as in the body centre of each cube.



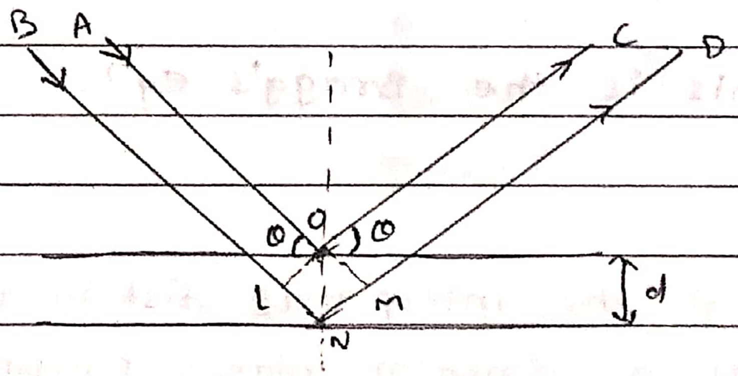
Diffraction of X-rays :

The Bragg eqn : -

Bragg pointed out that the reflection of X-rays can take place only at certain angles which are determined by the wave length of X-rays & the dist betn the planes in the crystal. The fundamental eqn which gives a simple reln betn the wavelength of the X-rays, the interplanar dist in the crystal & the angle of reflection, is known as Bragg eqn.

Derivation of Bragg eqn

Consider following fig.



The horizontal lines represent ||el planes in the crystal stru separated from one another by the dist d. Suppose a beam of X-rays falls on the crystal at galancing angle θ. Some of these rays will be reflected from the upper plane at the same angle θ while some others will be absorbed & get reflected from the successive layers. Let the rays AB & CD are the incident & reflected beam resp. The ray BD will be in phase with AC only if the extra dist travelled by ray BD is equal to an integral no. of wavelength

$\therefore LN + NM = n\lambda$

Since the triangles OLN & OMN are congruent, hence $LN = NM$

$$2LN = n\lambda \quad \text{— ①}$$

From fig $\sin\theta = \frac{LN}{ON}$

$$LN = \sin\theta \cdot ON$$

$$LN = d\sin\theta \quad \text{— ②}$$

putting ② in ①

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

This is the Bragg's eqn.

① Find the interplanar dist in a crystal in which a series of planes produce a first order reflection from a copper X-ray tube ($\lambda = 1.539 A^\circ$) at angle of 22.5°.

→

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

$d = \frac{\lambda}{2\sin\theta}$ $n = 1$

$\therefore d = \frac{1.539 A^\circ}{2\sin(22.5)} = \frac{1.539 A^\circ}{2(0.383)} = 2.01 A^\circ$

$= 2.01 \times 10^{-10}$ m

(2) Diffraction angle 2θ equal to 16.8° for a crystal having interplanar dist in the crystal is 0.400nm when second order diffraction was observed. Calculate the wavelength of X-rays used.

→

$n = 2$, $d = 0.400\,nm = \cancel{0.400 \times 10^{-9} m}$

$= 0.400 \times 10^{-9}\,m$

$2\theta = 16.8^\circ \quad \therefore \theta = 8.40^\circ$

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

$2 \times \lambda = 2 \times 0.400 \times 10^{-9}\,m \times \sin(8.4^\circ)$

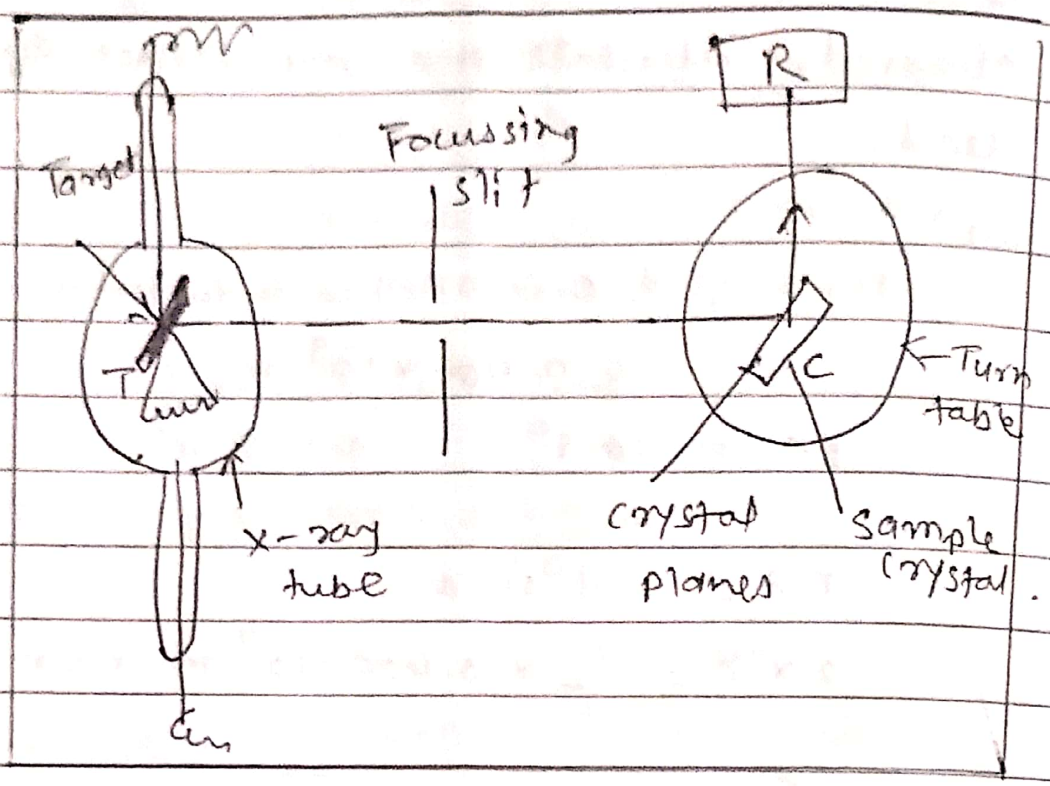
$\lambda = 0.400 \times 10^{-9}\,m \times 0.146$

