Announcement

Midterm Exam: Oct. 22, Wednesday, 2:30 – 4:30
The excitation error, $s$

• Bragg's Law and the Laue equations predict diffraction at only precise Bragg angles for an infinite crystal. Many diffraction experiments (especially in TEM) are carried out on specimens which are thin in at least one dimension.

• The effect of small dimensions is to allow diffraction over a range of angles close to the Bragg angle. This has the same effect as if the relative reciprocal lattice points (relpoints as shown in figure (a)) were stretched out in the direction of thinness of the sample. *The streaked reciprocal lattice points are now called relrods (figure b).*

• Why we still see diffraction, when the Bragg’s condition is not exactly satisfied?
The excitation error

The deviation parameter, $s$

- The Ewald sphere can intersect with a relrod even when it misses the actual reciprocal lattice point. Diffraction, at reduced intensity, can then still occur. The deviation parameter, $s$, defines how close a particular relrod is to the Ewald sphere. If we allow streaking, the diffraction vector $K$ is then given by vectorially adding the deviation parameter $s$ to the reciprocal vector $g$, so:

$$K = g + s$$

- The deviation parameter is defined to be positive in the direction of the beam (downwards) and negative if it points upwards as shown in figure b.
- The vector, $s$, is a measure of how far we deviate from the exact Bragg condition.
The excitation error

The deviation parameter, $s$

- In reciprocal space, the diffraction vector $\mathbf{K}$ is given by: $\Delta \mathbf{K} = \mathbf{k}_D - \mathbf{k}_I$

- A diffracted beam only arises when $\Delta \mathbf{K} = \mathbf{g}$ i.e. it is a vector between reciprocal lattice points. If we allow streaking of reciprocal lattice points, then the diffraction vector is given by:
  $$\Delta \mathbf{K} = \mathbf{g} + s$$

- In a thin crystal, diffraction may be thus be seen from a particular set of incident beam angles close together (not just a single angle), and/or a range of crystal orientations. The effect of streaking is that lattice points which do not touch Ewald's sphere but are close, can still give diffracted beams. However, they will have a reduced beam intensity. The intensity of the diffracted beam varies with the value of the deviation parameter $s$ as shown in figure b
Kinematical Theory of Electron diffraction

• Describing the angular dependence of the diffracted wave, $\psi(\Delta K)$, emitted from different arrangements of atoms.

• Explaining how a translationally-periodic arrangement of atom in a crystal permits strong constructive interference between individual wavelets, creating the Bragg diffractions.

• Assumption of kinematical theory is that the incident wave is scattered elastically coherently by individual atoms.

• Kinematical theory can be used to calculate the structure factor of the unit cell. For electron diffraction contrast from larger features such as crystal shapes and crystalline defects, kinematical theory is usually qualitative.

• Kinematical theory is more quantitative for X-ray diffraction because X-ray scattering is much weaker than electron diffraction.

• Quantitative results of strong electron diffraction require the dynamical theory, which will not be discussed in detail in this class. Check the textbook for more information about dynamic theory.
Electron diffraction from a material

\[ \frac{h^2}{8\pi m_0 e} \nabla^2 \psi(r') + [E - V(r')] \psi(r') = 0 \]

The incident electron wave inside the scattering atom satisfies the time-independent Schrödinger equation.

\( h \): Planck constant,
\( m_0 \): stationary electron mass,
\( r' \): atom coordinate
\( E \): potential of electron
\( V \): potential of material

Wave-vectors and position vectors for electron scattering

Detector
If the wave is undiminished and scattered only once by atom (this assumption is valid when the scattering is weak). We have the **first Born approximation solution**:

\[
\psi(r) = e^{2\pi i k_0 \cdot r} - \frac{2\pi m_0}{\hbar^2} \int \left( \psi^{'}\left( \frac{r'}{r} \right) \right) \cdot e^{-2\pi i \Delta k \cdot r'} d^3 r'
\]

