Bragg Law

\[ 2d_{hkl} \sin \theta = n\lambda \]
Equations connecting the Crystal Parameters \((h, k, l)\) and \(d\)-spacing with beam parameters \(\lambda\)

\[
n\lambda = 2d_{hkl} \sin \theta
\]

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

- \(d\) = Interlayer spacing of Atoms
- \(n=1\). This is also Index
- \(\lambda\) = Wavelength in nm
- \(a\) = Lattice parameter (nm)
- \((h k l)\) = Crystal Plane or Miller Indices
Mathematical definition of the reciprocal lattice

\[ \tilde{g}_{hkl} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^* \]

\[ d_{hkl} = \frac{1}{|\tilde{g}_{hkl}|} \]

where

- \( a^* b = a^* c = b^* a = b^* c = c^* b = c^* a = 0 \), i.e. \( a^* \) is normal to both \( b \) and \( c \), etc.
- \( a^* a = b^* b = c^* c = 1 \), only for cubic \( a^* \), \( b^* \), \( c^* \) are parallel to \( a, b, c \).

Just as \( a, b, \) and \( c \) need not be normal one another, \( a^*, b^*, \) and \( c^* \) also not necessarily normal one another.
Laue Condition: diffraction process in terms of scattering by individual atoms

As shown in Figure (b), diffraction occurs when $\mathbf{K}$ is a vector the reciprocal lattice ($\mathbf{g}_{hkl}$), i.e. $\mathbf{K} = \mathbf{K}_D - \mathbf{K}_I = \mathbf{g}_{hkl}$

(a) Reflection at the Bragg angle $\theta$ from crystal planes

(b) The vector diagram (vector triangle) describing the diffraction process

\[ \mathbf{K} = \mathbf{g}_{hkl}, \quad |\mathbf{K}| = \frac{1}{d_{hkl}} \]

and \[ |\mathbf{K}_I| = |\mathbf{K}_D| = \frac{1}{\lambda} \]
Construction of the Ewald's sphere, cont'

- Construct a circle with radius $1/\lambda$ (i.e. $|k_i|$), which passes through 0, (c).
- Wherever a rel-point touches the circle, Bragg's Law is obeyed and a diffracted beam will occur, (d).
- CO represents the incident beam and CG is a diffracted beam. The angle between them must be $2\Theta$.
- OG is the $g_{hkl}$ vector and thus has magnitude $1/d_{hkl}$, and since $|k| = 1/\lambda$.
- $OG = 2 \times (1/\lambda)\sin \Theta = 1/d_{hkl}$, rearranging this gives Bragg's equation with $n = 1$:
  $$n\lambda = 2d\sin \Theta$$
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 $K$ is given by: $K = k_D - k_I$

- A diffracted beam only arises when $K = g$, 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: $K = g + s$

- 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.
Learning Objectives:

After completing this section you should be able to:
• explain why non-primitive unit cells give rise to variations in the intensity of diffraction spots from different planes;
• predict which forbidden reflections for any non-primitive crystal structure;
• and write down the forbidden reflections for basic structures.
Intensity of diffraction

In structures with non-primitive cells, *scattering* from one atom in the cell can interfere with scattering from another to reduce or increase the intensity of diffraction.

Different diffraction intensity and diffraction patterns due to different structures of specimens
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:

\( \Delta K = K - K_0 \)

Detector

\( K_0 \)

\( K \)

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

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:

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

So the scattered part of the wave is

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

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

\[ \psi(r) = e^{2\pi i k_0 \cdot r} \left( \frac{\Delta \hat{k}}{|r|} \right) \cdot f(\Delta \hat{k}) \]

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

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

\[
f\left(\Delta k\right) = -\frac{2\pi n_0}{\hbar^2} \int V\left(\vec{r}'\right) \cdot e^{-2\pi i \Delta k \cdot \vec{r}'} d^3 \vec{r}' \\
V\left(\vec{r}'\right) = \sum_{R_j} V_{at}\left(\vec{r}' - R_j\right)
\]

Note that whenever \(\vec{r}' = R_j\), one of terms of \(V\) is \(V\) at (0), and the potential \(V (\vec{r}')\) gets a strong contribution from atom centered at \(R_j\)

Define a new coordinate: \(\vec{r} = \vec{r}' - R_j\)

Therefore, we can change the exponentials from full phase factors of independent wavelets into relative phase factors of wavelets from the different atoms, substitute the new coordinate into above equation
Only consider scattered wave inside the material (crystal), leave out the factor

\[ \frac{2\pi k_0 \cdot r}{r} \]

\[ \psi(\Delta \vec{k}) = -\frac{2\pi m_0}{\hbar^2} \int \sum_{R_j} V_{at,R_j}(\vec{r}) \cdot e^{-2\pi i \Delta k \cdot (\vec{r} + \vec{R})} d^3\vec{r} \]

\[ \psi(\Delta \vec{k}) = \sum_{R_j} \left( -\frac{2\pi m_0}{\hbar^2} \int V_{at,R_j}(\vec{r}) \cdot e^{-2\pi i \Delta k \cdot \vec{r}} d^3\vec{r} \right) \cdot e^{-2\pi i \Delta k \cdot \vec{R}_j} \]

