Diffraction from Crystals
“Structure Factor”

Lecture 5
Coherent elastic scattering

Incident plane wave: \( \Psi_{\text{incident}} = \exp\left[2\pi i (k_i \cdot r' - \omega t)\right] = \exp\left[2\pi i (k_i \cdot r')\right] \)

Scattered wave:
\[
\Psi_{\text{scattered}} = f(k_i, k_d) \frac{\exp\left[2\pi i k_d \cdot (r - r')\right]}{|r - r'|} = f(\theta) \frac{\exp\left[2\pi i k_d \cdot (r - r')\right]}{|r - r'|}
\]
Scattering from a lattice

\[ V_{\text{atom}}(\vec{r}') = \sum V_{\text{at}}(\vec{r}' - \vec{R}_j) \]

\[ \Psi_{\text{scattered}}(\vec{k}, \vec{r}) = -\frac{m}{2\pi\hbar^2} \exp\left[2\pi i (\vec{k}_d \cdot \vec{r})\right] \int \sum V_{\text{at}}(\vec{r}' - \vec{R}_j) \exp\left[-2\pi i (\vec{k} \cdot \vec{r}')\right] d^3\vec{r}' \]
Scattering from a lattice

\[ \Psi_{\text{scatt}}(\mathbf{K}) = \frac{-m}{2 \pi \hbar^2} \int \sum V_{\text{at}, \mathbf{R}_j}(\mathbf{r}) \exp[-2\pi i (\mathbf{K} \cdot (\mathbf{r} + \mathbf{R}_j))] d^3 \mathbf{r} \]

\[ = \sum_{\mathbf{R}_j} \frac{-m}{2 \pi \hbar^2} \int V_{\text{at}, \mathbf{R}_j}(\mathbf{r}) \exp[-2\pi i (\mathbf{K} \cdot \mathbf{r})] d^3 \mathbf{r} \exp[-2\pi i (\mathbf{K} \cdot \mathbf{R}_j)] \]

\( \mathbf{r} \equiv \mathbf{r}' - \mathbf{R}_j \) (i.e. \( \mathbf{r}' = \mathbf{r} + \mathbf{R}_j' \))

Ignore the \( 1/r^2 \) term to give:

\( f_{\text{el}}(\mathbf{R}_j, \mathbf{K}) \approx f_{\text{el}}(\mathbf{R}_j) \)

[\( [\mathbf{R}_j] \)- atom locations]
Scattering from a lattice

So scattered wave from an array of N atoms:

\[ \Psi_{\text{scatt}}(\mathbf{K}) = \sum_{j=1}^{N} f_{\text{el}}(\mathbf{R}_j) \exp[-2\pi i (\mathbf{K} \cdot \mathbf{R}_j)] \]

Notes:
- Now have \( \Psi(\mathbf{K}) \) only, \( \mathbf{R}_j \) are fixed. Means scattered wave depends on incident wave vector.
- This is a Fourier Transform (FT)

Diffraction intensity is proportional to the Fourier Transform of the scattering factor distribution in the material.
Scattering from a lattice

In simplest form, a crystal is:

Crystal = lattice + basis + defect displacements

$$\tilde{R}_j = \tilde{r}_{\text{lattice}} + \tilde{r}_{\text{basis}} + \tilde{r}_{\text{defects}} = \tilde{r}_l + \tilde{r}_b + \tilde{r}_d$$

For now, consider a defect free crystal:

Crystal = lattice + basis

$$\tilde{R}_j = \tilde{r}_{\text{lattice}} + \tilde{r}_{\text{basis}} = \tilde{r}_l + \tilde{r}_b$$

Scattered wave:

$$\Psi_{\text{scatt}}(\tilde{K}) = \sum_{\tilde{r}_l} \sum_{\tilde{r}_b} f_{\text{el}}(\tilde{r}_l + \tilde{r}_b) \exp[-2\pi i (\tilde{K} \cdot (\tilde{r}_l + \tilde{r}_b))]$$

