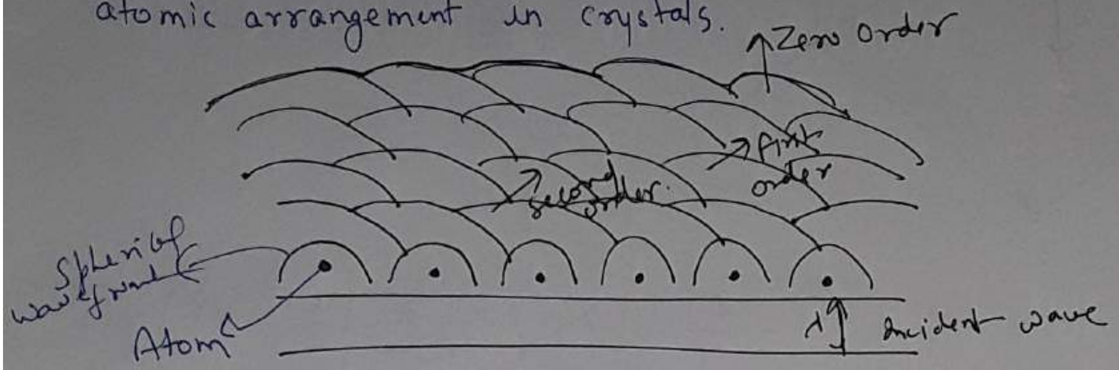
# Diffraction of X-rays by crystals → (37)

(1) X-rays are diffracted by crystals in same way as visible light by a diffraction grating.

(2) Diffraction — Serves the purpose of "direct exploration of the interior of crystals".

(3) Intensities of diffracted beams & their directions are related to atomic arrangement in crystals.




Reinforcement of scattered waves producing diffracted beams of different orders.

(4) An atom exposed to monochromatic X-rays ⊙ ⇇ X-rays

↓

Electric field vector of radiation forces its e⁻ to carry out harmonic vibrations of freq = incident beams & undergo acceleration.

↓

These Accelerated charges re-emit radiation at same frequency of their vibration

↓

Emitted wave ⟹ spherical wavefront centered about atom (and energy goes off in all directions)

↓

Consider above for a group of atoms arranged in a regular pattern

↓

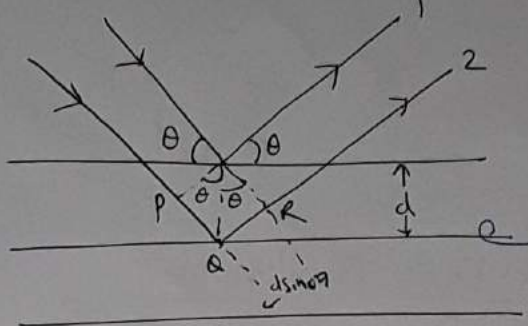
~~bb~~ Envelope of wavelets emitted by atoms form new wave crests & there are ~~two others~~ beams in few other directions also (apart from the incident direction)

↓

only in few directions these wavelets reinforce each other to produce plane waves
↓
These are diffracted waves of 0, 1st, 2nd order etc. 38
↓
But still crystal is in 3D, not a single 1D row of atom. Hence there are two ways of calculating conditions of diffraction ——
↓
(1) Due to Bragg (2) Von laue.

## (1) Bragg Treatment

WL Bragg investigated the conditions of X-ray diffraction by a model (simplified)




Assumptions: X-rays are specularly reflected (mirror-like) from the ‖ atomic planes in crystal & multiple reflections interfere constructively in those directions.

In figure → Horizontal lines ⇒ ‖ planes of atom, which partly reflect incident rays.

$d$ = Distance b/w successive planes.

$\theta$ = Angle of incidence = Angle of reflection.

1 and 2 are rays reflected from adjacent planes

$PQR$ = path diff b/w 1 and 2

⇒ Rays reflected from adjacent planes will be in phase & their amplitudes will reinforce to give strong reflection only if path diff = integral multiple of $\lambda$.

or $\boxed{2d\sin\theta = n\lambda}$

Above is called Bragg's law ($n$ = order of diffraction)

$\sin\theta \le 1$ ⟹ $\lambda \le 2d$ are essential for Bragg reflection to occur.

Note ⇒ There are only certain directions $\theta$ in which reflections of a given $\lambda$ from all ‖ planes add up in phase to give a strong diffracted beam.

Q) If $\lambda = 4 \times 10^{-5}$ cm, then is it bragg reflected.

Ans $d \simeq 10^{-8}$ cm



$\lambda \le 2d$ → Condition for bragg's law

→ $2d = 2 \times 4 \times 10^{-5}$ cm $= 8 \times 10^{-5}$ cm

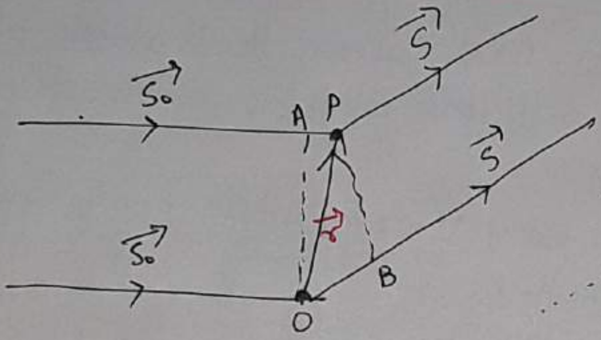
$\lambda \le 2d \Rightarrow$ $8 \times 10^{-5}$ cm $\le 10^{-8}$ cm ✗ Not satisfied.

