Powder X-ray Diffraction

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Uses of Powder Diffraction

Qualitative Analysis
- Identification of single-phase materials
- Identification of multiple phases in microcrystalline mixtures
- Recognition of amorphous materials in partially crystalline mixtures

Quantitative Analysis
- Lattice Parameter Determination
- Phase Fraction Analysis

Peak Shape Analysis
- Crystallite Size Distribution
- Microstrain Analysis
- Extended Defect Concentration

Structure Refinement
- Rietveld Method

Structure Solution
- Reciprocal Space Methods
- Real Space Methods

Thermal expansion and Phase Transitions

Three Unique Features of Synchrotron Radiation

•Intensity

•*Enables Rapid Data Collection*
- Kinetics
- Unstable Compounds
- Environmental Cells

–*Enables Focussing*
- Small Samples
- Small areas/volumes

•Energy Range

•*Enables Spectroscopy*
- –Elemental Identification
- –Bonding Studies
- –Speciation

•*Enables Optimal Conditions*
- –Environmental Cells
- –Selected Elements

•Low Divergence

Enables High Resolution

•Micro Beams

•Small Volumes

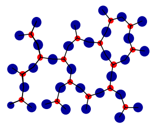
•Complex Materials

What is special about a crystal?

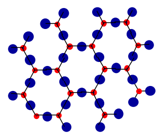
Solid phases are often crystalline, but need not be - e.g. glass an "amorphous material"

Glass
- Fractures into shards
- Takes on any shape, depending on preparation
- Properties do not vary with orientation.

Crystal
- Cleaves along preferred directions
- Grows with well developed crystal faces
- Properties depend on orientation in which they are measured.



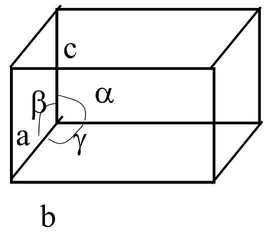
• Si ● Oxygen



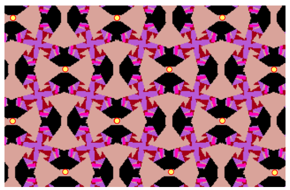
Crystal Structure

- CRYSTAL: Contains a periodical array of atoms/ions. This can be represented by a simple lattice of points.
- A group of atoms is associated with each lattice points.
- LATTICE: An infinite array of points in space, in which each point has identical surroundings to all others.
- CRYSTAL STRUCTURE: The periodic arrangement of atoms in the crystal.

The Unit Cell



The unit cell is a basic parallelopiped shaped block from which the whole volume of the crystal may be built by repetition in 3 dimensions. Any point in the unit cell may be specified with respect to the origin by parameters x, y, z measured parallel to the unit cell axes and expressed as fractions.



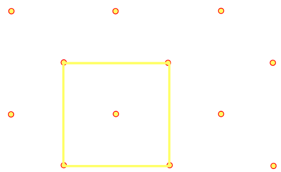
Example of 2D symmetry in a wallpaper pattern

To show symmetry:

1. Pick a point

2. Find all equivalent points

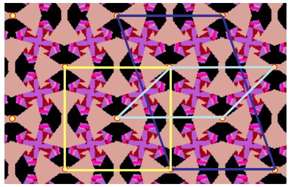
(http://www.clarku.edu/~djoyce/wallpaper/)



Example of 2D symmetry in a wallpaper pattern

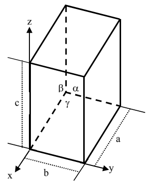
To show symmetry:

- 1. Pick a point
- 2. Find all equivalent points
- These points form a 2D lattice
- Connecting 4 lattice points to form a parallelogram gives a possible *unit cell*



Example of 2D symmetry in a wallpaper pattern

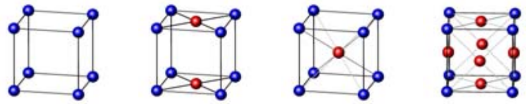
- Connecting 4 lattice points to form a parallelogram gives a possible *unit cell*
- *Unit cell* – the basic unit that repeats in every direction
- Different *unit cells* can be chosen
- But some *unit cells* are preferable for higher symmetry



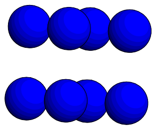
Lattice parameters: a, b, c; α, β, γ

Name	Bravis Lattice	Conditions
Triclinic	1 (P)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, C)	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$
Orthorhombic	4 (P,F,I,A)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2 (P, I)	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$
Cubic	3 (P, F,I)	$a = b = c$ $\alpha = \beta = \gamma = 90°$
Trigonal	1 (P)	$a = b = c$ $\alpha = \beta = \gamma < 120° \neq 90°$
Hexagonal	1 (P)	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$

P **C** **I** **F**



PC Lattice



α-Po is **primitive-Cubic**

Identical atoms at corners but nothing at the and body or face centers.

