Crystal structures from X-Ray diffraction

for $a \sim \text{Å}$ necessary wavelength $\lambda \sim \text{Å} = 10^{-8}\,\text{cm}$

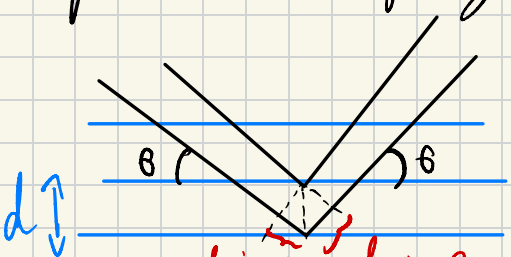
$$E = \hbar\omega = h\frac{c}{\lambda} \sim 10^3\,\text{eV} \rightarrow \text{keV}$$, x-Ray energies

→ Atomic vibrations are not considered, They will affect intensity & noise but do not change the general formulation.

Bragg Formulation

→ real space approach (crystallographers).

→ elastic scattering, specular reflection from parallel planes, with spacing d



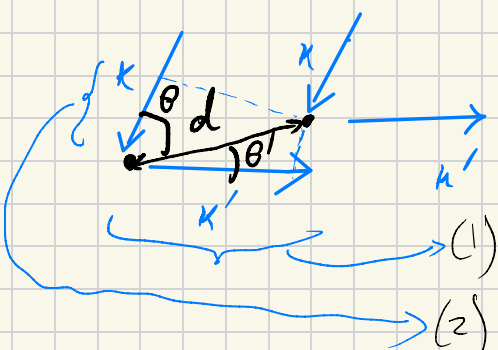
Constructive interference

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

→ path difference

Von Laue Formulation

- much more powerful, physicists approach
- No specular reflection assumed
  - Crystall: infinite repetition of atoms (lattice points, scatterers). Signal strong when scattered x-rays interfere constructively. X-ray scattered from all lattice points



$$\vec{K} = K\hat{n} = \frac{2\pi}{\lambda}\hat{n}$$

$$K' = K\hat{n}' = \frac{2\pi}{\lambda}\hat{n}'$$

(1) $d\cos\theta' = -d\hat{n}'$ — d and $\hat{n}'$ in opposite directions

(2) $d\cos\theta = d\cdot\hat{n}$

Path difference: $(1)+(2) = d\cos\theta' + d\cos\theta = d(\hat{n}-\hat{n}')$

$$d(\hat{n}-\hat{n}') = m\lambda \xrightarrow{\times 2\pi} \vec{d}(\vec{K}-\vec{K}') = 2\pi m$$

$\vec{d}$ is a lattice vector $\Rightarrow \vec{R}(\vec{K}-\vec{K}') = 2\pi m$ { m integer; $\vec{R}$ => all lattice vectors

$\Rightarrow e^{i\vec{R}(\vec{K}-\vec{K}')} = 1$ for all lattice vectors

$\Rightarrow$ This means $\vec{K} - \vec{K}' = \vec{G}$ a Reciprocal lattice vector!

→ elastic scattering:

$|\vec{K}'| = |\vec{K}| = K$ $\qquad$ $\vec{K} - \vec{K}' = \vec{G}$ or $\vec{K}' = \vec{K} + \vec{G}$

$|G| = G$ $\qquad$ $|\vec{K}'| = |\vec{K} + \vec{G}|$

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

$\Rightarrow G^2 + 2\vec{G}\vec{K} = 0$

$\vec{K}\hat{n} = \frac{1}{2}G$

with $\hat{n} = \frac{\vec{G}}{|G|}$ unitary vector along $\vec{G}$

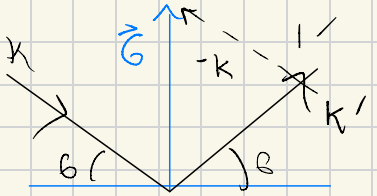
$K \underbrace{\frac{\vec{G}}{|G|}}_{\hat{n}} = \frac{1}{2}G$

$\Rightarrow$ Component of the incident W.V $\vec{K}$ along the reciprocal lat. vec. G must be $\frac{1}{2}|\vec{G}|$

$\Rightarrow$ The plane $\perp \vec{G}$ at $\frac{1}{2}G$ is called a Bragg Plane

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

Von Laue: $\begin{cases} \vec{K} \cdot \frac{\vec{G}}{|G|} = \frac{1}{2}G \\ e^{i(K-K')R} = 1 \end{cases}$ → change in W.V is a RLV



$\vec{G} = \vec{k}' - \vec{k}$

$\sin\theta = \frac{1}{2} G/k \Rightarrow G = 2k\sin\theta$

$\vec{G}$ is a RLV, it must be a multiple of the shortest RLV in the same direction G_0.

