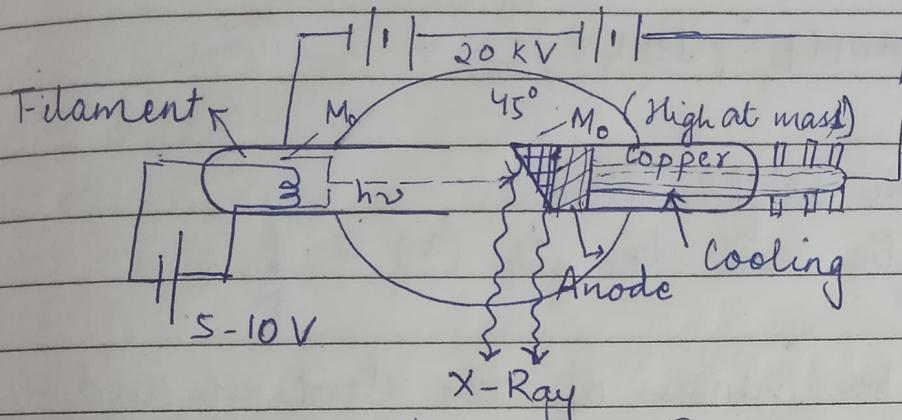


X-Ray Crystallography

Date: 11

XRC

Production of X-rays by Coolidge tube.



W. Roentgen
1895

Pressure $\rightarrow 10^{-4}$ to 10^{-5} torr.

* Properties of X-Rays and Applications.

- (i) Short wavelength 1 \AA° to 6 \AA° .
- (ii) Invisible to naked eyes.
- (iii) Can be reflected and refracted.
- (iv) Can show polarisation, diffraction.
- (v) Not deflected by electric and magnetic field.
- (vi) Very high energy, $h\nu = \frac{hc}{\lambda}$, can penetrate in substances.
- (vii) Ionize gases & show photoelectric effect.
- (viii) Can produce secondary X-rays.
- (ix) Destructive effect on tissues.

* Applications.

- Industrial and engineering.
- To see the quality of weld.
- To detect cracks in surfaces.
- To study the crystal structure.
- Scientific and research.
- Determination of atomic no. and chemical

elements.

$$eV = h\nu = \frac{hc}{\lambda} - (1)$$

$$\lambda = \frac{hc}{eV} = \frac{12.4}{V} - (2)$$

V = kilovolt (10 kV).

* Electron Diffraction

$$\text{de-Broglie wavelength } (\lambda) = \frac{h}{p}$$

Let m be mass of the electron and v is the velocity, then momentum $p = mv$

$$\lambda = \frac{h}{mv} - (1)$$

If V is the potential applied to electron to accelerate it, then energy = eV.

$$\text{Kinetic energy} = \frac{1}{2}mv^2$$

$$\text{So, } \frac{1}{2}mv^2 = eV - (2)$$

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

$$\lambda = \frac{\sqrt{150}}{V}$$

$$V \approx 50 \text{ kV}$$

* Neutron Diffraction

$$\lambda = \frac{h}{p} = \frac{h}{M_n v}$$

where, M_n = mass of neutron, which is 2000 times more than the mass of e^- , the wavelength associated with a neutron is about $1/2000$ that of an electron velocity.

The energy E of the suitable neutrons may be calculated by recalling,

$$E = \frac{P^2}{2}$$

2 Mn

$$\lambda = \frac{h}{\sqrt{2M_n E}}$$

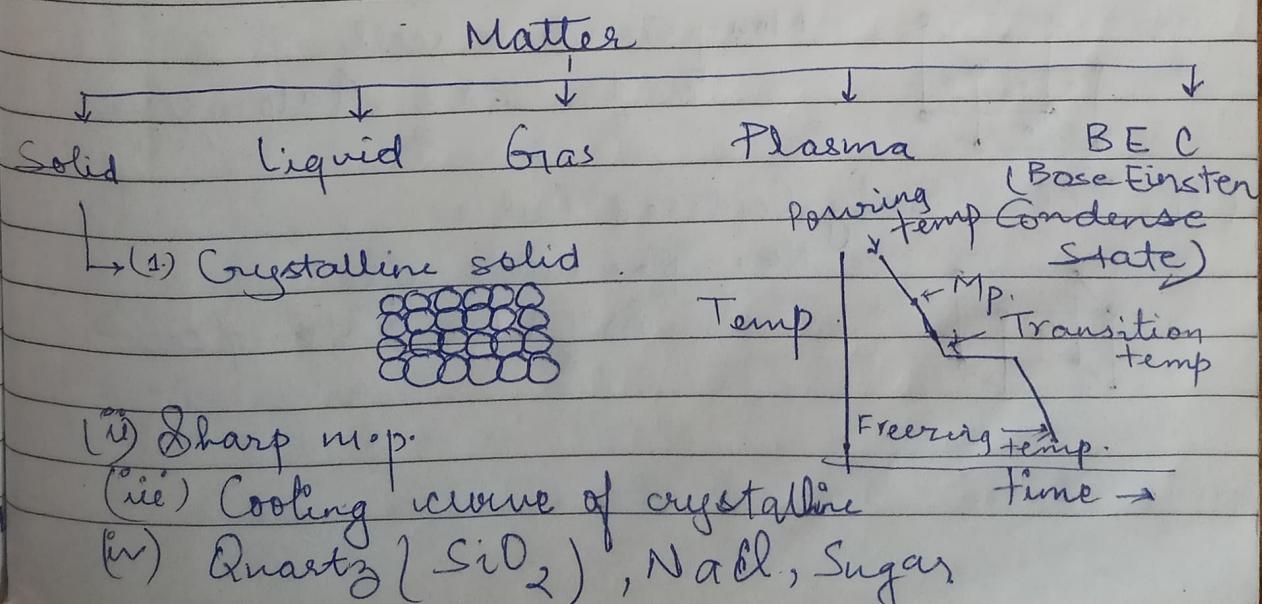
$$\lambda \approx \frac{0.28}{\sqrt{E}} \quad \text{--- (2)}$$

Here, λ is expressed in \AA° and E in eV
 $E = 0.1 \text{ eV}$, $\lambda = 1 \text{ \AA}^\circ$.

$$E = 0.01 \text{ eV}, \quad \lambda = 1 \text{ \AA}.$$

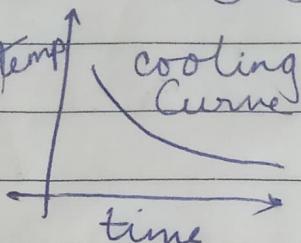
A particularly major role of the neutron diffraction has been investigating the magnetic structure of solids. This is the result of the facts that the neutrons possesses magnetic moments and that these moments interact with the magnetic moment of the scattering atom of the solids. This gives an additional scattering mechanism for neutrons.

Classification of Matter and Solids.



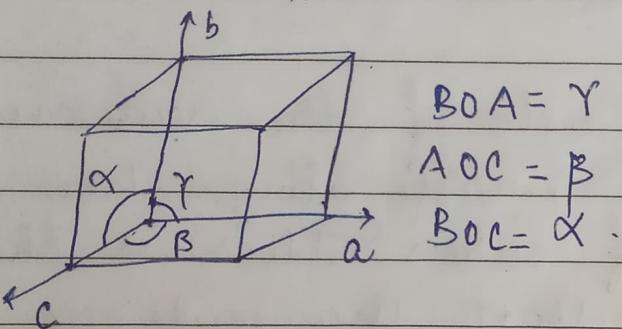
(2) Amorphous Solids.

