



FIG. 7. Use of the Fly's Eye.



Prof.W.H.Bragg





Sir W.L.Bragg

X-ray Diffraction

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Types of Forces

- 1) Strong forces
- 2) Weak forces
- 3) Electromagnetic forces
- 4) Gravity

Types of Matter

- 1) Atoms
- 2) Molecules
- 3) Crystals
- 4) Particles, Solids, Surfaces, Liquids, Glasses, Gases



Electromagnetic Radiation at a Synchrotron

Energy transmitted in the form of waves or particles

γ-rays	X-rays	UV	Vis	IR	µ-waves

higher energy \rightarrow lower energy

For particles:

de Broglie wavelength = Planck's const./momentum [λ = h/p]

For an electron accelerated through 100 Volts, $\lambda = 1.2$ Å,

Why is wavelength important?

To probe a sample you need radiation with a wavelength of similar, or smaller, magnitude to the size of the "object" under investigation.



To investigate atomic/molecular structure, we use X-rays, electrons, and neutrons, since they can have wavelengths about the sizes of atoms.

X-rays

- Hard X-ray wavelengths ~ 0.1 Å to 60 Å
- Soft X-ray wavelengths ~ 60 Å to 120 Å
- Interact weakly, ie. penetrating therefore, can see inside of a structure, but most of the beam passes through, unperturbed.
- 10 x more photons are absorbed than scattered.
- X-rays scatter off of valence electrons (~ 1% off nuclei).



Scattering.

coherent, incoherent

elastic (Thomson), inelastic (Compton)

Absorption.

atoms: can then be emitted as fluorescence, photoelectrons, Auger electrons

molecules: can emit fluorescence, phosphorescence, transfer heat, (stimulated emission)

Diffraction. The bending of waves due to obstructions and small apertures, as with crystals.

Refraction. The bending of a wave as it passes from one medium to another

Reflection. Radiation bouncing back from one medium to the original medium, where the wavelength << size of the object.

Photoelectric Effect

Ionization occurs when a light has sufficient energy to eject an electron. The kinetic energy of the emitted electron is diagnostic of the orbital from which it was ejected. Allows Photoelectron spectroscopy.



 E_{hv} = electron kinetic energy + electron binding energy

Valence spectroscopy: information on bonding Core spectroscopy: qualitative and quantitative analysis, "chemical shift"

X-ray Scattering

Coherent scattering occurs when the Xray particle collides with an atom and deviates without a loss in energy.



Coherent

Incoherent scattering is where the incident X-ray loses some of its energy to the scattering electron. As total momentum is preserved, the wavelength of the scattered photon is increased.



Incoherent

Compton Scattering

Compton scattering occurs when the incident x-ray photon is deflected from its original path by an interaction with an electron. The electron is ejected from its orbital position and the x-ray photon loses energy because of the interaction but continues to travel through the material along an altered path. Energy and momentum are conserved in this process. The energy shift depends on the angle of scattering and not on the nature of the scattering medium.

$$\lambda_{scattered} - \lambda_{initial} = \left[\frac{h}{m_e c}\right](1 - \cos\theta)$$

where h is Plancks constant; m_e the mass of the electron; c the speed of light; and θ the angle the photon is deflected by.

Since the scattered x-ray photon has less energy, it has a longer wavelength and less penetrating than the incident photon.

Thompson Scattering

• An electron will oscillate in phase with an x-ray beam according to the following equation:

$$I = \frac{I_0}{r^2} \left[\frac{e^2}{m_e c^2} \right]^2 \frac{1 + \cos^2(2\theta)}{2}$$

where I_0 is the intensity of the incident beam; *e* the charge on the electron; m_e the mass of the electron; *c* the speed of light; and *r* the distance from the scattering electron to the detector.

Clearly (by the second term) the scattered energy from a single electron is quite low. Third term, involving the cosine function, is called the *polarisation factor* because it indicates that the incoming non-polarised xray is polarised by the scattering process, resulting in a directional variation in the scattered intensity.



When X-rays pass through a material, the intensity is attenuated (decreased) through absorption by the elements in the material.

Attenuation is due to two effects:

Compton scattering (σ) of the beam, which diverts photons in directions different from the primary beam: **Photoelectric absorption** (^T), which produces fluorescence or Auger electrons.



Absorption

These two effects may be combined into a single bulk mass absorption coefficient μ). This coefficient is different for each element and wavelength and is defined as a the sum of photoelectric and Compton scattering:

$$\mu = \tau + \sigma$$

Where τ = photoelectric absorption coefficient and σ is the Compton Scattering coefficient In many materials photoelectric absorption accounts for about 95 percent of the absorption and Compton scattering can be ignored. Further, Compton scattering is not important at wavelengths less than 1 Å.

Fluoresence



If an X-ray photon of sufficiently high energy strikes an inner shell electron the electron can be ejected it from the atom.

Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent Xrays.

Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent Xrays.

