Basic Crystallography: Reciprocal Space (a Gentle Introduction)

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Introduction

• Notions of **reciprocal space** and the **reciprocal lattice** are indispensable for understanding X-ray Crystallography.

• Diffraction by a lattice gives a lattice as a diffraction pattern.

• There is a precise mathematical relationship between the original diffracting lattice and the resulting pattern.

• However, this is a (mostly) non-mathematical introduction to help you qualitatively understand the concepts of reciprocal space and the reciprocal lattice.
Direct Space & Reciprocal Space

- We live in direct space
- Distances and orientations between isolated objects
- Reciprocal space is a “spatial frequency” space (e.g. number of Tim Horton’s per kilometre)
- In NMR time and frequency are related by a Fourier transform (units: time $t$ and frequency $t^{-1}$)
- In X-ray Crystallography direct space and reciprocal space are related by Fourier transform (units: distance Å and spatial frequency Å$^{-1}$)
Bragg’s Law

- $n\lambda = 2d\sin\theta$
- Rewrite as:
  - $\sin\theta = 0.5n\lambda(1/d)$
- Reciprocal relationship between diffraction angle, $\theta$, and the $d$ spacing
- The smaller the $d$ spacing, the higher the diffraction angle
Reciprocal Quantities

- $1/d = d^*$
- $d^*$ is a reciprocal quantity and typically has units of Å$^{-1}$
- The ‘*’ in general means a reciprocal space quantity
- A direct space unit cell with parameters $a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$ has a corresponding reciprocal unit cell: $a^*$, $b^*$, $c^*$, $\alpha^*$, $\beta^*$, $\gamma^*$
- There are exact mathematical relationships which relate the direct space and reciprocal space unit cell parameters
Reciprocal Relationships

- The relationships between the direct axes and reciprocal axes is strictly reciprocal.
- Any statement about the two lattices remains true if you simply replace all starred (*) quantities by unstarred quantities and vice-versa.
- $a^* \perp bc$(face) and $a \perp b^*c^*$(face).
- Any direct axis has as family of reciprocal lattice planes which are perpendicular to that axis.
- Conversely, any reciprocal axis has a family of direct lattice planes which are perpendicular to that axis.
X-ray Diffraction Patterns

- The X-ray diffraction pattern is the reciprocal lattice of a crystal’s direct lattice
- Referred to as the **intensity weighted reciprocal lattice**
- Diffraction maxima are reciprocal lattice points
- Intensity distribution of diffraction pattern is related to the electron density distribution in the crystal
Reciprocal Lattice Points

- Are designated by their Miller index, hkl
- Assigning hkl values to the reciprocal lattice points is called *indexing the crystal* or *indexing the diffraction pattern*
- Reciprocal lattice points represent the diffraction from a *set of planes* designated by the hkl value and have a corresponding d* value
- Normal to the set of planes and therefore represent a direction in reciprocal space
Graphical Construction of Reciprocal Lattice from Direct Space Lattice

- For a set of planes in direct space, we draw a vector normal to these planes.
- Terminate the vector at a distance $1/d$.
- For a given lattice row:
  - $d^*(nh,nk,nl) = nd^*(hkl)$.
- Graphic:
  
  ![Graphical Construction of Reciprocal Lattice](http://www.xtal.iqfr.csic.es/Cristalografia/parte_04-en.html)
Indexing a Diffraction Pattern

- Synthesized reciprocal lattice layer (hk0) from an actual crystal
- Vertical axis has closer packed reciprocal lattice points
- Vertical axis has larger direct space unit cell parameter
Indexing a Diffraction Pattern

- First assign the lattice directions
- Notice there are systematic absences along the $h00$ and $0k0$ reciprocal axes
- Indicative of two screw axes (translational symmetry elements)
Indexing a Diffraction Pattern

- Assign hkl values to each reciprocal lattice point
- Use Bragg’s Law to calculate the interplanar spacing associated with each reciprocal lattice point
- Measure angle between a* and b* to obtain γ*
- Repeat process with other zero layers (0kl and h0l)
How to think about this

- Each reciprocal lattice point represents both a direction and d spacing.
- With each reciprocal lattice point measured, we are “sampling” the electron density with certain spatial frequency in a given direction.
The Swiss Cheese Analogy

- We want to map where all the holes are in a block of Swiss cheese
- We (virtually) slice the block using various thicknesses and at various orientations
- We then take these slices and use them to map the size and shapes of the all the holes in the block
Resolution of Our Mapping

- Slicing our cheese every 10 mm will cause us to miss some of the smaller holes in the cheese.
- We make finer and finer slices to map even the smaller holes within the cheese.
- Why not just use all fine slices rather than both low and high resolution slices?
- Analogy breaks down at this point.
- In X-ray we need both the low resolution data and high resolution data.