- (i) Irregular arrangement of atoms
- (ii) No sharp m.p.
- (iii) Continuous cooling curve

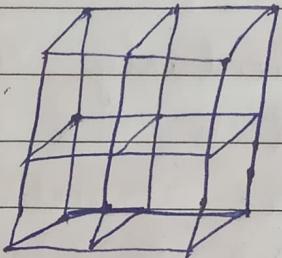


CRYSTAL LATTICE AND UNIT CELL

It is a regular 3-D arrangement of constituent particles in space — Crystal lattice
Unit cell — smallest 3D part of the crystal lattice



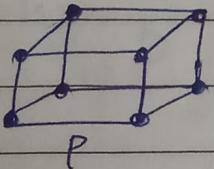
$$\begin{aligned} BOA &= \gamma \\ AOC &= \beta \\ BOC &= \alpha \end{aligned}$$



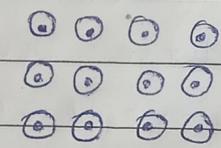
Lattice + Basis = Crystal ~~structure~~ structure

Classification of Unit Cells

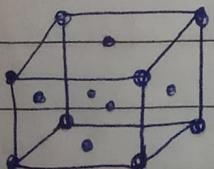
- (1) SCC - Simple Cubic Unit cell



Primitive or simplest - Constituent particles are situated at 8 corners of the cell



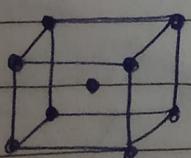
- (2) FCC - Face Centered Cubic



Non-primitive cell

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \text{ atoms/unit cell}$$

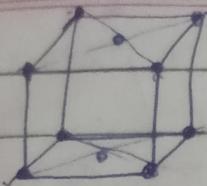
- (3) BCC - Body Centered Cubic



Non-primitive cell

$$8 \times \frac{1}{8} + 1 = 2 \text{ atoms/cell}$$

(4) BCC (Base Centered Cubic)



Non-primitive

$$8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2 \text{ atoms/unit cell}$$

Three Dimensional Bravais Lattice

a, b, c α, β, γ

1, 2, 3, 4, 6 - permissible rotation

Fourteen Bravais Lattice and Seven Crystals

(1) Cubic

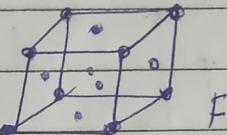
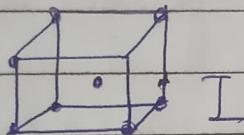
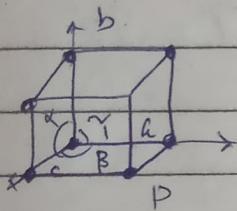
$$a = b = c$$

$$\alpha = \beta = \gamma = \pi/2$$

(1) P

(2) Body centered I

(3) Face centered, F



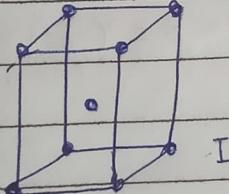
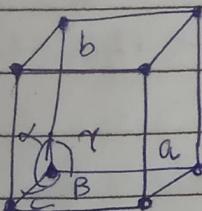
(2) Tetragonal

$$a = b \neq c$$

$$\alpha = \beta = \gamma = \pi/2$$

(1) P

(2) Body centered I



(3) Orthorhombic, $a \neq b \neq c$,

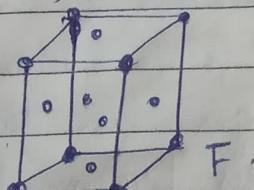
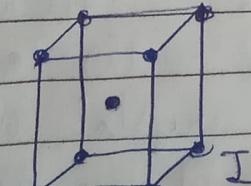
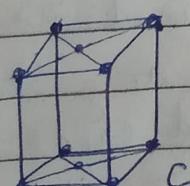
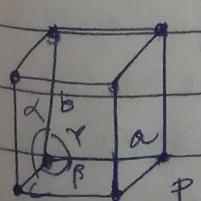
$$\alpha = \beta = \gamma = \pi/2$$

(1) P

(2) Base centered C

(3) Body centered, I

(4) Face centered, F



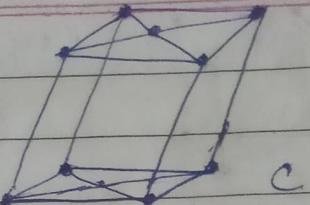
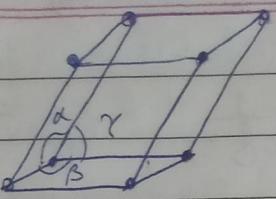
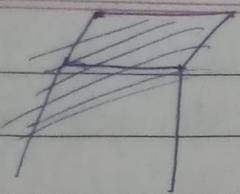
(4) Monoclinic

$$a \neq b \neq c$$

$$\alpha = \beta = 90^\circ \neq \gamma$$

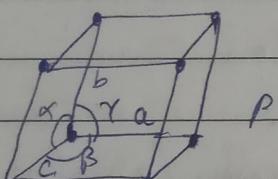
(1) Simple

(2) Base centered C



(5) Triclinic $a \neq b \neq c$

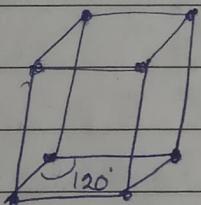
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



(1) Simple

(6) Hexagonal $a = b \neq c$

$$\alpha = 120^\circ, \beta = \gamma = 90^\circ$$

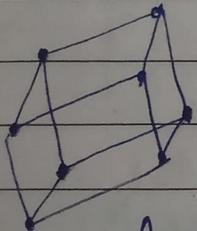


(7) Trigonal

$$a = b = c$$

(1) Simple P or R

$$\alpha = \beta = \gamma \neq 90^\circ, \text{ but } < 120^\circ$$



Crystal Planes and Miller Indices

.....

The miller indices are

.....

determined as follows

(i) Take any atom as the

origin in the crystal and erect coordinate axes from the atom to the direction of the basis vectors. The axis may be primitive or non-primitive.

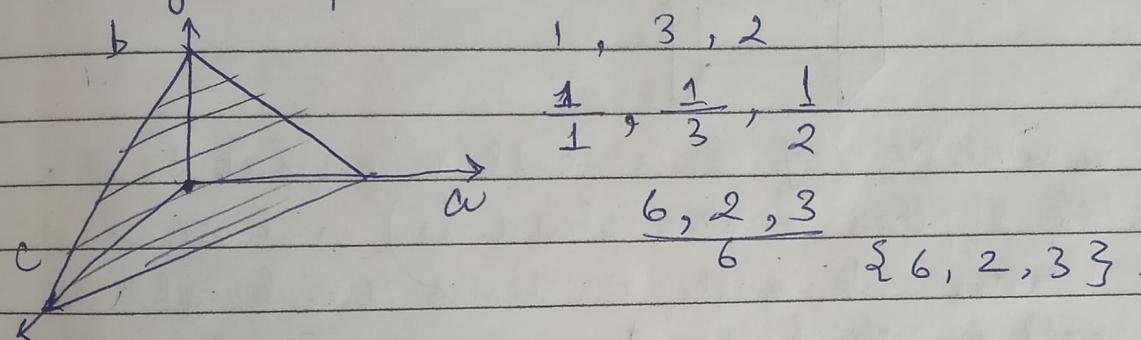
(ii) Choose the plane of the set of

interest and note its intercept on axes a, b, c in terms of lattice constants.

