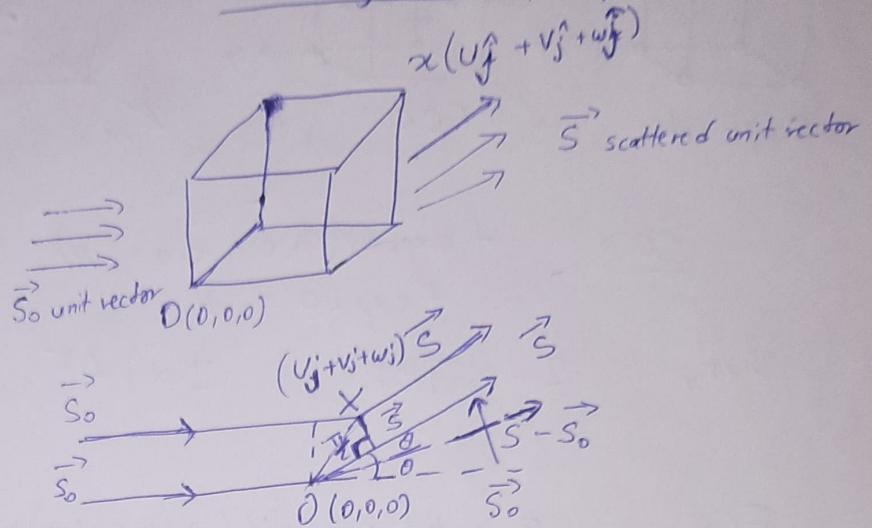


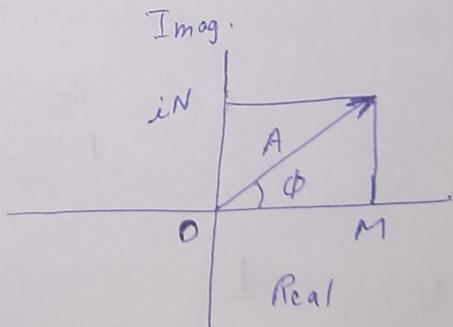
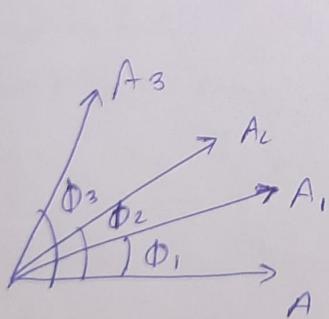
3) X-ray hitting electrons in 1st and 2nd orbit
(B' ignore)

Scattering of X-rays by unit cell



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

$$\begin{aligned} \phi &= 2\pi(ha^* + kb^* + lc^*)(u_j \vec{a} + v_j \vec{b} + w_j \vec{c}) \\ &= 2\pi(hu_j + kv_j + lw_j) \end{aligned}$$



$$\begin{aligned} A \cos \phi + i A \sin \phi \\ = A e^{i\phi} = A \exp(i\phi) \end{aligned}$$

f_j = scatt. factor of j^{th} atom

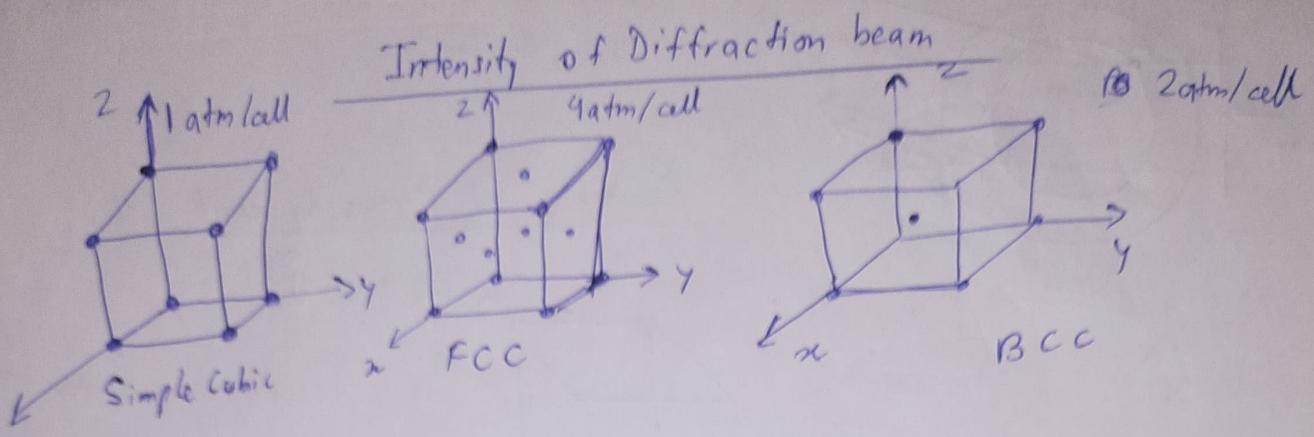
$$f_j \times A_e = \frac{A_j}{A_e} A_e = A_j \quad (A_j = \text{amplitude})$$

