A Very Abbreviated Introduction to Powder Diffraction

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Outline

- Diffraction properties of atoms with x-rays and neutrons
- Diffraction from single-crystals vs. powders
- Why do we use powder diffraction?
- Materials effects in powder diffraction
- Instruments for powder diffraction collection
- Crystallographic analysis of powder diffraction data
- Appendices:
  - More on peak shapes
  - More on crystallography
  - Where to go for more information
Coherent Atomic Scattering Power (diffraction)

Structure factors: \[ F_{hkl} = n \sum f_i \exp[2\pi i (hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2) \]

- **X-rays**: The scattering power (form factor, \( f_i \)) of an atom depends on the number of electrons in the atom and \( Q (Q \propto \sin \theta / \lambda) \)
  - X-ray scattering changes near absorption edges
- **Neutrons**: The scattering power (scattering length, \( b_i \)) of an atom depends on the isotope and is independent of \( Q \)
  - A few isotopes scatter with opposite phase to most, for these we write \( b(f) \) as negative
  - Some isotopes atoms have neutron resonances (similar to x-rays)
  - Magnetic scattering is from electrons; \( f_M(Q) \) similar to x-rays

Comparison of Neutron and X-ray Atomic Scattering Powers
Neutrons and x-rays “see” atoms differently

Incoherent and inelastic scattering

Incoherent and inelastic scattering create background. This is usually significant only with neutrons and most commonly for powder (less so single crystal) diffraction.

With neutrons, some type of atoms have large incoherent cross sections (phase is lost during the scattering).

Hydrogen (not deuterium) is the poster child for this: it has a huge incoherent scattering cross-section (~80 barns) that tends to overpower coherent scattering (typically <1 barns for most atoms). Samples with more than a few atom % (not mass %!) will have a significant background.
Resonant scattering: scattering at a resonance edge causes atoms to “light up”

Experiments are sometimes performed at wavelengths close to absorption edges to enhance the scattering from particular elements.

**X-rays**

The x-ray form factor has in fact three components:

- \( f(Q) + f'(\lambda) + i f''(\lambda) \)
  - \( f \) is determined by \( Q \) and the number of electrons in an atom and is independent of wavelength.
  - \( f' \) and \( f'' \) are small except at wavelengths very close to an atom’s absorption edge.

At wavelengths close to an edge absorption becomes high; fluorescence occurs above the edge.

**Neutrons**

Scattering lengths for most atoms are wavelength-independent.

A similar “resonant scattering” type experiment can sometimes be performed comparing samples containing different isotopes (\( \text{^{235}U} \) to \( \text{^{238}U} \)).

A few isotopes (mostly lanthanides and actinides) have absorption edges at accessible wavelengths.

- This is usually a curse rather than a blessing: it makes TOF neutron scattering had to analyze.

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**Single-crystal vs. Powder Diffraction**
Single crystal diffraction: the movie

Video from Diamond synchrotron (U.K.)

Bragg scattering in single crystals

- Reflection positions (Bragg’s law)

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

Note that \( d \) above is a reciprocal space quantity (actually \( d = 1/d^* \)), \( |d^*| = |h a^* + k b^* + l c^*| \), better: \( \lambda = 4 \pi \sin \theta / Q \)

- Reflection intensities are related to the square of “structure factor”, \( F_{hkl} \)

\[ F_{hkl} \propto \sum f_j \exp(2\pi i(hx_j + ky_j + lz_j)) \exp(-U_j Q^2/2) \] sum over all atoms in the crystal (or unit cell).

\( x, y, z \): position of atom in unit cell

\( U \): atom displacements

\( f_j \) (or \( b_j \)): scattering power of atom
Diffraction from random polycrystalline material

In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.

A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction.

Diffraction occurs only at specific angles, those where Bragg’s Law is satisfied.

Bragg cones in powder diffraction

Since there is a random distribution of crystals then diffraction occurs in all directions for each Bragg angle, 2θ, thus powder diffraction arises in cones.

All reflections occurring at a single 2θ value (as well as reflections at nearly the same value) are superimposed and only the sum of their intensities can be measured. For this reason a powder diffraction pattern gives less information than a single crystal measurement.
Measuring powder diffraction

- Angular dispersion: a single detector is moved over a range of 2θ angles.
  - Sample irradiated with monochromatic radiation

Comparison of \( \text{Tb}_2\text{TiO}_3 \) with x-rays & neutrons

- **X-ray**
- **Neutron**

<table>
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<th>Intensity</th>
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<tr>
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<tr>
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Why do we do powder diffraction?

