**Handout 7**
**Reciprocal Space**

Useful concepts for the analysis of diffraction data

http://homepages.utoledo.edu/clind/

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**Concepts versus reality**

- “Reflection from lattice planes” is just a concept that helps us to visualize what is happening in a diffraction experiment
- In reality, X-rays are scattered by the electrons in the atoms
  - X-ray wavelength is similar to size of electron cloud
  - a periodic crystal corresponds to a periodic variation in electron density
  - the scattering event leads to a phase change of 180°
- Neutrons are scattered by nuclei
  - nuclei are much smaller than the neutron wavelength
  - neutrons can also interact with magnetic moments in a material
Phase change on scattering

What do we actually measure?

- We measure the intensity distribution of scattered radiation as a function of scattering angle
  - for single crystals, we get 3D resolution
  - for powder experiments, all information is compressed into 1D

- The intensity distribution of scattered radiation is a result of the electron density distribution inside the crystal
  - the electron density distribution is the same in each unit cell
    ⇒ periodic array of electron density
Reciprocal space

- We do not see the periodic electron density directly during a diffraction experiment
  - we only observe the intensity distribution of X-ray scattering from the crystal(s)
- The diffraction intensity is correlated to the electron density in the crystal by a Fourier transform
  - often referred to as direct space and reciprocal space
- This means that we sample reciprocal space with our diffraction experiments
  - we can define a reciprocal lattice that corresponds to the direct (crystal) lattice

Real and reciprocal space

<table>
<thead>
<tr>
<th>CRYSTAL SPACE</th>
<th>DIFFRACTION SPACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal lattice ↔ reciprocal lattice</td>
<td></td>
</tr>
<tr>
<td>crystal</td>
<td>diffraction pattern of crystal</td>
</tr>
<tr>
<td>unit cell contents ↔ structure factors</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 3.11. Relationships between a crystal (in crystal space) and its reciprocal lattice (in diffraction space).  
The reciprocal lattice

◆ The reciprocal lattice has the same symmetry as the crystal lattice
◆ It can be derived from the crystal lattice graphically
  - draw lattice planes
  - pick an origin and draw normals to the lattice planes
  - mark points along the normals spaced d*(hkl) from the origin, where
    \[ d^*(hkl) = \frac{1}{d(hkl)} \]
◆ The reciprocal lattice constants a*, b* and c* are defined so that
  they correspond to d*(100), d*(010) and d*(001)
  - note that the direction of a*, b* and c* will only coincide with that of a, b
    and c if the crystal lattice has \( \alpha = \beta = \gamma = 90^\circ \)

The reciprocal lattice – graphical construction

“Structure Determination by X-ray Crystallography”,
Reciprocal lattice constants

◆ The mathematical definition of the reciprocal lattice constants is

- \( a^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \)
- \( b^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \)
- \( c^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \)

where \( \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = V \)
\( V = \text{volume of the unit cell} \)

◆ Alternative formulation:

- \( \mathbf{g}_i \cdot \mathbf{h}_j = \delta_{ij} \)

Scattering from a material

◆ Assumption: Incoming beam is a plane wave, phase change on scattering is identical for all rays

◆ According to vector algebra:

- \( \Delta l_1 = \mathbf{r} \cdot \mathbf{s}_0 \)
- \( \Delta l_2 = \mathbf{r} \cdot \mathbf{s} \)
- total path difference: \( \Delta l = \Delta l_2 - \Delta l_1 = \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0) \)
Scattering from a material (2)

- Define: Scattering vector
  \[ \mathbf{S} = \mathbf{s} - \mathbf{s}_0 \]
- The phase difference \( \phi \) is given by
  \[ \phi = 2\pi \frac{\Delta l}{\lambda} = \frac{2\pi}{\lambda} \mathbf{S} \cdot \mathbf{r} = \mathbf{K} \cdot \mathbf{r} \]
- The change in scattering amplitude, \( dA(s) \), is given by the phase difference and the electron density in the volume element \( dV_r \)
  \[ dA(s) = e^{-\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV_r \]
  \[ A(s) = \int_{V_r} e^{-\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV_r \quad \text{Fourier transform!} \]

The relationship between \( A \) and \( \rho \)

- The scattering amplitude, \( A(s) \), and the electron density, \( \rho(\mathbf{r}) \), are correlated by a Fourier transform
  \[ A(s) = \int_{V_r} e^{-\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV_r \quad \rho(\mathbf{r}) = \int_{V_r} e^{\mathbf{K} \cdot \mathbf{r}} A(s) dV_r \]
- Problem: We cannot measure \( A(s) \), but only the intensity \( I \), which is given by
  \[ I = A(s) \cdot \mathbf{A}^*(s) \]
- Note that these equations are valid for any material, we have not yet made any assumptions about periodicity!
Scattering from crystals

♦ To describe the electron density distribution in a crystal, we only need to describe it in one unit cell:

\[ \rho(r) = \rho(r_0 + \tau_1), \text{ where } \tau_1 = m_1a + m_2b + m_3c \]

♦ Over all space, this gives us

\[ A(s) = \int_{V_c} e^{-iK(r_0 + \tau_1)} \rho(r_0) dV_r \quad \text{or} \]

\[ A(s) = \left[ \int_{V_c} e^{-iK r_0} \rho(r_0) dV_r \right] \sum_{m_1} e^{-iK m_1a} \sum_{m_2} e^{-iK m_2b} \sum_{m_3} e^{-iK m_3c} \]