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

Amp. of scatt. x-ray due to unit cell (all the atoms)

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

$$\text{Crystal Struct. Factor } F = \frac{A}{A_e} = \sum_j f_j \exp 2\pi i (h u_j + k v_j + l w_j)$$



$$\underline{\text{SC}} = F = f \exp 2\pi i (h_0 + k_0 + l_0) \\ = f \exp i 0 = f$$

Thus, $I \cancel{\propto} |F|^2 \quad I \propto |f|^2$

$$\underline{\text{FCC}} \quad F = f [\exp 2\pi i (h_0 + k_0 + l_0) + \exp 2\pi i (h_{\frac{1}{2}} + k_{\frac{1}{2}} + l_{\frac{1}{2}}) \\ + \exp 2\pi i (h_{\frac{1}{2}} + k_0 + l_{\frac{1}{2}}) + \exp 2\pi i (h_0 + k_{\frac{1}{2}} + l_{\frac{1}{2}})]$$

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

$$\begin{array}{c} \text{If } h, k, l \text{ are mixed} \\ \text{Case 1 - } \left. \begin{array}{l} 2 \text{ odd} \\ 1 \text{ even} \end{array} \right\} \begin{array}{l} h=1 \\ k=3 \\ l=2 \end{array} \Rightarrow \\ h+k=4, k+l=5, l+h=3 \end{array}$$

$$\text{Case 2 - } \left. \begin{array}{l} 2 \text{ even} \\ 1 \text{ odd} \end{array} \right\} \begin{array}{l} h=0 \\ k=1 \\ l=4 \end{array} \Rightarrow \\ h+k=3, k+l=5, l+h=6$$

$$\exp \pi i n = -1 \quad \text{and} \quad \exp \pi i n = +1 \\ (\text{odd}) \qquad \qquad \qquad (\text{even})$$

• Case 1 - $F = 0$

Case 2 - $F = 0$

If h, k, l are unmixed

$$\text{All odd } F = 4f$$

$$\text{All even } F = 4f$$

$$I \propto |4f|^2$$

BCC

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

$$= f (1 + \exp \pi i (h+k+l))$$

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

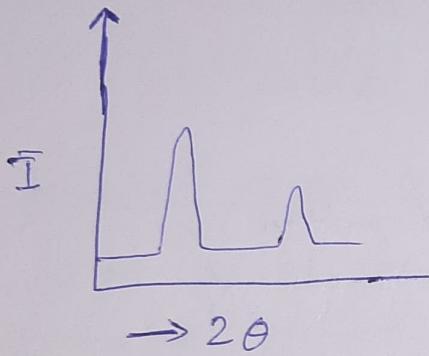
$$F = f [1 + (-1)] = 0$$

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

$$F = 2f$$

$$\cancel{I \propto |F|^2} \quad I \propto |2f|^2$$

XRT Peak



Experimental method of X-rays Diffraction and determination of Crystal Structure

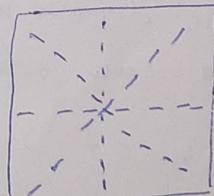
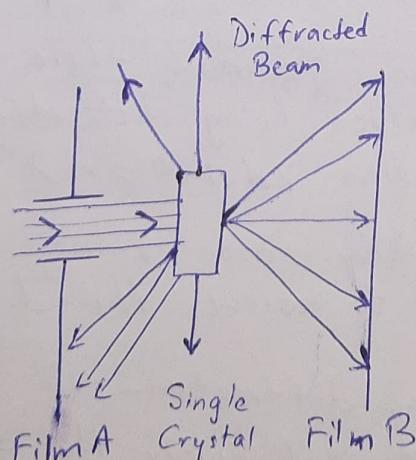
- ① Laue Method
- ② Rotating Crystal Method
- ③ Powder Method