Secondary Fluorescence

The absorption of an incident X-ray to produce another X-ray produces an effect termed secondary fluorescence. Secondary fluorescence produces an excess intensity. Some elements undergo self-absorption: K-line X-rays may be absorbed by other atoms of same element to produce L-line X-rays. For a given element of interest, any X-rays of energy higher than E_c produced from other elements can cause fluorescence. The energy at which the mass absorption coefficient increases abruptly is the absorption edge and corresponds to Ec exactly.

For example, consider a material composed of 1/3 Fe, 1/3 Ni, and 1/3 Co. One would expect about 33.3% of the total X-rays observed to be produced by each element, but instead we see 40% Fe, 28% Ni, and 32% Co. The Fe in the material is fluoresced by Ni-K α producing Fe-K α X-rays and absorbing Ni-K α .

Plot of the X-ray absorption curves for Fe (black), Co (red), and Ni (blue), showing the K α absorption edges. The locations of the K α lines for these elements is also shown. Note than Ni-K α x-rays have sufficient energy to fluoresce Fe-K α x-rays.



Scattering and Diffraction Techniques

3-Dimensional

2-Dimensiional

X-ray crystallography Phasing methods Grazing incidence diffraction

Low-angle scatter

Dynamics Equilibrium: B factors, diffuse scatter Non-equilibrium: Laue method

Other Synchrotron Techniques

Scattering:

- Raman (inelastic, due to vibrations)
- visible Rayleigh (elastic, information on particle size
- and dynamics)

Absorption and related techniques:

EXAFS (measure fluorescence in an excitation spectrum)

UV, vis, IR (electronic, vibrations)

- absorption (CD, linear, time-resolved)

-fluorescence

-phosphorescence (luminescence)

Infra-red Spectroscopy

Displacement of atoms during vibration lead to distortion of electrical charge distribution of the molecule.



atoms (mass) are connected with bonding electrons. r_e is the equilibrium distance and F: force to restore equilibrium.

 $\omega_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$

F(x) = -kx where X is displacement from equilibrium k_i is the force constant and μ_i is reduce mass of a particular motion.

Molecular vibration lead to oscillation of electric charge governed by vibration frequencies of the system.

Oscillating molecular dipole can interact directly with oscillating electric vector of electromagnetic radiation of the same frequency

 $h v = h \omega$

Energy is quantized and vibrations are in the range 10^{11} to 10^{13} Hz => 30 - 3,000 cm⁻¹

Circular Dichroism

• CD measures the difference between the absorption of left and right handed circularly-polarized light by a chiral chromophore.



 This difference is measured as a function of wavelength, and is always very small (<<1/10000 of total). Therefore CD spectroscopy requires a high flux source that provides stable linear polarization over and extended wavelength range (VUV-Near IR)

X-ray Scattering by an Atom

- Scattering by an atom is essentially the sum of the scattering of the electron "cloud" around the nucleus.
- Scattering from each electron follows the Thompson equation. Because of the distance between electrons scattering within the atom and the fact that the x-ray wavelength is of the same order as the atomic dimensions, there will be path differences between the scattered waves. These differences will always be less than one wavelength, so the interference will always be partially destructive.



Figure 3.12. The scattering of X-rays from a real atom extended in space.

•This phenomenon is called the *atomic scattering factor*, described by the quantity f_0 . This function is normalized in units of the amount of scattering occurring from a single electron in the Thompson equation. At zero degrees, f_0 will be equal to the number of electrons surrounding the atom or ion. At higher scattering angles, the factor will be less.

Intensity

- The intensity of the diffracted beam can be given by: $I = SLP \big| F_{hkl} \big|^2$
- S is a scale factor that is dependent on the intensity of the source and the detector efficiency.
- LP is a combination of the Lorentz and polarisation factors which for a non-polarised X-ray beam is given by:

$$LP = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}$$

The Structure Factor F_{hkl}

- For a reflection from a plane *hkl*. The structure factor F_{hkl} is:

$$F_{hkl} = \sum_{i=1}^{unit-cell} f_i \cdot \exp\left[-B_i \frac{\sin^2 \theta_{hkl}}{\lambda^2}\right] \cdot \exp[2\pi i hkl \cdot x_i]$$

- x_i = (x_iy_iz_i) are the fractional coordinates for atom i in the cell
- hkl are the Miller indices for the reflection
- B_i is the Debye-Waller displacement (thermal) factor for atom (in Å²)
- f_{i} . Is the scattering factor.

X-ray Diffraction

• In X-ray diffraction f_i is given by:

$$f_i^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

- $\Delta f'$ and $\Delta f''$ are the real and anomalous dispersion terms.
- The first term f_0 depends on the diffraction angle 2 θ .

Anomalous X-ray Scattering $f_i^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$

• Anomalous scattering or anomalous dispersion occurs when the incident X-ray energy is sufficient to cause photoelectric x-ray production in a target atom. The process is called fluorescence. This phenomenon is responsible for "absorption edge" observed when certain elements interacting with particular wavelength x-rays. In this process a characteristic X-ray photon is produced in the target; subsequent interaction produces coherent X rays which are slightly out of phase with other coherently scattered X-rays. The net result is a reduction of the scattered intensity from the element.

Bi Wavelength Dependence

Just as the absorption coefficient shows large jumps at "edges" the scattering power of elements shows rapid changes near edges.

