

[5/10/21]

fast moving e^-

Wave
Dual
Nature
Particle

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Electron Diffraction

$$\text{de-Broglie wavelength for matter } / e^- : \lambda = \frac{h}{p}$$

Let 'm' be the mass of the e^- and 'v' be the velocity,
then momentum 'p' = mv

$$\text{So, } \lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{--- (1)}$$

If 'V' is the potential applied to e^- to accelerate it,
then energy = eV

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

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

$$\text{WKT, } \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{150V}}$$

where $\lambda = \sqrt{\frac{150}{V}}$ (where $\lambda \rightarrow \text{in } \text{\AA}$
 $V \rightarrow \text{in volt}$)

Neutron Diffraction

According to de-Broglie wavelength,

$$\lambda = \frac{h}{mp} = \frac{h}{M_n v} \quad \text{--- (1)}$$

where M_n is the mass of neutron, which is 2000 times more than the mass of electron, the wavelength associated with neutron is about $\frac{1}{2000}$ that of an electron velocity.

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

$$E = \frac{p^2}{2M_n}$$

(Here
particles
neutron)

X-ray diffractometer will determine crystalline, polycrystalline and amorphous materials.

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$$\text{do, } \lambda = \frac{h}{P} = \frac{h}{\sqrt{2M_n E}}$$

$$\Rightarrow \lambda \approx \frac{0.28}{\sqrt{E}} \quad (2) \quad (\text{where } \lambda \rightarrow \text{expressed in } \text{\AA} \text{ and } E \rightarrow \text{expressed in eV})$$

$$\text{for } E = 0.1 \text{ eV}, \lambda = 1 \text{ \AA}.$$

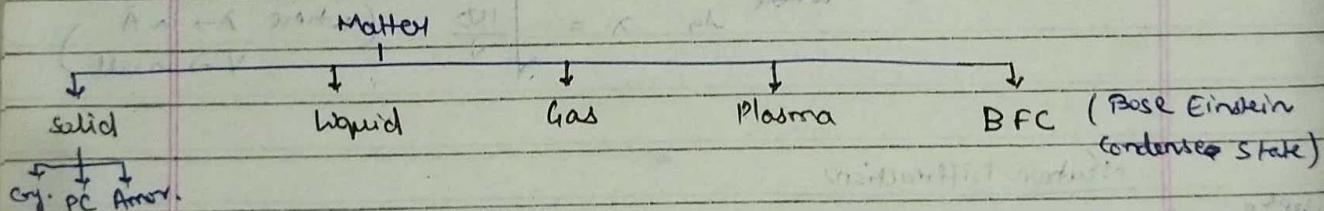
(small value) \rightarrow neutron diffraction.

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

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Classification of Matter and Solids

occupies
space &
volume



repetition of
unit cell = λ

Crystalline solid - (i) Atoms are periodically arranged for the long range

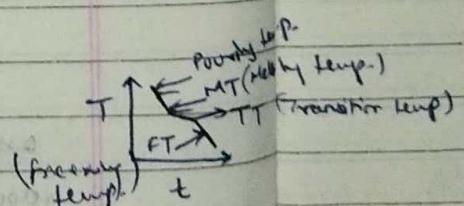


Lattice points

(ii) It gives sharp melting point.

(iii) Cooling curve of crystalline solids is discontinuous.

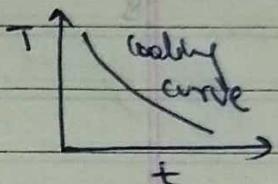
(Discontinuous)



Amorphous solid - (i) Irregular (not proper periodicity) arrangement of the constituent particles or supercooled liquid.



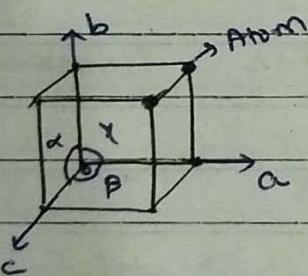
(ii) It gives continuous cooling curve.



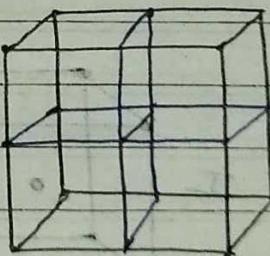
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Crystalline Lattice & Unit Cell

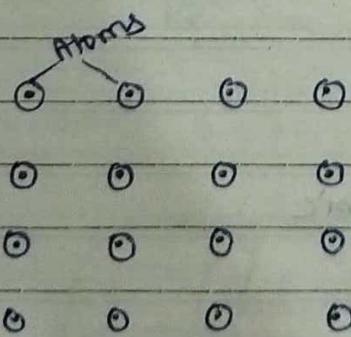
Regular arrangement of ~~3D~~ constituent particles in space.



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



Lattice points
Atoms



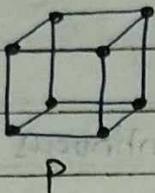
Lattice + Basis = Crystal structure

Classification of unit cell - Primitive & Non-primitive.

Classification of Unit Cells

1) SCC - Simple cubic unit cell

$$P = 8 \times \frac{1}{8} = 1 \text{ atom/cell}$$

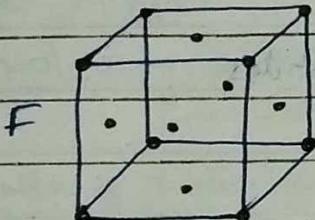


Primitive or Simplest - (P)

Constituent particles are situated at 8 corners of the cell.

2) FCC - Face-centred cubic

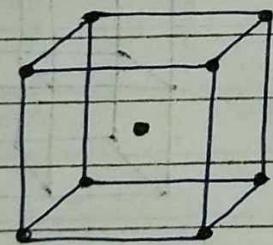
$$\begin{aligned} F &= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \\ &= 4 \text{ atoms/cell} \end{aligned}$$



Non-primitive cell.

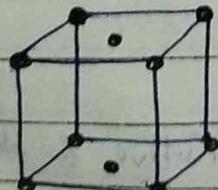
3) BCC - Body-centred cubic

$$\begin{aligned} I &= 8 \times \frac{1}{8} + 1 \\ &= 2 \text{ atoms/cell} \end{aligned}$$



4) BCC - Base centred cubic

$$\begin{aligned} C &= 8 \times \frac{1}{8} + 2 \times \frac{1}{2} \\ &= 2 \text{ atoms/cell} \end{aligned}$$



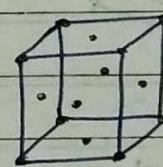
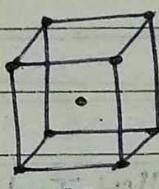
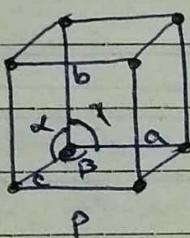
Non-primitive cell

Three-dimensional Bravais LatticeLattice parameters - a, b, c Angles - α, β, γ Permissible rotations - $1, 2, 3, 4, 6$ + } Identical environment
 $\vec{r} = -\vec{r}$ 14 Bravais Lattice and 7 crystals

① Cubic

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ / \text{f.c.c.} \quad P, I, F$$



②

Tetragonal

$$a = b \neq c$$

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

P, I

③

Orthorhombic

$$a \neq b \neq c$$

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

P, C, I, F



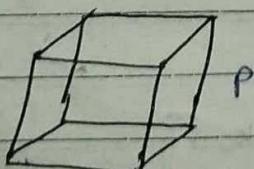
④

Monoclinic

$$a \neq b \neq c$$

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

P, C



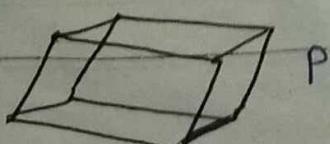
⑤

Triclinic

$$a \neq b \neq c$$

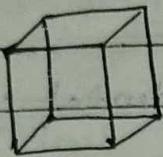
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

