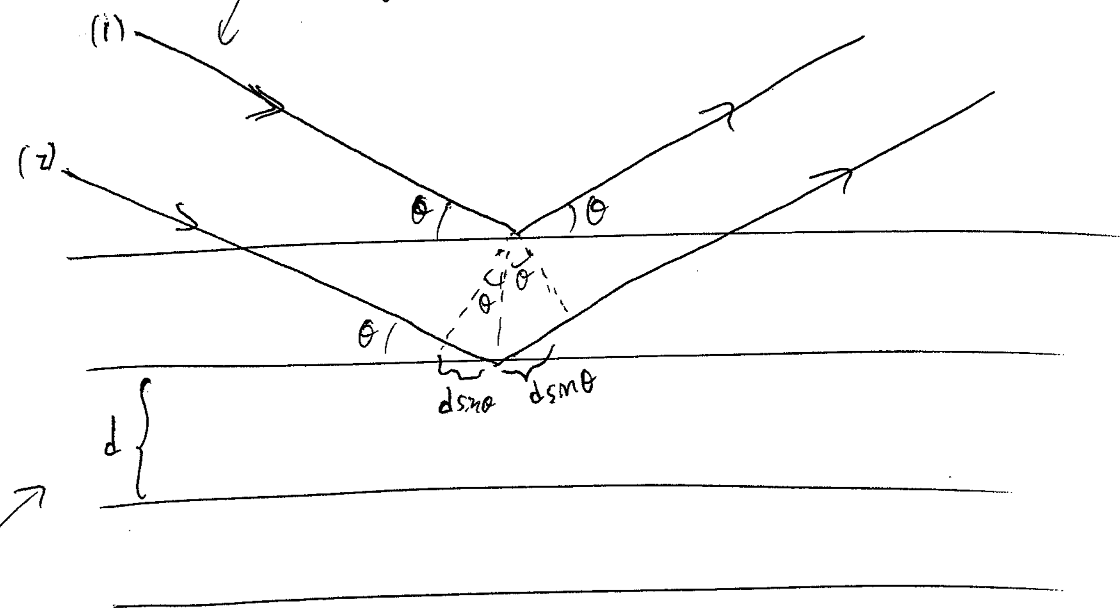
Scattering / Diffraction → Probing Crystal Structure

- Q: How do we <u>measure</u> crystal structure?

  A: Scatter some particles off our sample.

<u>Bragg Picture</u>: wavelength λ.



Think of crystal as a bunch of planes spaced distance d apart.

- Extra path length of (2) is $2d\sin\theta$
- For constructive interference, need $2d\sin\theta = n\lambda$

$$\Rightarrow \sin\theta = \frac{n\lambda}{2d}$$

- Want $\lambda \sim d$ ($\lambda \gg d$ can't satisfy Bragg condition)
  ($\lambda \ll d$ has very small spacings between allowed scattering angles → harder to measure.)

- $d \sim 1$ Å in solids.

