Diffraction

(The crystal as a diffraction lattice)

1. Requirements: $\lambda \sim a^0$

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

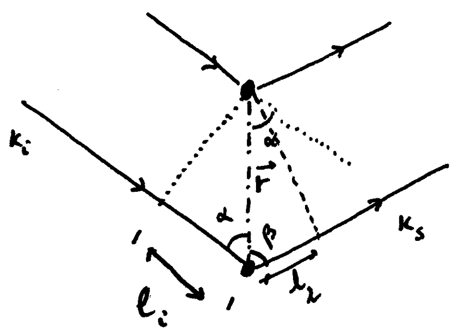
(Elastic, inelastic, and coherent scattering)

2. Basics:

$$\Psi = A\, e^{i\vec{k}\cdot\vec{r}}$$

(Detects the intensity of the beam for a given solid angle)

2.1 - Scattering from two particles:



$$l_i = r\cos\alpha$$

$$\vec{k}_i\cdot\vec{r} = |\vec{k}_i|\, r\cos\alpha$$

$$l_i = \frac{\lambda}{2\pi}\cdot\vec{k}_i\cdot\vec{r}$$

$$\frac{2\pi l_i}{\lambda} = \vec{k}\cdot\vec{r}$$

Similarly, $l_2 = r\cos\beta$; $\vec{k}_s\cdot\vec{r} = |\vec{k}_s|\, r\cos(180^\circ - \beta) =$

$$= -\frac{2\pi}{\lambda}\, r\cos\beta$$

$$l_2 = -\frac{\lambda}{2\pi}\,\vec{k}_s\cdot\vec{r}$$

The total phase difference will then be:

$$\frac{2\pi}{\lambda}(l_1 + l_2) = \vec{k}_i \cdot \vec{r} - \vec{k}_s \cdot \vec{r} = \underbrace{(\vec{k}_i - \vec{k}_s)}_{\vec{Q}\ =\ \text{scattering vector.}} \cdot \vec{r}$$

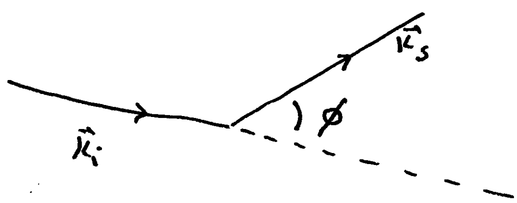
Therefore, the wave scattered by atom-1 $\left(\psi_1(\vec{r}) = e^{i\vec{k}_s \cdot \vec{r}}\right)$ will be out of phase with respect to the wave scattered by atom-2.

$\left(\psi_2(\vec{r}) = e^{i\vec{k}_s \cdot \vec{r}} \cdot e^{i\vec{Q}\cdot\vec{r}}\right)$

The total scattered wave, seen by the detector, will be:

$$\psi_1(\vec{r}) + \psi_2(\vec{r}) = e^{i\vec{k}_s \cdot \vec{r}}\left[1 + e^{i\vec{Q}\cdot\vec{r}}\right]$$

The amplitude of the scattered beam is affected by the phase factor $\left[1 + e^{i\vec{Q}\cdot\vec{r}}\right]$



$$\vec{Q}\cdot\vec{Q} = |\vec{k}_i|^2 + |\vec{k}_s|^2 - 2\,\vec{k}_i \cdot \vec{k}_s$$

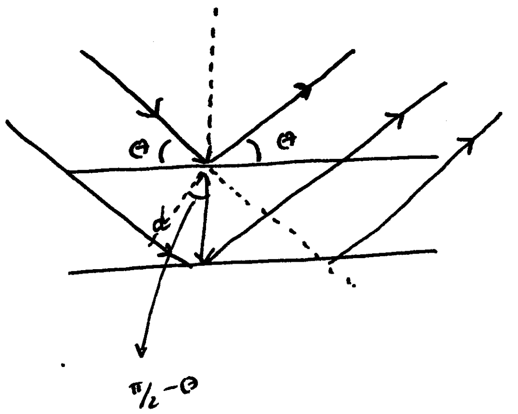
$$Q^2 = 2\left(\frac{2\pi}{\lambda}\right)^2 - 2\left(\frac{2\pi}{\lambda}\right)^2 \cos\phi$$

$$= \frac{8\pi^2}{\lambda^2}(1 - \cos\phi) =$$

$$= \frac{16\pi^2}{\lambda^2}\sin^2\left(\frac{\phi}{2}\right)$$

$|\vec{Q}| = \frac{4\pi}{\lambda}\sin\theta$ (with $\theta = \frac{\phi}{2}$)

Remark : consider a reflection of an incident ray on a set of lattice planes: Bragg's law :