P



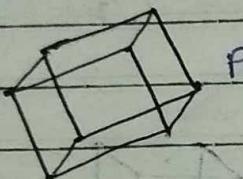
(6) Hexagonal

$a = b \neq c$, $\alpha = 120^\circ$, $\beta = \gamma = 90^\circ$, Simple P



(7) Trigonal

$a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$, Simple P or R
but $< 120^\circ$



Crystal Planes and Miller Indices

$a \ b \ c$
2 3 4

$\frac{1}{2} \ \frac{1}{3} \ \frac{1}{4}$

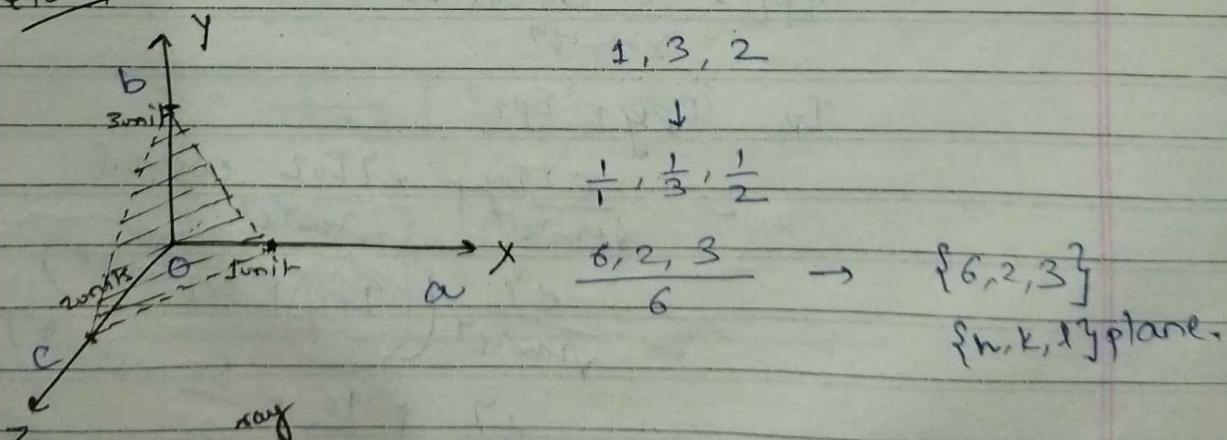
$\frac{6,4,3}{12}$

so, $\{6,4,3\} = \{h,k,l\}$
plane

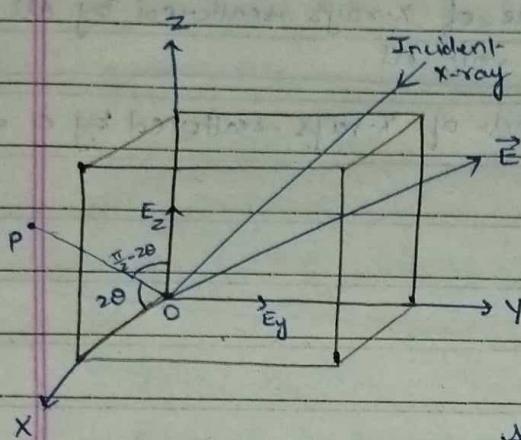
The miller indices are determined as follows-

- 1) Take any atom as the origin in the crystal and erect coordinate axes from the atom to the direction of the basis vectors. The axes may be primitive or non-primitive.
- 2) Choose the plane of the set of interest and note its intercepts on the axes a, b, c in terms of the lattice constants. The plane must be chosen so that no intercept is at the origin.
- 3) Take the reciprocal of these intercepts & convert these into the smallest set of integers that can be obtained by \times each of the fractions by the same number.
- 4) The result is conveniently enclosed in the parenthesis $\{h, k, l\}$ by taking reciprocals.

Example



^{ray}
 x -diffractometer measures the $\{h, k, l\}$ plane of the crystal str.

Polarization factorIncident
X-ray

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

$$\Rightarrow E_y^2 = E^2 - E_z^2$$

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

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

Now,

$$I_0 = E^2$$

$$\therefore I_{0y} = E_y^2, I_{0z} = E_z^2$$

$$I_{py} = I_{0y} \frac{e^4}{\pi^2 m^2 c^4} \sin^2 \frac{\pi}{2}$$

$$= I_{0y} \frac{e^4}{\pi^2 m^2 c^4}$$

$$\text{and, } I_{pz} = I_{0z} \frac{e^4}{\pi^2 m^2 c^4} \sin^2 \left(\frac{\pi}{2} - 2\theta \right)$$

$$= I_{0z} \frac{e^4}{\pi^2 m^2 c^4} \cos^2 2\theta$$

$$\text{Now, } I_p = I_{py} + I_{pz}$$

$$= I_{0y} \frac{e^4}{\pi^2 m^2 c^4} + I_{0z} \frac{e^4}{\pi^2 m^2 c^4} \cos^2 2\theta$$

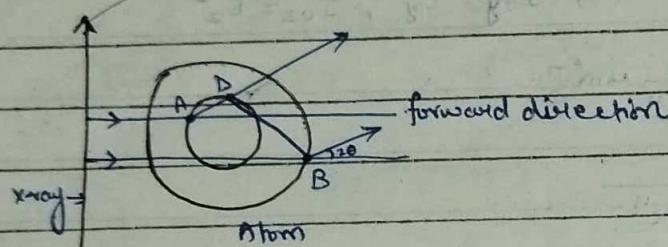
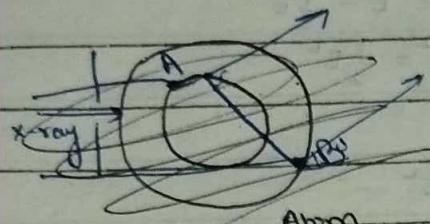
$$= \frac{e^4}{\pi^2 m^2 c^4} (I_{0y} + I_{0z} \cos^2 2\theta)$$

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

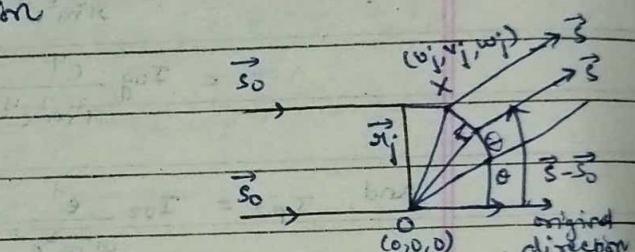
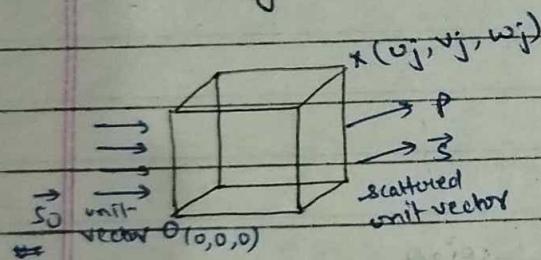
$$I_p = \frac{e^4 I_0}{\pi^2 m^2 c^4} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

Crystal structure factor

Crystal structure factor, $f =$ Amplitude of x-rays scattered by all the atoms in a unit cell
 Amplitude of x-rays scattered by a single e-



