Basic Crystallography

Crystals and Bragg's Law

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Crystallography – what is it?

- 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?

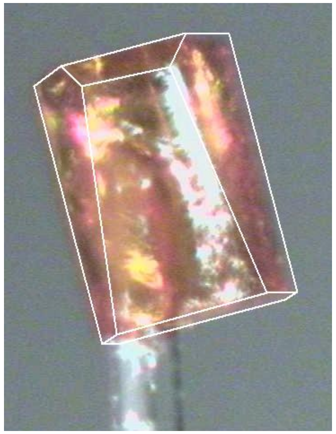
- Solid state structure determination
  - No gas/liquid phase information
  - Limited dynamics
  - Usually energetically minimized
  - No ab initio elemental analysis
- Synthetic limitations
  - Must have a crystalline material
  - Must be large enough
  - Must be stable
    - Can overcome temperature/humidity/oxidation/light within limits

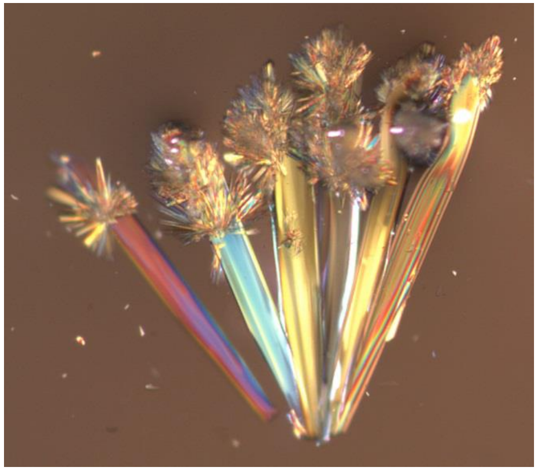
Some History

- 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?

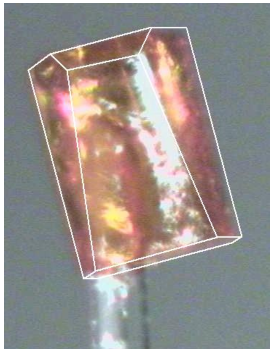
- What is a crystal?
  - Regularly shaped
  - High degree of long-range order and repetition
  - Yields a sharp diffraction pattern
- What is a good crystal?
  - Single
  - No re-entrant faces
  - Appropriately sized
    - Typically 0.05-0.6mm
  - Not just pretty on the outside

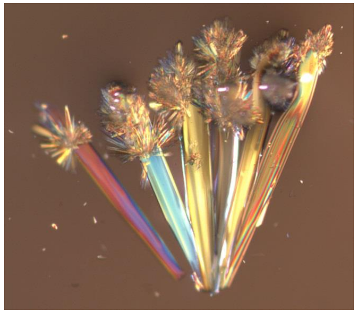


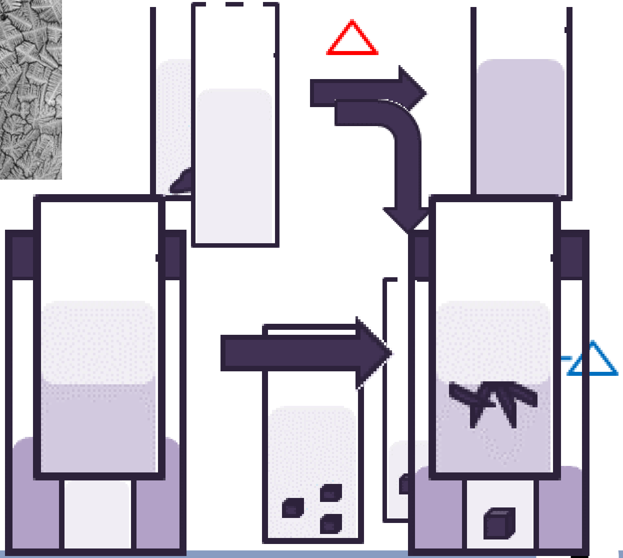


Crystals – how do you get them?