So not bragg reflected

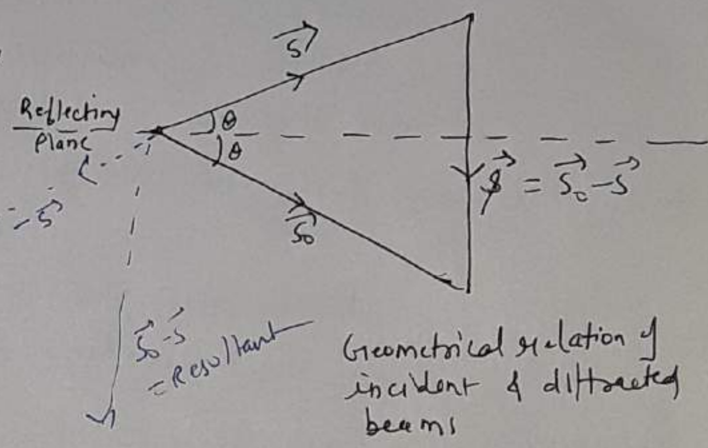
$8 \times 1 \le 10^{-3}$

$8 \le 10^{-3}$ ✗

## (2) Von laue Treatment




PO = $\vec{r}$




Geometrical relation of incident & diffracted beams

(1) P, O are two scattering centres

(2) $\vec{S_0}$ = unit vector in direction of incident beam.

$\vec{S}$ = " " " arbitrary scattering direction.

PA, OB → Projections of $\vec{r}$ on incident & scattered waves directions

(3) $\vec{r}$ = Distance b/w two identical scattering centres.

$PA - OB = \vec{r}\cdot\vec{S_0} - \vec{r}\cdot\vec{S} = \vec{r}\cdot(\vec{S_0} - \vec{S}) = \vec{r}\cdot\vec{\mathcal{S}}$

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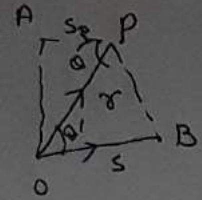
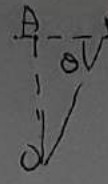
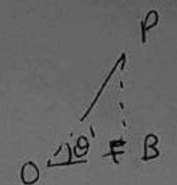



$\cos\theta = \frac{PA}{OP} = \frac{PA}{r} \Rightarrow PA = r\cos\theta$

$\vec{r}\cdot\vec{S_0} = |\vec{r}|\,|\vec{S_0}|\cos\theta = r\cos\theta = PA$

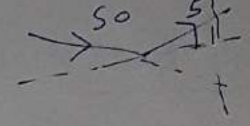
$\vec{r}\cdot\vec{S} = |\vec{r}|\,|\vec{S}|\cos\theta' = r\cos\theta' = OB$




$\cos\theta' = \frac{OB}{OP} = \frac{OB}{r}$

$r\cos\theta' = OB$

$\vec{S} \Rightarrow$ Represent direction of $\perp$ to a plane which reflects incident direction into scattering (Reflection plane)




$2\theta$ = Angle b/w $\vec{S_0}$ and $\vec{S}$

$|\vec{S}| = 2\sin\theta$

$\phi_r$ = Phase diff b/w radiation scattered at two points

$= \frac{2\pi}{\lambda} \times$ path diff $= \frac{2\pi}{\lambda}(PA - OB) = \frac{2\pi}{\lambda}(\vec{r}\cdot\vec{S})$

for $\vec{S}$ to be direction of diffraction maxima $\Rightarrow$ $\phi_r$ should be integral multiple of $2\pi \times$ An integer

$\Downarrow$

$$\boxed{\phi_r = \frac{2\pi}{\lambda}(\vec{r}\cdot\vec{S}) = 2\pi \times \text{Integer.}}$$

Above is true when, radiation scatt. from nearest-neighbor atoms add up in phase.