Lattice type P

BCC Lattice

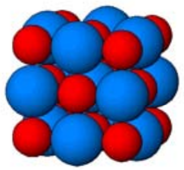
α-Iron is **Body-Centered Cubic**

Identical atoms at corners and body center (nothing at face centers)

Lattice type I

Also Nb, Ta, Ba, Mo...

FCC Lattice



Sodium Chloride (NaCl) Na is much smaller than Cl

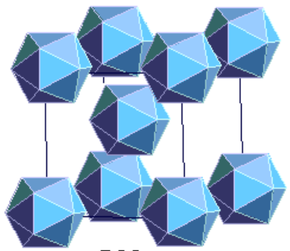
Face Centered Cubic

Rocksalt structure

Lattice type F

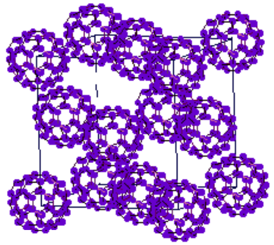
Also NaF, KBr,MgO….

FOOT & MOUTH VIRUS



BCC

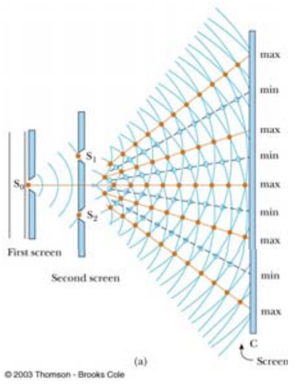
BUCKMINSTERFULLERENE



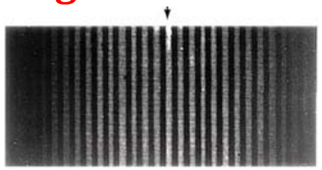
FCC

Young's Double Slit Experiment

- Thomas Young first demonstrated interference in light waves from two sources in 1801
- Light is incident on a screen with a narrow slit, S_o
- The light waves emerging from this slit arrive at a second screen that contains two narrow, parallel slits, S_1 and S_2
- The narrow slits, S_1 and S_2 act as sources of waves
- The waves emerging from the slits originate from the same wave front and therefore are always in phase



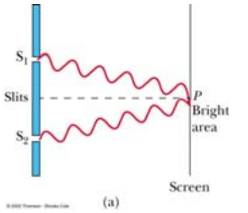
Resulting Interference Pattern



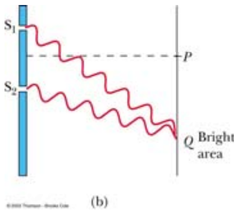
- The light from the two slits form a visible pattern on a screen
- The pattern consists of a series of bright and dark parallel bands called *fringes*
- ***Constructive interference*** occurs where a bright fringe occurs
- ***Destructive interference*** results in a dark fringe

Interference Patterns

- Constructive interference occurs at the center point
- The two waves travel the same distance
  - Therefore, they arrive in phase

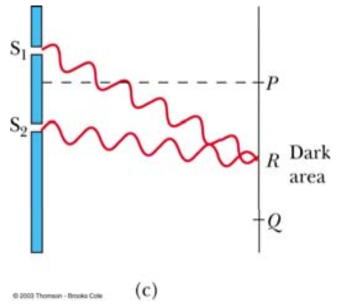


- The upper wave travels one wavelength farther than the lower wave
  - Therefore, they arrive in phase
- A bright fringe occurs



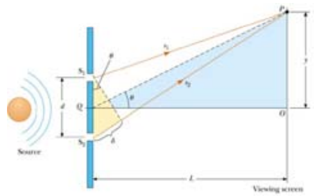
Interference Patterns

- The upper wave travels one-half of a wavelength farther than the lower wave
- The trough of the bottom wave overlaps the crest of the upper wave (180° phase shift)
- This is destructive interference
  - A dark fringe occurs