Define single atomic factor for electron scattering

\[ f_{el}(\vec{R}, \Delta \vec{k}) = -\frac{2\pi m_0}{\hbar^2} \int V_{at,R_j}(\vec{r}) \cdot e^{-2\pi i \Delta k \cdot \vec{r}} d^3\vec{r} \]
Considering $\Delta K$ is very small, we treat $f_{el}$ as a number only depending on the type of atom located at $R_j$. So the scattered wave from $N$ atoms is written most simply as

$$\psi(\Delta \vec{k}) = \sum_{j}^{N} f_{el}(R_j) \cdot e^{-2\pi i \Delta k \cdot \vec{R}_j}$$

The diffracted wave is proportional to the Fourier transforms of the scattering factor distribution in the material.
Diffraction from a lattice with a basis

In both real space and in reciprocal space, it is useful to divide a crystal composed of atoms at locations $r$ into parts according to prescription:

**Crystal**= lattice + basis + defect displacements

$$r = r_g + r_k + \delta r_{g,k}$$

The lattice is one of the 14 Bravais lattice type.

The crystal typically has numerous unit cells on its lattice and numerous $r_g$

The basis is the atom group associated with each lattice site, the unit cell typically has a few $r_k$

For example, bcc structure $\{r_k\} = \{(0,0,0), (1/2,1/2,1/2)\}$

$\{r_g\} = \{m,n,l\}$, any integers

For a defect-free crystal, the atom positions, $R$, are provided by vector to each unit cell

$$R = r_g + r_k$$
Diffraction from a lattice with a basis

So the scattered wave for the case of an infinitely large, defect-free lattice with a basis

\[
\psi(\Delta \mathbf{k}) = \sum_{R} f_{at}(\mathbf{R}) \cdot e^{-2\pi i \Delta \mathbf{k} \cdot \mathbf{R}}
\]

\[
\mathbf{R} = \mathbf{r}_g + \mathbf{r}_k
\]

\[
\psi(\Delta \mathbf{k}) = \sum_{\mathbf{r}_g} \sum_{\mathbf{r}_k} f_{at}(\mathbf{r}_g + \mathbf{r}_k) \cdot e^{-2\pi i \Delta \mathbf{k} \cdot (\mathbf{r}_g + \mathbf{r}_k)}
\]

The atom basis is identical for all unit cells, \( f_{at}(\mathbf{r}_g + \mathbf{r}_k) = f_{at}(\mathbf{r}_k) \)
\[ \psi(\Delta \vec{k}) = \sum_{\vec{r}_g} e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_g} \cdot \sum_{\vec{r}_k} f_{at}(\vec{r}_k) \cdot e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_k} \]

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

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

\[ F(\Delta \vec{k}) = \sum_{\vec{r}_k} f_{at}(\vec{r}_k) e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_k} \quad \text{structure factor} \]
Since the structure factor of unit cell is identical for all lattice points, it is usually convenient to write the diffracted wave as:

\[ \psi(\Delta k) = \sum_{r_g}^\text{lattice} f_{at}(r_k) e^{-2\pi i \Delta k \cdot r_g} \]

The intensity of the diffracted wave at detector, I, is the product of the wave-function with its complex conjugate:

\[ I_{\text{diff}}(\Delta k) = \psi(\Delta k) \cdot \psi(\Delta k)^* \]
Structure factor rules

1. Structure factor for sc lattice

For a sample cubic (sc) lattice, we can show easily that strong diffraction occurs for any integer combination, \((h,k,l)\).

A general sc reciprocal lattice vector, \(g\),

\[
g = h a^* + k b^* + l c^*
\]

For atoms located on the sites of a simple cubic lattice:

\[
\{ \vec{r}_g \} = \{ m \vec{a} + n \vec{b} + o \vec{c} \}
\]

and

\[
\{ \vec{r}_k \} = \{ 0 \vec{a} + 0 \vec{b} + 0 \vec{c} \}
\]
Structure factor rules

