volume of primitive cell $= \vec{a}\cdot\vec{b}\times\vec{c} = a^3/2$

$$\therefore \vec{a}^* = 2\pi \frac{\vec{b}\times\vec{c}}{\vec{a}\cdot\vec{b}\times\vec{c}} = \frac{2\pi}{a}(\hat{i}+\hat{j}),$$

$$\vec{b}^* = 2\pi \frac{\vec{c}\times\vec{a}}{\vec{a}\cdot\vec{b}\times\vec{c}} = \frac{2\pi}{a}(\hat{j}+\hat{k}).$$

$$\vec{c}^* = 2\pi \frac{\vec{a}\times\vec{b}}{\vec{a}\cdot\vec{b}\times\vec{c}} = \frac{2\pi}{a}(\hat{i}+\hat{k}).$$

Reciprocal of fcc lattice $\quad \vec{a} = \frac{a}{2}(\hat{i}+\hat{j}),\ \vec{b} = \frac{a}{2}(\hat{j}+\hat{k})$

$$\vec{c} = \frac{a}{2}(\hat{i}+\hat{k})$$

volume of primitive cell $= \vec{a}\cdot\vec{b}\times\vec{c} = a^3/4$.

and $a^* = \frac{2\pi}{a}(\hat{i}+\hat{j}-\hat{k}),\quad b^* = \frac{2\pi}{a}(-\hat{i}+\hat{j}+\hat{k}),\quad c^* = \frac{2\pi}{a}(\hat{i}-\hat{j}+\hat{k})$

∴ Reciprocal bcc lattice vectors = primitive fcc lattice vectors
Reciprocal fcc lattice vectors = primitive bcc lattice vectors

Crystal diffraction

Why use X-ray for crystollagraphy?

Atomic spacing (say for NaCl) is 2.8 Å. When X-ray is produced by accelarating electrons through a potential difference V,

$$eV = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{eV} = \frac{6.62\times10^{-34}\times3\times10^{8}}{1.6\times10^{-19}\times10^{4}} \quad (\text{say } V = 10\,kV)$$

$$= 1.24\ \text{Å}.$$

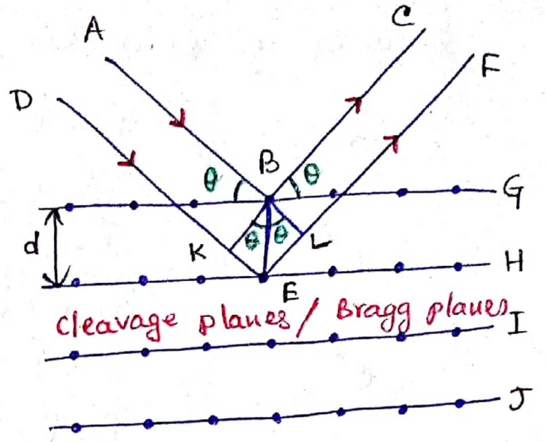
$\lambda_{x\text{-ray}} \approx a$ (elastic scattering without change in λ)

$\lambda_{visible/UV} \gg a$ (reflection or refraction)

$\lambda_{\gamma\text{-ray}} \ll a$ (small angle diffraction)

Bragg's law for crystal diffraction

Maximum intensity from reflected beam (waves) from two different atomic planes (cleavage planes) with path difference equal to integral multiple of $\lambda_{x\text{-}ray}$.



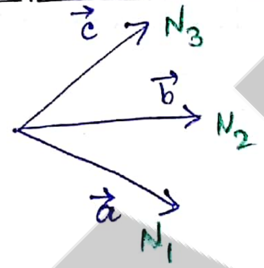
Path difference between ray [AB, BC] & [DE, EF] is KE + EL