The plane must be chosen so that no intercept is at the origin.

(iii) Take the reciprocal of these intercepts and convert them into the smallest set of integers by the same no.

(iv) The result is conveniently enclosed in the parentheses $h, k, l \rightarrow \{h, k, l\}$ by taking reciprocals.



Reciprocal Lattice

→ P. P. Ewald has simplified the description developed a useful method to represent such sets of inter-penetrating planes.

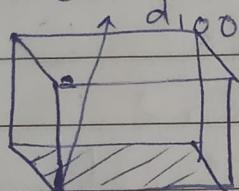
→ The normal to each plane from a common origin has been drawn.

→ A point on a normal at a distance from the origin equal to $\frac{1}{a_n k_l}$ has been placed.

→ Indeed the collection of such point form a periodic array. This array is called the reciprocal lattice, because distance in this lattice are reciprocal to those in the crystal.

→ Let's now define a reciprocal lattice vector \vec{a}_{hkl} . It is a vector whose magnitude is $1/d_{hkl}$ and whose direction is proportional to the normal to the hkl planes.

→ The parallelopiped by three non coplanar reciprocal lattice vectors $\vec{a}_{100}, \vec{a}_{010}, \vec{a}_{001}$ in the unit cell is reciprocal lattice. Its volume is obviously directly reciprocal to the unit cell volume in the crystal.



The volume 'V' of this cell is equal to the area ~~of~~ of the base (shaded) whose sides are ~~b, c~~ b and c times the height of the cell, which is d_{100} respectively,

$$V = \text{area} \times d_{100} \rightarrow \frac{1}{d_{100}} = \frac{\text{Area}}{\text{Volume}}$$

$$\Rightarrow \frac{1}{d_{100}} \hat{n} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad -(1)$$

where \hat{n} is the unit vector which is normal to the plane b or c .

$$\vec{a}_{hkl} = \frac{1}{d_{hkl}} \hat{n} \quad -(2)$$

Combining (1) and (2)

$$\vec{a}_{100} = \frac{1}{d_{100}} \hat{n} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{a}_{010} = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \quad \vec{a}_{001} = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

~~or~~

(3)

Properties of Reciprocal Lattice Vectors.

$$\begin{aligned}\overline{\sigma}_{100} &= \vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \\ \overline{\sigma}_{\bar{1}00} &= \vec{b}^* = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \\ \overline{\sigma}_{001} &= \vec{c}^* = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}\end{aligned}\quad \left. \right\} - (4)$$

$$\begin{array}{l} \rightarrow \vec{a}^* \cdot \vec{b} = 0 \\ \cdot \vec{b}^* \cdot \vec{c} = 0 \\ \vec{c}^* \cdot \vec{a} = 0 \end{array} \quad \left. \begin{array}{l} \vec{a}^* \cdot \vec{c} = 0 \\ \vec{b}^* \cdot \vec{a} = 0 \\ \vec{c}^* \cdot \vec{b} = 0 \end{array} \right\} \quad \left. \begin{array}{l} \vec{a}^* \cdot \vec{a} = 1 \\ \vec{b}^* \cdot \vec{b} = 1 \\ \vec{c}^* \cdot \vec{c} = 1 \end{array} \right\} - (5)$$

$$\rightarrow \vec{a}^* = \overline{\sigma}_{100} = \frac{1}{d_{100}} \hat{n}$$

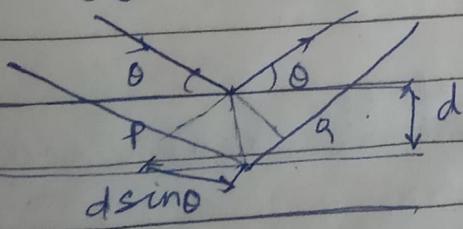
$$\rightarrow 2\vec{a}^* = 2\overline{\sigma}_{100} = \frac{2}{d_{100}} \hat{n} = \frac{1}{d_{200}} \hat{n}$$

$$\rightarrow \overline{\sigma}_{200} = \frac{1}{d_{200}} \hat{n}$$

$$3\vec{a}^* = 3\overline{\sigma}_{100} = \frac{3}{d_{100}} \hat{n} = \frac{1}{d_{300}} \hat{n}$$

$$\overline{\sigma}_{300} = \frac{1}{d_{300}} \hat{n}$$

Bragg Diffraction

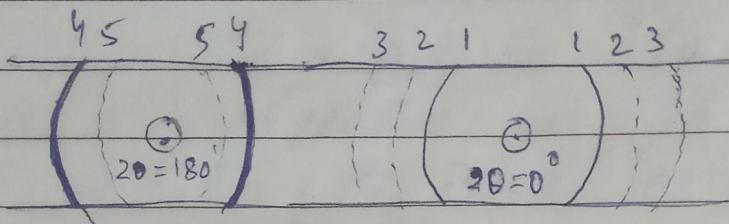


$$2d \sin \theta = n\lambda$$

$$\sin \theta \leq 1$$

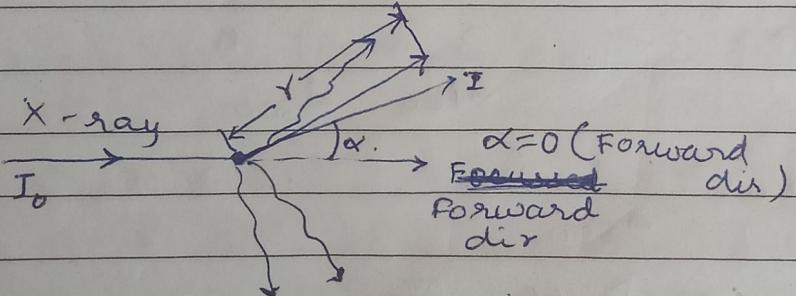
$$2d \geq \lambda$$

Intensities of Diffracted Beams.



Factors affecting the value of intensity of the diffracted beam.

- (1) Polarisation factor.
- (2) Atomic scattering factor.
- (3) Crystal Structure factor.
- (4) Multiplicity factor.
- (5) Lorentz factor.
- (6) Absorption factor.
- (7.) Temperature factor.



$$I = I_0 \frac{e^4}{r^2 m^2 c} \sin^2 \alpha$$

where $I =$ intensity of the observed beam scattered by an electron

$I_0 =$ intensity of the incident beam

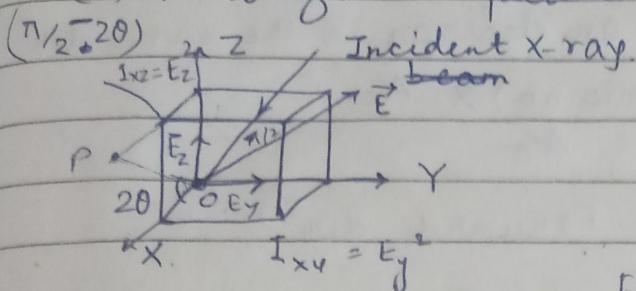
$c =$ velocity of light

$\alpha =$ angle bet' the scattering dirⁿ and the dirⁿ of the accelerating of the e⁻, that is the forward dirⁿ

$c =$ charge on the electron

$r =$ distance from the electron where the intensity is measured.