Nearest neighbors are separated by primitive translation distances $\vec{a}, \vec{b}, \vec{c}$ $\Rightarrow$

$$\frac{2\pi}{\lambda}(\vec{a}\cdot\vec{S}) = 2\pi h' = 2\pi nh$$

$$\frac{2\pi}{\lambda}(\vec{b}\cdot\vec{S}) = 2\pi k' = 2\pi nk$$

$$\frac{2\pi}{\lambda}(\vec{c}\cdot\vec{S}) = 2\pi l' = 2\pi nl$$

r can be equal to a, b, c) simultaneously conditions

$\alpha, \beta, \gamma \rightarrow$ Angles b/w $\vec{S}$ and $\vec{a}, \vec{b}, \vec{c}$ axes

$\vec{a}\cdot\vec{S} = aS\cos\alpha = a(2\sin\theta)\cos\alpha = 2a\sin\theta\cos\alpha$

$$\Rightarrow \left.\begin{aligned} 2a\sin\theta\cos\alpha &= h'\lambda = n h\lambda \\ 2b\sin\theta\cos\beta &= k'\lambda = n k\lambda \\ 2c\sin\theta\cos\gamma &= l'\lambda = n l\lambda \end{aligned}\right\} \rightarrow \text{Laue's Conditions}$$

(41)

**Note** ⇒ (1) $\vec{S}$ is identical to normal to (hkl) plane. Hence (hkl) plane may be regarded as reflecting planes in the sense of Bragg treatment.

(2) we can get diffraction maxima by reflecting in a lattice plane

**Using laue's eqn**

$$d = \frac{a}{h}\cos\alpha = \frac{b}{k}\cos\beta = \frac{c}{l}\cos\gamma$$

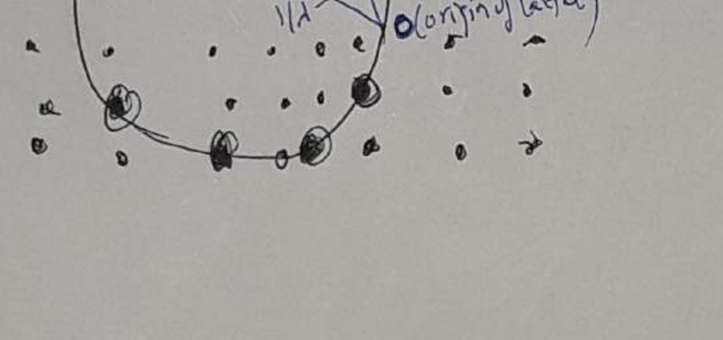
$$2a\sin\theta\cos\alpha = n h\lambda$$

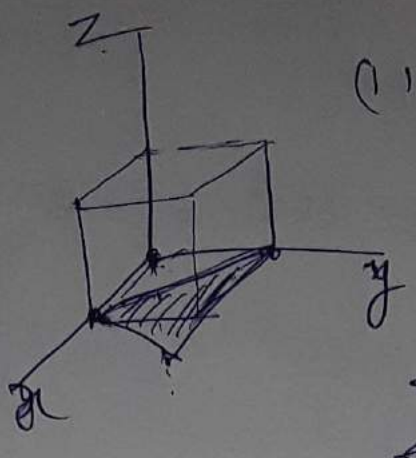
$$2\times\left(\frac{dh}{\cos\alpha}\right)\sin\theta\cos\alpha = nh\lambda$$

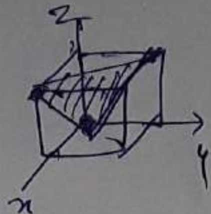
$$2d\sin\theta\,(\cancel{h}) = n\cancel{h}\lambda$$

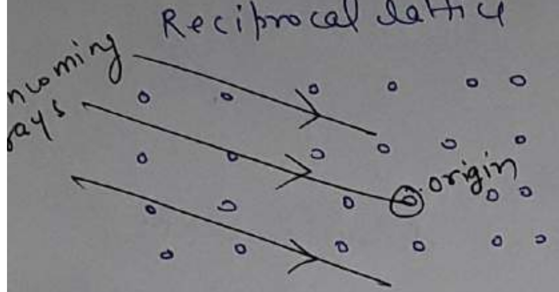
$$2d\sin\theta = n\lambda \rightarrow \text{Bragg from vonlaue}$$

## Geometrical Interpretation of Bragg Condition






Choose any X-ray beam (incident) terminating at origin of reciprocal lattice.

Then Mark its length as $1/\lambda$ from origin

& $|\vec{AO}| = 1/\lambda$

Then construct a sphere of radius $1/\lambda$ about 'A'

& suppose sphere cuts at 'B' (which is some point of reciprocal lattice) 2|3

B point $\longrightarrow$ $(h', k', l')$

A point $\longrightarrow$ Need not to be lattice point

Vector $\vec{OB}$ $\Rightarrow$ A vector containing origin & B at $(h'k'l')$

$\Rightarrow$ It must be $\perp$ to $(h'k'l')$ plane of direct lattice

$\Rightarrow$ AE is this $\perp$ plane

$\angle EAO = \angle EAB = \theta$ (Bragg Angle)

Also $|\vec{OB}| = n/d$ (n being largest integral factor common to $(h'k'l')$

In $\Delta$ AEO $\quad \sin\theta = \frac{EO}{AO} = \frac{EO}{1/\lambda}$

(43)

$$\frac{\sin\theta}{\lambda} = EO$$

$$2\frac{\sin\theta}{\lambda} = 2(EO) = |\overrightarrow{OB}|$$

$$\Rightarrow (\overrightarrow{OB}) = \frac{n}{d} = 2\frac{\sin\theta}{\lambda} \longrightarrow \boxed{n\lambda = 2d\sin\theta}$$