A crystal’s interference function

♦ The summation part in the formula for the scattering amplitude describes a crystal’s interference function:

\[ \sum_{m_1} e^{-iK m_1a} \sum_{m_2} e^{-iK m_2b} \sum_{m_3} e^{-iK m_3c} \]

remember that

\[ e^{-\frac{2\pi m_i \cdot S \cdot a}{\lambda}} = \cos\left(\frac{2\pi m_1 \cdot S}{\lambda} \cdot a\right) - i \sin\left(\frac{2\pi m_1 \cdot S}{\lambda} \cdot a\right) \]

♦ This will lead to reinforcement for

\[ a \cdot S = n_1\lambda \quad b \cdot S = n_2\lambda \quad c \cdot S = n_3\lambda \]

or, using unit vectors

\[ \begin{align*}
a \cdot S &= \frac{n_1}{a} & b \cdot S &= \frac{n_2}{b} & c \cdot S &= \frac{n_3}{c}
\end{align*} \]

Laue conditions!
A crystal’s interference function (2)

- Each of these conditions describes a family of planes spaced 1/a (1/b, 1/c) as a solution for $S$
  - for a one dimensional array of scatterers, the solutions are planes
  - for a two dimensional array, the solutions are lines
  - for a three dimensional array, the solution consists of points: The reciprocal lattice points

The Ewald sphere

- Remember that we defined
  \[ S = s - s_0 \]
  where $s$ and $s_0$ were unit vectors

- We can choose a frame of reference in which $s_0$ is fixed, and the end point of the vector $s_0/\lambda$ is the origin of reciprocal space

- This allows us to define an Ewald sphere, also known as sphere of reflection, with radius $1/\lambda$ around the crystal
Fulfilling four conditions

- The Ewald construction is also known as *wavelength condition*
- The three Laue conditions and the wavelength condition must be fulfilled simultaneously for diffraction to occur
- This means that a reciprocal lattice point must lie on the Ewald sphere for diffraction to occur
- Rotation of crystal is equivalent to rotation of reciprocal lattice

Bragg’s law in reciprocal space

- If we define the distance of a lattice point from the origin of reciprocal space as $d^*$, we get
  
  $$d^* = \frac{|\mathbf{s}|}{\lambda}$$

- We can also show that
  
  $$\frac{2\sin \theta}{|d^*|} = \lambda$$

- It follows that
  
  $$|d| = \frac{1}{|d^*|}$$
Calculating d-spacings

- The distance of reciprocal lattice points from the origin of the reciprocal lattice is given by

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

- \( h, k \) and \( l \) are the Miller indices

- By definition, \( d \) can be calculated from \( d^* \) by

\[ |d| = \frac{1}{|d^*|} \]

- Calculation is only straightforward for orthogonal crystal lattices

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**d-spacing formulae**

<table>
<thead>
<tr>
<th>System</th>
<th>( d^*(hkl) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>( \frac{h^2a^2 + k^2b^2 + l^2c^2 + 2hbk \cos \alpha + 2hl \cos \beta + 2kla \cos \gamma}{\sin \beta \sin \gamma} )</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( \frac{h^2a^2 + k^2b^2 + l^2c^2 + 2hka \cos \beta + 2hl \cos \alpha + 2kla \cos \gamma}{\sin \beta \sin \gamma} )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( \frac{h^2a^2 + k^2b^2 + l^2c^2}{a^2b^2c^2} )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( \frac{h^2a^2 + k^2b^2 + l^2c^2}{a^2b^2c^2} )</td>
</tr>
<tr>
<td>Hexagonal and trigonal (P)</td>
<td>( \frac{4(k^2a^2 + k^2b^2 + k^2c^2 + 2hk \cos \alpha \cos \beta \cos \gamma)}{(a^2b^2c^2)} )</td>
</tr>
<tr>
<td>Trigonal (R) (rhombohedral)</td>
<td>( \frac{4(k^2a^2 + k^2b^2 + k^2c^2 + 2hk \cos \alpha \cos \beta \cos \gamma)}{(a^2b^2c^2)} )</td>
</tr>
<tr>
<td>Cubic</td>
<td>( \frac{h^2a^2 + k^2b^2 + l^2c^2}{a^2b^2c^2} )</td>
</tr>
</tbody>
</table>

In the monoclinic system, \( a^0(001) = \sin \beta, d^0(001) = \sin \beta \), and hence \( d = K/\sin \beta \) and \( d^* = \sin \beta \).
In the hexagonal system (and trigonal P), \( a = \frac{a}{\sqrt{3}}, d = K/\sin \beta \).
In general, the expressions for \( d^* \) are simpler in form than the corresponding expressions for \( d^2 \).

Observations from single crystals and powders

- For a single crystal, there is one orientation in real space, resulting in one orientation of the reciprocal lattice
  - reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere
- A powder sample consists of many crystallites with random orientations
  - we get many overlapping reciprocal lattices, resulting in a “sphere” of reciprocal lattice points that fulfill the Bragg condition at a given 2θ
  - the sphere will intersect the Ewald sphere in a circle
  - we will observe “powder rings”

Powder diffraction rings


- If we assume an infinite number of randomly oriented crystallites, every point $P_n$ at distance $d^*$ from the origin of reciprocal space fulfills the Laue conditions