- Learn where the atoms are (single crystals, when available and appropriate, are better for this.)
- Determine the chemical phase(s) in a sample
- Measure lattice constants
- Quantify the components of a mixture
- Learn about physical specimen characteristics such as stress, preferred orientation or crystallite sizes
- Occupancies of elements amongst crystallographic sites (usually needs neutrons)

A Conceptual Basis for Understanding Materials Effects in Powder Diffraction
Materials effects on Powder Diffraction

For real materials, the powder diffraction pattern shows not only the crystal structure, but also shows microstructure details:

- How the crystallites are oriented, if not random (texture)
- The average sizes of the crystallites (peak broadening)
- Residual stress (peak broadening)

Less commonly:

- Stacking faults
- Modulated structures
- Extinction
- Compositional inhomogeneity
- Differences in ordering by atom type

Texture (non-random arrangement) affects reflection intensities

- Crystallite orientation will increase the intensity of reflections in orientations that are over-represented and will decrease other reflections
- If we have an overabundance of crystals aligned in along the (100) face, the reflections in that direction will have enhanced intensity
Crystallite (size) broadening

The Fourier transform (FT) from an *infinite* array of regularly spaced objects is an array of delta functions.

The FT from a *finite* length array is broadened; all maxima are broadened equally in Q (or d).

Microstrain (residual stress) broadening

Strain & stress changes the lattice constants of a material

- In a material with residual stress
  - some crystallites are under tension,
  - others are compressed

Shift of peak $\approx Q$, broadening increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d$ constant)
Comparison of microstrain and crystallite broadening

Crystallite broadening
- $\Delta Q \approx \Delta d^* = \text{constant}$

\[
\Delta d^* = \frac{\Delta d}{d^2} = \frac{\Delta \Theta \cot \Theta}{\lambda}
\]

\[
= \frac{\Delta 2 \Theta \cot \Theta \sin \Theta}{\lambda}
\]

\[
\Delta 2 \Theta = \frac{\lambda \Delta d}{d^2 \cos \Theta} = \frac{k}{\cos \Theta}
\]

Microstrain broadening
- $\Delta Q/Q \approx \Delta d^*/d^* = \text{constant}$

\[
\Delta d \frac{\Delta d^*}{d^*} = \Delta \Theta \cot \Theta
\]

\[
\Delta 2 \Theta = \frac{2 \Delta d}{d} \tan \Theta
\]


Types of Powder Diffraction Measurements
Area Detection

- With an area detector, a complete powder diffraction pattern can be collected in a fraction of a second.
  - Fast
  - Medium resolution
  - High background

Highest resolution requires high collimation. Optimal is a crystal analyzer between the sample and detector: 11-BM Diffractometer

Huber 480 rotation stage:
- High precision (~0.35arcsec)
- High accuracy (~1arcsec)
- Slew or step scans

12 analyzer array
- Si(111) crystals
- LaCl$_3$ scintillator detectors
- 2° apart in 2θ.

Mitsubishi robot custom "fingers"

Complete pattern is measured in <1 hour
11-BM Robotic Data Collection

(Matt Suchomel: [http://youtu.be/sowojskY7e4](http://youtu.be/sowojskY7e4) or search APS 11-BM on YouTube)

Reactor Source Neutron Diffraction
**Powder Instruments: Constant Wavelength**

- **Beamline HB2a at HFIR**
- **Beamline BT1 at NIST (NCNR)**

**Spallation Sources**

A pulse of protons impacting the target produces a shower of fast neutrons that are slowed down in a moderator. A new pulse is created ~30 times/sec.
Time of Flight Diffraction

Time of flight diffraction uses the fact that neutrons with different energies (velocities) have different wavelengths, \( \lambda = \frac{h}{mv} \) (de Broglie relationship).

Detector

Detector

Neutrons to sample

Protons into target

\( 2d \sin \Theta = \lambda \)

(Pulsed sources: e.g. SNS)

\( \lambda \) varies

\( 2\Theta \) fixed
Spallation source provides a broad band of wavelengths in sharp pulses
- TOF detection allows measurement of intensity versus wavelength
- Each detector provides a full diffraction pattern
- Data collection times:
  - Seconds to hours

3rd Generation TOF Instruments: High Intensity and High Resolution

GEM (ISIS TS-I)

WISH: A high-resolution magnetic diffractometer for TS-II

Super HRPD (JSNS)
Fitting of Powder Diffraction Data (Rietveld Analysis)

Why did Crystallography Revolutionize Science?

1. Crystallography was the first scientific technique that provided \textit{direct} information about molecular structure
   - Early work was intuitive: structures assigned based on patterns and symmetry (some results predate X-rays!)
2. X-ray and neutron diffraction observations can be modeled very accurately directly when the molecular structure is known
3. Diffraction can provide a very large number of independent observations
   - Probability of finding an incorrect structure model that is both plausible and is in good agreement with the diffraction observations is very small (but not zero!)
4. Computer-assisted least-squares optimization allows structural models to be improved, limited only by the quality of the data
5. Statistical and brute-force techniques overcomes the incomplete nature of diffraction observations (direct methods vs. “the phase problem”).