Bragg's law

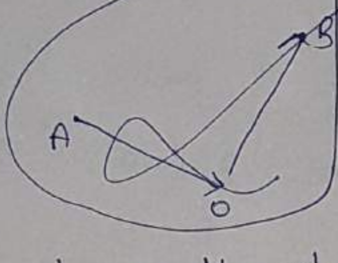
<u>Again</u>, $\overrightarrow{AO}$ = Incident beam

$\overrightarrow{OB}$ = $\perp$ to reflecting plane

$\overrightarrow{AB}$ = vector in direction of diffracted beam

Angle b/w $\overrightarrow{AO}$ & plane $\perp$ to $\overrightarrow{OB}$ (i.e. AE) = Appropriate Bragg Angle

Same figure can be redrawn

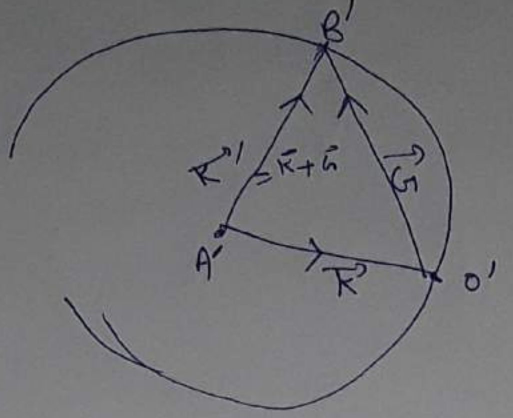



* If the sphere passes through no lattice point $\Rightarrow$ That particular wavelength would not be diffracted by that crystal in that orientation.
* X-ray diffraction can't occur if $\lambda > 2a$, bcoz a sphere of radius $\overrightarrow{AO} < \frac{1}{2a}$ can't pass through any point of lattice & above construction is not possible. We also note that as $\overrightarrow{AO}$ increases (length), greater is likelihood of sphere's intersecting a point, & hence of diffraction. This is known as Ewald Construction.

Again

Magnify all the vectors in last figure by a constant scale factor of $2\pi$

44




$\vec{G} = 2\pi \times \vec{OB}$

$\vec{K} = 2\pi \times \vec{AO}$

$\Rightarrow$ A'B' must be equal to A'O' (Both radius)

$\Rightarrow (\vec{K}+\vec{G})^2 = \vec{K}^2$

$(\vec{K}+\vec{G})\cdot(\vec{K}+\vec{G}) = K^2$

$K^2 + G^2 + 2\vec{K}\cdot\vec{G} = K^2$

$\boxed{2\vec{K}\cdot\vec{G} + G^2 = 0} \rightarrow$ vector form of Bragg equation.

Also $\vec{K}' = \vec{K} + \vec{G}$ (vector sum)

$\boxed{\vec{K}' - \vec{K} = \vec{G}}$

Scattering changes only direction of $\vec{K}$ & scattered wave differs from incident wave by a reciprocal lattice vector $\vec{G}$.

$\vec{k}' \rightarrow$ Scattered wave vector

$\vec{k} \rightarrow$ Incident " "

## BRILLOUIN ZONE

(MS)

Whether or not a K-value is reflected depends upon Ewald sphere's intersecting a point of the reciprocal lattice of the crystal. Under construction:

① Construct locus of all those points (k-values) which are Bragg reflected,

Ex → simple square lattice.

$$\vec{a} = a\hat{i} \; , \; \vec{b} = a\hat{j}$$

$$\vec{a}^{*} = \frac{1}{a}\hat{i} \; , \; \vec{b}^{*} = \cancel{\frac{b}{b}}\frac{1}{a}\hat{j}$$

Reciprocal lattice Vector $= \vec{G} = 2\pi\left(h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}\right)$

$$\vec{G} = 2\pi\left(h\frac{1}{a}\hat{i} + K\frac{1}{a}\hat{j}\right)$$

$$= \frac{2\pi}{a}\left(h\hat{i} + K\hat{j}\right)$$

(h, K are integers
i, j are unit vectors

② wave vector $\vec{K} = K_x\hat{i} + K_y\hat{j}$. (from origin of reciprocal lattice)

Bragg's condition ⇒ $2\vec{K}\cdot\vec{G} + \vec{G}^2 = 0$

$$2\left(K_x\hat{i} + K_y\hat{j}\right)\cdot\frac{2\pi}{a}\left(h\hat{i} + K\hat{j}\right) + \left(G_x^2 + G_y^2\right) = 0$$

$$\frac{4\pi}{a}\left(hK_x + KK_y\right) + \left(\frac{2\pi}{a}\right)^2\left(h^2 + K^2\right) = 0$$

$$\boxed{\left(hK_x + KK_y\right) + \frac{\pi}{a}\left(h^2 + K^2\right) = 0}$$

③ Take all possible combinations of h and K, by which we can get all values of K which will be Bragg reflected.