So the scattered part of the wave is

\[
\psi_{\text{scatt}}(r) = \frac{e^{2\pi i k_0 \cdot r}}{f\left( \Delta k \right)}
\]

\[
f\left( \Delta k \right) = -\frac{2\pi m_0}{\hbar^2} \int \left( \psi^{'}\left( \frac{r'}{r} \right) \right) \cdot e^{-2\pi i \Delta k \cdot r'} d^3 r'
\]
The scattered part of the wave

\[ \psi(r) = \frac{e^{2\pi i \mathbf{k}_0 \cdot r}}{r} \cdot f(\Delta \mathbf{k}) \]

\[ f(\Delta \mathbf{k}) = -\frac{2\pi m_0}{\hbar^2} \int V(r') e^{-2\pi i \Delta k \cdot r'} d^3 r' \]

• \(f(\Delta \mathbf{k})\) is the scattering factor. **The scattered wave is proportional to the Fourier transform of the scattering potential.**

• we will simply this term to apply it.
\[
\psi(\Delta \vec{k}) = \sum_{\vec{r}_g} e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_g} \cdot \sum_{\vec{r}_k} f_{at}(\vec{r}_k) \cdot e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_k}
\]

\[
\psi(\Delta \vec{k}) = S(\Delta \vec{k}) \cdot F(\Delta \vec{k})
\]

\[
S(\Delta \vec{k}) = \sum_{\vec{r}_g} e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_g} \quad \text{shape factor}
\]

\[
F(\Delta \vec{k}) = \sum_{\vec{r}_k} f_{at}(\vec{r}_k) e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_k} \quad \text{structure factor}
\]
So, bcc structure factor ruler: The sum of the three integers \( h, k, l \) must be an even number.

For example, bcc W, the lowest-order allowed diffractions are \((110), (200), (211), (220), (310), (222), (321), (440), (330), (411), (420), \) etc., but diffractions such as \((100), (111), (210), \) etc. are forbidden.

This rule applies to the other centered lattice: body centered, thorhombic, and body centered tetragonal.
Only real part determines the structure factor in below equation, if the term $\Delta \mathbf{k} \cdot \mathbf{r}_k$ is integer for crystal

$$F(\Delta \mathbf{k}) = \sum_{\mathbf{r}_k} f_{at}(\mathbf{r}_k) e^{-2\pi i \Delta \mathbf{k} \cdot \mathbf{r}_k}$$

structure factor

$\mathbf{g} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$

$\mathbf{r}_k = x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c}$

$\mathbf{r}_k$ is a vector which defines the location of each atom within unit cell, then we can write structure factor as:

$$F_{hkl} = \sum_i f_i e^{2\pi i (hx_i + ky_i + lz_i)}$$

For same atom in unit cell, $f_i$ has identical value
\[
F_{hkl} = \sum_{i} f_i e^{2\pi i (hx_i + ky_i + lz_i)}
\]

For bcc crystal: the lattice points includes (0,0,0), (1/2,1/2,1/2)

\[
F_{bcc} = \sum_{i} f_i e^{2\pi i (hx_i + ky_i + lz_i)}
= f \left\{ 1 + e^{\pi i (h+k+l)} \right\}
\]

- \(F_{bcc} = 2f\) if \(h + k + l\) is even
- \(F_{bcc} = 0\) if \(h + k + l\) is odd

For fcc factor rule: the three integers \(h,k,l\) must be all even or all odd. For example, the lowest –order diffractions are (111), (200), (220), (311), (222), (400), (331), (420), but other diffractions such as the (100), (110), (210), (211), etc. are forbidden.
Superlattice Diffractions

Applying the bcc analysis to B2 structure such as NiAl intermetallics

For B2 structure, the atom in the center is different from atoms at corner. For NiAl, Al is in center, and Ni is in corner.