\textit{100+ years later, no other technique offers as much power for learning about molecular structure!}
Fitting crystallographic data -- what is it all about?

- We perform an experiment:
  - Get lots of intensity and position measurements in a diffraction measurement: what do they tell us?
- Obtain an unit cell that fits the diffraction positions (indexing)
- “Solve the structure”: determine an approximate model to match the intensities
- Add/modify the structure for completeness & chemical sense
- Optimize the structure (model) to obtain the best fit to the observed data
  - This is usually done with Gauss-Newton least-squares fitting
  - Parameters to be fit are structural and may account for other experimental effects
- Least Squares gives us a Hessian matrix; inverse is variance-covariance matrix which gives uncertainties in the parameters

Crystallography from powder diffraction: before Rietveld

How did crystallographers use powder diffraction data?

- Avoided powder diffraction
- Manually integrate intensities
  - discard peaks with overlapped reflections
  - rewrote single-crystal software to refine using sums of overlapped reflections

Simulation of powder diffraction data was commonly done

- Qualitative reasoning: similarities in patterns implied similar structures
- Visual comparison between computed and observed structure verifies approximate model
- Fits, where accurate (& precise) models were rarely obtained

Error propagation was difficult to do correctly (but not impossible)
Hugo Rietveld’s technique

- Hugo Rietveld realized that if a pattern could be modeled, the fit between a computed pattern and observed data could be optimized.

  - Similar to single-crystal diffraction, except that now “experiment dependent parameters” must now be fit as well.
    - Background
    - Peak broadening
    - Lattice constants
  - Must have approximate model to start
  - Fewer data are available (usually)

Calculation of Powder Diffraction: Graphical Example

<table>
<thead>
<tr>
<th>hkl</th>
<th>mult</th>
<th>D-space</th>
<th>$F_{hkl}$</th>
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1) Generate reflection list
2) Compute $F_{hkl}$ from model
3) Peak heights are generated from $|F_{hkl}|^2 \times$ multiplicity
4) Convolute peaks & add background
5) Optimize model, peak widths, etc. to improve fit
Hugo Rietveld in the Petten Reactor (~1987)

Single crystal fitting

Minimize equation \( \sum w_i [y_i - Y(x_i, p)]^2 \) where

Data: \( y_i = F_{hkl} \) (obs)

Model: \( Y(x_i, p) = F_{hkl} \) (calc)

Parameters \( (p_1, p_2, p_3, \ldots p_m) \):
- atomic coordinates,
- displacement (T) factors

Powder data fitting

\( y_i = \) observed powder diffraction intensities

\( Y(x_i, p) = \) computed diffraction intensities from \( F_{hkl} \) (calc),
- background model, profile convolution, preferred orientation correction,
- + lattice parameters
- + “experimental” parameters for peak shapes, background…
Hugo Rietveld’s other breakthrough

- Based on intensities from the model, estimates for $F_{hkl}$ can be made, even when reflections are completely overlapped:

Location 1:
- 20% to A
- 40% to B
- 40% to C

Location 2:
- 100% to C

Rietveld Applications

- Crystallographic structure determination
- Quantify amounts of crystalline phases
  - (Amorphous content possible indirectly)
- Engineering properties
  - Residual stress/Crystallite sizes
  - Preferred orientation
- Lattice constant determination
What sort of data are needed for Rietveld Analysis?

- Must be possible to fit peak shapes
- Q range and resolution demands dictated by structural complexity
- Data from lab instruments should be used *with caution* for structure determination
- Neutron data are usually necessary for occupancy determination

Disadvantage of Rietveld:
Many non-structural parameters need to be fit

- Background
  - fixed
  - functions
- Peak shape
  - “fundamental parameters”
  - functions
- Lattice constants
  - zero correction
  - flat plate terms
- Scaling
  - Phase fractions
- Structural parameters
  - atom positions
  - occupancies
  - displacement parameters
- Preferential Orientation
- Absorption

*Powder diffraction offers fewer observations and worse peak-to-background than single crystal diffraction*
Limitations of Rietveld

- Rietveld can only discern parameters that have effects on the powder diffraction pattern
  - Some things cannot ever be determined from powder diffraction:
    - Absolute configuration
    - "in symmetry plane" magnetic moment directions

- If two parameters have approximately the same effect on the powder diffraction pattern, they correlate and they cannot be differentiated (e.g. occupancies & displacement parameters)