$= 0.0584 \times 10^{-9}\,m$

$= 0.584 \times 10^{-10}\,m$

$= 0.584\,A^\circ$.

Experimental methods: Rotating crystal:



X-rays generated in the tube T are passed thro' a slight so as to obtain a narrow beam which is then allowed to strike a single crystal c mounted on the turn-table. The crystal is rotated gradually by means of the turn-table so as to increase the glancing angle at which the x-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recording device R, such as a photographic plate. The angle for which reflections are maxm give the value of θ. The process is carried out for each plane of crystal. The ~~lowest~~ lowest angle at which the maxm reflections occurs corresponds to n=1. This is called first order reflection. The next higher angle at which the maxm reflection occur again, corresponds to n=2. This is the second order reflection, & so on.

Powder method :- This method is more widely used particularly for crystals with simple structures. In this method, no rotation is necessary since the powder sample already contains microcrystals arranged in all possible orientations. The powder consist of many small crystals which are oriented in all possible directions. As a result of this, X-rays are scattered from all sets of planes. The scattered rays are detected by using an X-ray sensitive film. i.e the sub to be examined is finely powdered & is kept in the form of a cylinder inside a thin glass tube. A narrow beam of X-rays is allowed to fall on the powder. The diffracted X-rays strike a strip of photographic film arranged in the form of a circular arc, as shown in fig below. As a result of this we get lighted areas in the form of arcs of lines at diff distances from the incident beams. These distances can be converted into scattering angles to be used in the Bragg's eqⁿ for diff planes of the crystal.

Determination of crystal stru of NaCl & KCl on the basis of Bragg's.

The values of θ for the first order reflection from the three faces of NaCl crystal are found to be 5.9°, 8.4° & 5.2° resp. Applying the Bragg eqⁿ & knowing that n & λ are the same in each case, the dist d betⁿ successive planes in the three faces will be in the ratio of

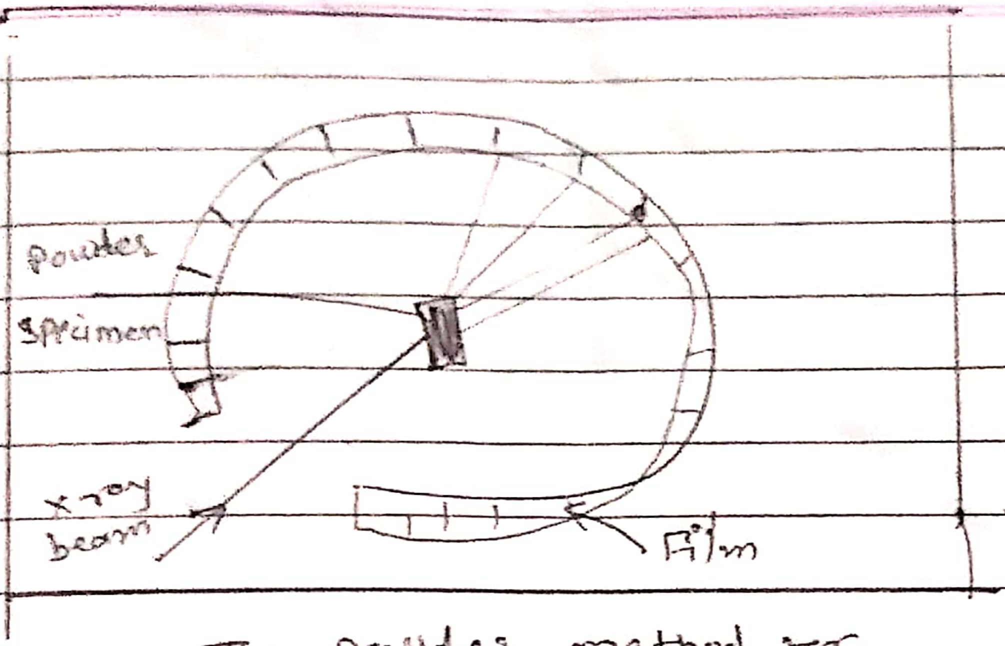
$$\frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ}$$

9.61 : 6.84 : 11.04

1 : 0.70 : 1.14

This ratio is very close to the spacin along the three ~~phases~~ planes of a face-centred cube. Thus NaCl has face-centred cubic stru

The same face-centred cubic stru was found in KCl.



The powder method for x-ray diffraction