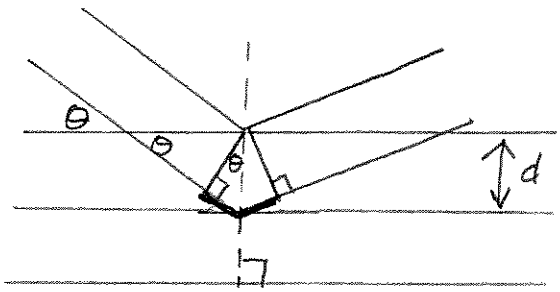
X-Ray Diffraction – Chpt. 6

Typical lattice space = few $\text{Å} = 10^{-10}\,m$

$$h\frac{c}{\lambda} = \frac{(4\times10^{-15}\,eV\cdot s)(3\times10^{8}\,m/s)}{10^{-10}\,m} = 12\times10^{3}\,eV$$

→ X-rays

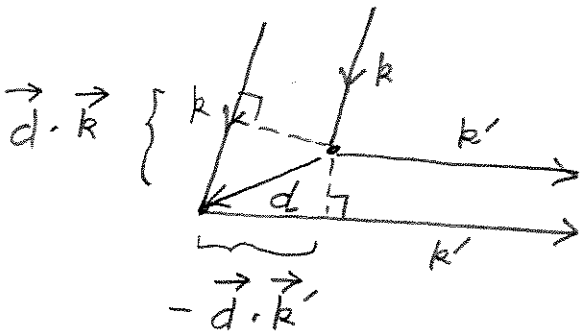
Bragg diffraction:



lattice planes

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

Von Laue formulation:



$$|k| = |k'| = \frac{2\pi}{\lambda}$$

$$\vec{d}\cdot\vec{k} - \vec{d}\cdot\vec{k}' = \frac{2\pi\overbrace{\Delta\ell}^{m\lambda}}{\lambda} = 2\pi m$$

$\vec{d}$ is any lattice vector $\vec{R}$ so we want for all $\vec{R}$ to have

$$e^{i\vec{R}\cdot(\vec{k}-\vec{k}')} = 1$$

→ $\boxed{\vec{K} = \vec{k} - \vec{k}'}$ (or $\vec{k}'-\vec{k}$)

$\vec{K}$ reciprocal lattice vector

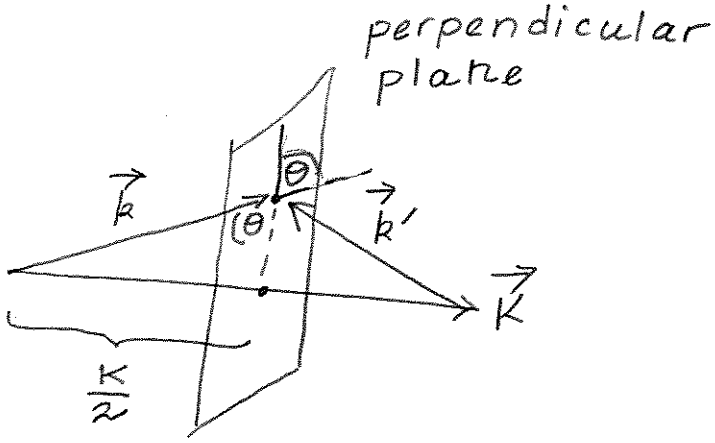
$$\vec{k}' = \vec{k} - \vec{K}$$

$$|k'| = |k| = |k - K|$$

$$\rightarrow \quad k^2 = k^2 - 2\,k\cdot K + K^2$$

$$\rightarrow \quad k\cdot K = \frac{1}{2}K^2$$

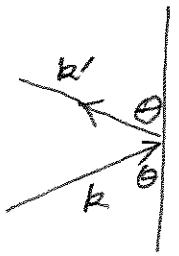
$$\rightarrow \quad \vec{k}\cdot\hat{K} = \frac{1}{2}K$$



<u>Equivalence Bragg & von Laue:</u>

Assume von Laue: $\vec{K} = \vec{k} - \vec{k}'$, $|k| = |k'|$

k & k' make angle θ with plane ⊥ to $\vec{K}$, which is also a lattice plane.



$$|K| = \frac{2\pi n}{d}$$ ← shortest lattice plane spacing in $\hat{K}$.

$$\frac{K}{2} = k\sin\theta$$

$$2k\sin\theta = K = \frac{2\pi n}{d}$$

($k = 2\pi/\lambda$)

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

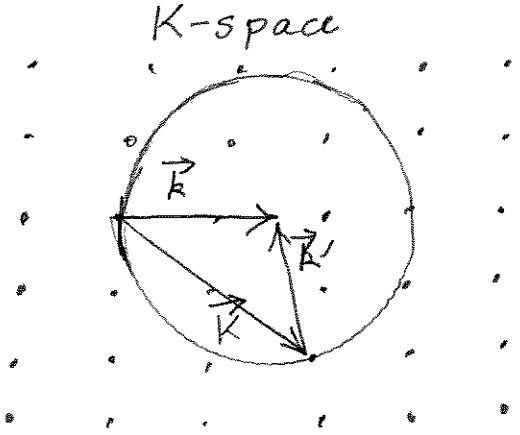
Same argument goes in reverse (Bragg → von Laue) because of the equivalence of lattice planes & $\vec{K}$ vectors.