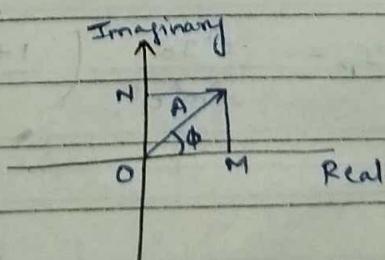
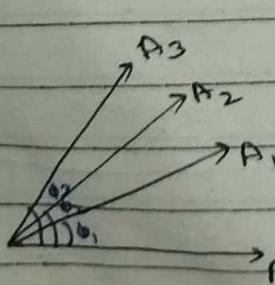
Scattering of x-rays by unit-cell



$$\text{Phase angle } \phi = 2\pi (\vec{S} - \vec{S}_0) \cdot \vec{s}_j = 2\pi (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \vec{s}_j$$

$$\phi = 2\pi (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot (u_j \vec{a} + v_j \vec{b} + w_j \vec{c})$$

$$\phi = 2\pi (hu_j + kv_j + lw_j)$$



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

$$A e^{i\phi} = A \exp(i\phi)$$

f_j = Atomic scattering factor of j th atom

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

$$f_j A_e \exp 2\pi i (h u_j + k v_j + l w_j)$$

Amplitude of the scattered X-ray due to unit cell (all the atom)

$$A = \sum_j f_j A_e \exp 2\pi i (h u_j + k v_j + l w_j)$$

$$\text{Crystal Structure factor (F)} = \frac{A}{A_e}$$

$$F = \sum_j f_j \exp 2\pi i (h u_j + k v_j + l w_j)$$

Intensity of diffracted beams -

1) Simple cubic

$$F = f \exp 2\pi i (h \cdot 0 + k \cdot 0 + l \cdot 0)$$

$$= f \exp 0$$

$$= f$$

$$I \propto |F|^2 \quad \text{do, } I \propto |f|^2 \quad (\text{for SC})$$

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

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

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

If h, k, l are mixed

$$\begin{array}{c} 20 \text{ ad} \\ 1 \text{ even} \end{array} \left\{ \begin{array}{c} h=1 \\ k=3 \\ l=2 \end{array} \right\} \quad \frac{h+k}{4} \quad \frac{k+l}{5} \quad \frac{h+l}{3}$$

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

Then

$$F = 0$$

When h,k,l is unmixed + pol) insq of it

n, l, k or hkl	If it is odd $F = 4f$
odd even	If it is even $F = 4f$

$$(I + \mu x^2 + \mu d^2) \text{ in } \mathcal{O} \Rightarrow I \propto |F|^2 \Rightarrow I \propto 16f^2$$

3)

BCC

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

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

$$F=0 \quad \text{and} \quad (x+1)^2 \sin \theta + x(2x+3) \cos \theta = 0$$

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

$$F = 2f$$

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

Simple Cubic \rightarrow $I \propto |f|^2$

$$fcc \Rightarrow I \propto 14f^2$$

$$Bcc \rightarrow J \propto 12f^2$$

Broadening of Spectral Line -

- * As we know, the atoms do not emit radiations 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 mechanisms is necessary for the development of laser sources with sufficient spectral purity.

To account for purity dependence of absorption, we can write

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

where,

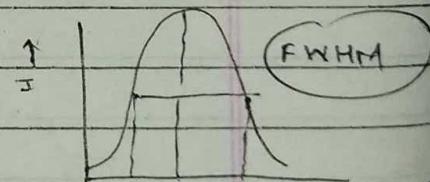
$g(\omega)$ is the line shape function representing the frequency behaviour of $K(\omega)$

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

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

Line Broadening Mechanism can be classified

into 2 grps. -



Two Grps

Homogeneous
Broadening

Ex: Natural broadening,
Collision broadening

Inhomogeneous
Broadening

Ex: Doppler

Avg. grain size = $0.94 \times$
in microns

$B \cos \theta$
in radian

broadening.

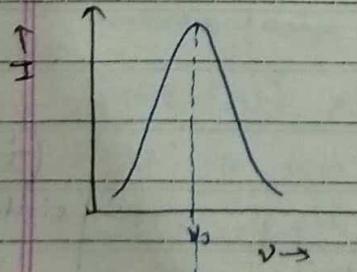
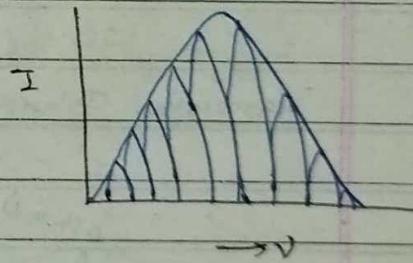
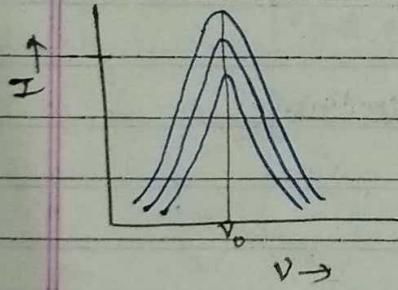
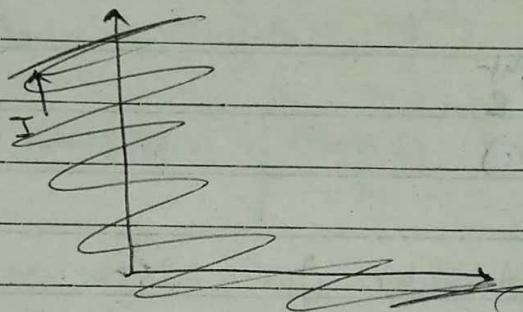
A line broadening mechanism is referred to as homogeneous if it broadens the response of each individual atom equally and hence has the same effect of all the atoms. Every

A line broadening mechanism is referred to as inhomogeneous when it leads to the atomic resonant frequency being distributed over a

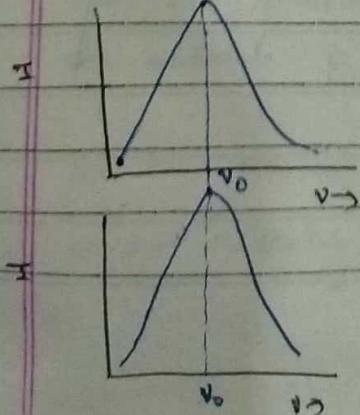
above therefore has the same central frequency and same atomic line shape.

band of frequencies (central frequencies of individual atom varies). therefore the resultant - in a broadened line of the whole system without broadening the line of individual atoms.

(Homogeneous broadening
is Lorentzian
in shape)



(Inhomogeneous broadening is Gaussian
in shape.)



Polarization by Scattering -

Scattering -
(Vibrations in all possible directions)

Scattered (size of the scattered will be comparable with 'x')

Polarized light along Y-axis)

polarized
light along x-axis)

\Rightarrow (Observing light-
I to Y-axis &
II to X-axis)

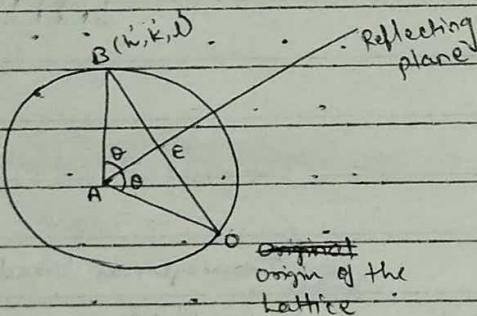
$I \propto F^2$ for simple cubic

$$I \propto 14f^2 \text{ for fcc}$$

$$I \propto |2f|^2 \text{ for BCC}$$

- But requires Lorentz correction factor
and Polarisation correction factor

Geometrical Interpretation of the Bragg condition -



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

$$\angle EAO = \theta \quad \text{and}$$

$$OB = \frac{n}{d}$$

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

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

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

\vec{r} = radius
circle \rightarrow evolved sphere
evolved construction

Lorentz Correction Factor → Time taken by the X-ray to reach the evolved sphere.