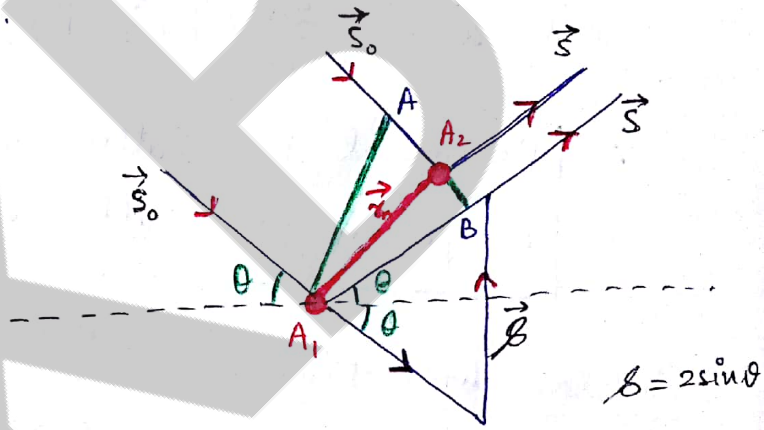
$= d\sin\theta + d\sin\theta = 2d\sin\theta$. So for constructive interference,

$\boxed{2d\sin\theta = n\lambda}$, $n = 1, 2, 3 \dots \Rightarrow$ "Bragg's law."

λ, θ = known, d = unknown.

Laue's equation of XRD





Assumptions : (a) The primary X-ray beam travels within the crystal at the speed of light. (b) Each scattered wavelet travels through the crystal without getting rescattered.

Say N_1 number of points along direction $\vec{a}$

N_2 number of points along direction $\vec{b}$

N_3 number of points along direction $\vec{c}$

Total $N = N_1 N_2 N_3$ points in the crystal lattice.

Path difference between two x-rays is $d = \vec{r}_n \cdot \vec{s} - \vec{r}_n \cdot \vec{s}_0 = \vec{r}_n \cdot \vec{\delta}$

$\therefore$ Phase difference is $\frac{2\pi}{\lambda} d = \frac{2\pi}{\lambda} \vec{r}_n \cdot \vec{\delta} = K \vec{r}_n \cdot \vec{\delta}$

remember: $\vec{s}, \vec{s}_0$ unit vector, $|\vec{\delta}| = \delta = 2\sin\theta$, $\vec{r}_n = n^{th}$ lattice point from origin $= \vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$.

If y is the displacement of the scattered wave from origin at a distance R at time t with amplitude A_0, then

$$y_0 = \frac{A_0}{R} e^{i\omega t}. \quad \therefore \text{ displacement from } \vec{r}_n \text{ is}$$

$$y = \frac{A_0}{R} e^{i\omega t} e^{iK\vec{r}_n \cdot \vec{s}}$$

$\therefore$ Total displacement due to the whole Bravais lattice is

$$Y = \sum_{\text{all points}} \frac{A_0}{R} e^{i\omega t} e^{iK\vec{r}_n \cdot \vec{s}}$$

$$= \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} e^{iK[(n_1\vec{a} + n_2\vec{b} + n_3\vec{c})\cdot\vec{s}]} \frac{A_0}{R} e^{i\omega t}$$

$$= \frac{A_0}{R} e^{i\omega t} \sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}} \sum_{n_2=0}^{N_2-1} e^{iKn_2\vec{b}\cdot\vec{s}} \sum_{n_3=0}^{N_3-1} e^{iKn_3\vec{c}\cdot\vec{s}}$$

Now $$\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}} = 1 + e^{iK\vec{a}\cdot\vec{s}} + e^{i2K\vec{a}\cdot\vec{s}} + \cdots + e^{i(N_1-1)K\vec{a}\cdot\vec{s}}$$

$$= \frac{1 - e^{iN_1(\vec{a}\cdot\vec{s})K}}{1 - e^{i(\vec{a}\cdot\vec{s})K}}$$

$$\therefore \left(\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}}\right)\left(\sum_{n_1=0}^{N_1-1} e^{iKn_1\vec{a}\cdot\vec{s}}\right)^*$$

$$= \frac{1 - e^{iN_1(\vec{a}\cdot\vec{s})K}}{1 - e^{i(\vec{a}\cdot\vec{s})K}} \times \frac{1 - e^{-iN_1(\vec{a}\cdot\vec{s})K}}{1 - e^{-i(\vec{a}\cdot\vec{s})K}}.$$