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



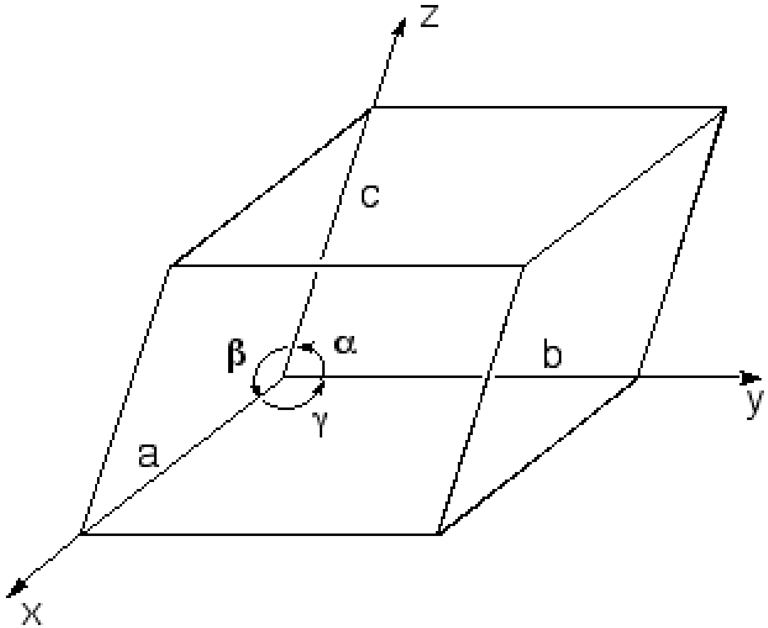




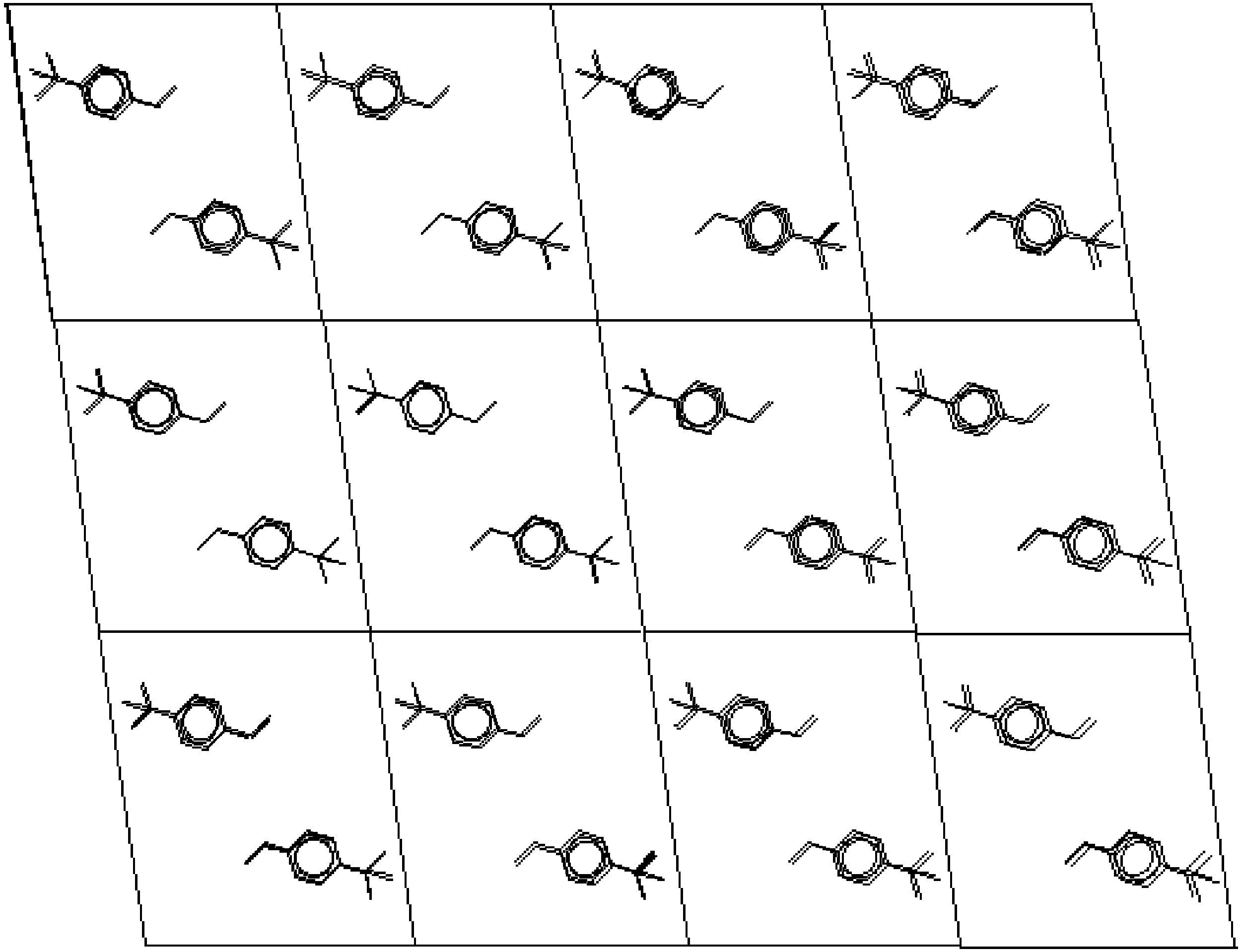
http://xray.chem.uwo.ca/Guides.html

Unit Cells

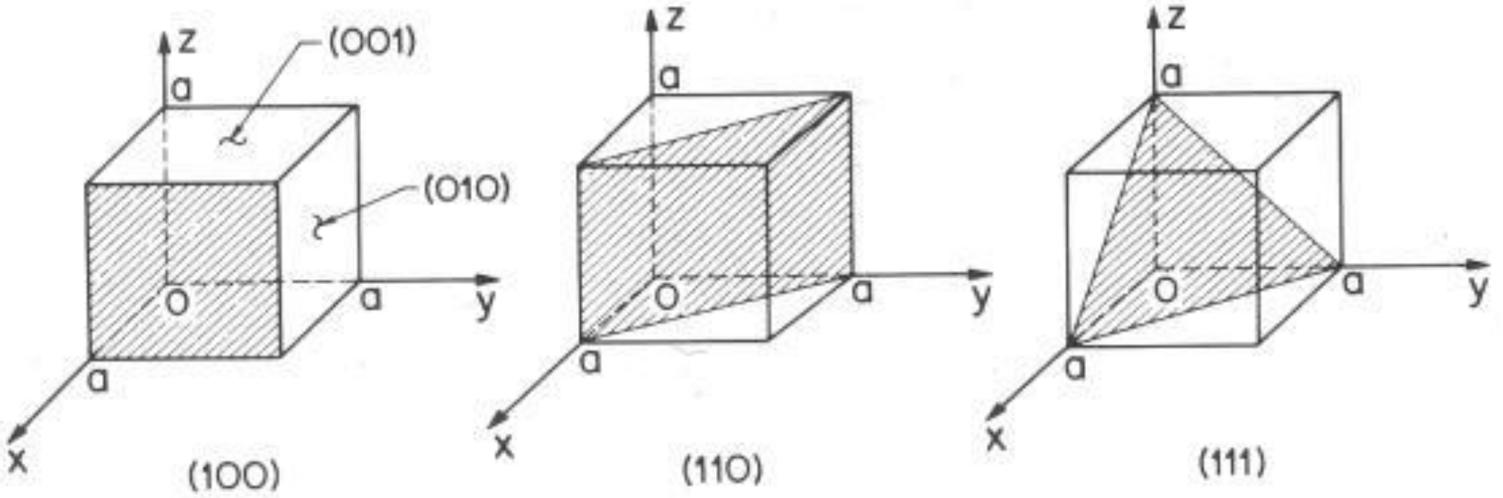
- Smallest unique part of a crystal that can be translated *through space* to reproduce the entire crystal
- Parallelepiped defined by 3 non-coplanar vectors
  - Magnitudes = a, b, c
  - Angles = α,β, γ
  - Atomic coordinates = x, y, z