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

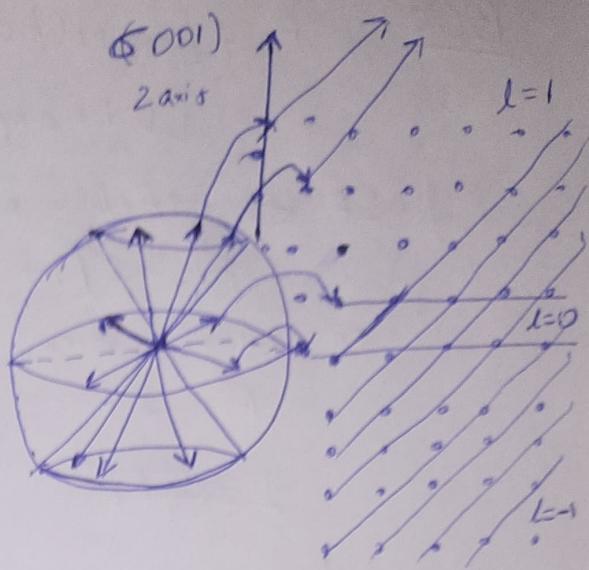
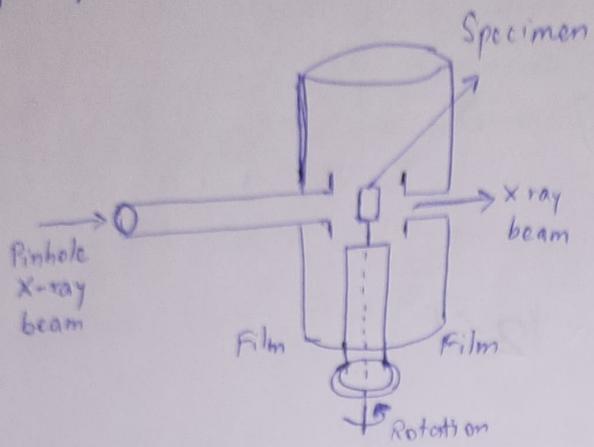
$d = \text{interplanar distance}$
 $n = \text{integral number}$

Laue Method

$(\lambda = 0.2 \text{\AA} \text{ to } 2 \text{\AA})$
X-ray
Pinhole Colimator



Rotating Crystal Method



Powder Method

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

Two cases are there -

- (i) Either change θ and observe the diff. pattern.
 - (ii) Either λ is changed and diff. pattern is observed.

Debye & Scherer - Scientists

Devised by Debye & Scherer in 1920 to determine the structure of finely powdered polycrystalline material. A finely powdered crystalline material is kept in a capillary tube & a narrow beam of monochromatic rays is ~~not~~ allowed to fall on the ~~opposite~~ capillary tube.

In infinitely small polycrystalline specimen, there are many crystals, so we have different x-ray values being diffracted only when Bragg's Law ~~of~~ equation $2d \sin\theta = n\lambda$ is satisfied.

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

Two cases may arise for x-ray diffraction -

- 1) Either θ will change and observe the diff. pattern.
 - 2) Either λ will change and observe the diff. pattern.

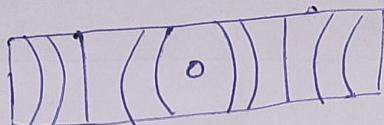
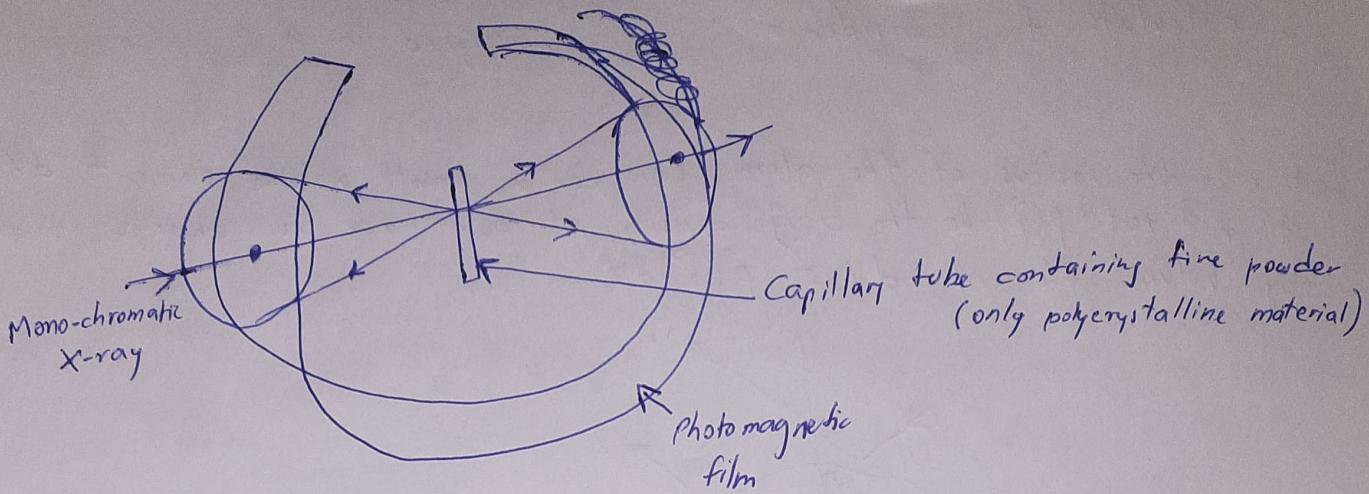
$f(n)$ n^{th} deg.