• Minimum absorption is obtained near 13.31 eV (0.93 Å)

Maximum Δf' is ca 8 electrons by measuring at 13.3 and 13.5 eV.



Dynamics

Equilibrium

Non-equilibrium

B factors

• Diffuse scatter

- Laue crystallography
- Rapid Mixing and Small angle scattering

The temperature (B) factor

- Atoms are not located at fixed points undergo vibrations about their mean positions.
- The amplitude of these vibrations increase as the temperature increases.
- Due to such motion, the scattering factor falls off exponentially. The greatest reduction in intensity is at high angles (low d-values).

$$f_B = f \cdot e^{-B\left(\sin\theta/\lambda\right)^2}$$

Debye-Waller temperature factor B = $8\pi^2 < u^2$

Where $\langle u \rangle^2$ is mean-square amplitude of atomic vibration. This is directional and can be anisotropic

The temperature (B) factor

ATOMIC SCATTERING FACTOR CURVE FOR ELEMENT BI - WEBSCAT by B.Rupp



Increasing motion of an atom induces an angular dependent reduction in intensity. The greatest reduction is at high angles (low d-values).

$$f_B = f \cdot e^{-B(\sin\theta/\lambda)^2}$$

Debye-Waller temperature factor B = $8\pi < u > 2$

Effect of Temperature Ag₂O



Diffuse Scatter

- Diffuse Scatter is the scatter that is not in the Bragg reflections. Every crystal has it.
- Diffuse scatter can arise from:
 - Thermal displacement
 - Occupational disorder
 - Displacive Disorder
 - Short Range Order
 - Stacking Faults

Diffuse Scatter



Powder X-ray Diffraction

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.



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



Example of 2D symmetry in a wallpaper pattern

To show symmetry:

.1. Pick a point

0

0

.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)	$a \neq b \neq c$ $\alpha = \beta = 90^{\circ} \neq \gamma$
	Orthorhombic	4 (P,F,I,A)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$
	Tetragonal	2 (P, I)	$a = b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$
	Cubic	3 (P, F,I)	a = b = c $\alpha = \beta = \gamma = 90^{\circ}$
•	Trigonal	1 (P)	a = b = c $\alpha = \beta = \gamma < 120^{\circ} \neq 90^{\circ}$
	Hexagonal	1 (P)	$a = b \neq c$ $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$
I		_	

Ρ

С

F









PCC Lattice



α -Po is primitive-Centered Cubic

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

Lattice type P

BCC Lattice



$\begin{array}{l} \alpha \text{-Iron is Body-} \\ \textbf{Centered Cubic} \end{array}$

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

<u>Rocksalt structure</u> Lattice type F Also NaF, KBr, MgO....

FOOT & MOUTH VIRUS



BUCKMINSTERFULLERENE



Diffraction of X-ray Waves

 <u>Diffraction</u>: 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







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

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: <uvv>

Miller Indices:

- 1. Find the intercepts on the axes in terms of the lattice constant a, b, c
- 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



(100)





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



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 $\lambda/2$ 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 I 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	У	Ζ	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



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 kth Bragg reflection,
- k₁ ... k₂ 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 $R_p = \frac{\sum |y_{iobs} - y_{icalc}|}{\sum}$

The weighted Profile R
 R

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

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

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

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

• The Goodness of fit

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 SrRuO₃



The background

- Fluorescent radiation from the sample
- Diffraction from the continuous spectrum
- Diffuse scattering
 - Incoherent
 - Temperature diffuse
- Other materials
 - Specium 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).

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



 The width of peaks is usually not constant.

 $H^2 = Utan^2\theta + Vtan\theta + W$



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

60000

50000

40000

- The fit to a single phase sample looks good
 - BUT.....
 - The detail of the fit is not satisfactory the model is missing something!



R 2.42% R 3.85%

254

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

Limitations

- 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

- 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.









Neutron Diffraction

XRD 0.85A PF





Powder Diffraction Software

http://www.ccp14.ac.uk/

- Structure Solution from Powder Diffraction
 - Some pathways for Structure Solution from Powder Diffraction
- Search-Match phase Identification
- Powder Diffraction Data Conversion / Interconversion
- Powder Diffraction Data Visualisation
- Peak finding and Peak Profiling
- Powder Indexing (finding a unit cell from powder data)
- Unit Cell Refinement
- Le Bail Whole Profile Fitting
- Pawley Whole Profile Fitting
- Rietveld Refinement

- Restrained Rietveld Structure Refinement of Organics
- View Fourier Maps from Rietveld Refined Data
- Structure Conversion and Transformation
- Structure Drawing and Visualisation
- Modelling of Amorphous Materials
- Incommensurate/Modulated Structure solution and refinement
- Anharmonic Thermal Refinement
- Bond Length and Bond Angle Calculation
- Bond Valence Calculations
- Pole Figure and Texture Analysis Software
- Polyhedral Volume Calculations
- High Q Powder Diffraction Analysis for PDF/Local
 Order Determination
- TOF (Time of Flight) Neutron Diffraction
- Variable Count Time (VCT) Data Collection for Powder Diffraction
- Integration of Image Plate Data