$|G_0| = \frac{2\pi}{d}$ (we learned this in the Miller indices!)

family of planes distance $\Rightarrow |G| = G = \frac{2\pi n}{d}$

$\Rightarrow 2k\sin\theta = \frac{2\pi n}{d} \Rightarrow \boxed{d\sin\theta = n\lambda}$ → Bragg condition.

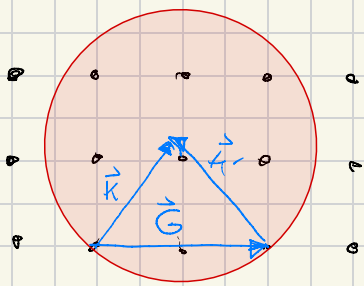
($k = \frac{2\pi}{\lambda}$)

$\Rightarrow$ A Laue diffraction peak associated with a change in W.V $\vec{G}$ corresponds to a Bragg reflection from a family of planes $\perp$ to $\vec{G}$; the order n of the reflection

$$n = \frac{|G|}{|\text{shortest RLV} \parallel \text{to } \vec{G}|}$$

Ewald Construction

Draw a sphere in k-space with radius $\vec{k}$ (incident W.V). The origin of $\vec{k}$ at the surface. The Laue condition will be satisfied if there is another RL Point at the surface of the sphere:



- in general this will not be satisfied unless we choose carefully the origen.

How?

1. - Laue method: Fix directions, change wavelenthe
2. - Rotating crystal: Fix λ, $\vec{k}$, rotate crystal
3. - Powder diffraction → equivalent to performing all possible rotations.

Geometrical structure factor

→ Diffraction By a Monoatomic lattice + basis

→ In the previous derivations we assumed that the atoms (scatterers) are placed at the lattice points

But crystal ≡ B.L + basis

⟹ identical scatterers at basis sites (monoatomic)

⟹ $\vec{d}_i$ location of basis atoms in U. Cell

⟹ Condition of phase difference between scattered rays at $\vec{d}_i$ or $\vec{d}_j$ at a Bragg Peak $(\vec{k}-\vec{k}')=\vec{G}$

$\vec{G}\cdot(\vec{d}_i-\vec{d}_j)$; The amplitude of the two rays will differ by a factor $e^{i\vec{G}(\vec{d}_i-\vec{d}_j)}$

$$S_h = \sum_{j=1}^{n} e^{i\vec{G}\cdot\vec{d}_j}$$

→ Amplitude for rays scattered by the entire U. Cell

↪ Geometrical structure factor

Intensity $I \propto |S_k|^2$

. Note S_k is N.T the unique source of k dependence of the intensity.

Example : BCC as a SC + Basis

$\vec{d}_1 = 0,0,0$

$d_2 = \frac{a}{2}(1,1,1)$

$\Rightarrow S_k = 1 + e^{i\vec{k}\frac{a}{2}(1,1,1)}$

$\vec{k} = \sum_i n_i b_i = \frac{2\pi}{a}(n_1, n_2, n_3)$

$S_k = 1 + e^{i\pi(n_1+n_2+n_3)} = 1 + (-1)^{n_1+n_2+n_3} = \begin{cases} 2 & \sum_i n_i = \text{even} \\ 0 & \sum_i n_i = \text{odd} \end{cases}$

$\Rightarrow$ No associated Bragg reflection if $\sum_i n_i = \text{odd}$ $\Rightarrow$ Converts the SC into an FCC lattice as we would have had if we treated the lattice as BCC.

Ex: Monoatomic Diamond Lattice

FCC + Basis $\begin{cases} \vec{0} \\ \frac{a}{4}(1,1,1) \end{cases}$

Reciprocal of FCC = BCC with $a_{cubic} = \frac{2\pi}{a}$

$$b_1 = \frac{2\pi}{a}(-1,1,1) \quad b_2 = \frac{2\pi}{a}(1,-1,1) \quad b_3 = \frac{2\pi}{a}(1,1,-1)$$

$$S_K = 1 + e^{\frac{1}{2} i\pi (n_1+n_2+n_3)} = \begin{cases} 2 \sum_i n_i = 2k \; 2\pi & \leftarrow \text{Twice even} \\ 1 \pm i & \sum_i n_i = \text{odd} \\ 0 & \sum_i n_i = 2(2n+1) \end{cases} \leftarrow \text{Twice odd}$$