Interference Equations

- The path difference, δ, is found from the tan triangle
- $\delta = r_2 - r_1 = d \sin \theta$

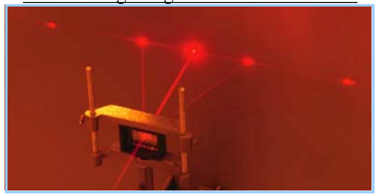


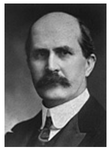
- For a bright fringe, produced by constructive interference, the path difference must be either zero or some integral multiple of of the wavelength
- $\delta = d \sin \theta_{bright} = m \lambda$
  - $m = 0, \pm 1, \pm 2, \ldots$
  - m is called the *order number*

Diffraction of X-ray Waves

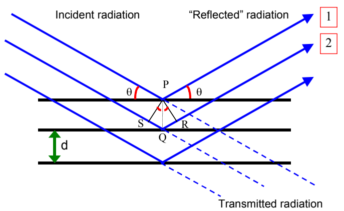
- **Diffraction:** When light passes sharp edges or goes through narrow slits the rays are deflected and produce fringes of light and dark bands.

Diffraction grating and helium-neon laser





Bragg's Law



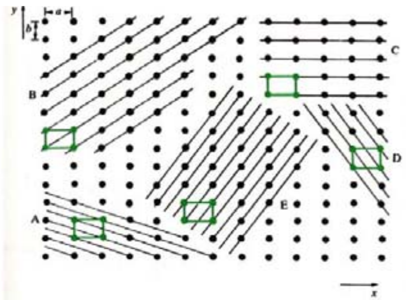
Beam "2" travels the extra distance SQR

$$n\lambda = \overline{SQ} + \overline{QR}$$
$$= d_{hkl} \sin \theta + d_{hkl} \sin \theta$$
$$= 2d_{hkl} \sin \theta$$

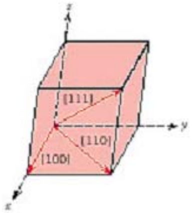
But not all planes result in diffraction !!!

Lattice Planes

- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of integers referred to as Miller Indicies



Crystallographic Directions And Planes



Lattice Directions

Individual directions: [uvw]

Symmetry-related directions: <uvw>

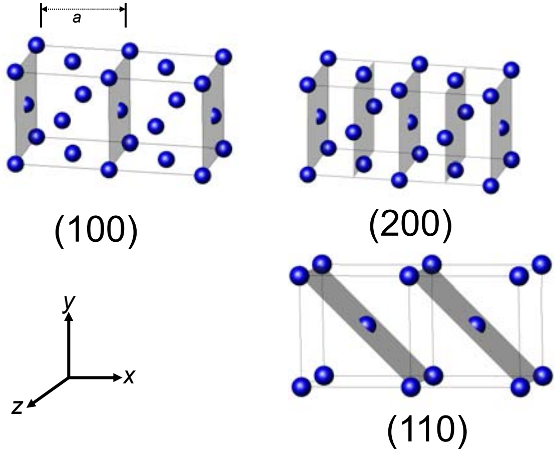
Miller Indices:

1. Find the intercepts on the axes in terms of the lattice constant a, b, c
2. Take the reciprocals of these numbers, reduce to the three integers having the same ratio

   (hkl)

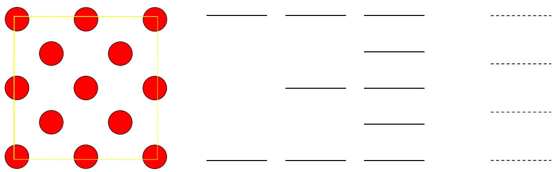
Set of symmetry-related planes: {hkl}

Examples of Miller Indices



Families of Planes

- Miller indices describe the orientation of a family of planes
  - the spacing between adjacent planes in a family is referred to as a "d-spacing"
- different families of planes
  - d-spacing between (400) planes is 1/4 that of the (100) spacing.
  - The (300) plane does not contain atoms and so is not observed

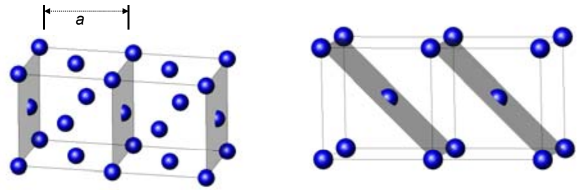


(100) (200) (400) (300)

