**X-Ray Diffraction**

A method to determine crystal structure.

Assumption: ignoring thermal vibrations of lattice (including zero-point vibrations) for now.

A charged particle of charge $q$ in an EM field:

$$H = \frac{1}{2m} \left( p - \frac{q}{c} A \right)^2 + V(r) = \frac{1}{2m} \left( p^2 - \frac{q}{c} A \cdot p - \frac{q^2}{c^2} A + \frac{m^2 c^2}{4} A^2 \right) + V(r)$$

Interaction: $\Delta H = \frac{1}{2m} \left( -\frac{q}{c} A \cdot p - \frac{q^2}{c^2} A + \frac{m^2 c^2}{4} A^2 \right)$, usually treated as a perturbation.

$\Delta H \propto \frac{1}{m}$

Rough estimates:

$$\frac{\text{Scattering prob. for protons}}{\text{Scattering prob. for electrons}} \propto \left( \frac{m_e}{m_p} \right)^2 \sim \left( \frac{1}{1840} \right)^2$$

X-ray scattering is dominated by electrons (nuclei can be ignored).
Still, x-ray interaction with electrons is weak, and so one can use single-scattering theory (kinematic theory) in most cases. For comparison, electron scattering involves a strong interaction; one must consider multiple scattering (dynamical theory) - complicated.

For example: double scattering

Consider elastic scattering only; \( k' = k \). Inelastic scattering by phonons will be considered later when we discuss neutron scattering.

\[
A = \text{total scattering amplitude at } \mathbf{r}' \text{ (detector)} \propto \int (\text{amplitude of incident plane wave}) \times (\text{number of electrons in } d^3 r) \times (\text{amplitude of scattered spherical wave at } \mathbf{r}')
\]
$A \propto \int_{\mathcal{V}} (e^{ik \cdot r})(n(r)d^3r)\left(\frac{e^{ik'[r'-r]}}{|r'-r|}f(\chi,\phi)\right)$,

where $f(\chi,\phi)$ = angular distribution factor, determined by $\langle\psi_f | \Delta H | \psi_i \rangle$.

Assume the crystal dimensions $\ll r'$ (far field approximation), $f(\chi,\phi)$, $k'$, $r'$, and $|r'-r| \sim r'$ are approximately constants.

$e^{ik'[r'-r]} = e^{ik'[r'-r]}$

$A \propto \frac{f}{r'} \int n(r) e^{ik \cdot r} e^{ik'[r'-r]} d^3r = \frac{f}{r'} e^{ik' \cdot r'} \int d^3r \ n(r) \ e^{-i\Delta k \cdot r} \propto f \int d^3r \ n(r) \ e^{-i\Delta k \cdot r}$

$\Delta k = k' - k =$ scattering wave vector

For a rigid perfect crystal structure, $n(r) =$ periodic $= \sum \ n_k \ e^{K \cdot r}$

$\int n(r) e^{-i\Delta k \cdot r} d^3r = \sum_k n_k \int e^{i(K-\Delta k) \cdot r} d^3r$

Remember -- $\int e^{i(K-\Delta k) \cdot r} d^3r \propto \delta(K-\Delta k)$

For a "large" crystal, $\int_v e^{i(K-\Delta k) \cdot r} d^3r = V\delta_{\Delta k,K}$.
1d proof: Consider a crystal of length \( Na \). Let \( p = K - \Delta k \)

\[
\int_{-\infty}^{\infty} e^{ipx} dx = \frac{e^{iNap} - 1}{ip}
\]

\[
\left| \int_{-\infty}^{\infty} e^{ipx} dx \right|^2 = \frac{4}{p^2} \sin^2 \left( \frac{Nap}{2} \right) \leq \frac{4}{p^2}
\]

(envelope function)

Example: \( N = 100, a = 1 \)

Peak height = \((Na)^2\) at \( p = 0 \)

Width of main peak \( \Delta p \)
determined by

\[
\frac{(Na)^2}{2} = \frac{4}{\Delta p^2} \sin^2 \left( \frac{Na\Delta p}{2} \right) \sim \frac{4}{\Delta p^2}
\]

\[
\Delta p = \frac{2\sqrt{2}}{Na} \sim \frac{1}{\text{size of crystal}} \to 0
\]

For x-ray diffraction, \( K, k, k' \) of order \( \frac{1}{a} \).
\( p = K - \Delta k \) is also of order \( 1/a \). So, \( \Delta p \sim \frac{1}{Na} \ll k, k', K \)

\[ \int_{o}^{Na} e^{ipx} dx \approx Na\delta_{p,o} \bigg( \text{width} \sim \frac{1}{Na} \bigg) \]

QED

Back to 3d diffraction, \( A \propto f \sum_{K} n_{K} \delta_{\Delta k, K} \)

Scattering intensity \( \propto |A|^2 \)

For unpolarized x-rays (after averaging over polarization), \( I \propto F(\chi) \left| \sum_{K} n_{K} \delta_{\Delta k, K} \right|^2 \)

where \( F(\chi) = \frac{1 + \cos^2 \chi}{2} \) \( \chi \): scattering angle

\( I \neq 0 \) if and only if \( \Delta k = K \) and \( n_{K} \neq 0 \)

\( K = k' - k \): an example of **conservation of crystal momentum** also known as the **von Laue condition** for x-ray diffraction.