According to Laue condition, the strong diffraction occurs at $\Delta \mathbf{K} = \mathbf{g}$

\[ g \cdot r_g = \left( h \hat{a}^* + k \hat{b}^* + l \hat{c}^* \right) \cdot \left( m \hat{a} + n \hat{b} + o \hat{c} \right) \]

\[ g \cdot r_g = hm + kn + lo = \text{integer} \]

for any integer $h, k, l$

and

\[ g \cdot r_k = \left( h \hat{a}^* + k \hat{b}^* + l \hat{c}^* \right) \cdot \left( 0 \hat{a} + 0 \hat{b} + 0 \hat{c} \right) = 0 \]
Therefore, when the Laue condition, $\Delta k = g$, is satisfied for the simple cubic lattice:

$$S(\Delta \vec{k}) = \sum_{\vec{r}_g = 0}^{N-1} e^{-2\pi i \text{integer}} = \sum_{\vec{r}_g = 0}^{N-1} 1 = N$$

$$F(\Delta \vec{k}) = \sum_{\vec{r}_k = (000)}^{1 \text{term}} f_{at}(\vec{r}_k) e^{-2\pi i \Delta \vec{k} \cdot \vec{r}_k} = f_{at}(0)e^{-0} = f_{at}(\Delta \vec{k})$$

The scattered wave is

$$\psi(\Delta \vec{k}) = S_{sc}(\Delta \vec{k}) F_{sc}(\Delta \vec{k}) = N f_{at}(\Delta \vec{k})$$

For sc crystal, any crystal (hkl) produces the strong diffraction
For bcc crystal, 

There are two basis vectors, \( \mathbf{r}_{k1} \) and \( \mathbf{r}_{k2} \):

\[
\{ \mathbf{r}_k \} = \{(0,0,0), (1/2, 1/2, 1/2)\}
\]

The lattice is

\[
\{ \mathbf{r}_g \} = \{m, n, l\}, \text{ any integers}
\]

According to Laue condition, the strong diffraction occurs at \( \Delta \mathbf{K} = \mathbf{g} \)

\[
F_{bcc}(\Delta \mathbf{k}) = \sum_{\mathbf{r}_{k1}, \mathbf{r}_{k2}} f_{at}(\mathbf{r}_k) e^{-2\pi i \Delta \mathbf{k} \cdot \mathbf{r}_k}
\]

\[
\Delta k \cdot \mathbf{r}_{k1} = g \cdot \mathbf{r}_{k1} = h0 + k0 + l0 = 0
\]

\[
\Delta k \cdot \mathbf{r}_{k2} = g \cdot \mathbf{r}_{k2} = h \frac{1}{2} + k \frac{1}{2} + l \frac{1}{2}
\]

\[
\therefore \quad F_{bcc}(\Delta \mathbf{k}) = f_{at}(0) \cdot e^0 + f_{at}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) e^{-i2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l\right)}
\]
The structure factor takes on two values depending on whether the sum \(h+k+l\) is odd or even:

\[
F_{bcc}(\Delta \vec{k}) = f_{at}(0) \cdot e^0 + f_{at}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})e^{-i2\pi \cdot \frac{N}{2}}
\]

\[
= f_{at}(0) - f_{at}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \text{N = h + k + l is odd number}
\]

\[
F_{bcc}(\Delta \vec{k}) = f_{at}(0) + f_{at}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})e^{-i2\pi \cdot N}
\]

\[
= f_{at}(0) + f_{at}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), N = h + k + l \text{ is even number}
\]
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

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

$\mathbf{r}_k$ 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
For bcc crystal: the lattice points includes (0,0,0), (1/2,1/2,1/2)

\[ F_{b_{cc}} = \sum_i f_i e^{2\pi i (hx_i + ky_i + lz_i)} \]

\[ = f \left\{ 1 + e^{\pi i (h+k+l)} \right\} \]

\[ F_{b_{cc}} = 2f \quad \text{if } h + k + l \text{ is even} \]

\[ F_{b_{cc}} = 0 \quad \text{if } h + k + l \text{ is odd} \]

HW#11: Prove the 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.

Due day: 10/13/08
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:

\[
I(100) \propto \left| f_{Ni} - f_{Al} \right|^2 \text{ weak}
\]

B2-NiAl unit cell

Ni

Al

B2-NiAl unit cell
\[ F_{\text{NiAl}} = \sum_i f_i e^{2\pi i (hx_i + ky_i + tz_i)} \]

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

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

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

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

On the other hand, the allowed diffractions from bcc crystal, the “fundamental diffractions”, e.g. the (200), have intensity:

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

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
So to obtain the superlattice diffractions of an ordered structure, first locate the fundamental diffraction of underlying lattice (ignore the atom type), e.g. Ni in above example. Next locate the diffractions from a modified lattice where one species of atoms is removed, e.g. Al in above example. The unit cell is now larger, so there are more diffractions. The superlattice diffraction occur at the locations of the new diffractions of this modified lattice.

HW#12: Fe3AlC phase in Fe-C-A system has a cubic structure: Al is corner, C is in the cubic center, and Fe is in the center of each face.

1. Derive an expression for the structure factor in terms of \( f_{\text{Al}} \), \( f_{\text{Fe}} \), and \( f_{\text{C}} \)

2. Sketch the (100)* section of the reciprocal structure for this Fe3AlC phase, labeling the low index diffractions and indicating relative intensities.

Due: 10/13/08