So, Ni basis is (0,0,0), and Al basis is (1/2,1/2,1/2)

Then

\[ F_{NiAl} = \sum_{i} f_i e^{2\pi i (hx_i + ky_i + lz_i)} \]

\[ = f_{Ni} e^{2\pi i (h0 + k0 + l0)} + f_{Al} e^{2\pi i \left( \frac{1}{2} + \frac{1}{2} + \frac{1}{2} \right)} \]

\[ = f_{Ni} + f_{Al} e^{\pi i (h+k+l)} \]

\[ F_{NiAl} = f_{Ni} + f_{Al} \text{ if } h + k + l \text{ is even} \]

\[ F_{NiAl} = f_{Ni} - f_{Al} \text{ if } h + k + l \text{ is odd} \]

Instead of zero diffracted intensity, the (100) diffracted from B2-ordered NiAl has an intensity proportional to:

\[ I(100) \propto \left| f_{Ni} - f_{Al} \right|^2 \text{ weak} \]
On the other hand, the allowed diffractions from bcc crystal, the “fundamental diffractions”, e.g. the (200), have intensity:

\[ I(200) \propto |f_{Ni} + f_{Al}|^2 \text{ strong} \]

The (100) diffraction is called a “superlattice diffraction”. It reflects the periodicity of sc lattice upon which B2 structure is constructed using a basis of two different atoms.
B2-NiAl super-lattice (001) diffraction pattern
Crystal Shape factor

\[
S(\Delta k) = \sum_{r_g} e^{-2\pi i \Delta k \cdot r_g} \quad \text{shape factor}
\]

\[
F(\Delta k) = \sum_{r_k} f_{at}(r_k) e^{-2\pi i \Delta k \cdot r_k} \quad \text{structure factor}
\]

For very large crystals, the shape factor gives little information about the crystal shape, and is not very interesting, e.g. for sc crystal:

\[
\psi(\Delta k) = S_{sc}(\Delta k) F_{sc}(\Delta k) = Nf_{at}(\Delta k)
\]

\[
I_{scatt} = \psi \cdot \psi^* = |f_{at}|^2 \cdot N^2
\]

So for very large crystal, the shape factor intensity becomes infinitely high and infinitesimally narrow.

The shape factor is most interesting for small crystals.
Crystal Shape factor

\[ S(\Delta \vec{k}) = \sum_{\vec{r}_g} e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_g} \]

For convenience, we sacrifice some generality by assuming that the small crystal is a rectangular prism with \( N_x, N_y, \) and \( N_z \) unit cells along the direction as shown in figure.

An thin-foil specimen modeled as a rectangular slab made up of rectangular unit cells of sides \( a, b, c \). There are \( N_x \) cell in the \( x \) direction, \( N_y \) cell in the \( y \) direction, and \( N_z \) in the \( z \) direction.

Let

\[ \vec{r}_n = n_x \vec{a} + n_y \vec{b} + n_z \vec{c} \]

\[ n_x = 0,1,\ldots,N_x-1 \]

\[ n_y = 0,1,\ldots,N_y-1 \]

\[ n_z = 0,1,\ldots,N_z-1 \]
The intensity of scattered wave \( \psi_{\text{scatt}} \), \( I \)

\[
I = |\psi_{\text{scatt}}|^2 = F^2 \left( \frac{\sin^2(\pi N_x \Delta k \hat{a})}{\sin^2(\pi \Delta k \hat{a})} \right) \left( \frac{\sin^2(\pi N_y \Delta k \hat{b})}{\sin^2(\pi \Delta k \hat{b})} \right) \left( \frac{\sin^2(\pi N_z \Delta k \hat{c})}{\sin^2(\pi \Delta k \hat{c})} \right)
\]

when \( \Delta k \hat{a} = \text{integer} \), This is the Laue condition and the intensity is a maximum \( I \rightarrow F^2 \cdot N^2 \)

when

\[
\pi N_x \hat{a} = \frac{\pi}{2} n, \text{ n is an integer,......}
\]

\[
\hat{a} = \frac{n}{2N_x}, \hat{b} = \frac{n}{2N_y}, \hat{c} = \frac{n}{2N_z}
\]