The path difference between the radiation scattered by two adjacent planes is :

$$2d \sin\theta$$

Detection will be possible if there is constructive interference : $2d \sin\theta = m\lambda$ (Bragg's law)

If this relation is replaced in the general equation $\left(|\vec{Q}| = \frac{4\pi}{\lambda}\sin\theta\right)$ we obtain :

$$|\vec{Q}_m| = \frac{4\pi}{2d\sin\theta}\sin\theta \cdot m = m\frac{2\pi}{d} ,$$

Suggesting that there is a relationship between diffraction and the reciprocal lattice (more of this later)

2.2 - Scattering from a collection of particles :

One can generalize the above considerations for N particles

Let $\vec{r}_j$ be the position of the j-particle with respect to an origin. Take a given $\vec{k}_i$ and a given $\vec{k}_s$. Add the phase shifts for each particle :

$$F(\vec{Q}) = \sum_j e^{i\vec{Q}\cdot\vec{r}_j}$$

The intensity of the scattering beam is

$$|F(\vec{Q})|^2 = \left|\sum_j e^{i\vec{Q}\cdot\vec{r}_j}\right|^2 = \sum_i\sum_j e^{i\vec{Q}(\vec{r}_i-\vec{r}_j)}$$

<u>Remark</u>: $F(\vec{Q}) = \sum_j e^{i\vec{Q}\cdot\vec{r}_j}$ (structural factor) is a complex number. Since only $|F(Q)|^2$ is detected, we loose information about the phase of this structural factor. [$\cdot$ $F(\vec{Q})' = A\,e^{i\Phi}$]

<u>Remark</u>: Imagine that we have a collection of particles of a different nature. Then, each particle will scatter the radiation by a different amount. To take this into account we must include a weighting factor for each type of particles (f_j):

$$\vec{F}(\vec{Q}) = \sum_j f_j\, e^{i\vec{Q}\cdot\vec{r}_j}$$

f_j is the scattering factor (factor de forma)

<u>Remark</u>: The continuous distribution of particles

$$dF(\vec{Q}) = \rho(\vec{r})\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}$$

$$F(\vec{Q}) = \int \rho(\vec{r})\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}$$

(particle density matters ....)

If X-rays are used, then electrons are important: (X-rays are scattered by electrons). Hence $\rho_{el}(\vec{r}) \rightarrow$

$$\rightarrow \quad f(\vec{Q}) = \int \rho_{el}(\vec{r})\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}$$

3. Scattering processes as Fourier transforms:

All the above equations look like Fourier transforms (and they are).

Consider the structural factor $F(\vec{Q})$ defined above. Start from a set of point-like particles. The density distribution is then:

$$\frac{1}{V}\sum_j \delta(\vec{r}-\vec{r}_j)$$

Hence

$$F(\vec{Q}) = \frac{1}{V}\sum_j \int \delta(\vec{r}-\vec{r}_j)\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}$$

$$= \sum_j e^{i\vec{Q}\cdot\vec{r}_j}$$

3.1- The idea of a convolution as a "decoration process" is very useful, along with the convolution theorem

One can think of a crystal structure of convolutions:

lattice $\otimes$ base $\otimes$ electrons in atoms $\otimes$ thermal motion

~~Because~~ Hence, the FT of a ~~cry~~ crystal structure is simply the product of the FT of these elements. We can consider each of them separately:

3.1.1- The FT of the lattice is the reciprocal lattice:

$$R(\vec{Q}) = \sum_{h,k,l} \delta\left[\vec{Q} - (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)\right]$$

(as seen)

This means that $\vec{k}_i - \vec{k}_s = \vec{G}$ is a necessary condition for a "Bragg peak". This condition corresponds to the von Laue requirement expressed in his PhD-thesis in 1903. It can be shown that this condition is equivalent to the Bragg's law. (see TP).

3.1.2. The basis: (the structural factor)

$$\sum_{i=1}^{N'} \delta(\vec{r}-\vec{r}_i) \xrightarrow{\text{F.T.}} e^{i\vec{Q}\cdot\vec{r}_i}$$

$\vec{r}_i$ = location of the i^{th} atom in the unit cell.