$$f(x) + 1 = (x+1)^q \cdot h$$

$$f(x) - 1 = (x+1)^3 \cdot k$$

$$Q = (x-1)^3 \cdot k - (x+1)^3 \cdot l$$

(3)

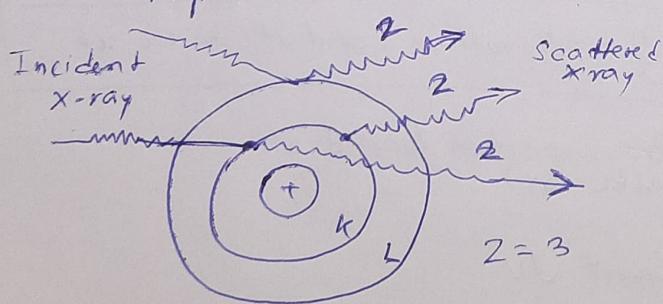


Advantages of powder method

1. Identification of unknown crystalline material.
2. Determination of unit cell dimension.
3. Measurement of sample's purity.
4. It helps to determine the lattice parameters (a, b, c)

Atomic Scattering Factor / Atomic Form Factor

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



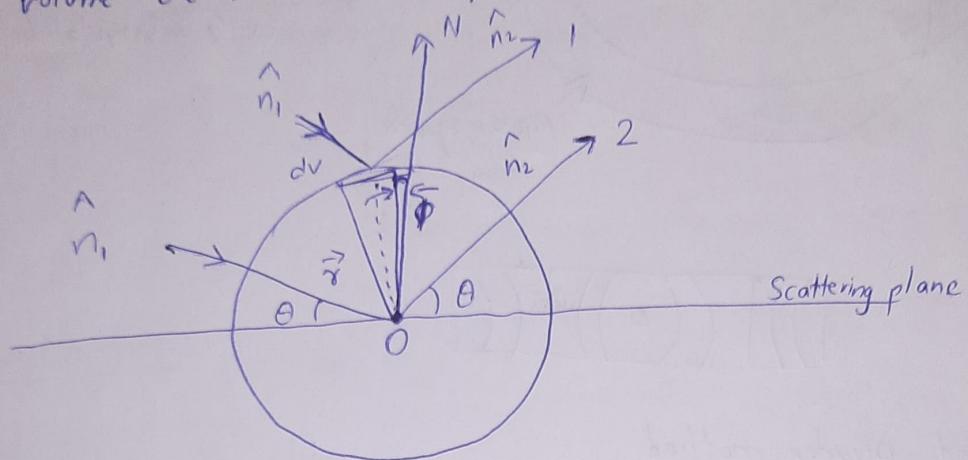
Ideally, there should not be any phase diff. but a phase diff. exists in real life.

The amp. of radiation scatt. by a single atom is not necessarily equal to the prod. of the amplitude of the radiation scattered by a single electron and the no. of electrons (Z) present in the atom. ~~This~~
It is generally < this val. The atomic scattering factor (f) describes the power of a single atom in relation to the scatt. pow of a single electron.

To calculate f , consider a

assigned in a s

Let r be the radius of the atom. Consider a small volume element dV at r . Let $\rho(\vec{r})$ be the charge density at point r . The charge enclosed by volume element $dV = \rho(\vec{r})dV$



Let \hat{n}_1 & \hat{n}_2 represent the directions of incident & scattered x-ray beam respectively. The phase difference bw the wave scattered from vol. element dV and that scattered from electron in $\phi_r = \frac{2\pi}{\lambda} \cdot \vec{r} \cdot \vec{N}$

when N is the normal to the scattering plane,

$$\phi_r = \frac{2\pi}{\lambda} r N \cos\phi$$

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

$$\phi_r = \left(\frac{4\pi}{\lambda} \sin\theta \right) (r \cos\phi) - \textcircled{1}$$

$\frac{4\pi}{\lambda} \sin\theta$ will be a constant for one set

Amplitude of wave scattered from electron located at origin $O = Ae^{i(kx - \omega t)} - \textcircled{2}$