$$= \frac{1 - \cos\{N_1(\vec{a}\cdot\vec{s})K\} + i\sin\{N_1(\vec{a}\cdot\vec{s})K\}}{1 - \cos\{(a\cdot\vec{s})K\} - i\sin\{(a\cdot\vec{s})K\}.} \times \frac{1 - \cos\{N_1(\vec{a}\cdot\vec{s})K\} + i\sin\{N_1(\vec{a}\cdot\vec{s})K\}}{1 - \cos\{(\vec{a}\cdot\vec{s})K\} + i\sin\{(\vec{a}\cdot\vec{s})K\}}$$

$$= \frac{\left(1 - \cos\{N_1(\vec{a}\cdot\vec{s})K\}\right)^2 + \left(\sin\{N_1(\vec{a}\cdot\vec{s})K\}\right)^2}{\left(1 - \cos\{(\vec{a}\cdot\vec{s})K\}\right)^2 + \left(\sin\{(\vec{a}\cdot\vec{s})K\}\right)^2}$$

$$= \frac{1 - \cos\{N_1(\vec{a}\cdot\vec{s})K\}}{1 - \cos\{(\vec{a}\cdot\vec{s})K\}} = \frac{\sin^2\{\frac{N_1(\vec{a}\cdot\vec{s})K}{2}\}}{\sin^2\{\frac{(\vec{a}\cdot\vec{s})K}{2}\}} = \frac{\sin^2(N_1\psi_1)}{\sin^2(\psi_1)}$$

where $\psi_1 = \frac{1}{2} K \vec{a}\cdot\vec{s}$.

$\therefore$ Total intensity $I = YY^* = \left(\frac{|A_0|}{R}\right)^2 \frac{\sin^2(N_1\psi_1)}{\sin^2\psi_1} \frac{\sin^2(N_2\psi_2)}{\sin^2\psi_2} \frac{\sin^2(N_3\psi_3)}{\sin^2\psi_3}$

$$\psi_1 = \frac{1}{2}K\vec{a}\cdot\vec{s} = \frac{1}{2}K|\vec{a}||\vec{s}|\cos\alpha = \frac{1}{2}\frac{2\pi}{\lambda}a\, 2\sin\theta\cos\alpha = \frac{2\pi a\sin\theta\cos\alpha}{\lambda}$$

Similarly $\psi_2 = \frac{1}{2}K\vec{b}\cdot\vec{s} = \frac{2\pi b\sin\theta\cos\beta}{\lambda}$,

$\psi_3 = \frac{1}{2}K\vec{c}\cdot\vec{s} = \frac{2\pi c\sin\theta\cos\gamma}{\lambda}$

[Notice the analogy of $\vec{s}$ with $[h,k,l]$ plane with angles α, γ, β]

In $\lim_{\psi_1\to h\pi}$, $\frac{\sin^2(N_1\psi_1)}{\sin^2\psi_1}$ is maximum $= N_1^2$

Similarly $\lim_{\psi_2\to k\pi} \frac{\sin^2(N_2\psi_2)}{\sin^2\psi_1} = N_2^2$, $\lim_{\psi_3\to l\pi} \frac{\sin^2(N_3\psi_3)}{\sin^2\psi_3} = N_3^2$

Then $I_{max} = \left(\frac{|A_0|}{R}\right)^2 N_1^2 N_2^2 N_3^2 = \frac{|A_0|^2}{R^2} N^2$

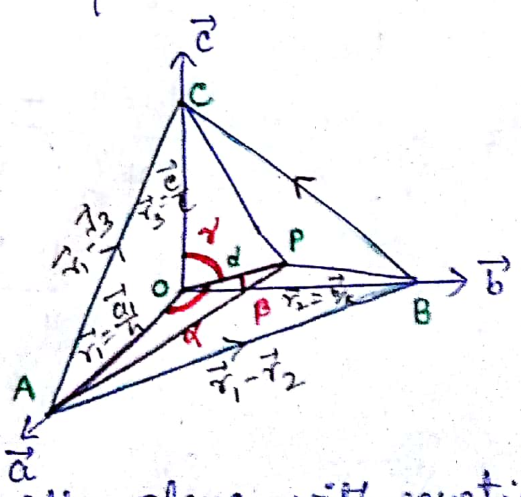
$\therefore$ $\frac{2\pi a\sin\theta\cos\alpha}{\lambda} = h\pi$, $\quad \boxed{2a\sin\theta\cos\alpha = h\lambda}$

$\frac{2\pi b\sin\theta\cos\beta}{\lambda} = k\pi$, $\quad \boxed{2b\sin\theta\cos\beta = k\lambda}$

$\frac{2\pi c\sin\theta\cos\gamma}{\lambda} = l\pi$, $\quad \boxed{2c\sin\theta\cos\gamma = l\lambda}$

"Laue equations".