~~[illegible]~~ $= \pm$

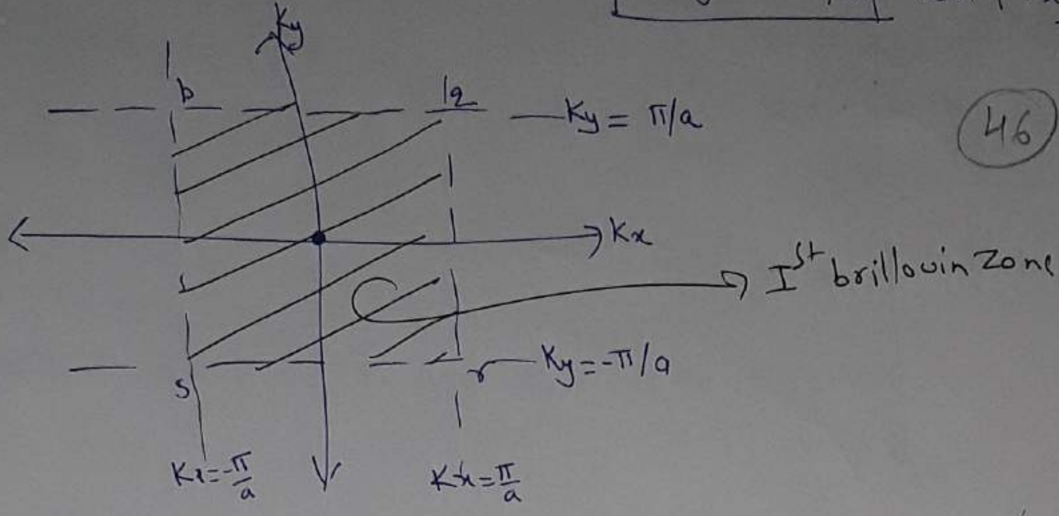
$h = \pm 1 , K = 0 \longrightarrow \quad \pm K_x + 0 = -\frac{\pi}{a}\left((\pm 1)^2 + 0\right)$

$\boxed{\pm K_x = -\pi/a}$ and $\boxed{K_y = \text{Arbitrary}}$

$h=0,\ k=\pm 1 \rightarrow \quad 0 + (\pm 1)K_y = \frac{-\pi}{a}\left(0 + (\pm 1)^2\right)$

$\boxed{\pm K_y = -\pi/a}$ and $\boxed{K_x = \text{Arbitrary}}$






pqrs → Area enclosed in $1^{st}$ B.Z.

→ All vectors originating at origin & terminating on these lines will produce Bragg reflection

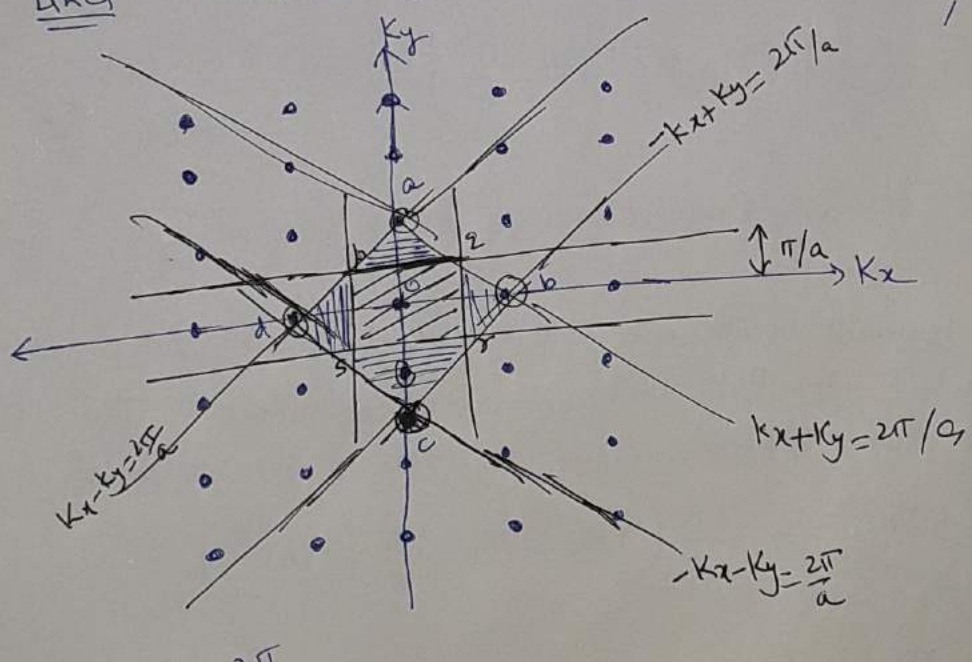
(4) Besides these lines other set of lines

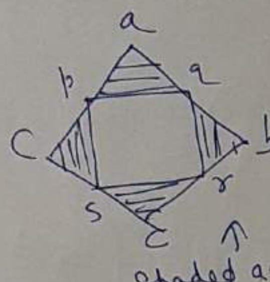
$\pm K_x \pm K_y = \frac{2\pi}{a}$ are also possible

Area enclosed by these lines (after subtracting area of $1^{st}$ B.Z)

is called $2^{nd}$ B.Z.