Amp. of wave scatt. from small vol. element 'dV'
 $Ae^{i(kx - \omega t) + i\phi_r} \times \rho(\vec{r})dV$

The ratio of amplitude of wave scatt. by the charge element dV to that scatt. by the electron at the origin is

$$df = \frac{Ae^{i(kx - \omega t) + i\phi_r} \times \rho(\vec{r})dV}{Ae^{i(kx - \omega t)}}$$

$$\Rightarrow df = e^{i\mu_r r} f(\vec{r}) dv \quad - \textcircled{3}'(3)$$

Using spherical polar coordinates it can be shown that

$$dv = 2\pi r^2 \sin\phi d\phi dr \quad - \textcircled{4}$$

Using $\textcircled{1}$ & $\textcircled{3}$

$$df = e^{i\mu_r r} f(\vec{r}) 2\pi r^2 \sin\phi d\phi dr \quad - \textcircled{5}$$

Integrating both sides,

$$f = \int_{\phi=0}^{\alpha} \int_{r=0}^{\infty} e^{i\mu_r r \cos\phi} f(\vec{r}) 2\pi r^2 \sin\phi d\phi dr \quad - \textcircled{6}$$

$$\int_0^{\pi} e^{i\mu_r r \cos\phi} \sin\phi d\phi = \frac{2 \sin(\mu_r)}{\mu_r} \quad - \textcircled{7}$$

Using $\textcircled{6}$ & $\textcircled{7}$,

$$f = \int_0^{\infty} f(\vec{r}) 2\pi r^2 \left(\frac{2 \sin(\mu_r)}{\mu_r} \right) dr$$

$$f = \int_0^{\infty} f(\vec{r}) 4\pi r^2 \frac{\sin(\mu_r)}{\mu_r} dr \quad - \textcircled{8}$$

Eqn. 8 is the general expression for scattering factor.

Broadening of spectral lines

- As we know, the atoms don't emit radiation at a precise freq. but over a range of frequencies, called as broadening of spectral lines.
- Various mechanisms cause this broadening and understanding of the mechanisms is necessary for the development of laser sources with sufficient spectral purity.
- To account for purity dependence of absorption, we can write

$$K(\omega) = \frac{\eta c^2 \pi^2 g_2 A_{21}}{g_1 \omega_0^2} \cdot \left(N_1 - \frac{g_1}{g_2} N_2 \right) \cdot g(\omega) \rightarrow \Delta\omega \text{ (FWHM)}$$

full width half maxima

Where $g(\omega)$ is line shape func. representing frequency behaviour of $K(\omega)$

ω_0 = central freq. of resonant freq. at which $g(\omega)$ is max and therefore $K(\omega)$ is max.

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

Two Groups

Inhomogeneous Broad
eg-doppler broad.

A line broadening mech is refrrd to as inhom. when it leads to the atomic resonant frequency being distributed over a band of frequencies (control frequency of individual atoms varies). Therefore the resultant is a broadened line of the whole system without broadening the individual lines of individual atoms.

Homogenous
Broadening
eg-natural, collision broad
A line brdng mech. is refrrd to as homog. if it broadens the response of each individual atom equally and hence has the same effect on all atoms.
Every atom has same freq. control freq. and same atomic line shape.

(22) X 3 - 1
(65)

| |
-1

DILR - ||| ||

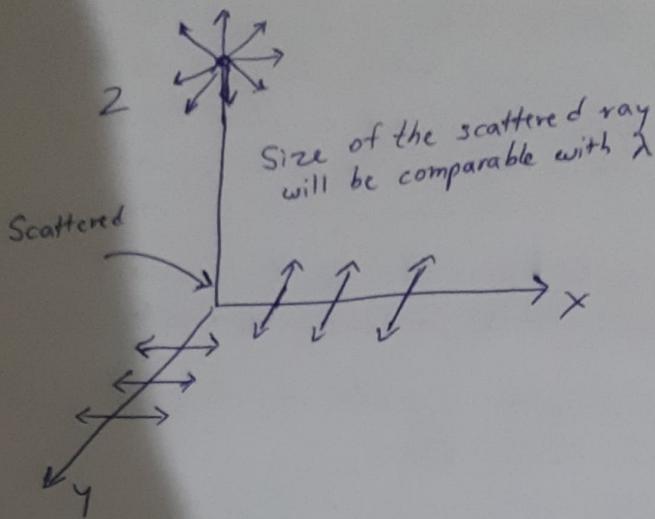
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QA - || ||