(1) Polarization factor



$$E^2 = E_y^2 + E_z^2$$

$$\begin{aligned} E_y^2 &= E^2 - E_z^2 \\ &= E^2 - \frac{1}{2} E^2 \end{aligned}$$

$$E_y^2 = \frac{1}{2} E^2$$

$$I_0 = E^2$$

$$I_{oy} = E_y^2, \quad I_{oz} = E_z^2$$

$$\begin{aligned} I_{py} &= I_{oy} \frac{e^4}{\pi^2 m^2 c^4} \sin^2 \frac{\pi}{2} \\ &= I_{oy} \frac{e^4}{\pi^2 m^2 c^4} \end{aligned}$$

$$\begin{aligned} I_{pz} &= I_{oz} \frac{e^4}{\pi^2 m^2 c^4} \sin^2 \left(\frac{\pi}{2} - 2\theta \right) \\ &= I_{oz} \frac{e^4}{\pi^2 m^2 c^4} \cos^2 2\theta \end{aligned}$$

$$\begin{aligned} I_p &= I_{py} + I_{pz} \\ &= \frac{e^4}{\pi^2 m^2 c^4} (I_{oy} + I_{ox} \cos^2 2\theta) \end{aligned}$$

$$= \frac{e^4}{\pi^2 m^2 c^4} \left(\frac{I_0}{2} + \frac{I_0 \cancel{\cos}}{2 \cos^2 2\theta} \right)$$

$$I_p = \frac{e^4 I_0}{\pi^2 m^2 c^4} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

5) Scattering factor $f = \text{Amplitude of the wave scattered by an atom}$

Amplitude of the wave scattered by an electron in the same dir.

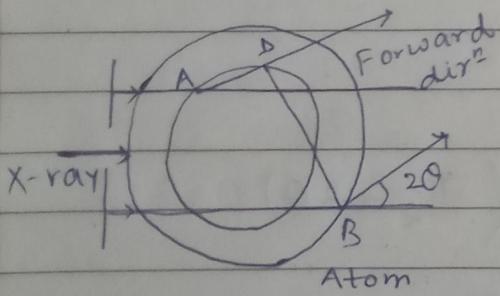
$$= Z \frac{(\text{Atomic no}) \times A_e}{A_e}$$

$$f = Z (\text{Forward dir}^n)$$

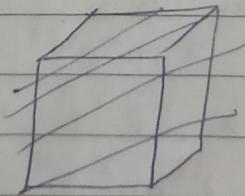
(3) Crystal Structure factor $F = \text{amplitude of X-rays scattered by all the atoms in a unit cell}$

Amplitude of X-rays scattered by a single electron

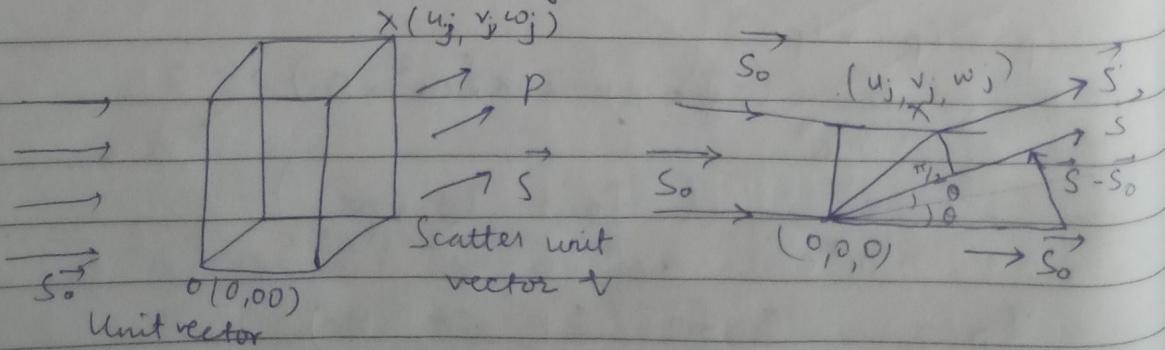
Scattering factor (f) =



Scattered X-rays by unit cell



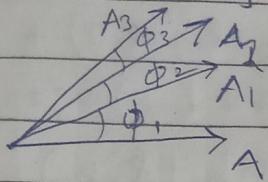
Scattered X-rays by unit cell



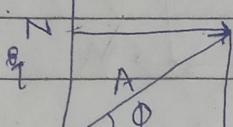
$$\text{Phase angle } \phi = \frac{2\pi(\vec{S} - \vec{S}_0)}{\lambda} \cdot \vec{r}_j = 2\pi (ha^* + kb^* + lc^*) \cdot \vec{r}_j$$

$$\phi = 2\pi(ha^* + kb^* + lc^*) \cdot (u_i \vec{a} + v_j \vec{b} + w_k \vec{c})$$

$$\phi = 2\pi(hu_i + kv_j + lw_k)$$



Imaginary



M. Real

$$A \cos \phi + i A \sin \phi$$

$$= Ae^{i\phi} = A \exp i\phi$$

$$f_j = \text{atomic scattering factor of } j\text{th atom}$$

$$= f_j \times A_e = \frac{A_j}{A_e} \times A_e = A_j$$

$$f_j A_e \exp 2\pi i (hu_j + kv_j + lw_j)$$

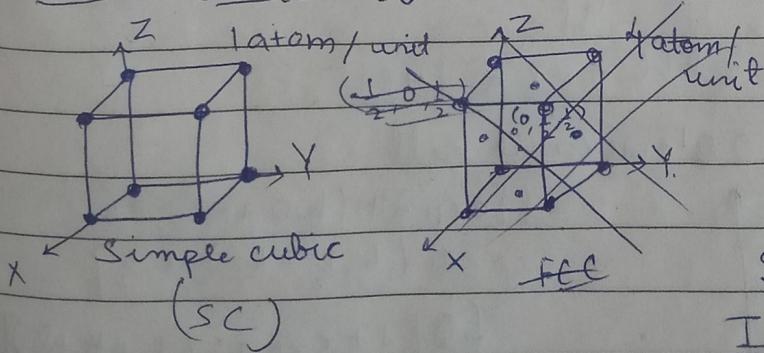
Amplitude of the scattered x-rays due to unit cell (all the atoms)

$$A = \sum_j f_j A_e \exp 2\pi i (hu_j + kv_j + lw_j)$$

$$\text{Crystal structure factor} = F = \frac{A}{A_e}$$

$$= \sum_j f_j \exp 2\pi i (hu_j + kv_j + lw_j)$$

Intensity of Diffracted Peaks

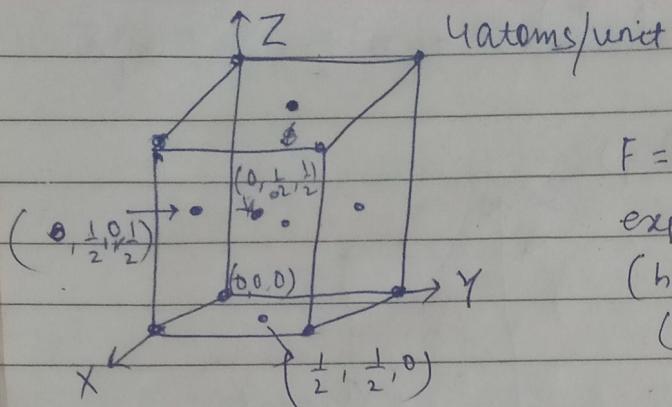


$$SC = F = f \exp 2\pi i (h_0 O + k_0 O + l_0 O)$$

$$SC = F = f \exp iO = f$$

$$I \propto |f|^2$$

FCC



FCC.