Lattice Spacing

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

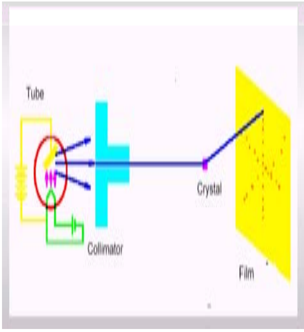
For cubic system with a = 4.0 A

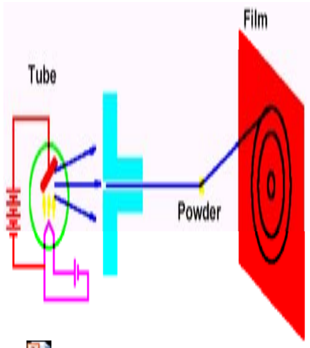


d_{100} = 4.0

d_{110} = 2.828

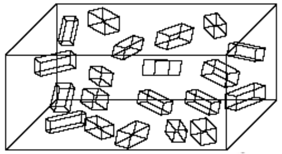
Single Crystal vs Powder





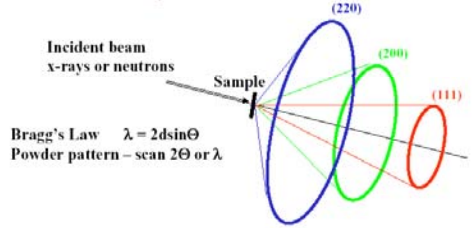
McCusker

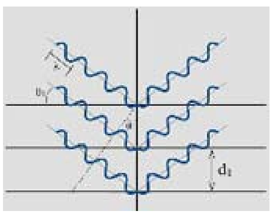
Powder – A Polycrystalline Mass

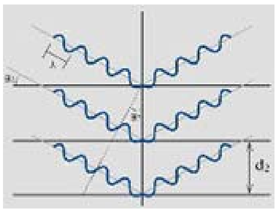


All orientations of crystallites possible

Single crystal reciprocal lattice - smeared into spherical shells

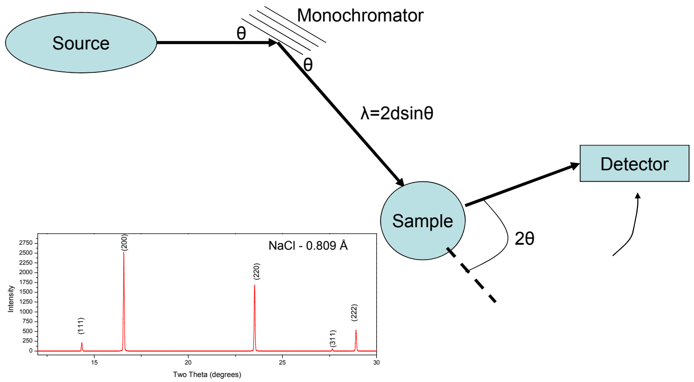






- By varying the angle θ, the Bragg's Law conditions are satisfied by different d-spacings in polycrystalline materials.
- Plotting the angular positions and intensities of the resultant diffracted peaks produces a pattern which is characteristic of the sample.

Powder Diffraction

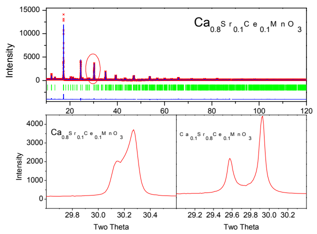


Information Contained in a Diffraction Pattern

Peak Positions
- Crystal System
- Space Group Symmetry
- Unit Cell Dimensions
- Qualitative Phase Identification

Peak Intensities
- Unit Cell Contents
- Point Symmetry
- Quantitative Phase Fractions

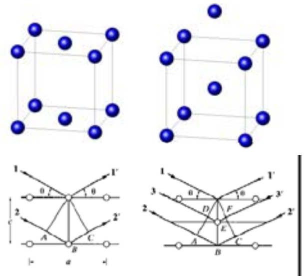
Peak Shapes & Widths
- Crystallite Size (2-200 nm)
- Non-uniform microstrain
- Extended Defects (stacking faults, etc.)