Page

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 $\rho(x, y, z)$

Hence to calculate (x_i, y_i, z_i)

The value to the observed structure factor amplitude

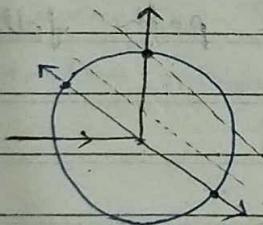
$$I_{0(hkl)} = |F_{0(hkl)}|^2$$

$$\Rightarrow |F_{0(hkl)}| = \sqrt{\frac{I_{0(hkl)}}{LP}} \quad \text{where } L \text{ is the Lorentz factor}$$

P is the polarization factor

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

$$|F_{\text{rel.}}(hkl)| = K' |F_{\text{obs.}}(hkl)| = \sqrt{\frac{I_{0}(hkl)}{LP}}$$



Lorentz factor arises from the time required of a reciprocal lattice (rl) point to pass through the evolved sphere. This time is not constant for all the rl points. This depends on the location of individual reciprocal lattice (rl) points and the speed and the direction from which it approached the ~~evolved~~ Ewald sphere.

If the crystal is rotated about ϕ or ω at a given angular velocity ω , the rl points also rotate at the same

angular velocity.

Therefore the linear velocity of a g.l. point located at d^* g.l. unit away from origin as it approaches to the Ewald ~~sphere~~ sphere.

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

$$d^* = \left(\frac{\lambda}{d} \right)$$

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

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

$$P = tv$$

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

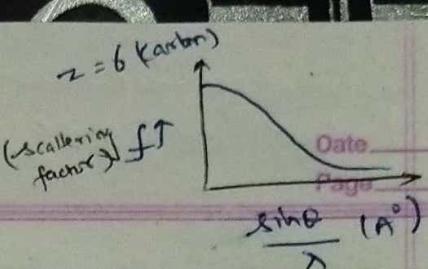
Now, 'P' depends on the angle θ between the surface of the sphere of reflection and the path followed by the g.l. point.

$$\text{Now, } P \propto \frac{1}{\cos \theta}$$

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

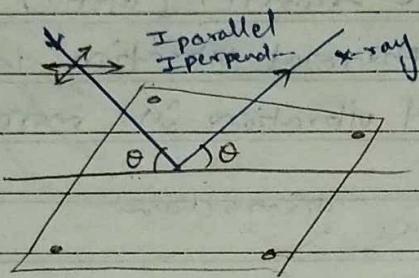
$$\Rightarrow t \propto \frac{1}{\sin 2\theta}$$

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



Polarization correction factor

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



$(\pi \text{ beam}) I_{\parallel} \rightarrow f(x, y, z)$ and independent of θ

$(\sigma \text{ beam}) I_{\perp} \rightarrow f(x, y, z)$ and dependent on θ

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

In case we are using crystal monochromator, the effect is important. The incident beam itself will be polarised.

Secondary polarization will influence the diffraction data.

$$p = \frac{1 + k \cos^2 \theta}{1 + k}$$

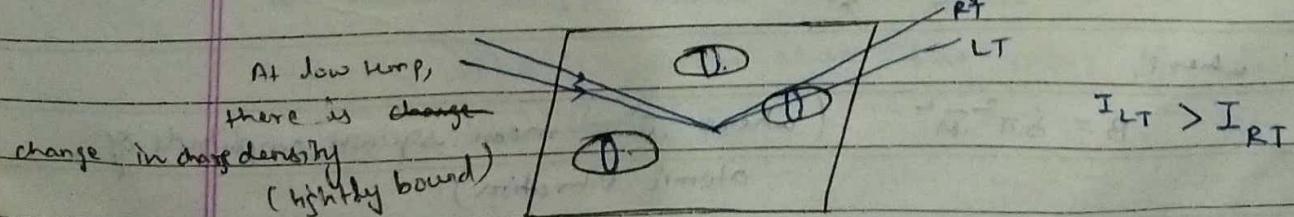
where, k is the ratio of power of π beam w.r.t σ beam from the crystal monochromator.

If ~~the~~

~~the~~

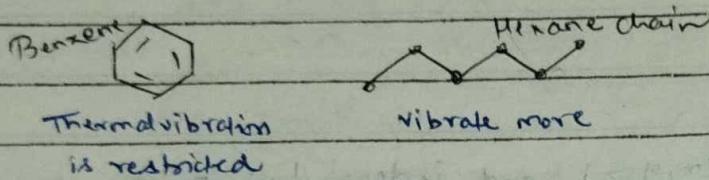
Temperature factor on the intensity of the diffracted beam-

Absolute scaling and the effect of temperature factor



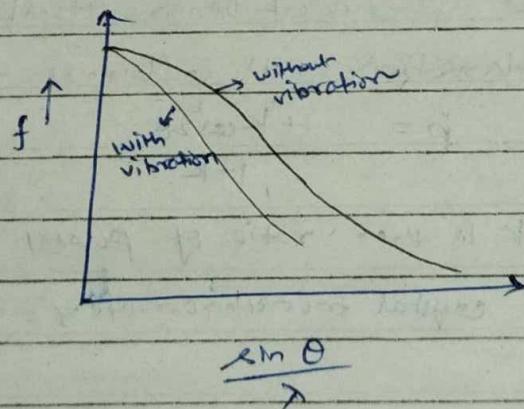
At high temperature, these vibrations will be made significant and hence will influence the diffracted intensity more
 $m = \text{mass of the scattered atom}$

for heavier elements, thermal vibration is less and for lighter, the thermal vibration is more.



The ~~eff.~~ effect of thermal vibration is to reduce the scattering power of an element, mostly lighter elements, and hence the diffracted intensity is weak.

Result \rightarrow Thermal vibration will lower the scattering factor (f)



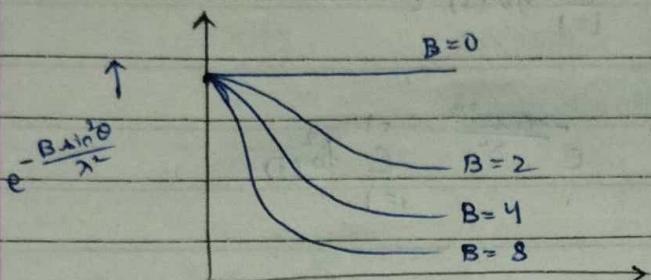
The variation in the atomic scattering factor is given by-

$$e^{-\frac{B \bar{u}^2 \theta^2}{\lambda^2}}$$

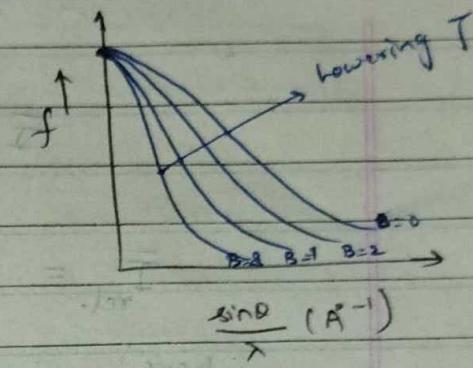
where,

$$B = 8\pi^2 \bar{u}^2 \quad (\text{where } \bar{u}^2 = \text{mean square amplitude of atomic vibration})$$

$$f = f_0 e^{-\frac{B \sin^2 \theta}{\lambda^2}}$$



$$\frac{\sin \theta}{\lambda} (\text{A}^{-1})$$



$$\frac{\sin \theta}{\lambda} (\text{A}^{-1})$$

The avg. observed intensity corrected for Lorentz and polarization factor.

$$\bar{I}_{\text{relative}} = \langle |F_{\text{rel.}}|^2 \rangle_{\text{avg.}}$$

If we have a unit cell with 'N' atoms then

~~$$\bar{I}_{\text{abs}} = \frac{1}{N} \sum_{i=1}^N f_i^2$$~~

$$\bar{I}_{\text{abs}} = \frac{1}{N} \sum_{i=1}^N f_i^2 \quad (\bar{I}_{\text{abs}} = \text{Theoretical avg. intensity})$$

Now, the ratio of $\frac{\bar{I}_{\text{abs}}}{I_{\text{rel}}}$ should be defined as the scale

factor to place the I_{rel} values on an absolute scale.

since f_i is not same over the range of $\frac{\sin \theta}{\lambda}$.