$$F = f \left[\exp 2\pi i (h \cdot 0 + k \cdot 0 + l \cdot 0) + \exp 2\pi i (h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot 0) + \exp 2\pi i (h \cdot \frac{1}{2} + k \cdot 0 + l \cdot \frac{1}{2}) + \exp 2\pi i (h \cdot 0 + k \cdot \frac{1}{2} + l \cdot \frac{1}{2}) \right]$$

$$F = f \left[1 + \exp \pi i (h+k) + \exp \pi i (h+l) + \exp \pi i (k+l) \right]$$

Case I: If h, k, l are mixed

$$\begin{cases} 2 \text{ odd} \\ 1 \text{ even} \end{cases} \quad \begin{cases} h=1 \\ k=3 \\ l=2 \end{cases} \quad \left\{ \begin{array}{l} \frac{h+k}{4}, \frac{k+l}{5}, \frac{l+h}{3} \end{array} \right.$$

$$\begin{cases} 2 \text{ even} \\ 1 \text{ odd} \end{cases} \quad \begin{cases} h=2 \\ k=1 \\ l=4 \end{cases} \quad \left\{ \begin{array}{lll} h+k & k+l & l+h \\ 3 & 5 & 6 \end{array} \right.$$

$$\exp \pi i n = -1 \quad \begin{matrix} \text{odd} \\ , \end{matrix} \quad \exp \pi i n = +1 \quad \begin{matrix} \text{even} \\ , \end{matrix}$$

$$F = 0.$$

Case II:-

If h, k, l are unmixed

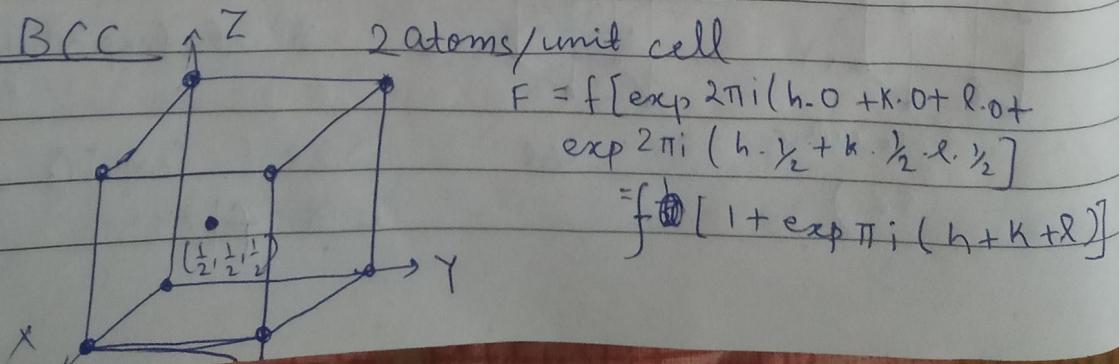
$$\begin{matrix} h, k, l \\ \text{odd} \end{matrix} \quad \text{or} \quad \begin{matrix} h, k, l \\ \text{even} \end{matrix}$$

If it is odd, $F = 4f$.

If it is even, $F = 4f$.

$$\text{FCC: } I \propto |4f|^2$$

BCC



$$F = f \left[\exp 2\pi i (h \cdot 0 + k \cdot 0 + l \cdot 0) + \exp 2\pi i (h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot \frac{1}{2}) \right]$$