Lines $\quad -K_x - K_y = 2\pi/a$, $K_x + K_y = 2\pi/a$, $K_x - K_y = 2\pi/a$, $-K_x + K_y = 2\pi/a$




shaded area is $2^{nd}$ BZ.

$\vec{ob} = \vec{G} = \frac{2\pi}{a}\hat{i}$

$\vec{od} = \vec{G} = \frac{-2\pi}{a}\hat{i}$

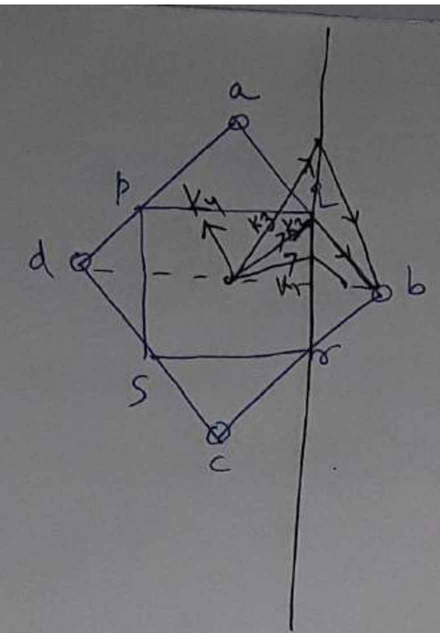
$\vec{oa} = \vec{G} = 2\pi/a\,\hat{j}$

$\vec{oc} = \vec{G} = -2\pi/a\,\hat{j}$

(1) $-K_x - K_y = \frac{2\pi}{a}$

If $K_x = 0 \rightarrow K_y = -2\pi/a$

$K_y = 0 \rightarrow K_x = \frac{-2\pi}{a}$




$\vec{K_1}, \vec{K_2}, \vec{K_3} \rightarrow$ Bragg reflected at zone boundaries

$\vec{K_4} \Rightarrow$ Does not get Bragg reflec.

(5) In 3-D $\Rightarrow$ $hK_x + KK_y + lK_z = -\pi/a\,(h^2+K^2+l^2)$

$1^{st}$ B.Z. $\Rightarrow$ Cube intersecting axes at $\pi/a$ ($K_x\, K_y\, K_z$)

$2^{nd}$ B.Z. $\Rightarrow$ Pyramids added to each face of $1^{st}$ B.Z. cube.

(6) <u>Brillouin Zone of FCC lattice</u>

Primitive Translation vectors of FCC

$$\vec{a} = \frac{a}{2}(\hat{i}+\hat{j})$$
$$\vec{b} = \frac{a}{2}(\hat{j}+\hat{k})$$
$$\vec{c} = a/_2\,(\hat{k}+\hat{i})$$

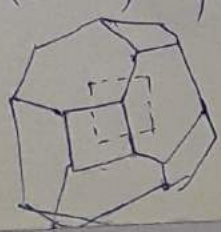
$\vec{a}^* = \frac{1}{a}(\hat{i}+\hat{j}-\hat{k})$, $\vec{b}^* = \frac{1}{a}(-\hat{i}+\hat{j}+\hat{k})$

$\vec{c}^* = \frac{1}{a}(\hat{i}-\hat{j}+\hat{k})$

$$\vec{G} = 2\pi(h\vec{a}^* + K\vec{b}^* + l\vec{c}^*) = \frac{2\pi}{a}\left[(h-K+l)\hat{i} + (h+K-l)\hat{j} + (-h+K+l)\hat{k}\right]$$

Shortest non-zero $\vec{G}$'s are eight vectors $\Rightarrow \frac{2\pi}{a}(\pm\hat{i} \pm\hat{j} \pm\hat{k})$

$\boxed{\text{First B.Z.}}$ $\rightarrow$ Determined by the 8 planes $\perp$ to these vectors at their mid points. But the corners of octahedron thus formed are truncated by planes which are $\perp$ bisectors of six reciprocal lattice vectors $\rightarrow$ $\frac{2\pi}{a}(\pm 2\hat{i})$ ; $\frac{2\pi}{a}(\pm 2\hat{j})$ ; $\frac{2\pi}{a}(\pm 2\hat{k})$



## 7) Brillouin Zone of B.C.C. lattice

48

Primitive Translation vector → Reciprocal lattice vectors

$\vec{a} = a/2\,(\hat{i}+\hat{j}-\hat{k})$ $\qquad \vec{a}^* = \frac{1}{a}(\hat{i}+\hat{j})$

$\vec{b} = a/2\,(-\hat{i}+\hat{j}+\hat{k})$ $\qquad \vec{b}^* = \frac{1}{a}(\hat{j}+\hat{k})$

$\vec{c} = a/2\,(\hat{i}-\hat{j}+\hat{k})$ $\qquad \vec{c}^* = \frac{1}{a}(\hat{k}+\hat{i})$

$$\vec{G} = 2\pi(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) = \frac{2\pi}{a}\left[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}\right]$$

Shortest non-zero $\vec{G}$'s are following 12 vectors →

$$\frac{2\pi}{a}(\pm\hat{i}\pm\hat{j}),\ \frac{2\pi}{a}(\pm\hat{j}\pm\hat{k}),\ \frac{2\pi}{a}(\pm\hat{k}\pm\hat{i})$$

$\boxed{1^{st}\ B.Z.}$ → Determined by 12 planes normal to these vectors at their mid points.