$\therefore I_{\text{abs}}$ also varies with $\frac{\sin \theta}{\lambda}$

To avoid this, we divide the Ewald's sphere into small infinite shells such that the value of f_i do not change within the shell.

f_i are all influenced by the thermal motion

$$\bar{I}_{abs} = \sum_{i=1}^N f_o(i) e^{-\frac{2B \sin^2 \theta}{\lambda^2}}$$

$$I_{abs.} = e^{-\frac{2B \sin^2 \theta}{\lambda^2}} \sum_{i=1}^N f_o(i)$$

$$\bar{I}_{rel.} = C \bar{I}_{abs}$$

where, C is the scale factor

$$\bar{I}_{rel.} = C e^{-\frac{2B \sin^2 \theta}{\lambda^2}}$$

$$\sum_{i=1}^N f_o^2(i)$$

JANUARY 2016				
S	M	T	W	F
31			1	2
3	4	5	6	7
10	11	12	13	14
17	18	19	20	21
24	25	26	27	28
			29	30

2015

DECEMBER 31
Thursday

XRC

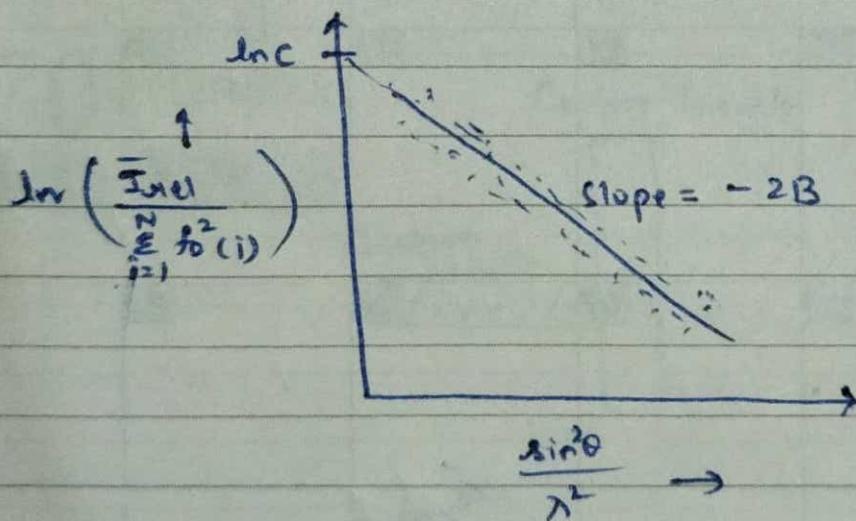
$$\frac{\bar{I}_{rel}}{\sum_{i=1}^N f_0^2(i)} = C e^{-\frac{2B \sin^2 \theta}{\lambda^2}}$$

↓
scale factor

Now,

$$\ln \left(\frac{\bar{I}_{rel}}{\sum_{i=1}^N f_0^2(i)} \right) = \ln C - \frac{2B \sin^2 \theta}{\lambda^2}$$

$\underbrace{\hspace{1cm}}_y \qquad \underbrace{\hspace{1cm}}_x$



Now,

$$\bar{I}_{rel} = C \bar{I}_{abs}$$

$$|F_{rel}|^2 = C |F_{abs}|^2$$

$$|F_{abs}| = \frac{1}{\sqrt{C}} |F_{rel}|$$

29 DECEMBER

2015

Tuesday

NOVEMBER 2015						
S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30					

$$|F_{abs}| = k |F_{rel}|$$

↓
scale

component =
constant

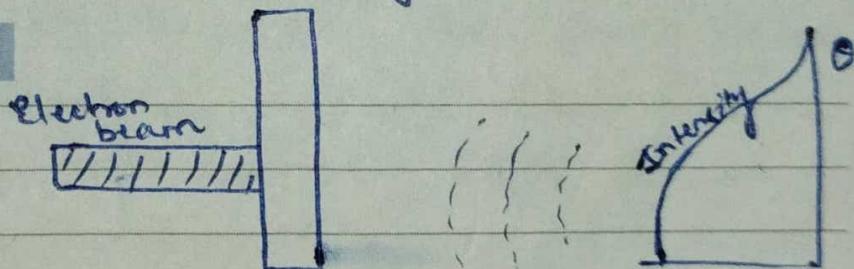
Electron Diffraction

If the e^- behave as a particle, the distribution of e^- will vary continuously as a function of angle. This distribution will vary only slightly with change in e^- energy.

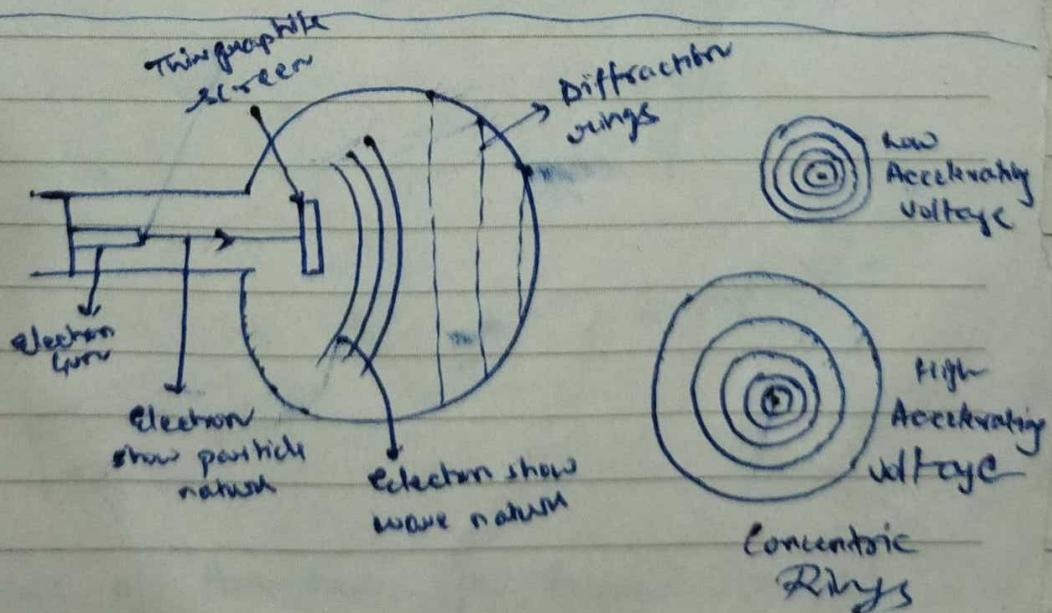
30 DECEMBER

Wednesday

Carbon target



Thin graphite
screen



25 DECEMBER

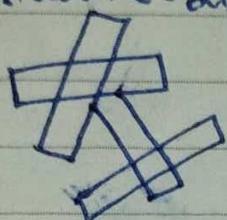
2015

Friday

NOVEMBER 2015						
S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30					

Selected Area Electron Diffraction (SAED)