$$= f \left[1 + \exp \pi i (h+k+l) \right]$$

If $h+k+l = \text{odd}$

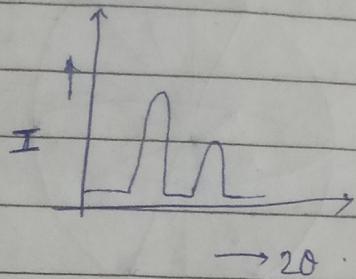
$$F = 0$$

If $h+k+l = \text{even}$

$$F = g_f$$

$$\therefore I \propto |F|^2$$

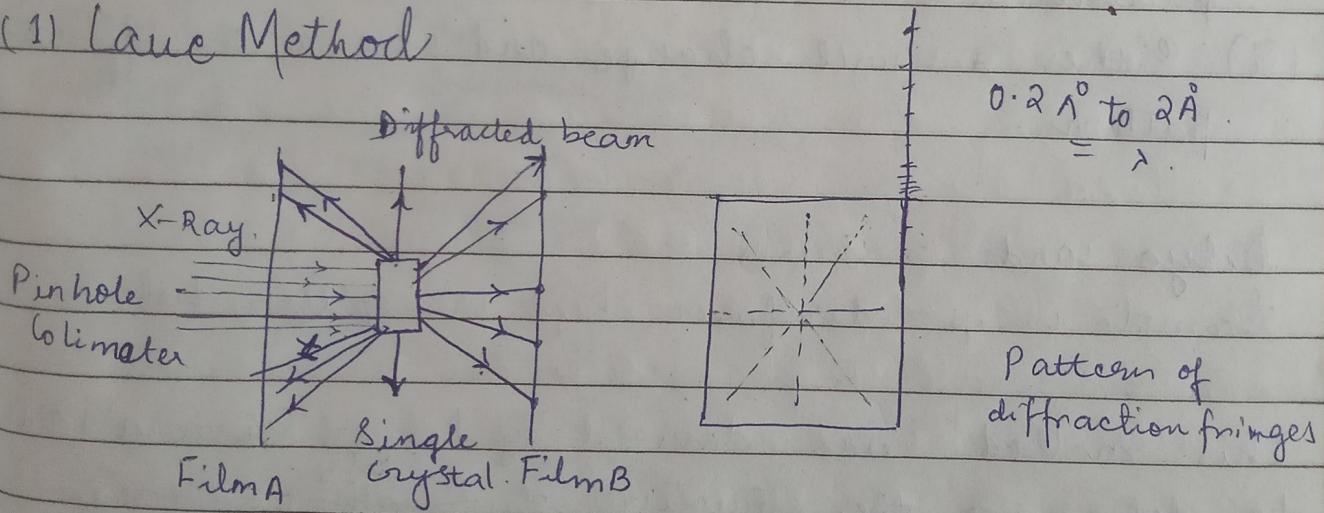
$$I \propto |2f|^2$$



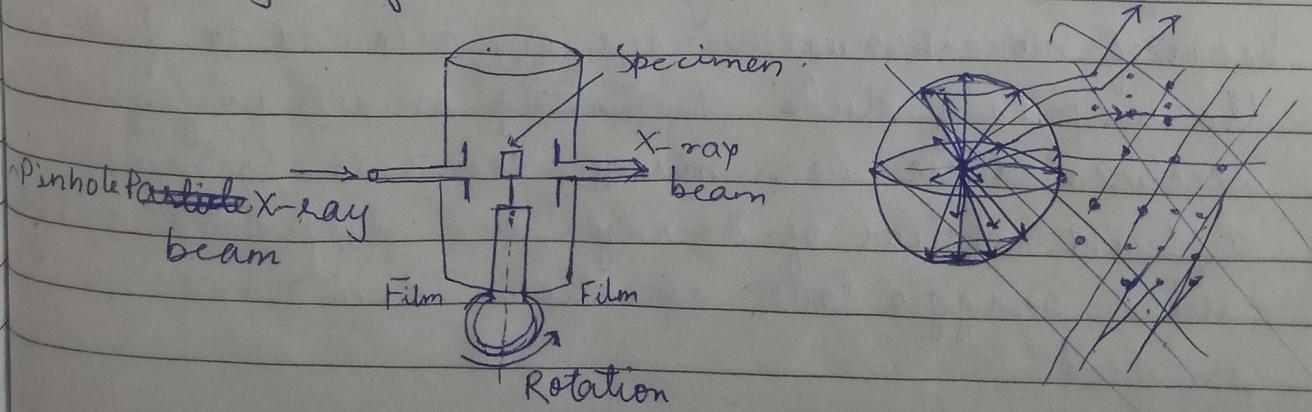
Experimental Method of X-rays diffraction and Determination of Crystal Structure.

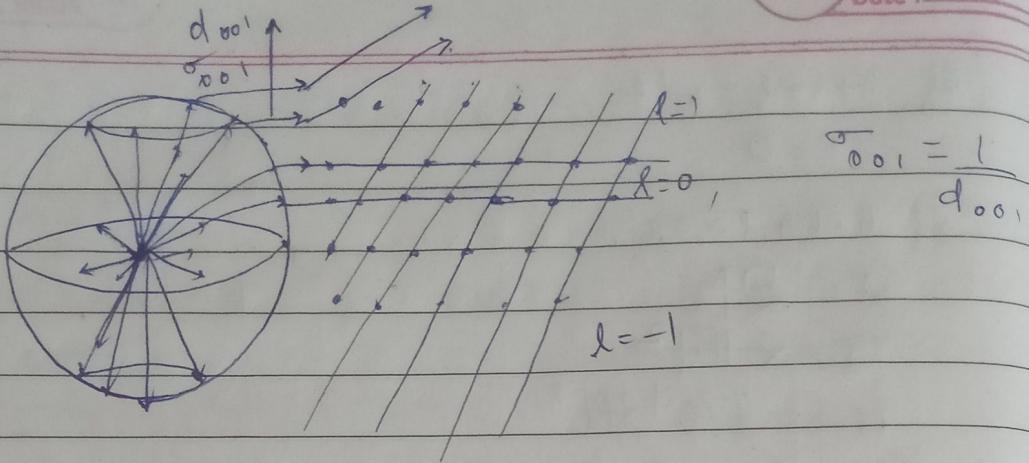
- (1) Laue Method
- (2) Rotating crystal Method
- (3) Powder Method

(1) Laue Method



(2.) Rotating crystal Method





3) Powder Method of X-rays.

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

θ = changed, λ = const

2 cases are there :-

- (i) Either θ will change and observe the diffraction pattern
- (ii) Either λ will change and observe the diffraction pattern.

Debye and Scherrer -

Sample in powder form kept in capillary tube

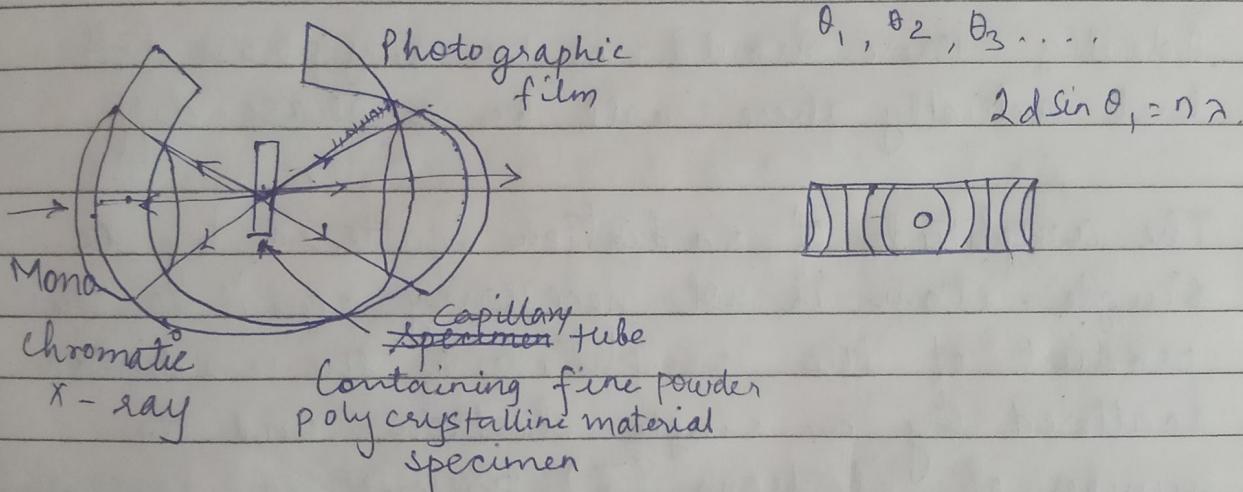
This method was devised by Debye & Scherrer in 1916 to determine the structure of ^{finely} powdered polycrystalline materials. Finely powdered material is kept in a capillary tube and a narrow beam of monochromatic rays is allowed to fall on the capillary tube. In ^{infinitely} small polycrystalline specimen. there are many crystals so we have different values of X-rays are diffracted only when Bragg's law equation $2d \sin \theta = n\lambda$ is satisfied.

The beam of X-rays are met monochromatic using a filter. A photographic film is used to receive the diffracted X-rays.

Two cases may arise for X-ray diffraction:

(I) Either θ will change and observe the diffraction pattern

(II) Either λ will change and observe the diffraction pattern.

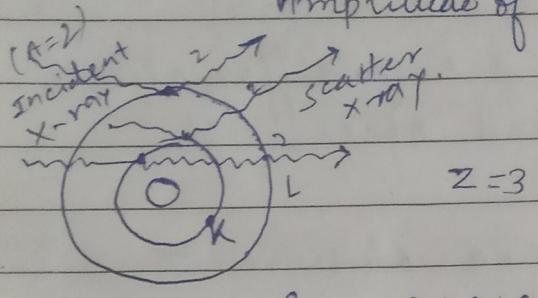


Advantages —

- (i) Identification of unknown crystalline material.
- (ii) Determination of unit cell dimension.
- (iii) Measurement of samples purity, then it helps to determine the lattice parameters a, b, c .