→ $1^{st}$ B.Z. is regular 12-faced solid – Rhombic dodecahedron

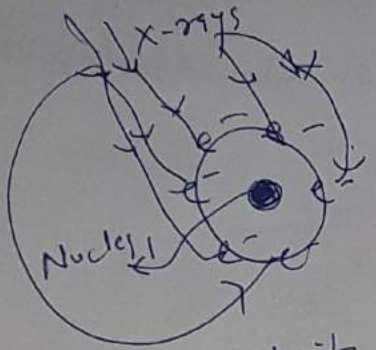
# Atomic Scattering Factor

Bragg's / laue equations → Diffraction from point scattering centres (or point electrons)

Actual Crystals → Scattering is actually done by cloud of e's which sorrounds the nuclei.

Neglecting the effect of atomic nuclei, which interact much less strongly with X-rays, we expect scattering from an atom would simply be scattering ~~with~~ from 1-$e^-$ multiplied by no of e's in atom.

~~But~~,

| Expectation | Reality |
|---|---|
|  Nucleus don't scatter<br><br>Total scatt. = Scatt. from one $e^-$ × No of $e^-$ | Total scatt = Scatt from one $e^-$ × Some no.<br>↓<br>Not equal to total no. of e's |

As size of atom is of the order of X-ray wavelength, hence all parts of atom do not scatter in phase to produce expected scattering.

Infact,,

$$\boxed{f = \frac{\text{Amplitude of radiation scattered from atom}}{\text{Amplitude of radiation scattered from } e^-}}$$

↓

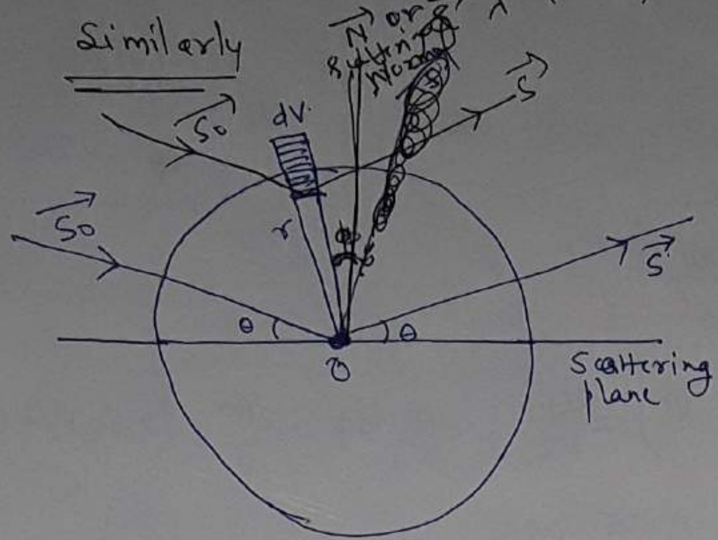
Atomic scattering factor / form factor.

$$\boxed{f < Z} \qquad f = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin \mu r}{\mu r} dr$$

## Derivation

In laue's equation we have two scattering centres separated by $\vec{r}$ distance $d$ $\phi_r = \frac{2\pi}{\lambda}(\vec{r}.\vec{s})$ where $\vec{s}$ is scattered beam.

Similarly




① O is origin at centre of atom.

② let an $e^-$ is located extremely near to centre or we can say $e^-$ lies at ~~centre~~ origin

③ $\rho(r)$ is charge density at a point which is at distance $\vec{r}$ from centre.

④ dv is volume about point $\vec{r}$.

⑤ $\vec{S}$ is direction of scattering.

~~⑥ Volume element dV is chosen to be an annular ring of radius r sin φ width r dφ thickness dr~~

⑥ $\vec{N}$ is scattering normal, or $\vec{s}$ is scattering norm

⑦ $\phi_r = \left(\frac{2\pi}{\lambda}\right)\vec{r}.\vec{N}$ (laue's eqn) $= \frac{2\pi}{\lambda}(\vec{r}.\vec{s})$

↓

Phase diff b/w wave scattered from charge $\rho(r)\,dr$ and scattered from electron.