Experimental geometries:

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

Fix λ. In general will not have $\vec{K} = \vec{k} - \vec{k}'$.
Only occurs at specific points.

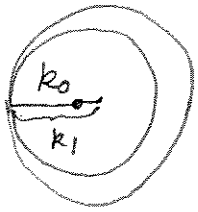
Ewald Construction



Given $\vec{k}$, draw sphere of radius $|k|$ and look for intersections w/ $\vec{K}$.

1. Laue Method

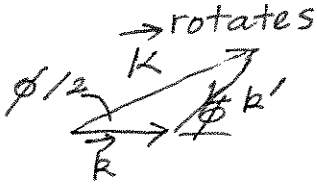
Vary energy (or k) between k_0 and k_1:



2. Rotating-Crystal Method

Sphere rotates. Will get all $|\vec{K}| < 2 \cdot \frac{2\pi}{\lambda}$.

3. Powder or Debye-Scherrer Method (effectively same as 2.)



$\}\rightarrow$ Get a cone: $K = 2k \sin(\phi/2)$

Geometric structure factor:

Identical scatterers at $\vec{d}_1, \ldots, \vec{d}_n$ in a unit cell.

$$\boxed{S_K = \sum_{j=1}^{n} e^{i\vec{K}\cdot\vec{d}_j}}$$

Intensity of Bragg peak $\propto |S_K|^2$.

Examples:

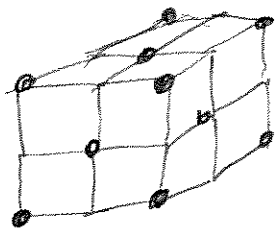
BCC: $\vec{d}_1 = \vec{0}$, $\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

$$S_K = 1 + \exp\left(i\vec{K}\cdot\tfrac{1}{2}a(\hat{x}+\hat{y}+\hat{z})\right)$$

$$K = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})$$

$$\rightarrow S_K = 1 + e^{i\pi(n_1+n_2+n_3)} = 1 + (-1)^{n_1+n_2+n_3}$$

$$= \begin{cases} 2, & n_1+n_2+n_3 \text{ even} \\ 0, & n_1+n_2+n_3 \text{ odd} \end{cases}$$

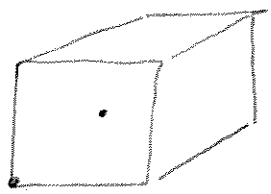


FCC w/ spacing $2\cdot\frac{2\pi}{a}$

Diamond: FCC w/ basis: $\vec{0}$, $\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$.

For FCC lattice reciprocal lattice is BCC w/ spacing of cube $4\pi/a$.

Let $K = \frac{4\pi}{a}(\nu_1\hat{x}_1 + \nu_2\hat{y} + \nu_3\hat{z})$.



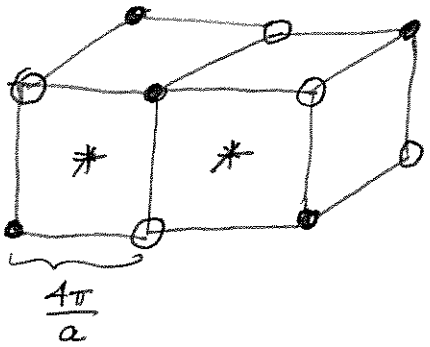
$$S_K = 1 + e^{i\pi(\nu_1+\nu_2+\nu_3)}$$

, ν's half integer on BCC lattice.

$\nu_1 + \nu_2 + \nu_3 = 0, \pm 2, \pm 4, \ldots$ $\quad S_K = 2$ $\quad |S_K|^2 = 4$ •

$\nu_1 + \nu_2 + \nu_3 = \pm 1, \pm 3, \pm 5, \ldots$ $\quad S_K = 0$ $\quad |S_K|^2 = 0$ o

$\nu_1 + \nu_2 + \nu_3 = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots$ $\quad S_K = 1 \pm i$ $\quad |S_K|^2 = 2$ *



Polyatomic crystal:

$$S_K = \sum_{j=1}^{n} f_j(K)\, e^{i\vec{K}\cdot\vec{d}_j}$$

$f_j(K)$: atomic formfactor

$$f_j(K) = -\frac{1}{e}\int d^3r\, e^{iK\cdot r}\rho_j(r)$$

$\rho_j(r)$: electronic charge density