<u>Bragg's law from Laue equations</u>



From Laue equation, direction cosines of $\vec{s}$ are

$\cos\alpha = \frac{h\lambda}{2a\sin\theta}$, $\cos\beta = \frac{k\lambda}{2b\sin\theta}$,

$\cos\gamma = \frac{l\lambda}{2c\sin\theta}$.

But also see that if (h,k,l) is a miller plane with equation

$\frac{x}{a/h} + \frac{y}{b/k} + \frac{z}{c/l} = 1$ then $\frac{a}{h}\cos\alpha = \frac{b}{k}\cos\beta = \frac{c}{l}\cos\gamma = d$.

∴ The direction cosines of $\vec{r}$ are also proportional to $h/a, k/b, l/c$, so the X-ray is diffracted from $\vec{r}_0$ to $\vec{r}$ by the miller plane (h,k,l).

$$\therefore\ d = \frac{a}{h}\cos\alpha = \frac{a}{h}\,\frac{h\lambda}{2a\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$= \frac{b}{k}\cos\beta = \frac{b}{k}\,\frac{k\lambda}{2b\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$= \frac{c}{l}\cos\gamma = \frac{c}{l}\,\frac{l\lambda}{2c\sin\theta} = \frac{\lambda}{2\sin\theta}$$

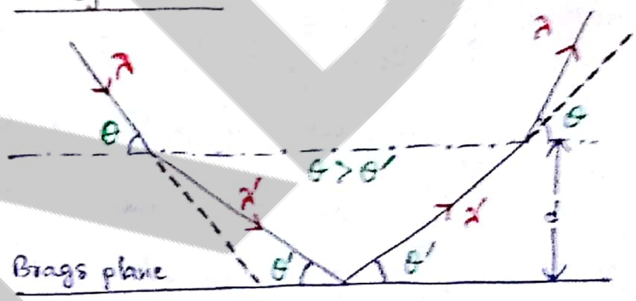
Note that h,k,l of Laue equation aren't necessarily identical with Miller indices but may contain a common factor n.

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

with d = adjacent interplanar spacing with Miller indices $\frac{h}{n}, \frac{k}{n}$ & $\frac{l}{n}$.

Modification of Bragg's law due to refraction

Refraction of X-rays due to change in wavelength & angle of incidence because of the refractive index of the crystal.



Bragg's equation $n\lambda' = 2d\sin\theta'$

Using Snell's law, the refractive index is $\mu = \frac{\lambda}{\lambda'} = \frac{\cos\theta}{\cos\theta'}$

$$\therefore\ n\frac{\lambda}{\mu} = 2d\sqrt{1-\frac{\cos^2\theta}{\mu^2}}$$

$$\text{or } n\lambda = 2d\sqrt{\mu^2-\cos^2\theta} = 2d\sqrt{\sin^2\theta-(1-\mu^2)} = 2d\sin\theta\sqrt{1-\frac{1-\mu^2}{\sin^2\theta}}$$

$$\simeq 2d\sin\theta\left(1-\frac{1-\mu^2}{2\sin^2\theta}\right)$$

$$\simeq 2d\sin\theta\left(1-\frac{2(1-\mu)}{2\sin^2\theta}\right)$$

$$\simeq 2d\sin\theta\left(1-(1-\mu)\frac{4d^2}{n^2\lambda^2}\right)$$

$[1-\mu^2 = (1+\mu)(1-\mu) \simeq 2(1-\mu)$ as $\mu \simeq 1]$

$[2d\sin\theta = n\lambda$ or $\frac{1}{\sin^2\theta} = \frac{4d^2}{n^2\lambda^2}]$

$$\boxed{n\lambda = 2d\sin\theta\left[1-\frac{4d^2(1-\mu)}{n^2\lambda^2}\right]}$$

[illegible] The correction term $\frac{4d^2(1-\mu)}{n^2\lambda^2}$ is small & becomes more small as "n" increases.