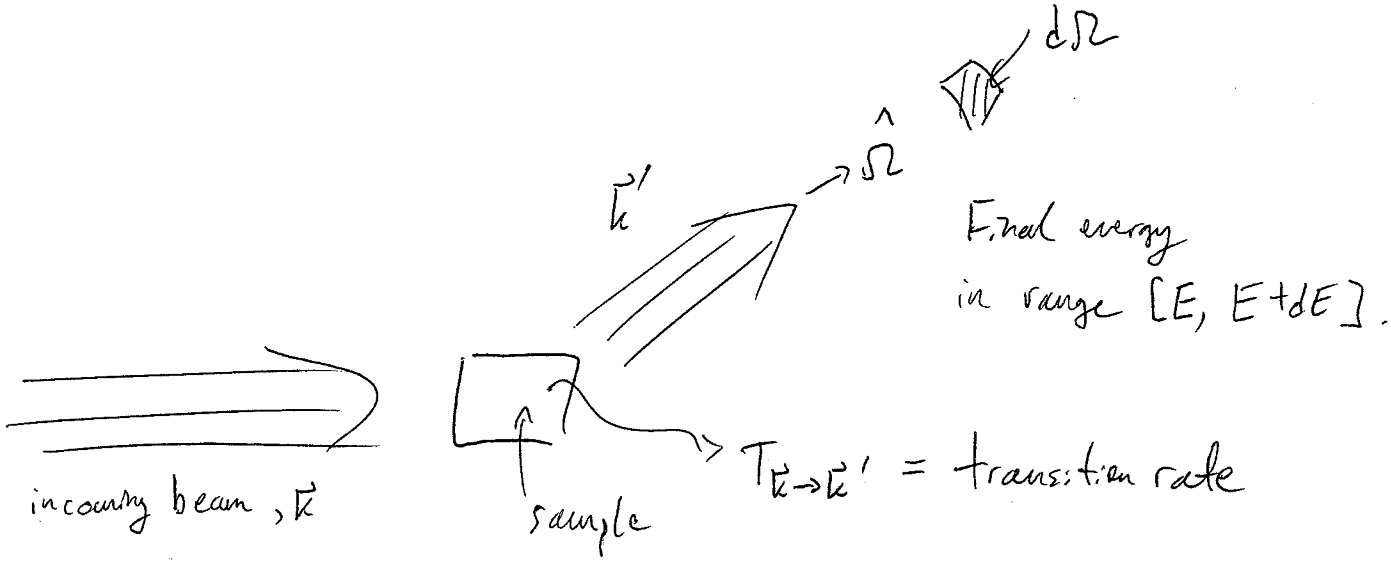
⇒ Possibilities

- Photons with $\lambda \sim 1$ Å ($E \sim 12$ keV → X-rays)
- Electrons $\lambda_{dB} \sim 1$ Å ($E \sim 150$ eV)
  ⇝ But electrons feel strong Coulomb interaction with solid
  ⇒ Multiple scattering except for very thin samples
- Neutrons $\lambda_{dB} \sim 1$ Å ($E \sim 0.1$ eV ⇔ $\frac{E}{k_B} \sim 400$ K)
  "thermal neutrons"

- X-rays: Hard to ~~..~~ resolve change in energy of scattered X-ray, so not great for probing excitations of the solid. (But it is possible with X-rays from synchrotrons.)

- neutrons: Require larger samples since they interact very weakly. But can probe excitations.

More Systematic Approach



- Incoming beam characterized by flux $\Phi = \dfrac{\#\text{ particles}}{\text{Area}\cdot\text{time}} = \dfrac{N_p \cdot v(k)}{V}$

(#/time)

Measure: $$\frac{d\sigma}{d\Omega\, dE}(\hat{\Omega}, E) = \frac{\#\text{ scattered into } d\Omega \text{ around } \hat{\Omega} \text{ and } dE \text{ around } E}{dE \cdot d\Omega \cdot \Phi}$$

$$\frac{d\sigma}{d\Omega}(\hat{\Omega}) = \frac{\#/\text{time scattered into } d\Omega \text{ around } \hat{\Omega}}{d\Omega \cdot \Phi}$$

$$= \int dE \frac{d\sigma}{dE\, d\Omega}$$

$$\sigma_{tot} = \frac{\text{total }\#/\text{time scattered}}{\Phi} = \int dE\, d\Omega \frac{d\sigma}{dE\, d\Omega}$$

- Want to relate $\frac{d\sigma}{d\Omega dE}$ and $T_{k\to k'}$.

Start with $\Phi \sigma_{tot} = N_p \sum_{k'} T_{\vec{k}\to\vec{k}'}$ $\left(\frac{\text{total \# scattered}}{\text{time}} \right)$

<u>NB</u>: We treat the scattering in the sample as if both sample <u>and</u> incident particle are inside a periodic box of volume V. (This is why, for example, $\vec{k}'$ above is treated as discrete.) This should be okay for large V. In this case, $\sum_{\vec{k}'} = V \int \frac{d^3k'}{(2\pi)^3}$, so:

$$\Phi \sigma_{tot} = N_p V \int \frac{d^3\vec{k}'}{(2\pi)^3} T_{\vec{k}\to\vec{k}'} = \frac{N_p V}{(2\pi)^3} \int dk' \, d\Omega' \, (k')^2 \, T_{\vec{k}\to\vec{k}'}$$