⑧ Scattering amplitude from point $e^-$ in direction $\vec{S} = A e^{i(kx-\omega t)}$

$x$ = Distance covered along $\vec{S}$

$k$ = Wave no

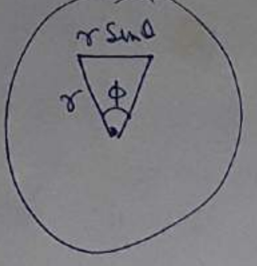
Scattering amplitude from charge $\rho(r)\,dv$ or volume element is proportional to amount of charge in dV & out of phase by $\phi_r$ given by $= A e^{i(kx-\omega t)+i\phi_r}\,\rho(r)\,dV$

⑨ Ratio of Amplitudes $=$ ~~df~~ $= \frac{A e^{i(kx-\omega t)+i\phi_r}\,\rho(r)\,dV}{A e^{i(kx-\omega t)}} = df$

$$f = \int df = \int \rho(r)\, e^{i\phi_r}\, dV$$

(51)

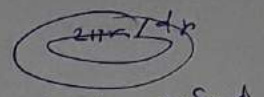
$$|\vec{N}| = |\vec{S}| = 2\sin\theta$$




$\rho(r)$ is function of $\vec{r}$ only

$dV = (2\pi r^2)\sin\phi\, d\phi\, dr$

0 to $2\pi$ gives $2\pi$ factor




height $= r\sin\phi$
$l \times b \times h$

$$\Rightarrow \phi_r = \frac{2\pi}{\lambda}(\vec{r}\cdot\vec{N}) = \frac{2\pi}{\lambda}(\vec{r}\cdot\vec{S}) = \left(\frac{2\pi}{\lambda}\right) rN\cos\phi = \frac{2\pi}{\lambda} r\,(2\sin\theta)\cos\phi$$

$$= \frac{4\pi}{\lambda}\, \underline{r}\sin\theta\cos\phi = \mu\, \cancel{r}\cos\phi$$

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

$$f = \int_{r=0}^{\infty}\int_{\phi=0}^{\pi} \rho(r)\, \underline{e^{i\mu r\cos\phi}}\; 2\pi r^2\, \underline{\sin\phi}\, \underline{d\phi}\, dr$$

$$= \int_0^{\infty} 2\,\frac{\sin\mu r}{\mu r} \times 2\pi r^2\, dr = \int_0^{\infty} 4\pi r^2 \rho(r)\, \frac{\sin\mu r}{\mu r}\, dr$$

Note:

(1) Further evaluation needs information about charge distribution, which may be obtained from Hartree approx. or Thomas Fermi theor.

(2) Values of f by these methods are only for free atoms

(3) These values of f also represent X-ray reflection intensities from crystals.

(4) For Magnesium, $Z=12$

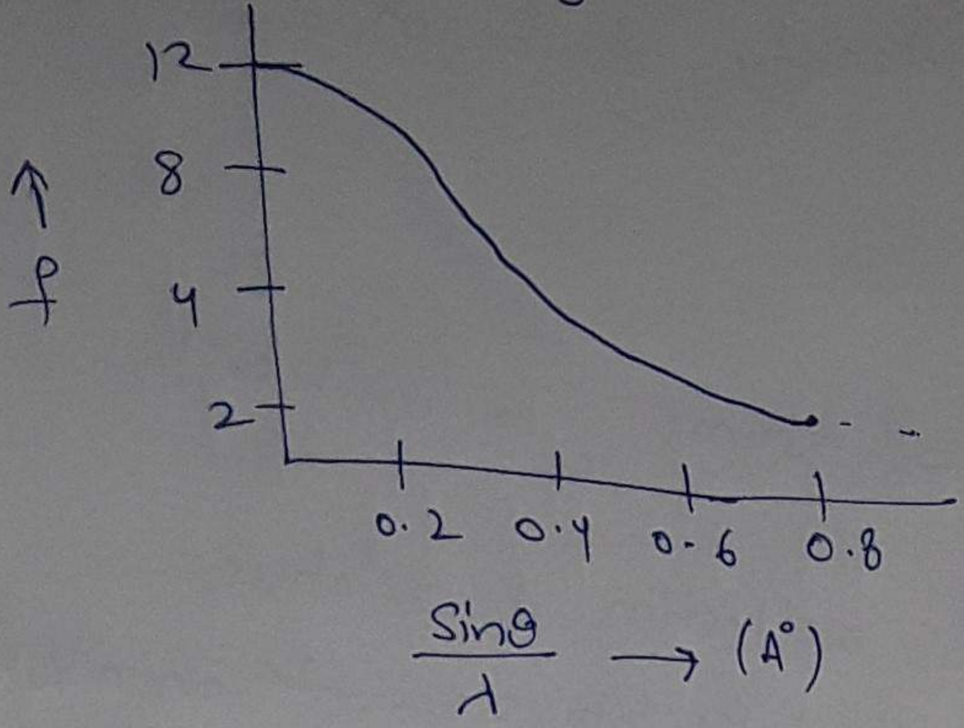
$f \to Z$

$\theta \to 0 \Rightarrow \mu \to 0$

$$\Rightarrow \frac{\sin\mu r}{\mu r} \to 1$$

$$\Rightarrow \quad f = \int_0^\infty 4\pi r^2 \rho(r)\, dr = Z$$

52




$f$ vs $\frac{\sin\theta}{\lambda}$ for Magnesium.