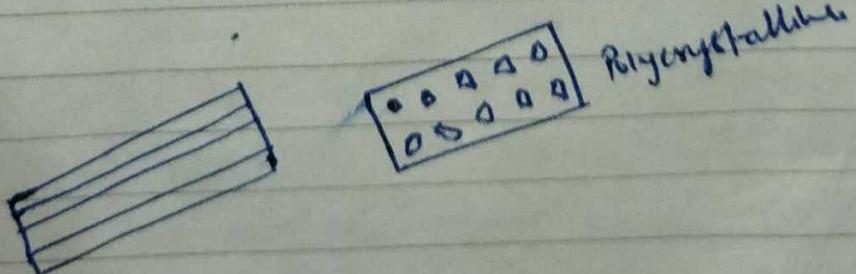
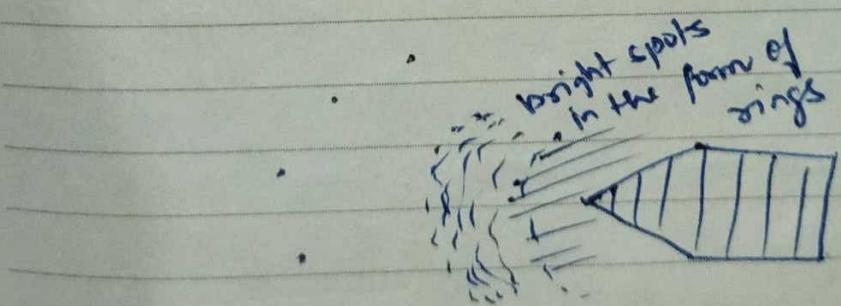
- ① single crystalline - diffraction of a single crystal gives



a discrete
a discrete spot

- ② Polycrystalline (consisting of many crystalline or single crystals), small spots making up

26 DECEMBER rings. Individual crystalline gives these spots arising from Bragg reflection resulting numerous discrete spots ~~not~~ line up and forming rings.



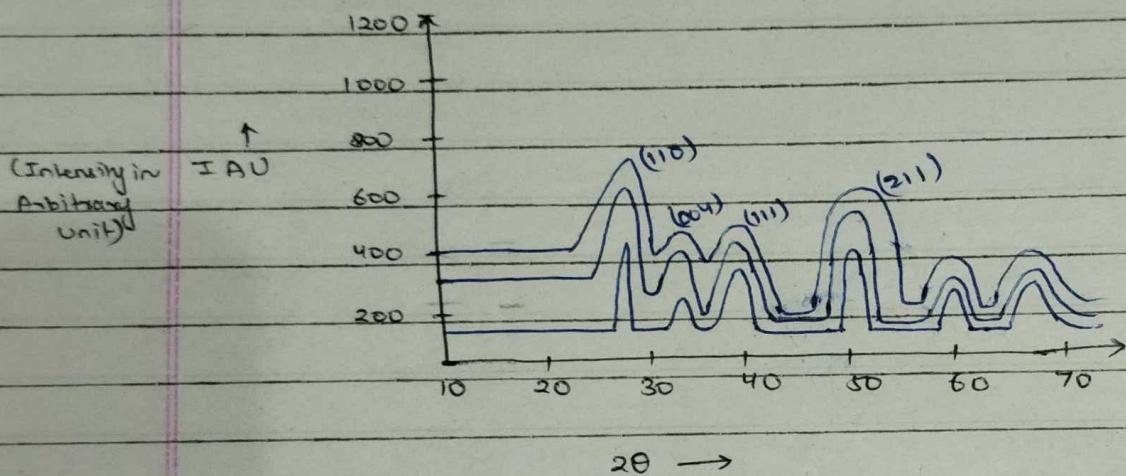
and in case of Amorphous, (diffused rings)

SAED

Amorphous - Diffuse Rings

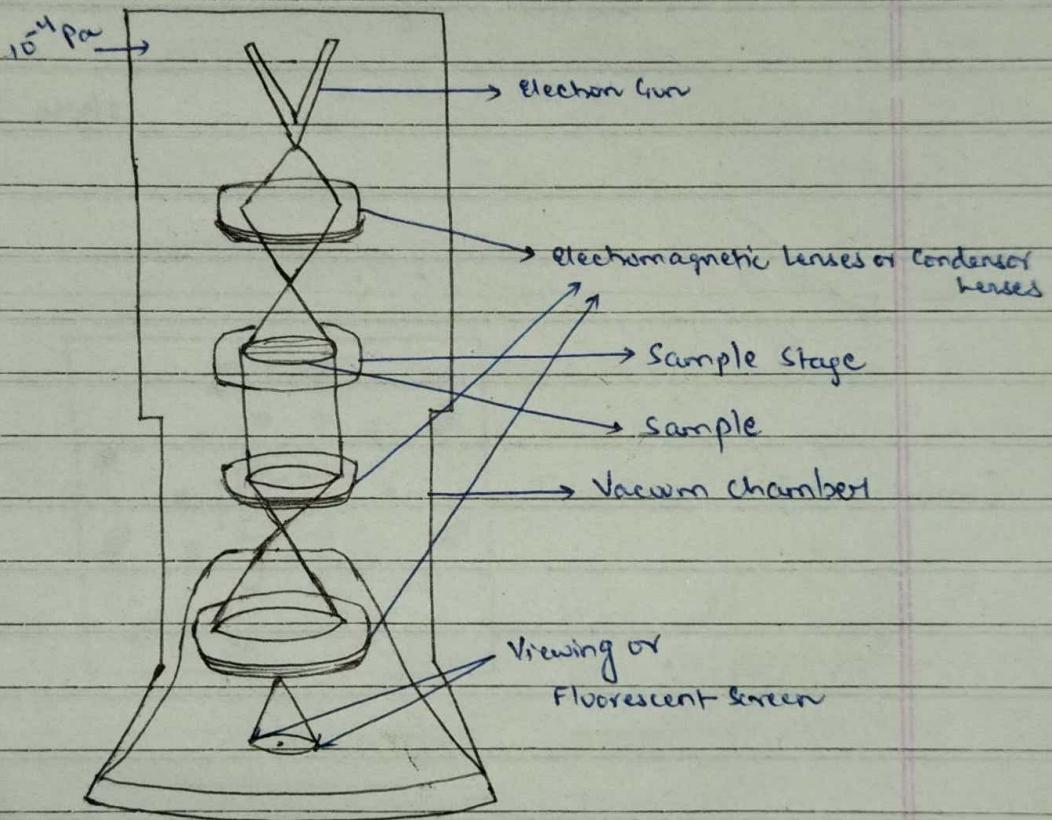
Single crystal - Bright spots

Polycrystalline - Bright Rings

The same information we can achieve by XRD Analysis -Transmission Electron Microscope (TEM)

TEM is a very imp. tool in nanotechnology in which e⁻ are made to fall on sample. These e⁻ interact with matter and get transmitted and strike a fluorescent screen and produces high resolution sample images.

Principle - TEM works on the same basic principle as the light microscope but uses e⁻ beam 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 resolution images of sample. TEM can reveal the finest details of images.

