X - ray Crystallography.
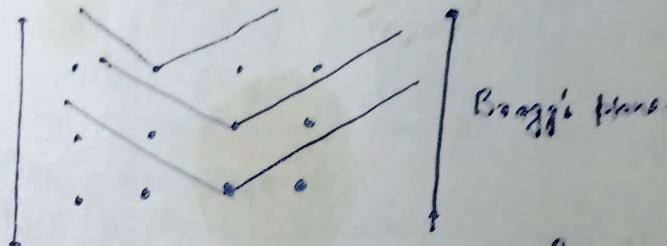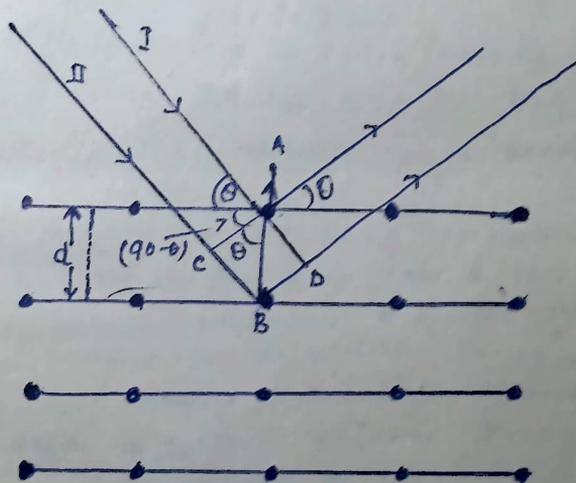
William H. Bragg (1913) used Polychromatic light.
William Lourence Bragg (son) elaborated the work of
his father. He found that crystal can be utillised in,
reflection, deffaction and grating.

He established a very simble and useful
relation Co-relating the wave length of x-ray and distance
between consecutive lattice Planes and this serves
as a very powerful tool for study of crystal structure
and Nature of x-ray

Bragg's Plane

Derivation of Bragg's Equation :—>

$PA1$ Ct and $\angle PAt = \theta$
∴ $\angle JAC = 90-\theta$
$AB \perp TM$
and $\angle AB = 90°$
∴ $\angle CAB = \theta$

In $\triangle ACB$
$\sin\theta = \dfrac{CB}{AB}$
∴ $CB = AB\sin\theta$

Consider a beam of monochromatic X-rays incident
on a set of parellel and equidistance lattice Called
Bragg's plane's in the crystal Substance.

 Let d cm be the distance between
Successive plane and θ be the glacial angle
i.e angle between the direction of incident angle
and the plane.
 The two Parallel rays I and II are reflected
by two atoms A and B in two adjacent Plane. B is
exactly below to A. The ray reflected from B travels a longer
distance than that reflected from A. Draw AC and AB
Perpendicular to the direction of the incident and reflected rays.
each of these line makes angle θ with AB, those length is
given by d.
 Further $CB = BD = AB\sin\theta$
       $= d\sin\theta$

The additional Path travelled by the ray reflected from the Second layer is equal to $(CB + BD)$

Thus the Condition for Consecutive interference {i.e maximum intensity} between the two rays is

$$CB + BD = n\lambda$$

or, $2BD = n\lambda$ [∵ $CB = BD$]

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

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

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

$(n = 1, 2 \cdots)$
order of reflection

and λ is const

then $d \propto \dfrac{1}{\sin\theta}$

where $n =$ Simple integer is $1, 2, 3 \cdots \cdots$

If monochromatic x-rays are used, λ has definite value for a given set of lattice plane. It also has a fixed value. There for the possibility of getting maximum reflection (Possibility of getting reflected wave in same phase with one another. dependens upon the glacial angle θ.

If θ is increase gradually, the number of Position will be found at which the reflection will be maximum.

then Path diff $= \lambda$

If $n = 1$

The reflection is of 1st order when Path diff $= \lambda$ i.e; $n = 1$

when Path diff $= 2\lambda$ i.e. $n = 2$

The reflection is of second order.

Experimental result :— In using sepctrometer, the crystal is kept in such position that θ is equal to Zero and the position of ionisation chamber is adjusted to receive the x-rays. The crystal is rotated in small step starting from $\theta = 0$ The ionisation Chamber accordingly rotated through twice that the angle of receive reflected X-ray

A graph is plotted between glacial angle θ and intensity of ionisation. The graph is known as X-ray spectrum, the peaks Corresponds to order of reflection.

