Basic Crystallography

Crystals and Bragg’s Law

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Some semantics (yes, it’s important)

- **Spectroscopy/Spectrometry vs. Diffraction**
  - **Spectrum:** an array of entities, such as light waves or particles, ordered in accordance with the magnitudes of a common physical property, such as wavelength or mass.
  - **Diffraction:** the breaking up of an incoming wave by some sort of geometrical structure – for example, a series of slits – followed by reconstruction of the wave by interference.
  - **Diffraction is NOT energy dispersive**
    - (that would be XPS, EDS, XRF)

- **The meaning of peaks...**
  - NMR/MS/IR etc. peaks have information about specific chemical moieties
  - Each XRD peak has information about EVERYTHING
Crystallography – what can it do?

• Solid state structure determination
  – Connectivity
  – Molecular morphology
  – Interactions
  – Packing
  – Surfaces
  – Porosity
• Phase transitions
  – Temperature / Pressure dependent
• Charge Density
• Modulation
Crystallography – what can’t it do?

• Solid state structure determination
  – No gas/liquid phase information
  – Limited dynamics
  – Usually energetically minimized
  – No ab initio elemental analysis

• Synthetic limitations
  – Must have a crystalline material
  – Must be large enough
  – Must be stable
    • Can overcome temperature/humidity/oxidation/light within limits
Some History

• X-Rays Discovered in 1895 by Wilhelm Röntgen
• First diffraction experiment theorized by Max von Laue
• Carried out by Friedrich and Knipping in 1912.
• Nobel Prizes:
  – 1901 – Röntgen
  – 1914 – von Laue
  – 1915 – Bragg’s
  – ... 29 in all (http://www.iucr.org/people/nobel-prize)
Why Crystals?

• What is a crystal?
  – Regularly shaped
  – High degree of long-range order and repetition
  – Yields a sharp diffraction pattern

• What is a good crystal?
  – Single
  – No re-entrant faces
  – Appropriately sized
    • Typically 0.05-0.6mm
  – Not just pretty on the outside
Crystals – how do you get them?

- Crystal growth
  - Directly from reaction
  - Slow and steady (literally)
  - Solvent/solution based
    - Slow evaporation
    - Slow cooling
    - Vapor diffusion
    - Liquid diffusion
  - Sublimation

http://xray.chem.uwo.ca/Guides.html
Unit Cells

- Smallest unique part of a crystal that can be translated *through space* to reproduce the entire crystal
- Parallelepiped defined by 3 non-coplanar vectors
  - Magnitudes = $a$, $b$, $c$
  - Angles = $\alpha$, $\beta$, $\gamma$
  - Atomic coordinates = $x$, $y$, $z$
Unit cells
Miller Indices

- (100)
- (010)
- (001)
- (110)
- (111)

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Diffraction

- The bending of a wave front around an object, as with light passing through a suitably small slit.
- Constructive interference
Diffraction gratings

- Two Rays (1 & 2) are diffracted by a grating.
  - AB = CD (on the way in)
  - FG = EH (on the way out)
- Difference in pathlengths
  - DE – BF = n\(\lambda\)
- Using geometry
  - DE = a\(\cos\alpha_o\)
  - BF = a\(\cos\alpha\)
  - Therefore: \(n\lambda = a(\cos\alpha_o – \cos\alpha)\)
- Laue Equations
  - \(a(\cos\alpha_o – \cos\alpha) = h\lambda\)
  - \(b(\cos\beta_o – \cos\beta) = k\lambda\)
  - \(c(\cos\gamma_o – \cos\gamma) = l\lambda\)
Bragg’s Law

- William Henry (father) and William Lawrence Bragg (son)
  - Lawrence did most of the work
  - Both won the Nobel Prize in 1915

- Conceptualized diffraction as a reflection

\[
\begin{align*}
\text{AB} + \text{BC} &= n\lambda \\
2\text{AB} &= n\lambda \\
2(d \sin \theta) &= n\lambda
\end{align*}
\]

\[
\boxed{n\lambda = 2d \sin \theta}
\]
Reciprocal Space

\[ n\lambda = 2d \sin \theta \]

- Rearrange Bragg’s Law: \[ \frac{2 \sin \theta}{n\lambda} = \frac{1}{d} \]

- Diffraction pattern is reciprocal of crystal lattice

- Reflection from planes \((hkl)\) is the r.l. point \(hkl\) at a distance \(1/d_{hkl}\) from the origin and perpendicular to the planes

- What is the relationship between the crystal (real, direct) lattice and the diffraction pattern (reciprocal lattice)?