Changes in symmetry and microstrain upon chemical substitution can be established by examination of the patterns

Centering and Absences

- The positions of the atoms in a unit cell determine the intensities of the reflections
- Consider diffraction from (100) planes in

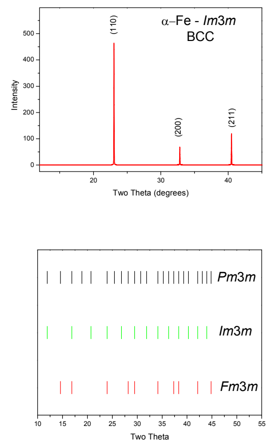


If the pathlength between rays 1 and 2 differs by λ, the path length between rays 1 and 3 will differ by λ/2 and destructive interference in (b) will lead to no diffracted intensity

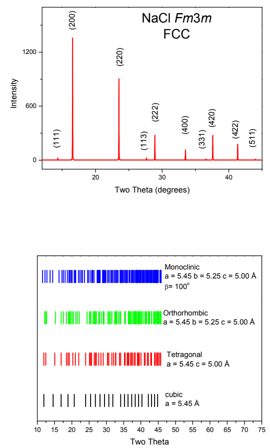
Centering and Absences

- We can extend these types of calculation to include other modes of lattice centering. They all lead to systematic absences

Bravais lattice	**Reflections that must be absent**
Simple (Primitive)	none
Base (C) centered	h and k mixed
Body (I) centered	(h+k+l) odd
Face (F) centered	h, k and l mixed



Influence of centering



Influence of symmetry

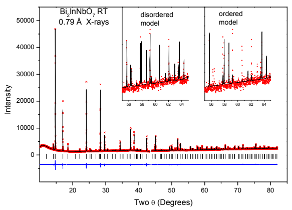
Multiplicity

- For high symmetry materials the Bragg angles and d-spacings for different reflections may be equivalent to one another
  For example (100), (010), (001) etc are equivalent in a cubic material
- In a powder, all planes with the same d-spacing contribute to the scattered intensity at a given Bragg angle
- The number of planes that are symmetry equivalent is referred to as the multiplicity and its appears as a multiplicative term in powder diffraction intensity calculations
- The multiplicity of a reflection depends upon the symmetry of the crystal
  Multiplicity of {100} for cubic is 6, but for tetragonal it would only be 4 as (100) and (001) are not equivalent

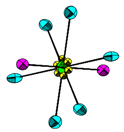
Diffraction Patterns

- Spacing of peaks depends on size of unit cell and the space group.
- The bigger the unit cell and/or the lower the symmetry the more diffraction peaks are observed.
- Intensity of peaks depends on (amongst other things) the arrangement of the atoms in the unit cell.
- For two materials that had identical unit cells, the peak positions would be IDENTICAL, however their intensities would be DIFFERENT.

Need for High Q



There are many more reflections at higher Q. Therefore, most of the structural information is at higher Q



Refinement of structure gave unusual displacement parameters for the Bi cations, indicative of cation disorder. The patterns could only be adequately fitted by including 6-fold disorder of the Bi. This involves a displacement along the (1 -1 0) direction

Atom	Site	x	y	z	B_{iso}
Model 1. Ordered Bi. R_p 4.08 R_{wp} 6.07%					
Bi	16d	0	0.25	0.75	2.74(6)
In/Nb	16c	0	0	0	3.00(8)
O(1)	48f	0.350(3)	0.125	0.125	7.6(7)
O(2)	8b	0.375	0.375	0.375	7.6(7)
Model 2. Disordered Bi R_p 3.09 R_{wp} 3.93%					
Bi	96h	0	0.2249(1)	0.7751(1)	0.96(7)
In/Nb	16c	0	0	0	0.61(3)
O(1)	48f	0.322(1)	0.125	0.125	1.7(2)
O(2)	8b	0.375	0.375	0.375	1.7(2)

Need for High Resolution

$$\frac{\Delta d}{d} = \frac{\Delta \lambda}{\lambda} + \frac{\Delta \theta}{\tan \theta}$$

Sample   Source   Source + Instrument

Differentiating Braggs Law gives the resolution as:

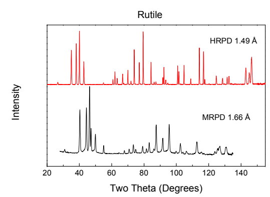
$$\lambda = 2d \sin \theta$$

Resolution

In Powder Diffraction it typically refers to the width of the peaks.