\( K \) is perpendicular to a family of planes with spacing \( d \).
\( \theta = \) angle of incidence

\( K = 2k \sin \theta \) (because \( k = k' \))

\[ K = \frac{2\pi}{d} n \]

\( n: \) integer (\( K \) not necessarily the shortest)

\( n = \) order of diffraction

\[ 2k \sin \theta = \frac{2\pi}{d} n \quad \lambda = \frac{2\pi}{k} \]

\[ n\lambda = 2d \sin \theta \quad \text{Bragg condition} \equiv \text{von Laue condition} \]

Elementary picture:

Constructive interference: path length difference = \( 2d \sin \theta = n\lambda \)
von Laue: \( \mathbf{k} + \mathbf{K} = \mathbf{k}' \), \( k = k' \)

**Bragg plane:** \( \perp \) bisector of \( -\mathbf{K} \) (or \( \mathbf{K} \)).

Laue condition implies tip of \( \mathbf{k} \) lies on a Bragg plane.

All Bragg planes form a discrete \( \infty \) set; in general tip of \( \mathbf{k} \) is not on one of them, i.e., no diffraction.

The Ewald construction:

1. Draw \( \mathbf{k} \) from origin \( O \) in reciprocal lattice.
2. Draw a sphere (Ewald sphere) with radius \( k \), centered at tip of \( \mathbf{k} \).
3. Laue condition is satisfied for reciprocal lattice points on the Ewald sphere surface.

In general, no diffraction.

**Laue method** for aligning crystals: use a broad-band x-ray source (such as the Bremsstrahlung radiation from an x-ray tube) to generate a continuous set of Ewald spheres; so a number of diffractions can be observed.
Implications of $n_\mathbf{k} \neq 0$:

$$n_\mathbf{k} = \frac{1}{V} \int_V n(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3r = \frac{1}{V} \int_V n_\mathbf{k}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3r \equiv \text{structure factor}$$

The integration could be over the whole volume or over a unit cell.

Within a unit cell, $n(\mathbf{r}) = \sum_{\text{basis}} n_\alpha (\mathbf{r} - \mathbf{r}_\alpha)$

$\mathbf{r}_\alpha$ : center of $\alpha$-th atom in unit cell; $n_\alpha$ electron density

$$n_\mathbf{k} = \sum_{\alpha} \frac{1}{V} \int_V n_\alpha (\mathbf{r} - \mathbf{r}_\alpha) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3r = \sum_{\alpha} \left( \frac{1}{V} \int_V n_\alpha (\mathbf{r} - \mathbf{r}_\alpha) e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_\alpha)} d^3r \right) e^{-i\mathbf{k} \cdot \mathbf{r}_\alpha}$$

$$= \sum_{\alpha} \frac{1}{V} \left( \int_V n_\alpha (\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3r \right) e^{-i\mathbf{k} \cdot \mathbf{r}_\alpha} \equiv \sum_{\alpha} f_\alpha (\mathbf{K}) e^{-i\mathbf{k} \cdot \mathbf{r}_\alpha}$$

$f_\alpha (\mathbf{K})$ = atomic form factor, largely independent of the solid state environment.

$$I \propto F(\chi) \left| \sum_{\mathbf{k}} n_\mathbf{k} \delta_{\Delta k, \mathbf{k}} \right|^2 = F(\chi) \left| \sum_{\mathbf{k}} \delta_{\Delta k, \mathbf{k}} \left( \sum_{\alpha} f_\alpha e^{-i\mathbf{k} \cdot \mathbf{r}_\alpha} \right) \right|^2$$
Example: \( \text{bcc} = \text{sc lattice + basis} \left\{ (0,0,0); \frac{a}{2} (1,1,1) \right\} \)

Reciprocal lattice = sc, with lattice constant \( \frac{2\pi}{a} \). \( \mathbf{K} = \frac{2\pi}{a} (\ell_1, \ell_2, \ell_3) \)

\[
n_{\mathbf{K}} = \sum_{\alpha} f_\alpha e^{-i\mathbf{K} \cdot \mathbf{r}_\alpha} = f + f e^{-i\pi(\ell_1 + \ell_2 + \ell_3)} = f \left[ 1 + (-1)^{\ell_1 + \ell_2 + \ell_3} \right]
\]

\( l = 0 \) for \( \ell_1 + \ell_2 + \ell_3 = \text{odd} \)

If we remove those \( \mathbf{K} \)'s with a zero structure factor \( (n_{\mathbf{K}} = 0) \), i.e., those with \( \ell_1 + \ell_2 + \ell_3 = \text{odd} \), we end up with an fcc lattice with lattice constant \( \frac{4\pi}{a} \), which is the reciprocal lattice of the original bcc lattice.

So, it works either way; you could treat bcc as a sc + basis. Same answers.

Another example: CsCl

\( \text{sc + basis} \left\{ \text{Cs} (0,0,0); \text{Cl} \frac{a}{2} (1,1,1) \right\} \)

\[
n_{\mathbf{K}} = f_{\text{Cs}} + f_{\text{Cl}} (-1)^{\ell_1 + \ell_2 + \ell_3} \neq 0 \text{ in general.}
\]

If, however, \( f_{\text{Cs}} = f_{\text{Cl}} \), \( n_{\mathbf{K}} = f_{\text{Cs}} + f_{\text{Cl}} (-1)^{\ell_1 + \ell_2 + \ell_3} = 0 \) for \( \ell_1 + \ell_2 + \ell_3 = \text{odd} \).

From intensity measurements, can determine \( f_{\text{Cs}} / f_{\text{Cl}} \).