θ_1 θ_2 θ_3 $\theta =$ Glacial angle

Intensity of Ionisation

θ_1 θ_2 θ_3 Glacial angle

INTENSITY OF IONISATION
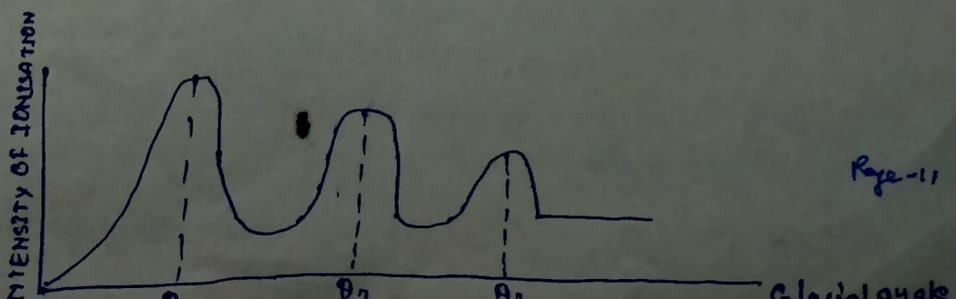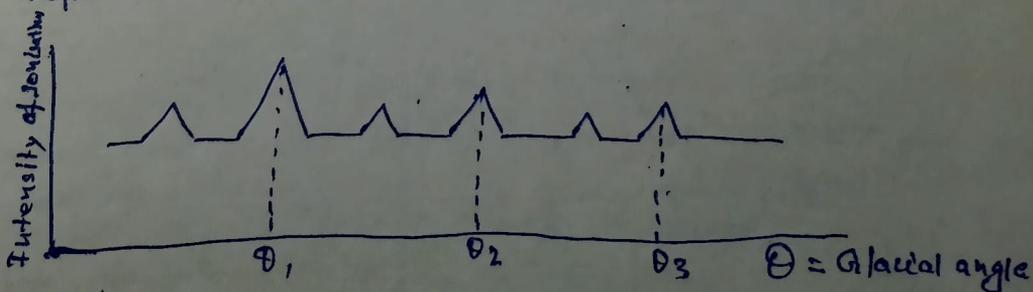
What do you mean by Weiss and Miller indices.

Weiss indices :

The law of rational indices states that intercept of any plane of a crystal along crystallographic axis are simple multiple of unit intercepts. The unit intercepts (or length) are shown as (a, b, c).

The $OA = a$, $OB = b$ and $OC = c$ are the unit intercepts.
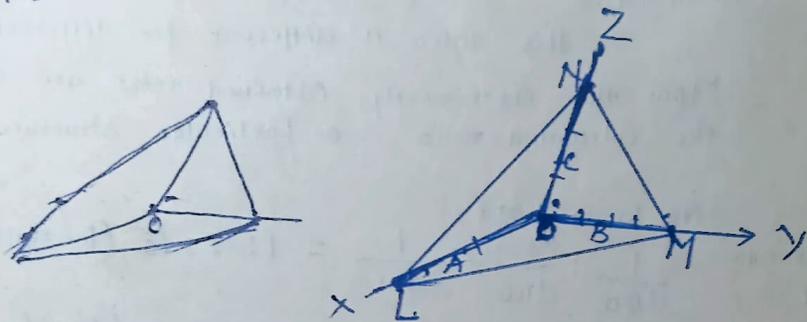
A Crystal Plane LMN has the intercepts OL, OM and ON along x, y and z axis where

$$OL = 2a$$
$$OM = 4b$$
$$\& \; ON = 3c$$

The Coefficient of unit intercepts of a crystal plane are called Weiss indices of a plane.

Weiss indices are not always integers. They may have fractional as well as infinite values. So, Weiss indices are not easy to be used, Hence it is replaced by Miller indices.

Miller indices :-

Miller indices of a crystal plane are obtained by taking the reciprocal of Weiss indices and multiplying throught by the lowest possible number in order to make all reciprocals as integers.

for KLM Crystal Plane : - We have the following data :-

I. Intercepts : - $2a, 4b, 3c$

II. Weiss indices : - $2, 4, 3$

III. Reciprocal of Weiss Indices : - $\frac{1}{2}, \frac{1}{4}, \frac{1}{3}$

IV. Multiplying by 12, : - $6, 3, 4$

∴ Miller indices : - $6.3,4$

If a plane is parallel to x and y axes and cuts z axes at unit intercept then (h, K, l) of the plane is 001.