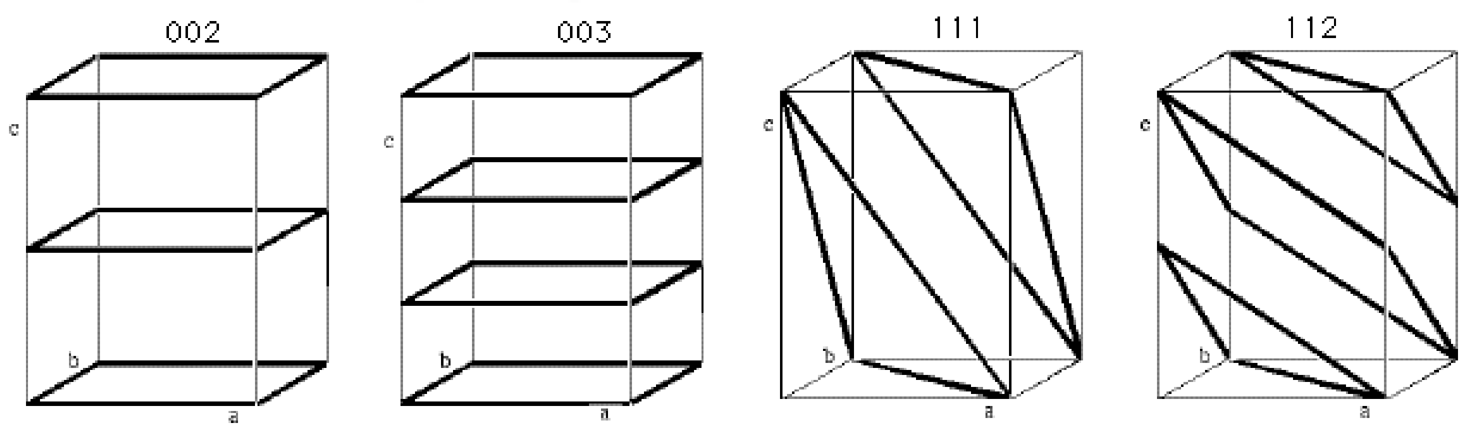


Unit cells



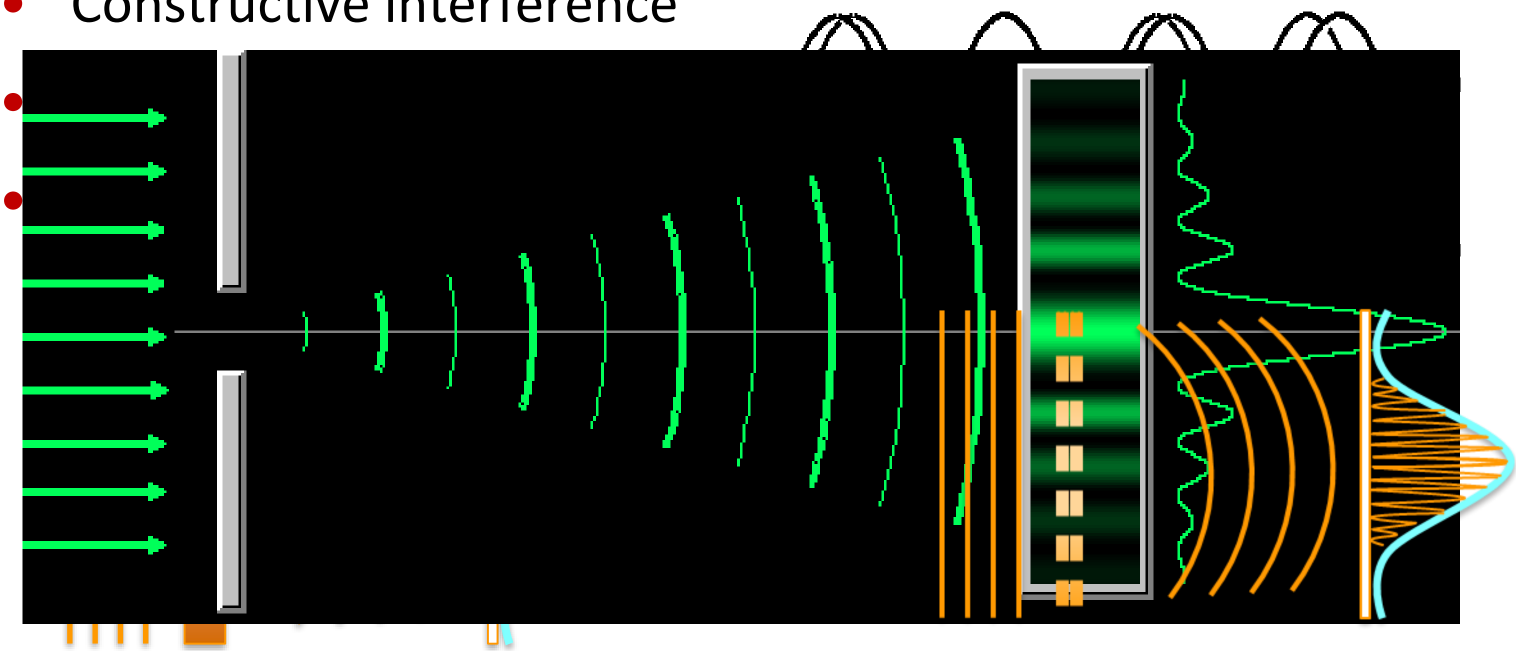
Miller Indices





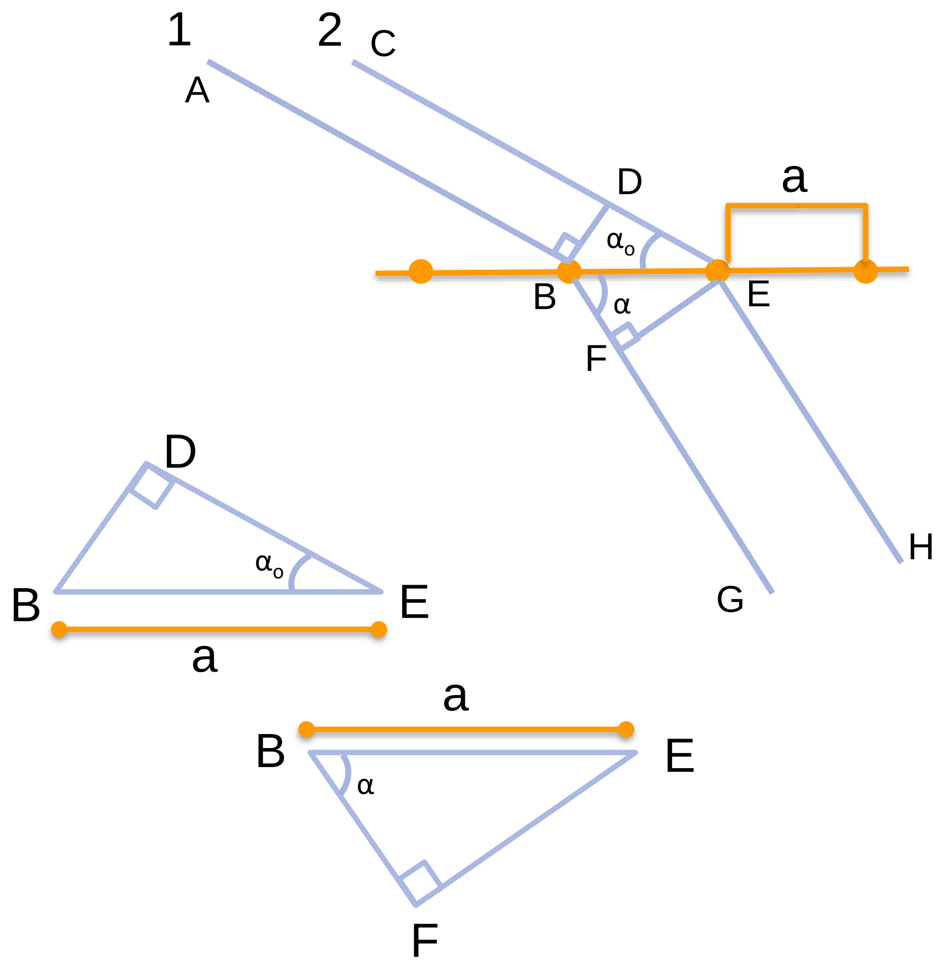
Diffraction

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



Diffraction gratings

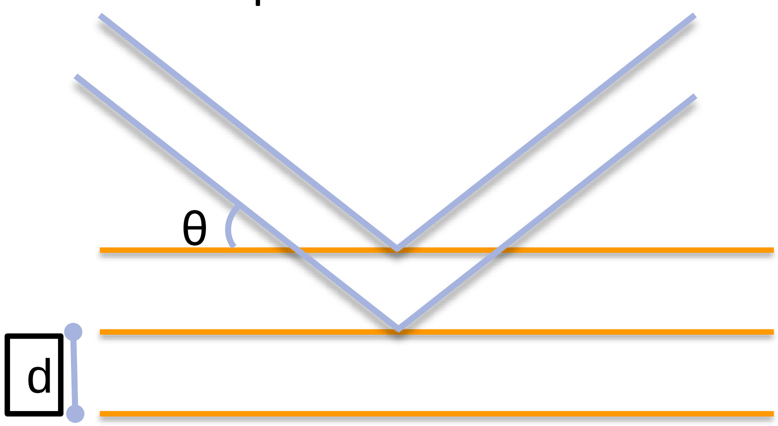
- Two Rays (1 & 2) are diffracted by a grating.
  - AB = CD (on the way in)