Atomic Scattering factor (f) or Atomic form factor

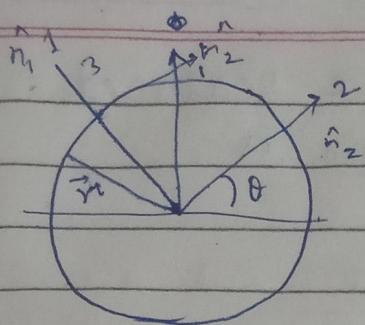
$f = \frac{\text{Amplitude of radiation scattered from an atom}}{\text{Amplitude of radiation scattered from an electron}}$



$$f = \frac{2+2+2}{2} = 3. \quad (\text{In actual situation, } f < 3)$$

Ideally, there should not be any phase diff., but actually there will be a phase diff.

The amplitude of radiation scattered by a single atom is not necessarily equal to the product of the amplitude of the radiation scattered by a single electron and the number of electrons (Z) present in the atom. It is generally less than this value. The atomic scattering factor (f) describes the scattering power of a single atom relating to the scattering power of a single electron. To calculate f , consider an atom containing Z electrons assigned in a concentric spherical symmetric configuration around its center which is taken as the origin. Let \vec{r} be the radius of the atom. Consider a small vol element dV at \vec{r} . Let $f(\vec{r})$ be charge density at point \vec{r} . The charge enclosed by volume element dV is $f(\vec{r})dV$.



Scattering plane

$$f(\vec{r}) = \text{charge density}$$

$$= \text{charge/vol}$$

$$\text{charge} = f(\vec{r}) dV.$$

Let \hat{n}_1 and \hat{n}_2 represent the direction of incident & scattered X-ray beam respectively. The phase diff between the wave scattered from volume element dV and that scattered from electron.

$$\Phi_r = \frac{2\pi}{\lambda} \vec{r} \cdot \vec{N}$$

where N is normal to the scattered plane

$$\Phi_r = \frac{2\pi}{\lambda} \cdot r \cdot N \cos \phi.$$

$$\Phi_r = \frac{2\pi}{\lambda} r (2 \sin \theta) \cos \phi \quad (N = 2 \sin \theta)$$

$$\Phi_r = \left(\frac{4\pi}{\lambda} \sin \theta \right) \cdot r \cos \phi. \quad -(1)$$

$$\text{let } \frac{4\pi}{\lambda} \sin \theta = \mu$$

Amplitude of wave scattered from electron located at origin is $A e^{i(kx - wt)}$ $-(2)$

Amplitude of wave scattered from small volume element dV .

$$A e^{i(kx - wt) + \frac{i}{k} \cancel{\frac{dV}{\cancel{k}}}} \times f(\vec{r}) dV$$

The ratio of amplitude of wave scattered by the electron at the origin is

$$df = \cancel{A e^{i(kx-wt) + idr}}$$

$$df = \frac{A e^{i(kx-wt) + idr} \times f(\vec{r}) dr}{A e^{i(kx-wt)}}$$

$$df = \cancel{A} e^{idr} \cdot f(\vec{r}) dr$$

Using spherical polar coordinate, it can be shown that

$$dr = 2\pi r^2 \sin \phi d\phi dr \quad (4)$$

$$df = e^{iur \cos \phi} \cdot f(\vec{r}) 2\pi r^2 \sin \phi d\phi dr \quad (5)$$

Integrating both sides we get.

$$f = \int_0^\pi \int_{r=0}^\infty e^{iur \cos \phi} \cdot f(\vec{r}) 2\pi r^2 \sin \phi d\phi dr \quad (6)$$

Using 6 & 7

$$f = \int_0^\infty f(r) 2\pi r^2 \frac{(2 \sin(\mu r))}{\mu r} dr \quad (7)$$

$$f = \int_0^\infty f(r) \cdot 4\pi r^2 \frac{\sin(\mu r)}{\mu r} dr$$

Broadening of Spectral Line.

As we know that the atoms do not emit radiation at a precise frequency but over a range of frequency called as broadening of spectral line. Various mechanisms cause broadening of spectral line and understanding of the mechanism is necessary for the development of LASER sources with sufficient spectral purity.

To account for purity dependence of absorption, we can write:

$$k(\omega) = \frac{\eta c^2 \pi^2 g_2 A_{21}}{g_1 \omega_0^2} \left(N_1 - \frac{g_1}{g_2} N_2 \right) g(\omega) \xrightarrow{\downarrow \text{FWHM}}$$

where $g(\omega)$ is the line shape function representing frequency behaviour of $k(\omega)$.

ω_0 = central frequency or resonant frequency at which $g(\omega)$ is maximum and therefore $k(\omega)$ is maximum.

These mechanisms determine the nature of ~~line~~ shape for $g(\omega)$.

$$\frac{0.94\lambda}{B \cos \theta} = \text{Avg grain size}$$

Classified in 2 groups.

Two groups

Homogenous broadening

Inhomogeneous broadening

Groups

Homogeneous broadening

e.g.: Natural broadening,

collision broadening

bonding broadening

A line ~~broadening~~ mechanism is referred to as homogeneous if it broadens the response of each individual atom equally and hence has the same effect on all the atoms.

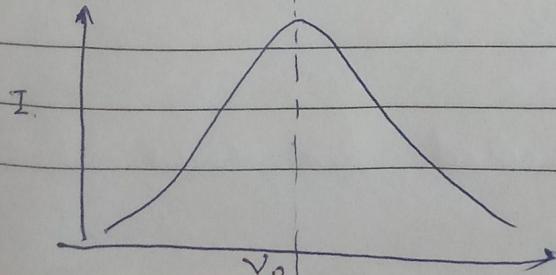
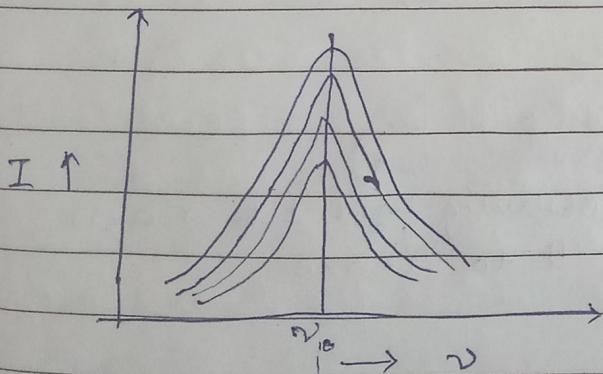
Every atom therefore has the same central frequency and the same atomic line shapes.

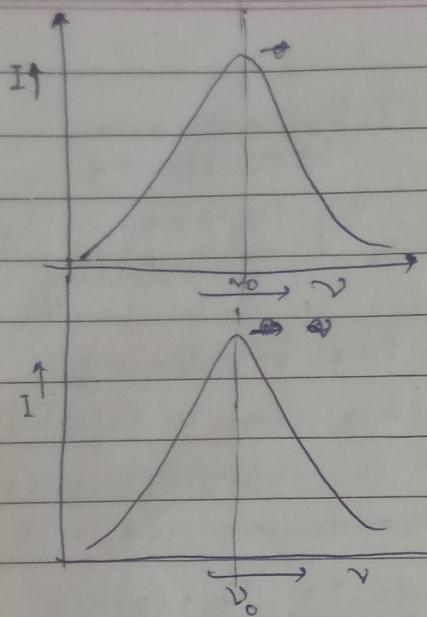
Inhomogeneous broadening

e.g.- Doppler

broadening

A line broadening mechanism is referred to as inhomogeneous broadening when it leads to the atomic resonant frequency being distributed over a band of frequencies (central frequency of individual atoms varies). Therefore the resultant is a broadened line of the whole system without broadening the line of individual atoms.