• This leads to the rel-rodd idea
• There are subsidiary maxima or minima for \( I \) as shown in figure
Deviation vector ($\mathbf{s}$): thin-foil effect

\[ \Delta k = g + s \]

or

\[ g = \Delta k - s \]

\[ s = s_a \, a + s_b \, b + s_c \, c \]

and

\[
S\left(\Delta \mathbf{k}\right) = \sum_{\mathbf{r}_g} \text{lattice} \, e^{-2\pi i \Delta \mathbf{k} \cdot \mathbf{r}_g}
\]

shape factor

\[
F\left(\Delta \mathbf{k}\right) = \sum_{\mathbf{r}_k} \text{basis} \, f_{at}\left(\mathbf{r}_k\right) e^{-2\pi i \Delta \mathbf{k} \cdot \mathbf{r}_k}
\]

structure factor

and noting that $g \cdot r_g = \text{integer}$
\[ S\left( \Delta \vec{k} \right) = \sum_{\vec{r}_g} \text{lattice} \ e^{-2\pi i \vec{k} \cdot \vec{r}_g} \]

\[ = \sum_{\vec{r}_g} \text{lattice} \ e^{-2\pi i \vec{g} \cdot \vec{r}_g} = \sum_{\vec{r}_g} \text{lattice} \ -2\pi i \left( \vec{g} + \vec{s} \right) \cdot \vec{r}_g \]

\[ = \sum_{\vec{r}_g} \text{lattice} \ e^{-2\pi i \text{integer}} e^{i2\pi \vec{s} \cdot \vec{r}_g} = \sum_{\vec{r}_g} \text{lattice} \ e^{i2\pi \vec{s} \cdot \vec{r}_g} \]

\[ \therefore \quad S\left( \Delta \vec{k} \right) = S\left( \vec{s} \right) \]

The shape factor depends only on \( \vec{s} \) not \( \vec{g} \)
The structure factor depends only on $\mathbf{g}$. Consider a bcc crystal

$$F(\Delta \mathbf{k}) = \sum_{a(000), a(\frac{111}{222})}^{2 \text{ term}} f_{at}(r_k, \Delta \mathbf{k}) e^{-2\pi \mathbf{g} \cdot r_k} \cdot e^{-2\pi s \cdot r_k}$$

$$= f_{at}(0, g) e^0 e^0 + f_{at}(\frac{111}{222}, g) e^{2\pi(h+k+l)/2} e^{2\pi(s_m+s_b n+s_c o)/2}$$

For a bcc crystal if

$h + k + l = \text{odd number}$

$$F(\Delta \mathbf{k}) = f_{at}(g) \left(1 + e^{i\pi(s_m+s_b n+s_c o)}\right) \approx 0$$

if $h + k + l = \text{even number}$

$$F(\Delta \mathbf{k}) = f_{at}(g) \left(1 + e^{i\pi(s_m+s_b n+s_c o)}\right) \approx 2f_{at}(g)$$

$$\therefore F(\Delta \mathbf{k}) = F(\mathbf{g})$$
The shape factor depends only on \( s \) not \( g \). The diffracted intensity is not a constant for any position along the rel-rod.