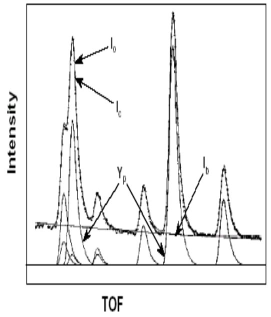
In Single Crystal Diffraction it typically refers to the minimum d-space studied.

Both definitions are relevant.



Peak Overlap

- Powder Diffraction patterns are a one dimensional representation of a three dimensional structure.
- Often peaks due to individual Bragg reflections overlap



The Solution - Rietveld

$$y_{icalc} = y_{iback} + \sum_{p} \sum_{k=k_1^p}^{k_2^p} G_{ik}^p I_k^2$$

- y_{ic} the net intensity calculated at point i in the pattern,
- y_{iback} is the background intensity,
- G_{ik} is a normalised peak profile function,
- I_k is the intensity of the k^{th} Bragg reflection,
- k_1 ... k_2 are the reflections contributing intensity to point i,
- the superscript p corresponds to the possible phases present in the sample.

The Answers

- The Profile R

$$R_p = \frac{\sum |y_{iobs} - y_{icalc}|}{\sum y_{iobs}}$$

- The weighted Profile R

$$R_{wp} = \left[\frac{\sum w_i (y_{iobs} - y_{icalc})^2}{\sum w_i y_{iobs}^2} \right]^{1/2}$$

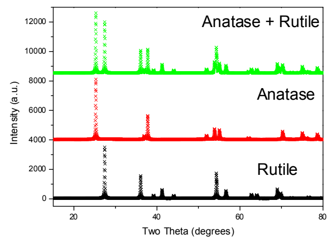
- The expected Profile R

$$R_{exp} = \left[\frac{N - P}{\sum w_i y_{iobs}^2} \right]^{1/2}$$

- The Goodness of fit

$$\chi^2 = \frac{\sum w_i (y_{iobs} - y_{icalc})^2}{N - P} = \left[\frac{R_{wp}}{R_{exp}} \right]^2$$

Phase Analysis



- Where a mixture of different phases is present, the resultant diffraction pattern is formed by addition of the individual patterns.
- The intensity of the peaks is proportional to the amount of the phase present.

Quantitative Phase Analysis

- Bragg scattering is proportional to N/V where N is the number of unit cells and V the unit cell volume. There for the weight of a phase in the beam is:

$$W_P = \frac{(SZMV)_P}{\sum_i (SMPV)_i}$$

S - the scale factor

Z the number of formula unites per unit cell

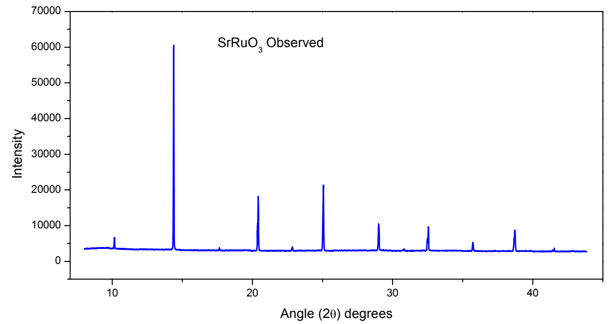
M the molecular weight of the formula unit

I is the index running over all phases

- Hence SZVM is proportional to the weight of the diffracting sample

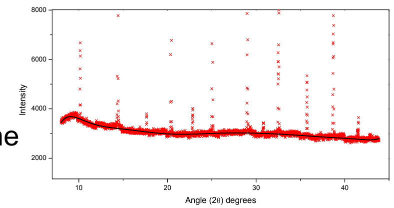
An Example

- Synchrotron X-ray Diffraction pattern for $SrRuO_3$



The background

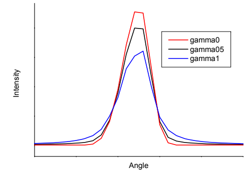
- Fluorescent radiation from the sample
- Diffraction from the continuous spectrum
- Diffuse scattering
  - Incoherent
  - Temperature diffuse
- Other materials
  - Specimen holder
  - air etc



- Background can be either fitted or estimated.
- Here the capillary is a feature.