Basis must be same for all unit cells: \( f(\tilde{r}_l + \tilde{r}_b) = f(\tilde{r}_b) \)

$$\Psi_{\text{scatt}}(\tilde{K}) = \sum_{\tilde{r}_l} \exp[-2\pi i (\tilde{K} \cdot \tilde{r}_l)] \sum_{\tilde{r}_b} f_{\text{el}}(\tilde{r}_b) \exp[-2\pi i (\tilde{K} \cdot \tilde{r}_b)]$$
Scattering from a lattice

Repeating:

\[ \Psi_{\text{scatt}}(\mathbf{K}) = \sum_{\mathbf{r}_l} \exp\left[-2\pi i (\mathbf{K} \cdot \mathbf{r}_l)\right] \sum_{\mathbf{r}_b} f_{\text{el}}(\mathbf{r}_b) \exp\left[-2\pi i (\mathbf{K} \cdot \mathbf{r}_b)\right] \]

\[ \Psi_{\text{scatt}}(\mathbf{K}) = S(\mathbf{K}) F(\mathbf{K}) \]

where:

\[ S(\mathbf{K}) = \sum_{\mathbf{r}_l} \exp\left[-2\pi i (\mathbf{K} \cdot \mathbf{r}_l)\right] \]

“Shape Factor”

\[ F(\mathbf{K}) = \sum_{\mathbf{r}_b} f_{\text{el}}(\mathbf{r}_b) \exp\left[-2\pi i (\mathbf{K} \cdot \mathbf{r}_b)\right] \]

“Structure Factor”

\[ F(\mathbf{K}) \text{ same for all lattice points:} \]

\[ \Psi(\mathbf{K}) = \sum_{\mathbf{r}_l} F(\mathbf{K}) \exp\left[-2\pi i (\mathbf{K} \cdot \mathbf{r}_l)\right] \]
**Structure Factor**

*Structure Factor:*
- Scattering from all atoms in the unit cell

\[
F(K) = \sum_{\vec{r}_b} f_{el}(\vec{r}_b) \exp [-2\pi i (\vec{K} \cdot \vec{r}_b)]
\]

In essence, Structure Factor determines whether or not constructive interference occurs at a given reciprocal lattice point.

This means our prior condition - \( \vec{K} = \vec{g} \) - is a necessary condition, but is not sufficient.
- There may not be intensity at a given \( \vec{g} \)!
Structure factor calculation

Consider $i$ atoms in the unit cell

$$F(K) = \sum_i f_i \exp \left[ -2\pi i (K \cdot \vec{r}_i) \right]$$

Location of $i^{th}$ atom (with respect to real lattice):

$$\vec{r}_i = x_i \vec{a} + y_i \vec{b} + z_i \vec{c}$$

Diffraction condition ($K = g$):

$$\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

General from:

$$F(K) = \sum_i f_i \exp \left[ -2\pi i (h x_i + k y_i + l z_i) \right]$$

Using defn of $a^*$, $b^*$ & $c^*$
Structure Factor

Simple cubic

\[ F = \sum_i f_i \exp[-2\pi i (hx_i + ky_i + lz_i)] \]

One atom basis: \( r = (0,0,0) \)

\[ F = f \{ \exp[-2\pi i (0 \cdot h + 0 \cdot k + 0 \cdot l)] \} \]
\[ = f \{ \exp[-2\pi i (0)] \} \]
\[ = f \{ \exp[0] \} \]
\[ = f \]

Simple result: intensity at every reciprocal lattice point
Structure Factor
body-centered cubic

Two atom basis: \( r = (0,0,0) \) & \( r = \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \)

\[
F = f \left\{ \exp \left[ -2\pi i \left( 0 \cdot h + 0 \cdot k + 0 \cdot l \right) \right] + \exp \left[ -2\pi i \left( \frac{1}{2} \cdot h + \frac{1}{2} \cdot k + \frac{1}{2} \cdot l \right) \right] \right\} \\
= f \left\{ 1 + \exp \left[ -\pi i (h+k+l) \right] \right\}
\]

\( h, k \) & \( l \) are integers, so \( h+k+l = N \) (where \( N \) is an integer)

The exponential can then take one of two values:

\[
\exp \left[ -\pi i (h+k+l) \right] = +1 \quad \text{if } N = \text{even} \\
\exp \left[ -\pi i (h+k+l) \right] = -1 \quad \text{if } N = \text{odd}
\]

So:

\[
F = 2f \quad \text{if } N = \text{even} \\
F = 0 \quad \text{if } N = \text{odd}
\]
Structure Factor
body-centered cubic

Allowed low order reflections are:
- 110, 200, 220, 310, 222, 321, 400, 330, 411, 420 ...