<table>
<thead>
<tr>
<th>Slice Width</th>
<th>Reciprocal Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Every 10.0 mm</td>
<td>1/10 or 0.1 mm^-1</td>
</tr>
<tr>
<td>Every 5.0 mm</td>
<td>1/5 or 0.2 mm^-1</td>
</tr>
<tr>
<td>Every 2.0 mm</td>
<td>1/2 or 0.5 mm^-1</td>
</tr>
<tr>
<td>Every 1.0 mm</td>
<td>1/1 or 1 mm^-1</td>
</tr>
<tr>
<td>Every 0.5 mm</td>
<td>1/(1/2) or 2.0 mm^-1</td>
</tr>
</tbody>
</table>
Resolution in Reciprocal Space

- The higher the diffraction angle, the finer the slice we are using to sample our crystal’s electron density.
- Diffraction condition only allows us to sample the electron density distribution at certain spatial frequencies (Bragg’s Law).
- We need to collect both high and low resolution data.
Ewald Construction

- Graphical depiction of Bragg’s Law
- Circle has radius of $1/\lambda$, centre at C such that origin of reciprocal lattice, O, lies on circumference
- XO is the X-ray beam, P is the reciprocal lattice point (in this case the 220 reflection)
- OP is the reciprocal lattice vector ($d^*$) and is normal to the (220) set of planes [aka the Scattering Vector]
- Angle OBP is $\theta$, the Bragg angle
- Angle OCP is 2$\theta$
- CP is the direction of the diffracted beam
- BP is parallel to the set of (220) planes
- Any time a reciprocal lattice point falls on the circumference, Bragg’s Law is fulfilled
Ewald Sphere

- 2D Ewald construction can be generalized to 3D to generate the “Ewald Sphere” (also called the “Sphere of Reflection”)
- Anytime a reciprocal lattice point is on the surface of the sphere Bragg’s Law is fulfilled
- Experimentally, we rotate the crystal (lattice) to bring a greater number of reciprocal lattice points pass through the surface of the sphere
- Image shows the detector slicing through part of the Ewald sphere and all the lattice points which were laying on the surface of the sphere
Ewald Spheres and Limiting Spheres

- Ewald sphere has a diameter of \( \frac{2}{\lambda} \)
- Every reciprocal lattice point within that distance can be brought into diffracting position
- Limiting sphere has a radius of \( \frac{2}{\lambda} \)
- The total number of reciprocal lattice points within the limiting sphere is approximated by
  \[ N \approx 33.5 \left( \frac{V_{\text{cell}}}{\lambda^3} \right) \]
Limiting Spheres of Common Radiations

- $N_{\text{MoK}\alpha} \approx \frac{33.5 V_{\text{cell}}}{0.71073^3} = 93.3 V_{\text{cell}}$

- $N_{\text{CuK}\alpha} \approx \frac{33.5 V_{\text{cell}}}{1.54178^3} = 9.14 V_{\text{cell}}$

- Normally, we don’t collect all reflections within the limiting sphere. In practice, we pick some maximum value of $\theta$

- $N_{\theta(\text{max})} \approx \frac{33.5}{\lambda^3} V_{\text{cell}} \sin^3 \theta_{\text{max}}$

- You will always get more data with a shorter wavelength
Wavelength Imposed Limits

- Maximum value of sine function = 1.0
- Imposes certain limits on the X-ray experiment
- Shorter wavelengths allow collection of more data points out to higher resolution

<table>
<thead>
<tr>
<th>Quantity</th>
<th>CuKα</th>
<th>MoKα</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>1.54178 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>((\sin \theta / \lambda)_{\text{max}})</td>
<td>0.648 Å(^{-1})</td>
<td>1.407 Å(^{-1})</td>
</tr>
<tr>
<td>( d_{\text{min}} )</td>
<td>0.771 Å</td>
<td>0.355 Å</td>
</tr>
<tr>
<td>Resolution Limit ((0.92d_{\text{min}}))</td>
<td>0.71 Å</td>
<td>0.33 Å</td>
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Practical Considerations for Data Collection

- Long axes give densely packed reciprocal lattice rows
- Integration is better if peaks aren’t overlapping
- Choose minimum crystal to detector distance as:
  \[ DX(\text{mm}) = 2 \times \text{longest primitive axis (Å)} \text{ [MoKα]} \]
  \[ DX(\text{mm}) = 1 \times \text{longest primitive axis (Å)} \text{ [CuKα]} \]
- For non-merohedrally twinned samples, move the detector back even farther