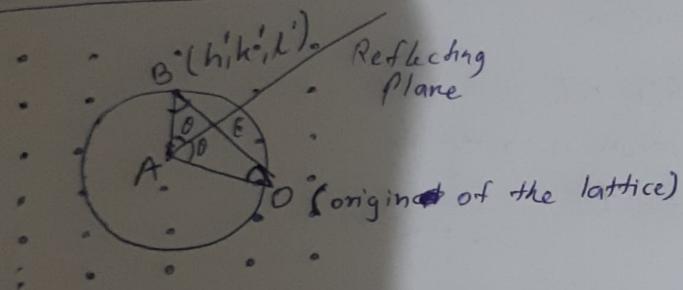
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Polarization by Scattering

(3)



Geometrical interpretation of the Bragg Condition



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

$$\angle EAO = \theta$$

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

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

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

Lorentz and Polarization Correction

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

Modulus of structure factor in cell of the structure amplitude. It is used to calculate $f(x, y, z)$

Hence to calculate (x, y, z)

Intrinsic value to the observed structure factor amplitude

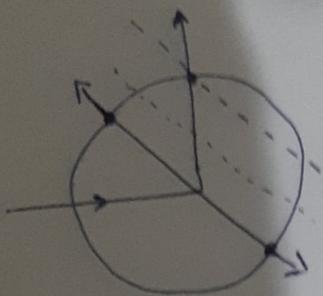
$$|F_0(hkl)| = |F_0(hkl)|^2$$

$$\Rightarrow |F_0(hkl)| = \sqrt{\frac{k I_0(hkl)}{LP}} \quad L = \text{Lorentz factor}$$

$\rho = \text{polarization factor}$

K depends upon crystal size, the beam intensity and few fundamental constants

$$|F_{rel}(hkl)| = K' |F_0(hkl)| = \sqrt{\frac{I_0(hkl)}{LP}}$$



Lorentz factor arises from the time required of a reciprocal lattice (rl) point to pass the Ewald Sphere. This time is not constant for all rl points. This depends on the location of individual rl points and the speed & direction from which it (rl points) approaches the Ewald sph.

As the crystal is rotated about ϕ or ω at a given velocity ω , the reciprocal lattice points will also rotate at the same angular velocity.

Therefore the line or vel of a r.l. point located at d^* r.l. units away from the origin as it approaches to the Ewald sphere,

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

$$d^* = \left(\frac{\lambda}{d}\right) \quad [\text{dimensionless}]$$

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

Now, the time 't' required for this r.l. point to pass through the full length P in the direction of motion is given by

$$P = tv \Rightarrow t = P/v = \frac{P}{2 \sin\theta \omega}$$

Now 'p' depends on the angle θ between the surface of the sphere of reflection and the path followed by the r.l. point

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

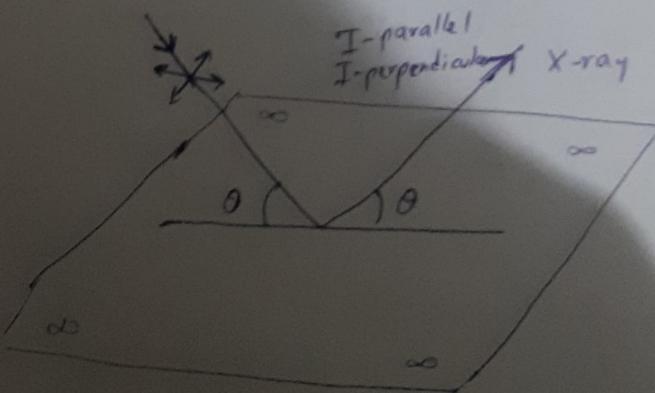
$$\Rightarrow t \propto \frac{1}{\sin 2\theta}$$

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

$$= \frac{1}{2 \sin\theta \omega}$$

Polarization Correction Factor

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



(3)

