Diffraction theory: Bragg's Law

Diffraction space:

Crystal lattice <-> Reciprocal lattice

Crystal <-> Diffraction pattern of crystal

Unit cell contents <-> Structure factors
Concept of diffraction (from a plane)

Cone of diffraction

Crystal

X-rays

Plane in crystal (real space)

Detector (reciprocal space)

Nature of scattering (diffraction):

Wavelength
Source (origin)

F(000) direct wave
Coherent scattering of X-rays by atoms:

When X-rays interact with atoms, the rapidly oscillating electric field of the radiation sets the electrons of the atoms into oscillation about their nuclei. This oscillation has the same wavelength as that of the incident radiation. The result is that the electron acts as an oscillation dipole that serves as a source of the secondary radiation.

Atomic scattering factors:
Since X-rays are scattered by electrons, the amplitude of the wave scattered by an atom is proportional to how many electrons there are around the atom. That is the atomic number $Z$. Atomic scattering factors $f_i$ are expressed as the ratio of scattering of an atom to the scattering by a single electron under the same condition.
Braggs Law:

Direction and indices of beams

In 1913, Bragg showed that scattered radiation from a crystal behaves as if the diffracted beam were “reflected” from a plane passing through points of the crystal lattice in a manner that makes these crystals-lattice planes analogous to mirrors.

Geometry of diffraction:

Braggs Law

Consider two waves (A,B) and their path length difference for constructive interference.

\[ \sin \theta = \frac{1}{2} \frac{PD}{d_{hkl}} \]

\[ PD = 2d_{hkl} \sin \theta \]
Fourier series:
Fourier showed that even the most complex periodic functions can be described as a sum of simple sine and cosine functions whose wavelengths are integral fractions of the wavelength of the complicated function.

\[ f(x) = a_0 + a_1 \cos \frac{2\pi}{h}(x) + a_2 \cos \frac{2\pi}{2}(2x) + \ldots + a_h \cos \frac{2\pi}{h}(hx) \]

\[ + b_1 \sin \frac{2\pi}{h}(x) + b_2 \sin \frac{2\pi}{2}(2x) + \ldots + b_h \sin \frac{2\pi}{h}(hx) \]

General one-dimensional Fourier

\[ f(x) = a_0 + \sum_{h=1}^{h} (a_h \cos \frac{2\pi}{h}(hx) + b_h \sin \frac{2\pi}{h}(hx)) \]

where \( h \) is an integer, \( a_h \) and \( b_h \) are constants, and \( x \) is a fraction of a period

Contributions to terms in a Fourier synthesis:

Individual terms:
(Bragg reflections)
0,0,0 to 10,0,0 (h,k,l)

Combined terms:
to give function
(Electron density)

Comments:
Importance of phase
Missing terms (800)
Calculating an Electron density map: 
Summation of scattering factors:

Hence for each Bragg reflection all electrons in the unit cell contribute to the resultant diffracted wave

\[ F_{hkl} = \sum f_{\text{atoms}} \quad \text{or} \quad \sum f_{\text{density}} \]

Electrons in the Bragg plane will have a larger resultant effect than those further away
And
Atoms with more electrons will have a larger effect than those with less

Fourier transforms

From reciprocal space to real space

\[ F(s) = F(\rho) \]

<table>
<thead>
<tr>
<th>Diffraction space</th>
<th>Electron density</th>
</tr>
</thead>
<tbody>
<tr>
<td>STRUCTURE FACTOR</td>
<td>ELECTRON DENSITY</td>
</tr>
</tbody>
</table>
Calculation of an electron-density map

Crystals precisely fits the definition of a periodic function
Hence we can combine Bragg reflections in a Fourier synthesis
to calculate an electron density map

\[ \rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} \left| F_{hkl} \right| \cos 2\pi \left( \frac{hx+ky+ lz - \alpha_{hkl}}{\lambda} \right) \]

\( \rho(x,y,z) \) electron density at a point \( x,y,z \) in a unit cell of volume \( V \)
\( F_{hkl} \) amplitude and \( \alpha_{hkl} \) phase angle of each
Bragg reflection \((h,k,l)\)

Assign:

The Bragg reflection \((h, k, l)\)
The \( F_{h,k,l} \) amplitude \( = \sqrt{I_{(h,k,l)}} \)
But cannot directly measure \( \alpha_{(h, k, l)} \) phase angle of each reflection