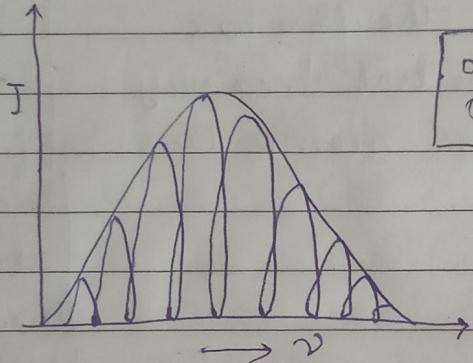




Homogeneous.

Homogeneous broadening
is Lorentzian in shape

Inhomogeneous

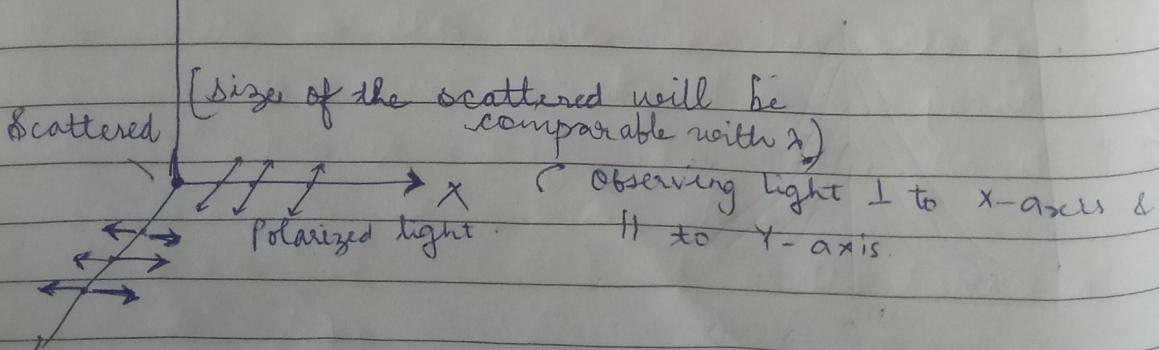


Inhomogeneous
broadening is
Gaussian in shape

Group of
atoms

Polarization by Scattering

\times^2 (Vibrations in all possible directions).

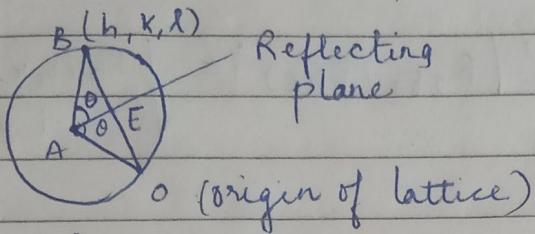


Y Observing light

I to Y-axis & II to X-axis

$I \propto |F|^2$ for simple cubic } But requires Lorentz
 $I \propto |4F|^2$ for FCC correction factor &
 $I \propto |2F|^2$ for BCC polarisation correction factor.

Geometrical Interpretation of the Braggs condition



$$\overrightarrow{AO} = \frac{1}{\lambda}$$

$$\angle EA0 = \theta \text{ and } OB = \frac{n}{d}$$

| l = radius
 \nearrow Ewald
 circle \rightarrow ~~sphere~~

$$\text{Now, } \overrightarrow{OB} = \frac{2 \sin \theta}{\lambda}$$

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

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

Lorentz Correction factor - Time taken by the X-ray to reach the ~~Ewald~~ sphere.

Lorentz and Polarization Correction

We know,

$$|F_{hkl}| \propto \sqrt{I_{hkl}}$$

Modulus of structure factor is called the structure amplitude. It is used to calculate $f(x, y, z)$ hence to calculate (x_i, y_i, z_i)

In I_{hkl} value to the observed structure factor amplitude

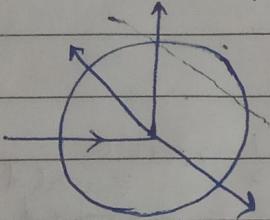
$$I_0(hkl) = |F_0(hkl)|^2$$

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$$\Rightarrow |F_0(hk\ell)| = \sqrt{\frac{k I_0(hk\ell)}{4}} \quad \text{when } L \text{ is the Lorentz factor, } p \text{ is polarization factor}$$

k depends on crystal size, the beam intensity and few fundamental constants.

$$|F_{\text{rect}(hk\ell)}| = k' |F_{\text{obs.}}(hk\ell)| = \sqrt{\frac{I_0(hk\ell)}{L_p}}$$



Lorentz factor arises from the time required of a reciprocal lattice ($r.l.$) point to pass the ~~Ewald~~ sphere. This time is not constant for all the $r.l.$ points. This depends on the location of individual reciprocal lattice ($r.l.$) points and the speed v the ~~dis-~~ from which it approaches the ~~Ewald~~ sphere.

As the crystal is rotated about ϕ or ω at a given ~~so~~ angular velocity ω , the $r.l.$ points also rotate at the same angular velocity. Therefore the linear velocity of a $r.l.$ point located at d^* $r.l.$ unit away from origin as it approaches to the Ewald Sphere.

$$v = d^* \omega \quad (\text{where } d^* \text{ is the distance in } r.l.)$$

$$d^* = \sqrt{d}$$

$$v = 2 \sin \theta \omega$$

Now, the time 't' required for this $r.l.$

point pass through the path length P in the dirⁿ of motion is given by

$$P = t v$$

$$t = \frac{P}{v} = \frac{P}{2w \sin \theta}$$

Now, 'p' depends on the angle θ betⁿ the surface of the sphere of reflection and the path followed by the el. point.

Now,

$$P \propto \frac{1}{\cos \alpha}$$

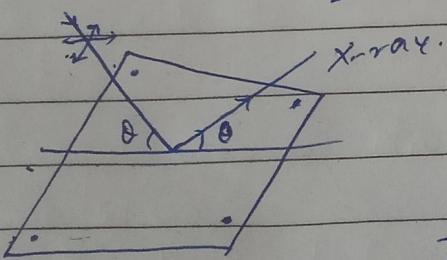
$$\Rightarrow t \propto \frac{1}{2 \sin \theta \cos \alpha}$$

$$t \propto \frac{1}{\sin 2\theta}$$

$$L = \frac{1}{\sin 2\theta} \quad \text{Lorentz correction factor}$$

Polarization Correction factor

$$p = \frac{1}{2} L (1 + \cos^2 2\theta) \rightarrow \text{polarization factor}$$



$I_{1r} \rightarrow f(x, y, z)$ and independent of θ

$I_{2r} \rightarrow f(x, y, z)$ and dependent on θ .

Note:- PLF is a very small value and so for the practical determination of intensity, PCF can be neglected.