Peak Shapes

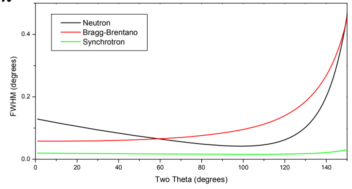
- Different Diffractometers have different peak shapes.
- The most widely function is a pseudo-Voigt (mixed Gaussian and Lorentzian).



$$G_{ik} = \gamma \frac{C_0^{1/2}}{H_k \pi}\left[1 + C_0 X_{ik}^2\right]^{-1} + (1+\gamma)\frac{C_1^{1/2}}{H_k \pi^{1/2}} \exp\left[-C_1 X_{ik}^2\right]$$

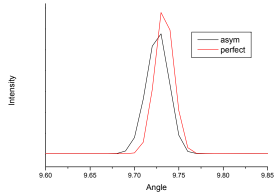
- The width of peaks is usually not constant.

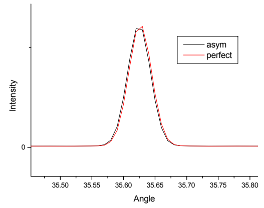
$H^2 = U\tan^2\theta + V\tan\theta + W$



Peak Asymmetry

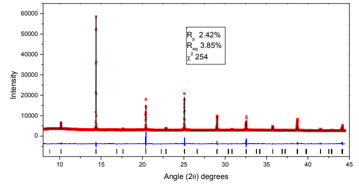
- Beam Divergence can results in asymmetric peaks at low angles.
- Results from not integrating over the entire Debye cone.



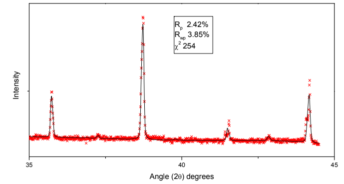


The Simple Structural Model

- The fit to a single phase sample looks good



- BUT……
- The detail of the fit is not satisfactory - the model is missing something!

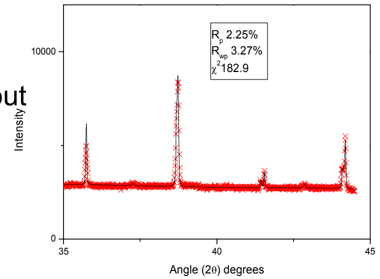


A Common Problem

- If the structural model is wrong then the most common response of Rietveld programs is to:
  - broaden the peaks,
  - Increase the displacement parameters,
- The former is most noticeable at high angles where intensity is lowest.
- Due to absorption of the X-rays powder X-ray diffraction often yields poor displacement parameters

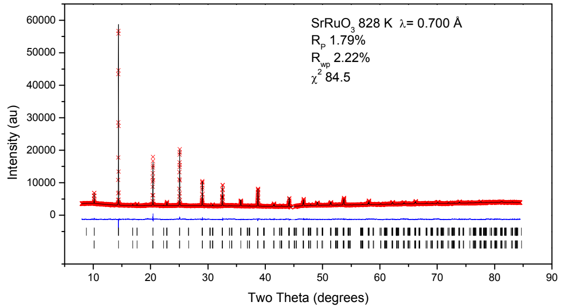
An Alternate Model

- The high angle splitting is well modeled by a tetragonal model - but this overestimates some intensities.



- The Truth lies somewhere in the middle

The finished Product



- The sample contains a mixture of both phases!

Strengths and Limitations of Powder X-ray Diffraction

Strengths

- Non-destructive – small amount of sample
- Relatively rapid
- Identification of compounds / phases – not just elements
- Quantification of concentration of phases – (sometimes)
- Classically for powders, but solids possible too
- Gives information regarding crystallinity, strain, crystallite size, and orientation

Limitations

- Bulk technique – generally – unless a microfocus source is used
- Not a “stand-alone” technique – often need chemical data
- Complicated appearance
- multiphase materials – identification /quantification can be difficult

Experiment Design Issues

What Wavelength?

- Absorption is your enemy!
- Short Wavelengths are best! BUT….
- Consider required resolution. And…
- Avoid Absorption Edges.

What Size Capillary?

- Small capillaries reduce absorption AND (with area detectors) improve resolution.
- BUT reduce amount of material.