  - FG = EH (on the way out)
- Difference in pathlengths
  - DE – BF = $n\lambda$
- Using geometry
  - DE = a $\cos\alpha_o$
  - BF = a $\cos\alpha$
  - Therefore: $n\lambda = a(\cos\alpha_o - \cos\alpha)$
- **<u>Laue Equations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



Bragg's Law

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

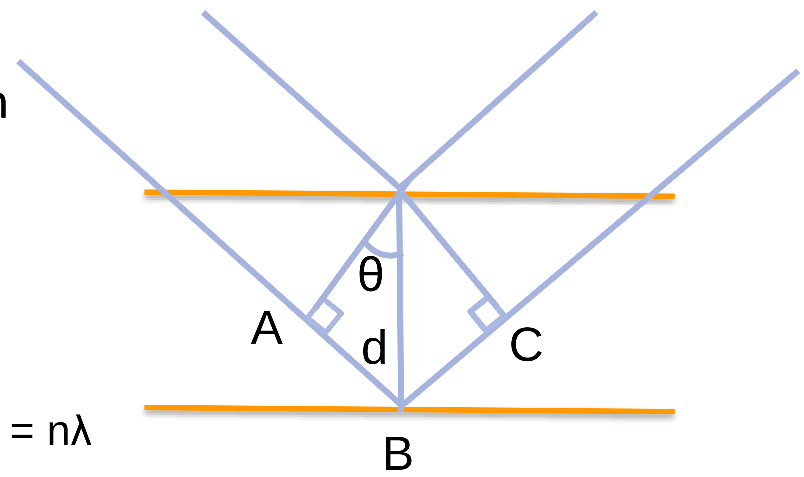
- Conceptualized diffraction as a reflection



$AB + BC = n\lambda$

$2AB = n\lambda$

$2(d \sin\theta) = n\lambda$



$$n\lambda = 2d \sin \theta$$

Reciprocal Space

$$n\lambda = 2d \sin \theta$$

- Rearrange Bragg's Law: $\frac{2 \sin \theta}{n\lambda} = \frac{1}{d}$ → d_{hkl}

- 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)?