$I_{||r} \rightarrow \rho(x, y, z)$ and independ. of θ

$I_{\perp r} \rightarrow \rho(x, y, z)$ and dependent on θ

SAED

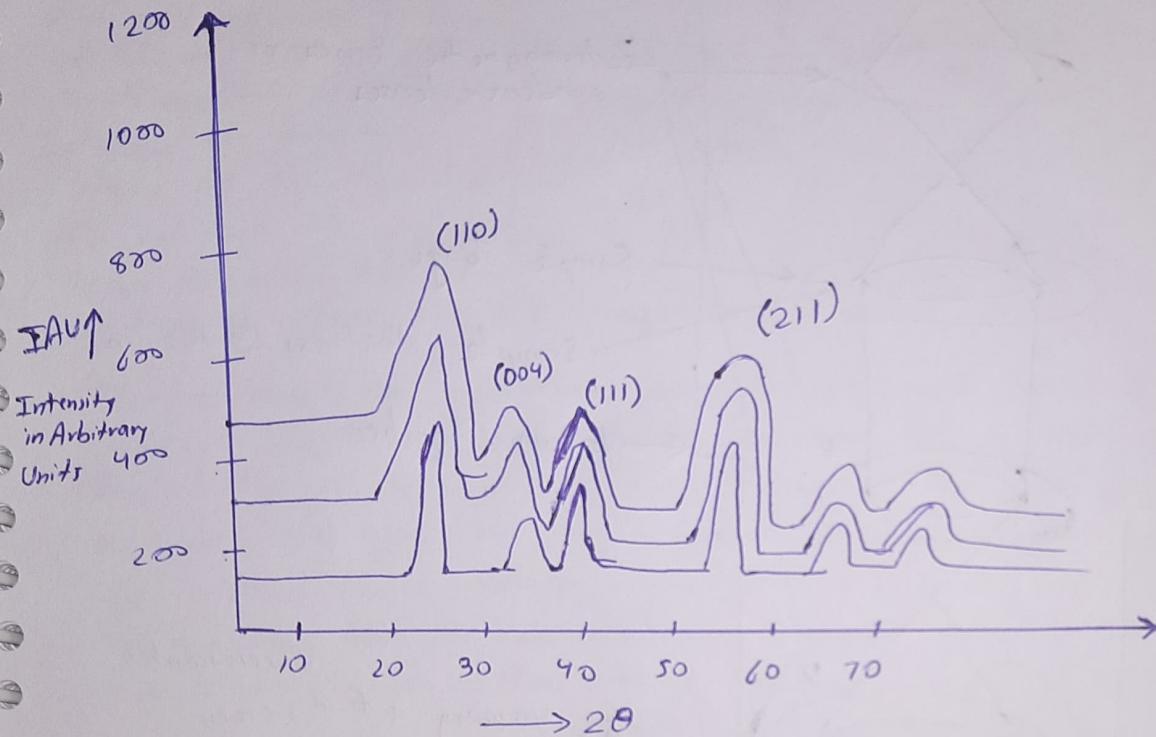
(3)

Amorphous \rightarrow Diffused rings

Single crystal \rightarrow Bright spots

Polycrystalline \rightarrow Bright rings

The same information we can achieve by XRD analysis



Transmission Electron Microscope (TEM) (1936)

TEM is very important tool in nano-technology in which electrons are made to fall on sample. These electrons interact with matter and get transmitted and strike a fluorescent screen and produce high resolution sample images.

TEM works on the same basic principle as the light microscope but uses electron beams instead of light beam to produce an image. As de-Broglie wavelength is much smaller than that of photons, TEM is capable of producing high-res images of sample. TEM can reveal the finest details of images.