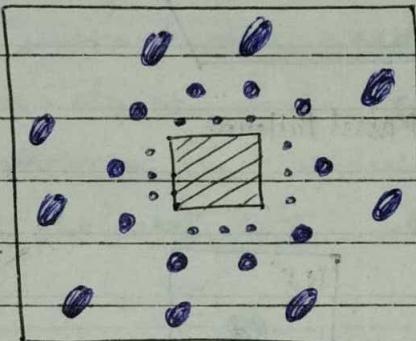
Construction -

Convergent Beam
Diffraction.
Electron

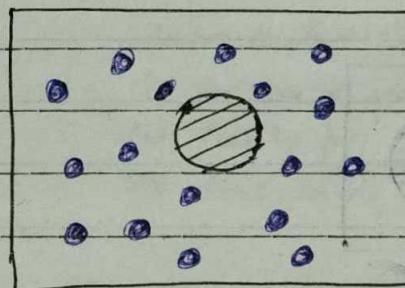
Parameters that can be determined by CBED -

- 1) Sample thickness
- 2) Convergence semi-angle
- 3) Camera length
- 4) Defocus.

(1) Sample thickness



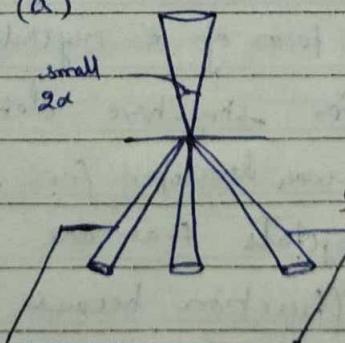
Thin Film ($t = 0.2 \mu\text{m}$)



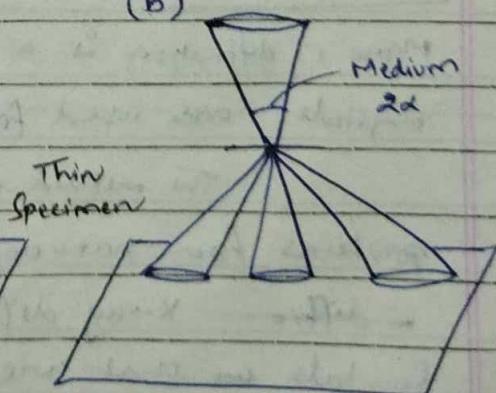
Thick film ($t > 1 \mu\text{m}$)

(2) Convergence semi-angle

(a)

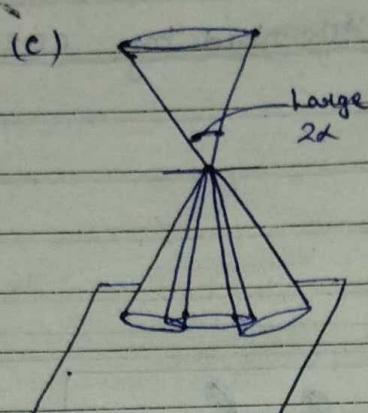


(b)

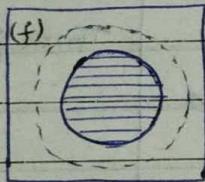
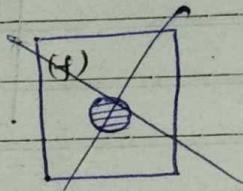
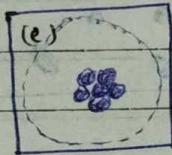
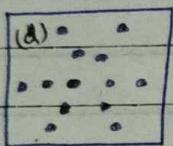


Kassel-Mitterstedt

Pattern (K.M.)



Kassel Pattern



Micro-crystal Electron Diffraction

Micro e^- diffraction is a form of e^- crystallography where thin 3D crystals are used for structure determination by e^- diffraction.

The method was developed for structure determination of proteins from nanocrystals that are typically not suitable for \leftarrow diffra x-ray diffraction because of their size.

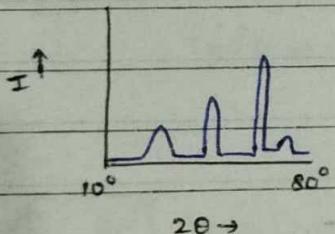
Crystals ~~are~~ that are 1 billion the size needed for x-ray crystallography can yield high quality data. The samples are frozen hydrated as for all other ~~cryo-~~ cryoem modalities but instead of using the TEM in imaging

mode, one uses it in diffraction mode with an extremely low e^- exposure.

The nano crystal is exposed to the diffracting beam and continuously rotated while the diffraction is collected on a fast camera as a movie. Micro e^- diffraction is then processed using traditional software for x-ray crystallography without the need for specialized software for structure analysis and refinements. Importantly, both the hardware & software used in a micro e^- diffraction experiment are standard and broadly available.

General features of the XRD pattern -

factors on which peak depends -



- (i) Position of peak
- (ii) Peak height
- (iii) Peak width

Huge database XRD patterns of XRD compounds -

- (i) International centre for diffraction data (ICDD)
- (ii) International crystal structure data base (ICSD)

Bragg Law and Peak Intensities -

$$\text{WKT}, \quad 2d \sin\theta = n\lambda$$

If $n=1$,

$$\text{Then } \lambda = 2d \sin\theta \quad \text{--- (1)}$$

$$\text{Now, } d_{hkl} = f(a, b, c, \alpha, \beta, \gamma, h, k, l)$$

for orthogonal system: $\alpha = \beta = \gamma = \frac{\pi}{2}$ Then, $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

for cubic system: $\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$

Atomic form factor -

XRD depends on scattering of X-rays by atoms.

Scattering Intensity, $f_p \propto \sum_{\text{Atomic No.}} (1 + \cos^2 \theta)$ $\begin{cases} \text{If } \theta \downarrow, f_p \uparrow \\ \text{If } \theta \uparrow, f_p \downarrow \end{cases}$

Similarly, it is difficult to detect C, N, O.

Geometry Structure factor (GSF) -

Interference b/w atoms of the basis of crystal

Unit cell - 7 types of unit cell

14 Bravais lattice -

$$I \propto |F_{hkl}|^2$$

↓
gsf

Two more factors that affect intensity -

① Temperature factor

② Refinement factor

Temperature factor $\rightarrow \rightarrow \rightarrow$
 $\dots \dots \dots$

$$f = f_0 \exp \left[-\frac{B \sin^2 \theta}{\lambda} \right]$$

where,

$$B = 8\pi^2 \bar{u}^2$$

↓
mean square displacement
proportional to T

Refinement
factor

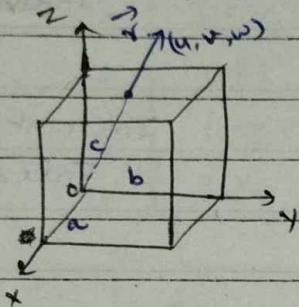
Rietveld Refinement

$$(F_{\text{obs}} - F_{\text{cal}}) = \text{Refine structure}$$

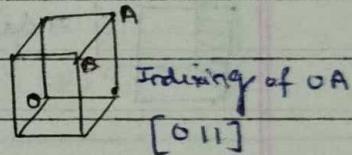
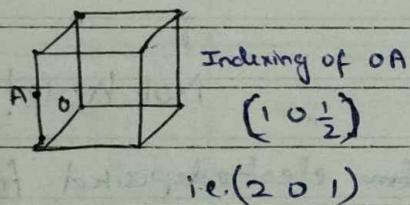
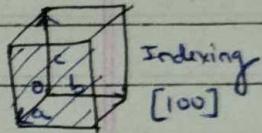
Date _____

Page _____

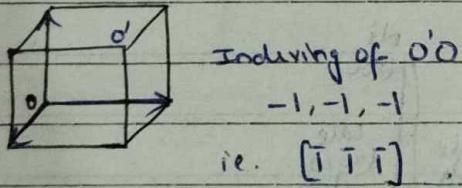
Crystal Plane and Directional Indexing



$$\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$$



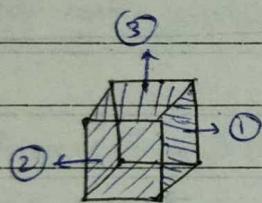
Indexing of OB
[111]



Indexing of Planes

- (i) Determine the intercepts of plane with crystal axes.
- (ii) Take the reciprocal of the intercepts.
- (iii) Remove the fractions by multiplying with the common factor.
- (iv) Reduce to the smallest integer values and enclose in the parenthesis without comma.
- (v) A negative intercepts will be denoted by a ^{bar} over the integer

(vi) If plane is passing through origin, take a parallel plane or shift the origin keeping same sense of crystal axes.