     If a plane cuts x, y and z axes at unit length, the Miller indices are 111 and hence the plane is designated as 111.

     <u>The distance between the parallel planes in a crystal are shown as $d_{h,k,l}$ for different Cubic Lattices,</u>

$$d_{h,k,l} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \ , \ \text{where } a = \text{Side length of the Cube.}$$

Q: – A crystal plane intercepts the Crystallographic axes of the following multiples of unit intercepts $\frac{3}{2}$, 2 and 1. Find out the Miller indices of the plane.

Ans: –

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

   2. Reciprocal of weiss · $\frac{2}{3}, \ \frac{1}{2}, \ 1$
            indices

   3. Multiplying by Six (6) :– 4, 3, 6

   ∴. Miller indices are, 4, 3, 6

The
Q: – Relative spacings for the unit cell for a f.c.c. lattice are $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ and $\frac{a}{\sqrt{3}}$. Find out the relation $d_{100} : d_{110} : d_{111}$.

Ans: – In the Cubic System, we know the relation.

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

$$\therefore \ d_{100} = \frac{a}{2\sqrt{1^2 + 0^2 + 0^2}} = \frac{a}{2 \times 1} = \frac{a}{2}$$

$$\therefore \ d_{110} = \frac{a}{2\sqrt{2}\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{2\sqrt{2}\cdot\sqrt{2}} = \frac{a}{4}$$

$$\text{for, } d_{111} = \frac{a}{\sqrt{3}\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}\cdot\sqrt{3}} = \frac{a}{3}$$

Now desired relation.

$$d_{100} : d_{110} : d_{111} \text{ are } \frac{a}{2} : \frac{a}{4} : \frac{a}{3} = \frac{1}{2} : \frac{1}{4} : \frac{1}{3}$$

Application of Bragg's Equation

(i) Determination of Crystal Structure by Bragg's Law:—

The X-ray beam is allowed to fall on crystal surface and the crystal is rotated. X-rays are reflected from various lattice planes. The intense reflection are noted with the help of Bragg's Spectrometer.

The Glancing angle (θ) for each intense reflection is recorded. Now using the Bragg's equation $2d\sin\theta = n\lambda$ the ratio of lattice spacing for various groups of planes can be obtained.

This ratio is different for different crystal.

Now the experimently obtained ratio are compared with the calculated ratio, a particular structure may be identified.

We know that,

Simple Cubic (S.C.)
$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \sqrt{3} \quad (\text{for simple cubic crystal})$$

(f.c.c)
$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2} \quad (\text{for f.c.c. crystal})$$

(B.C.C) and,
$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \frac{\sqrt{2}}{2} : \sqrt{3} \quad (\text{for b.c.c. crystal})$$

Let us consider that with Bragg's X-ray spectrometer. For the first order Intense reflection for plane (100) (110) & (111) the glancing angle are. $\theta_1, \theta_2 \& \theta_3$ respectively, then we have,

$$2d_{100}\sin\theta_1 = 2d_{110}\sin\theta_2 = 2d_{111}\sin\theta_3 = 1 \times \lambda \quad \left(\because \lambda \text{ is same for each case}\right)$$

$$\therefore \frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} :: \sin\theta_1 : \sin\theta_2 : \sin\theta_3$$

or, $d_{100} : d_{110} : d_{111} = \frac{1}{\sin\theta_1} : \frac{1}{\sin\theta_2} : \frac{1}{\sin\theta_3}$

In case of KCl crystal
$$\theta_1 = 5°23', \quad \theta_2 = 7°37' \quad \text{and} \quad \theta_3 = 9°25'$$

$$\therefore \frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = \sin 5°23' : \sin 7°37' : \sin 9°25'$$

$$= 5.09 : 0.1326 : 0.1056$$

$$= 1 : 1.414 : 1.744$$

$$= 1 : \sqrt{2} : \sqrt{3} \quad (\text{Approx.})$$

This shows that KCl is a simple cubic crystal. In this way crystal structure may be decided.

or, $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$