- Now $E = E(k)$; $\frac{1}{\hbar}\frac{dE}{dk} = v(k) = v(E)$ $\Rightarrow$ $dk = \frac{dE}{\hbar v(E)}$

$$\Rightarrow \Phi \sigma_{tot} = \frac{N_p V}{\hbar (2\pi)^3} \int dE' \, d\Omega' \, \frac{[k'(E')]^2}{v(E')} T_{\vec{k}\to\vec{k}'}$$

$$\Rightarrow \quad \sigma_{tot} = \frac{V^2}{\hbar(2\pi)^3} \int dE' d\Omega' \, \frac{[k'(E')]^2}{v(E)\, v(E')} \, T_{\vec{k} \to \vec{k}'}$$

$$\Rightarrow \quad \boxed{\frac{d\sigma}{d\Omega dE} = \frac{V^2}{\hbar(2\pi)^3} \frac{[k'(E')]^2}{v(E)v(E')} T_{\vec{k} \to \vec{k}'}}$$

- Most important part of this expression is the factor of V^2 in front. (Other factors can also be important.)

<u>Next</u>: Calculate $T_{\vec{k} \to \vec{k}'}$.

- We will do this for a "perfect solid" with no thermal / quantum ~~fluctuation~~ fluctuations of atomic positions. (Will later revisit this in more detail and include those effects.)

- Label atoms by α, positions $\vec{r}_\alpha$. ($\vec{r}_\alpha$ would be Bravais lattice in simplest case, could also be lattice with basis.)

- $H = H_{crystal} + H_{particle} + H_{int}$

$$H_{int} = U(\vec{r}) = \sum_\alpha U_\alpha(\vec{r}-\vec{r}_\alpha)$$

→ particle feels potential U_α from each atom.

- Treat H_{int} as a small perturbation. (If it isn't, then multiple scattering processes are important, and our scattering experiment will not be a good probe of crystal structure.)

⇒ Use Fermi's golden rule:

$$T_{\vec{k}\to\vec{k}'} = \frac{2\pi}{\hbar} \left| \langle \vec{k}' | H_{int} | \vec{k} \rangle \right|^2 \delta(E_{\vec{k}'} - E_{\vec{k}})$$

$$|\vec{k}\rangle \to \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$ plane wave (ignore, e.g. photon polarization, neutron spin.)

$$\boxed{\vec{q} = \vec{k}' - \vec{k}}$$

$$\langle \vec{k}' | H_{int} | \vec{k} \rangle = \frac{1}{V} \sum_{\alpha} \int d^3r \, e^{-i\vec{q}\cdot\vec{r}} \, U_\alpha(\vec{r} - \vec{r}_\alpha)$$

$$\Big\downarrow \ \vec{r} \to \vec{r} + \vec{r}_\alpha \ \text{change of variables}$$

$$= \frac{1}{V} \sum_{\alpha} e^{-i\vec{q}\cdot\vec{r}_\alpha} \int d^3\vec{r} \, e^{-i\vec{q}\cdot\vec{r}} \, U_\alpha(\vec{r})$$

$$= \frac{1}{V} \sum_{\alpha} \underbrace{U_\alpha(q)}_{\text{Fourier transform.}} \, e^{-i\vec{q}\cdot\vec{r}_\alpha} \equiv \frac{1}{V} M(\vec{q})$$

- Note: $M(\vec{q}) = \int d^3\vec{r} \, e^{-i\vec{q}\cdot\vec{r}} \, U(\vec{r})$ = Fourier transform of $U(\vec{r})$

- $U_\alpha(\vec{q})$ is called the form factor of atom α.