Intercept of Plane ①

$$\infty, 1, \infty$$

Reciprocal: $0, 1, 0$

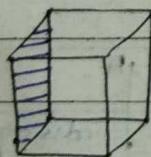
Indexing: (010)

Intercept of Plane ②

Indexing (100)

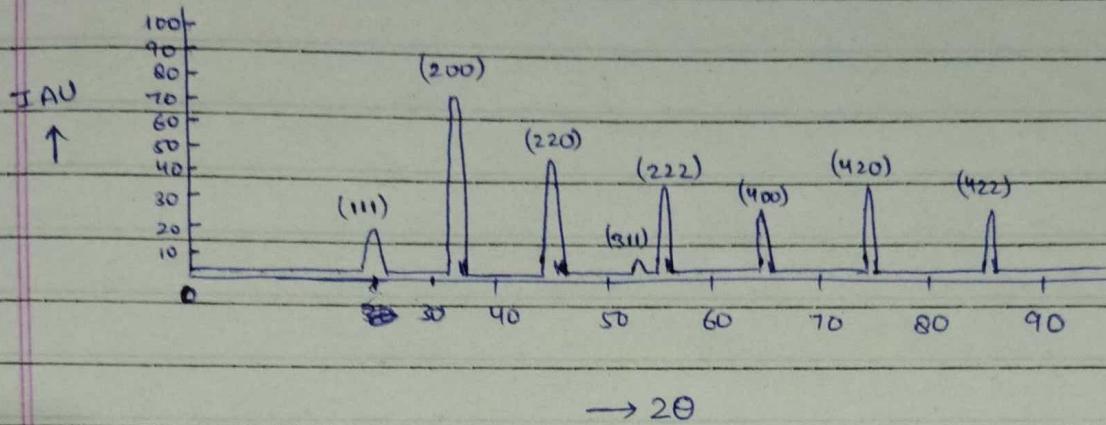
Intercept of Plane ③

Indexing (001)

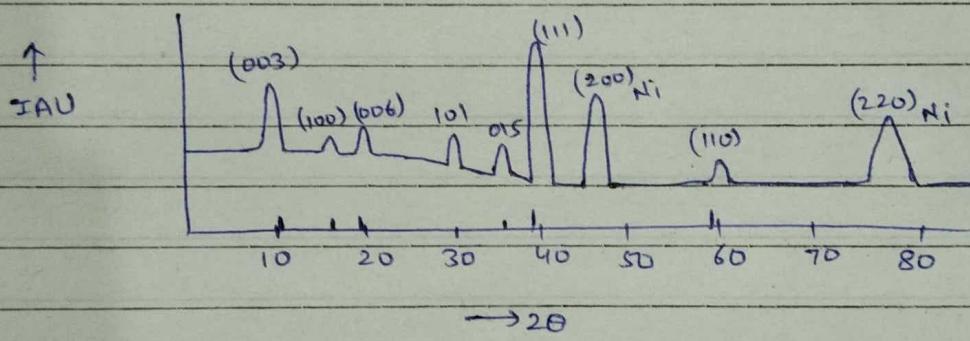


Indexing $(0\bar{1}0)$

NaCl Crystal



XRD Pattern in $\alpha\text{-Ni-Co(OH)}_2$ on Nickel -



$2\theta = 11.1, 16.8, 19.2, 33.8, 38.4, 59.6$

Planes (003), (100), (006), (101), (015), (110)

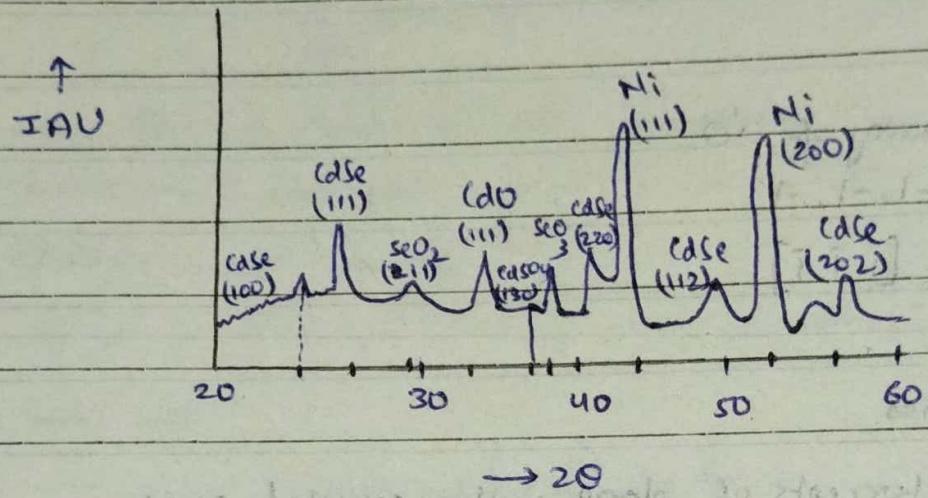
$$003 \rightarrow 8.0 \text{ \AA}$$

Intensity of the diffracted beam depends on following factors-

- 1) Polarization factor
- 2) Structure factor
- 3) Multiplicity factor
- 4) Lorentz factor
- 5) Absorption factor
- 6) Temperature factor

Applications of XRD

i) X-ray diffraction spectra of CdSe film electrodeposited film



Comparison of experimentally observed and standard values -

CdSe film	Standard d \AA	Crystalline plane	hkl	Reference ASTM file
20	d \AA			
24.64	3.69	CdSe Wurtzite	(100)	8-459
25.47	3.49	CdSe Zinc Blende	(111)	19-191

Case 2θ	Film $d\text{\AA}$	Standard $d\text{\AA}$	Crystalline Plane	hkl	Reference, ASTM File
29.69	3.00	3.00	SeO_2	(211)	22-1314
33.00	2.71	2.71	CdO	(111)	5-640
37.17	2.41	2.42	CdSe_4	(130)	15-86
42.05	2.14	2.14	CdSe Zinc Blende	(220)	19-191
44.54	2.03	2.03	Ni	(111)	4-850
49.79	1.82	1.83	CdSe Wurtzite	(112)	8-459
52.04	1.76	1.76	Ni	(200)	4-850
55.30	1.65	1.64	CdSe Wurtzite	(202)	8-459

(Volume - Serial No.)

Crystalline case	Relative Peak Height -	Peak width at half Maxima	Standard Values		
			d	Peak height	hkl
Wurtzite	45	0.90	3.72	100	(100)
	25	1.06	1.83	50	(112)
Zinc Blend	110	0.75	3.51	100	(111)
	62	0.75	2.14	55	(220)

{}