The intensity of scattered wave \( \psi_{\text{scatt}} \), \( I \)

\[
I = \left| \psi_{\text{scatt}} \right|^2 = F^2 \left( \frac{\sin^2(\pi N_x s \ a)}{\sin^2(\pi s \ a)} \right) \cdot \left( \frac{\sin^2(\pi N_y s \ b)}{\sin^2(\pi s \ b)} \right) \cdot \left( \frac{\sin^2(\pi N_z s \ c)}{\sin^2(\pi s \ c)} \right)
\]

This is the kinematical intensity distribution about any reciprocal lattice point. The intensity is proportional to \( N^2 \) whenever \( s=0 \). If the crystal has a uniform thickness (no variation in \( N_x \) for example), the intensity equation shows there are maxima and minima in the diffraction intensity with increasing value of \( |s| \).
The rel-rod at $g_{hkl}$ when the beam is $\Delta \theta$ away from the exact Bragg condition. The Ewald sphere intercepts the relrod at negative value of $s$ which defines the vector $\Delta K = g + s$. The intensity of the diffracted beam as a function of where the Ewald sphere cuts the rel-rod is shown on the right of the diagram. In this case, the intensity has fallen almost zero.
Application of shape factor, $S (\Delta k)$

1. Diffraction from wedge-shaped specimens

Figure shows diffraction from a wedged crystal.

- Rel-rod is always normal to the surface.
- when $s > 0$, the two rel-rods (rel-1 and rel-2) generate a doublet. Rel-1 spot is on the left. The middle is the matrix rel-rod.
Application of shape factor
1. Diffraction from wedge-shaped specimens

Figure shows diffraction from a wedged crystal.
• Rel-rod is always normal to the surface.
• when \( s<0 \), the two rel-rods (rel-1 and rel-2) generate a doublet. Rel-1 spot is on the right. The middle is the matrix rel-rod.
Application of shape factor

1. Diffraction from wedge-shaped specimens

Since the length of rel-rods is inversely proportional to the specimen thickness, the thinner the specimen, the more diffraction spots will occur in the pattern. As shown in the figure, a series of diffraction patterns were taken from a wedged crystal sample. The number of diffraction spots decreases as the thickness of the specimen increases.
Application of shape factor

2. Diffraction from planar defects

The effect of a thin inclined plate in a foil.

- When $s=0$, and there is no plate, we only see one spot in DP (diffraction pattern) because there is one rel-rod.
Application of shape factor
2. Diffraction from planar defects

The effect of a thin inclined plate in a foil.
- When $s=0$, and there is no plate, we only see one spots in DP (diffraction pattern) because there is one rel-rods.
- When $s<0$, and there is a plate, we see two spots because there are two rel-rods.
Application of shape factor

3. Diffraction from particles

The principles in determining the shape factor intensity distribution for various particles or crystals are simply "small becomes large" and vice versa.

These rel-rod shapes also approximately reflect the diffraction intensity distribution.
Application of shape factor

3. Diffraction from particles

Examples of how spots in reciprocal space have different shapes, depending on the particles which are diffracting.

The principles in determining the shape factor intensity distribution for various particles or crystals are simply “small becomes large” and vice versa.

These rel-rod shapes also approximately reflect the diffraction intensity distribution.

Diffuse scattering
Application of shape factor

4. Diffraction from thin crystalline plates which is parallel to the electron beam

(a) Schematic representation of the specimen showing the precipitates, thin crystalline plates, are parallel to the electron beam.

(b) The corresponding diffraction pattern shows the long streaks (diffuse scattering) caused by these thin plate-like particles.
Application of shape factor

5. Diffraction from finely twin structure which is normal to the electron beam

Fig. a shows finely twinned martensitic Co$_2$NiGa foil. The twin structure divides the crystal space into separate regions with varying widths, and thereby will give rise to some sort of streak in diffraction pattern. The direction of streak is, of course, perpendicular to the twin planes.

Fig. b shows the corresponding zone axis diffraction pattern. The streaks are normal to the twin planes. Each reciprocal lattice point has two pairs of modulation satellites, which also give rise to streaks.
HW#13: A precipitate has the shape of a tetrahedron with length of $a$ as shown below. What should be the shape of the diffuse scattering around the fundamental diffractions (i.e. the rod shape)? Sketch it as precisely as possible, and indicate the length in reciprocal space corresponding to $AB$ in real-space. Note that $AB=BC=AC=OC=a$

Due: Oct. 15/08