Construction

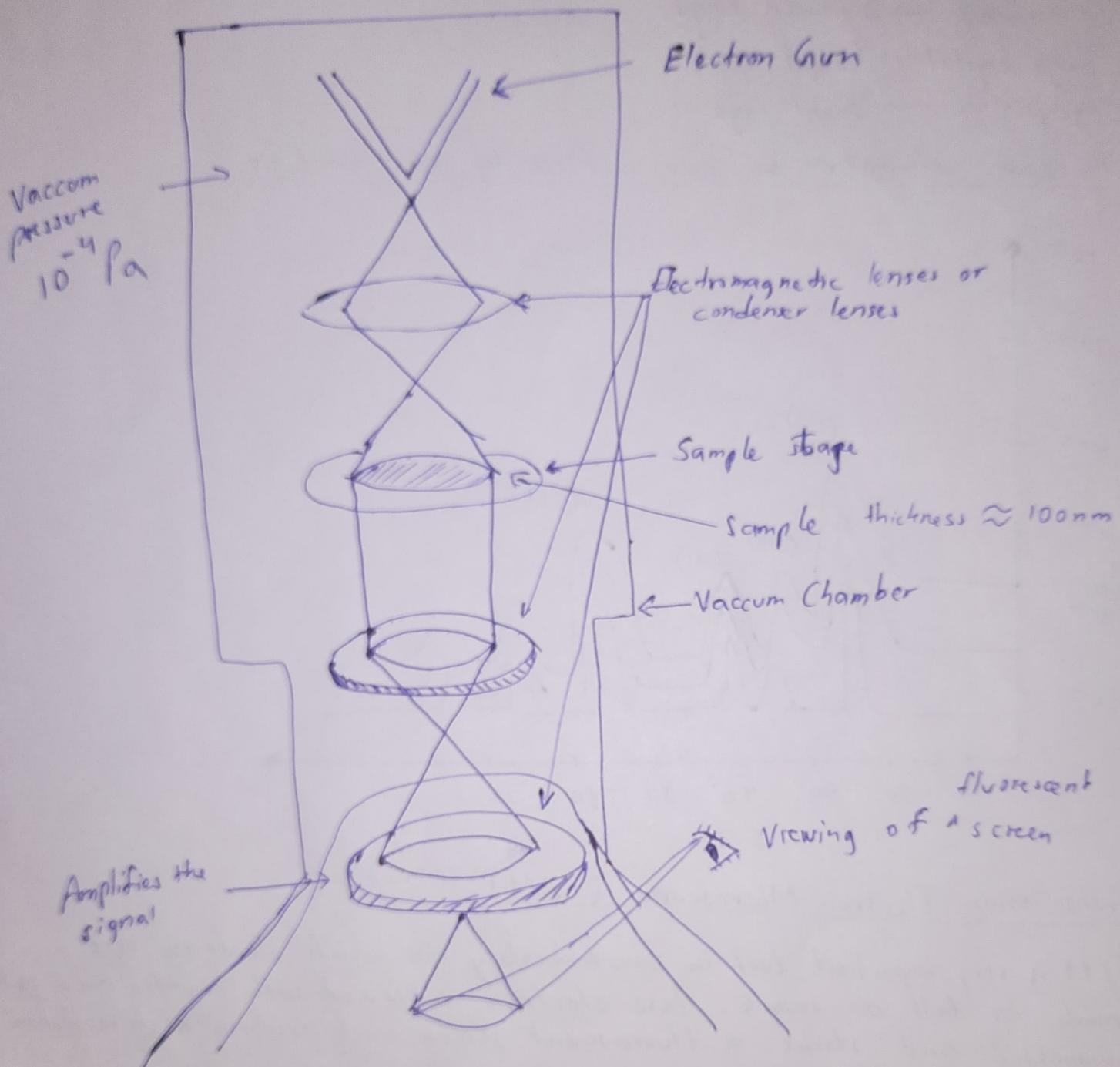
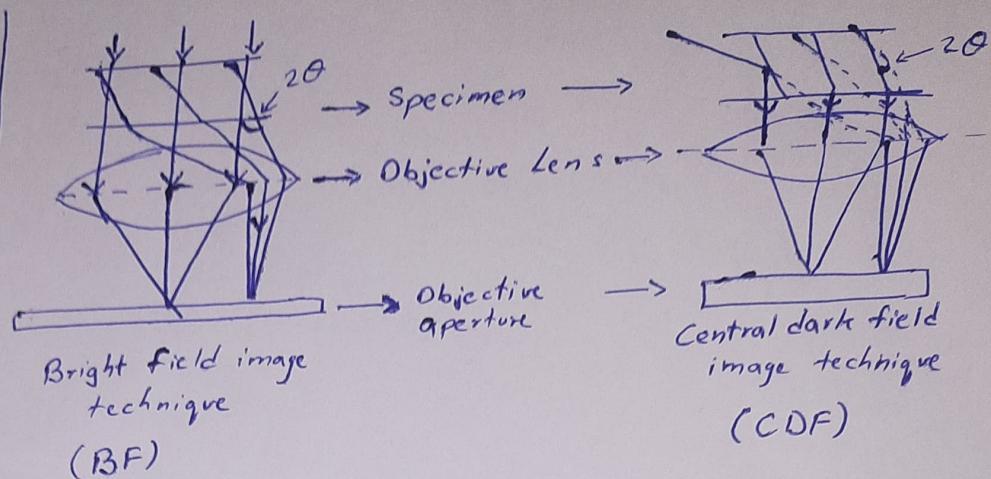


Image made - Bright & Dark field Images

- Bright field (BF) and CDF are most commonly used imaging modes for crystalline materials. Most of the analysis of crystal defects involve comparison between of BF and CDF. If a small aperture is inserted between the back-focal plane of the objective to intercept the diffracted beam to allow the beam to form an image, the the image is BF image.



- Alternatively, the aperture can be displaced from the optical axis to intercept the transmitted beam to form an image with the diffracted beam. This is known as CDF image. This displaced aperture method decreases the quality of image because of spherical aberration. In order to retain the resolution, electrons incident on the specimen is tilted so that the diffracted electrons travel along the optic axis and thus aberration can be avoided. This is CDF imaging technique.

Selected area diffraction (SAD) vs. Convergent Electron Beam Diff. (CEBD)