- $U(\vec{r})$ is similar to the atom density $n(\vec{r}) = \sum_\alpha \delta(\vec{r} - \vec{r}_\alpha)$.

$$n(\vec{q}) = \int d^3r \, e^{-i\vec{q}\cdot\vec{r}} \, n(\vec{r}) = \sum_\alpha e^{-i\vec{q}\cdot\vec{r}_\alpha}$$

$\Rightarrow$ Monatomic solid, $U_\alpha(\vec{q}) = U_1(\vec{q})$ and

$$M(\vec{q}) = U_1(\vec{q}) \cdot n(\vec{q}) \longrightarrow \text{Can measure } n(\vec{q}).$$

Putting things together,

$$\frac{d\sigma}{d\Omega\, dE} = \frac{1}{\hbar^2 (2\pi)^2} \frac{[k'(E')]^2}{v(E)v(E')} |M(\vec{q})|^2 \delta(E-E')$$

$$= \frac{1}{\hbar^2 (2\pi)^2} \left[\frac{k(E)}{v(E)}\right]^2 |M(\vec{q})|^2 \delta(E-E')$$

- We focus on $|M(\vec{q})|^2$
  - ~~Either we don't keep track of~~
- There are other contributions when $E \neq E'$ having to do with excitations of the solid. ~~This has to~~ (We don't see this because we assumed the $\vec{r}_\alpha$ were fixed.) ~~What~~ We'll see later that the $E=E'$ piece is actually dominant.

Toy model: 1D monatomic crystal

Lattice constant.

$$\Rightarrow M(q) = U_1(q) \sum_{\alpha} e^{-iqr_\alpha} \quad ; \quad r_\alpha = a \cdot n$$

integer

$$= U_1(q) \sum_{n} e^{-iqan}$$

- If $q = \frac{2\pi m}{a}$, then $e^{-iqan} = 1 \Rightarrow \sum_n e^{-iqan} = N$

\# atoms

- If $q \neq \frac{2\pi m}{a}$, then e^{-iqan} oscillates $\Rightarrow \sum_n e^{-iqan} = 0$.

$$\Rightarrow \boxed{M(q) = N\, U_1(q) \sum_{Q} \delta_{q,Q} \quad ; \quad Q = \frac{2\pi m}{a}}$$

~~• Large-V limit, $\delta_{q,Q} \to \frac{2\pi}{L}\delta(q-Q)$~~

~~Length of 1D system.~~

$$\cancel{|M(q)|^2 = N^2 |U_1(q)|^2 \sum_{Q,Q'} \delta_{q,Q}\, \delta_{q,Q'}}$$

$$|M(q)|^2 = N^2 |U_1(q)|^2 \sum_{Q,Q'} \delta_{q,Q}\,\delta_{q,Q'}$$

$\Rightarrow$

$$\boxed{|M(q)|^2 = N^2 |U_1(q)|^2 \sum_{Q} \delta_{q,Q}}$$

- Cross section $\propto N^2 \Rightarrow$ coherent scattering process! (constructive interference)

3D Monatomic Crystal, Bravais lattice:

$$M(\vec{q}) = U_1(\vec{q}) \sum_{\alpha} e^{-i\vec{q}\cdot\vec{r}_\alpha}$$

$$= U_1(\vec{q}) \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}}$$

$\vec{R}$ ↳ Bravais lattice vectors

- If $e^{-i\vec{q}\cdot\vec{R}} = 1$ for all $\vec{R}$, then $M(\vec{q}) = N U_1(\vec{q})$
- Otherwise, $e^{-i\vec{q}\cdot\vec{R}}$ oscillates $\rightarrow M(\vec{q}) = 0$.

- Let $\{\vec{Q}\}$ be the set of all vectors satisfying $e^{i\vec{Q}\cdot\vec{R}} = 1$ for all $\vec{R}$. (For a given Bravais lattice.)

$$\Rightarrow \quad M(\vec{q}) = N \sum_{\vec{Q}} U_1(\vec{Q})\, \delta_{\vec{q},\vec{Q}}$$

$$\Rightarrow \quad \boxed{|M(\vec{q})|^2 = N^2 \sum_{\vec{Q}} |U_1(\vec{Q})|^2\, \delta_{\vec{q},\vec{Q}}}$$

- Large-V limit, $\delta_{\vec{q},\vec{Q}} \rightarrow \frac{(2\pi)^3}{V}\, \delta(\vec{q}-\vec{Q})$,

$$|M(\vec{q})|^2 = \left(\frac{N}{V}\right)^2 (2\pi)^3 \sum_{\vec{Q}} |U_1(\vec{Q})|^2\, \delta(\vec{q}-\vec{Q})$$

- $\{\vec{Q}\}$ is called the reciprocal lattice