Forbidden reflections are:
- 100, 111, 210

Origin of forbidden reflections?
- Identical plane of atoms halfway between causes destructive interference

Real bcc lattice has an fcc reciprocal lattice
Structure Factor

face centered cubic

Four atom basis: \( r = (0,0,0), r = \left( \frac{1}{2}, \frac{1}{2}, 0 \right), r = \left( \frac{1}{2}, 0, \frac{1}{2} \right) \) & \( r = \left( 0, \frac{1}{2}, \frac{1}{2} \right) \)

\[
F = f \left\{ 1 + \exp[-\pi i (h+k)] + \exp[-\pi i (k+l)] + \exp[-\pi i (h+l)] \right\}
\]

So:

\( F = 4f \) if \( h,k,l \) all even or odd

\( F = 0 \) if \( h,k,l \) are mixed even or odd
Structure Factor
face centered cubic

Allowed low order reflections are:
- 111, 200, 220, 311, 222, 400, 331, 310

Forbidden reflections:
- 100, 110, 210, 211

Real fcc lattice has a bcc reciprocal lattice
Structure Factor
NaCl (rock salt) structure

Na on each fcc site, but with a two atom basis:

\[ r_{Na} = (0,0,0) & \quad r_{Cl} = \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \]

\[ F = \left\{ f_{Na} + f_{Cl} \exp\left[-\pi i (h+k+l)\right] \right\} \times \]
\[ \left\{ 1 + \exp\left[-\pi i (h+k)\right] + \exp\left[-\pi i (k+l)\right] + \exp\left[-\pi i (h+l)\right] \right\} \]

\[ F = 4\left(f_{Na} + f_{Cl}\right) \quad \text{if } h,k,l \text{ all even} \]
\[ F = 4\left(f_{Na} - f_{Cl}\right) \quad \text{if } h,k,l \text{ all odd} \]
\[ F = 0 \quad \text{if } h,k,l \text{ mixed} \]

If \( h,k,l \) all odd have ‘chemically sensitive’ reflections
Structure Factor

Ni$_3$Al (L1$_2$) structure

Simple cubic lattice, with at four atom basis

\[ r_{\text{Al}} = (0,0,0), \quad r_{\text{Ni}} = \left( \frac{1}{2}, \frac{1}{2}, 0 \right), \quad r_{\text{Ni}} = \left( \frac{1}{2}, 0, \frac{1}{2} \right) \quad \text{&} \quad r_{\text{Ni}} = \left( 0, \frac{1}{2}, \frac{1}{2} \right) \]

\[ F = f_{\text{Al}} + f_{\text{Ni}} \exp\left[ -\pi i (h + k) \right] + \exp\left[ -\pi i (k + l) \right] + \exp\left[ -\pi i (h + l) \right] \]

So:

\[ F = f_{\text{Al}} + 3f_{\text{Ni}} \quad \text{if} \quad h, k, l \text{ all even or odd} \]

\[ F = f_{\text{Al}} - f_{\text{Ni}} \quad \text{if} \quad h, k, l \text{ are mixed even or odd} \]

Again, since simple cubic, intensity at all points.

But each point is ‘chemically sensitive’.
Chemically sensitive reflections

Dark field images formed from chemically sensitive reflections produce a real space map of (highly) local chemistry.
Long period superlattices

Figure 16.8. (A) Artificial GaAs/Al$_x$Ga$_{1-x}$As structure in which order is created by alternating four layers of GaAs and four of (Al$_x$Ga$_{1-x}$)As. (B) DP showing three superlattice spots between the fundamental reflections in the 020 direction.

Figure 16.9. (A) Artificial superlattice of Si and Mo layers \( \sim 5 \text{ nm} \) thick (B) Expanded DP around 000 showing many superlattice spots (arrowed). The large spacing of the superlattice in real space results in very small spacing of the superlattice reflections in the DP in reciprocal space. Compare with Figure 16.8.