3.1.3: the atomic form factor. f_j

$$f_j \smile \rho_{el}(\vec{r})$$

Hence:

$$F(Q_{hkl}) = \sum_j f_j \, e^{2\pi i [h\vec{a}^* + k\vec{b}^* + l\vec{c}^*]\cdot(x_j\cdot\vec{a} + y_j\cdot\vec{b} + z_j\cdot\vec{c})}$$

$$= \sum_j f_j(Q_{hkl}) \, e^{2\pi i (hx_j + ky_j + lz_j)}$$

3.1.4 - Thermal motion:

Thermal motion (the Debye-Waller factor):

Assume that the thermal motion is isotropic and harmonic then the spread of the positions about the equilibrium will be a Gaussian, whose width is given by the mean-squared atomic displacement $\langle u_j^2 \rangle$. Let us see this

$$\vec{r}_j = \vec{r}_j + \vec{u}$$

↳ thermal motion ; $|\vec{u}| \ll 1$

The structural factor will be:

$$\sum_j f_j \, e^{-i\vec{G}(\vec{r}_j + \vec{u}_j)} = \sum_j f_j \, e^{i\vec{G}\cdot\vec{r}_j} \cdot e^{-i\vec{G}\cdot\vec{u}_j}$$

$$e^{-i\vec{G}\cdot\vec{u}_j} \simeq 1 - i\,\vec{G}\cdot\vec{u}_j - \frac{1}{2} G^2 u^2 + \cdots$$

on overall

$$\langle e^{-i\vec{G}\cdot\vec{u}_j} \rangle = 1 - i\langle \vec{G}\cdot\vec{u}_j \rangle - \frac{1}{2} \langle \vec{u}\cdot\vec{G} \rangle^2 + \cdots$$

$$\downarrow$$

$$0$$

$$\langle(\vec{G}\cdot\vec{u})^2\rangle = G^2 \langle u^2 \rangle \underbrace{\langle \cos^2\theta \rangle}_{\text{average over a sphere}} = G^2 \langle u^2 \rangle \frac{1}{3}$$

↓ 1/3

$$\langle e^{-i\vec{G}\vec{u}_j} \rangle = 1 - \frac{1}{6} \langle u^2 \rangle G^2 + \cdots = e^{-\frac{1}{6}\langle u^2 \rangle G^2}$$

For harmonic motion $\frac{3}{2} kT \simeq \frac{1}{2} M \omega^2 \langle u^2 \rangle$

So $\langle e^{-i\vec{G}\cdot\vec{u}_j}\rangle = e^{-\frac{1}{6}G^2\frac{3KT}{M\omega^2}}$ — The Debye-Waller factor.

Hence, the structural factor becomes:

$$F(Q_{hkl}) = \sum_j f_j(Q_{hkl})\, e^{i\vec{G}\cdot\vec{r}_j} \cdot e^{-\frac{1}{6}G^2\frac{3KT}{M\omega^2}}$$

□

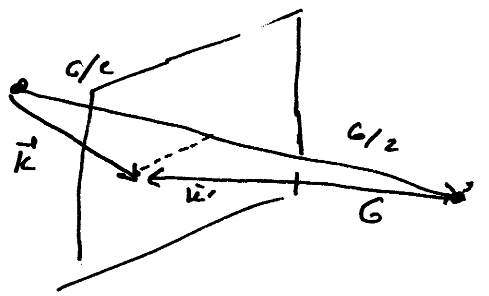
4. Von Laue and Bragg conditions and their equivalence.

Von Laue: $\vec{K}_i - \vec{K}_s = \vec{G}$ ~~In other words for exp~~

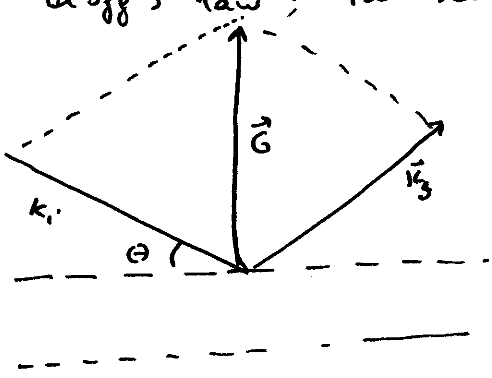
$\vec{K}_i - \vec{G} = \vec{K}_s$

$K_i^2 + G^2 - 2\vec{K}_i\cdot\vec{G} = K_s^2 \Rightarrow \boxed{\vec{K}_i\cdot\vec{G} = \frac{G}{2}}$ Von Laue.

An incident wave vector satisfies the von Laue condition if the tip of the ~~wave~~ vector lies in a plane $\perp$ $\vec{G}$, that is the bisector of a line joining O & $\vec{G}$.



Let us now see that this condition is equivalent to the Bragg's law: The scattering can be viewed as a Bragg reflection



$\vec{G} = \vec{k}_s - \vec{k}_i$

But, as we have seen

$|\vec{G}| = \frac{2\pi}{d}$, where d is the distance between adjacent planes.

Also (from the figure above), $k_i \sin\theta = \frac{|G|}{2} = \frac{\pi}{d}$ $\Rightarrow$

$\Rightarrow$ $\frac{2\pi}{\lambda} \sin\theta = \frac{\pi}{d}$ or $2d \sin\theta = \lambda$ (Bragg's law).

□

5. Ewald construction

6. Experimental methods

} See slides