Introduction to Powder X-ray Diffraction

21st National School on Neutron and X-ray Scattering

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History of Powder Diffraction

- Discovery of X-rays: Roentgen, 1895 (Nobel Prize 1901)
- Diffraction of X-rays: von Laue, 1912 (Nobel Prize 1914)
- Diffraction laws: Bragg & Bragg, 1912-1913 (Nobel Prize 1915)
- Powder diffraction: Developed independently in two countries:
  - Debye and Scherrer in Germany, 1916
  - Hull in the United States, 1917
- Original methods: Film based
- First commercial diffractometer: Philips, 1947 (PW1050)
  - Detectors and optics have improved a lot, but basic design remains similar!

http://www.msm.cam.ac.uk/xray/images/pdiff3.jpg
Original Powder Setups

◆ Oldest method: Debye-Scherrer camera
  - Capillary sample surrounded by cylindrical film
  - Simple, cheap setup
Physical Basis of Powder Diffraction

- Powder diffraction obeys the same laws of physics as single crystal diffraction
- Location of diffraction peaks is given by Bragg’s law
  - \(2d \sin \theta = n\lambda\)
- Intensity of diffraction peaks is proportional to square of structure factor amplitude
  - \(F(hkl) = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j)) \cdot \exp[-8\pi^2 \langle u^2 \rangle (\sin^2(\theta)/\lambda^2)]\)
Resonant X-ray Scattering Experiments

- Also referred to as “anomalous diffraction”; this type of experiment is carried out close to an absorption edge
- The elastic scattering is given by
  \[ f(E,Q) = f_o(Q) + f_o'(E,Q) + I f_o''(E,Q) \]
- \( f' \) and \( f'' \) undergo drastic changes close to the absorption edges of atoms
  - Great way to emphasize contribution of specific atoms
  - Especially useful for mixed site occupancies
  - In most cases, multiple patterns at different wavelengths are collected and analyzed simultaneously
Absorption Edges and Anomalous Scattering

- $f''$ “mirrors” the absorption coefficient

$$f''(E) = \left( \frac{2 \pi mc}{e^2 h} \right) E \mu_a$$

- $f'$ is intimately related to the absorption coefficient

$$f'(E) = \left( \frac{2}{\pi} \right) \int_0^\infty \frac{Ef''(E)}{(E_0^2 - E^2)} dE$$
Neutrons: Coherent and Incoherent Scattering

- For X-ray diffraction, we are generally only concerned with coherent elastic scattering
- For neutron powder diffraction, we unfortunately need to be aware of incoherent scattering as well
  - Phase is lost during incoherent scattering
  - Contributes to background
  - Less of an issue for single crystal experiments, but can be very significant for powder experiments
  - H is one of the worst culprits (not D!) – talk to beamline scientist what their setup can tolerate!
Goal of crystallography: Get structure

- **Single crystal experiments**
  - Grow crystals (often hardest step)
  - Collect data (usually easy, both access and setup)
  - Determine unit cell (very easy for good quality single crystal)
  - Reduce data and solve (=determine approximate structure) (often easy)
  - Optimize structure (=refinement) (requires some care)

- **Powder experiments**
  - Prepare powder sample (often easy)
  - Collect data (usually easy, but easy to make mistakes, too!)
  - Determine unit cell (can be very hard)
  - “Solve structure” (can be even harder – requires expert knowledge!)
  - Optimize structure – Rietveld refinement (requires considerable care)
What is a Powder?

◆ A perfect powder sample consists of an infinite number of small, randomly oriented crystallites
  – Note that this is the underlying definition for many quantitative analysis methods!
  – In real life, the number is of course not infinite, but should be large to give good averaging
  – Small particle size: 1-5 μm is ideal

◆ “Powder samples” can come in many different forms:
  – Loose powders
  – Films, sheets, blocks, wires…
  – Basically any “polycrystalline” sample can be used in PXRD – if it is not a single crystal, it is considered a “powder sample”
Observations from Single Crystals

- For a single crystal, there is one orientation in real space, resulting in one orientation of the reciprocal lattice
  - reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere
  - Rotating the crystal rotates the reciprocal lattice
Observations from Powders

- A powder sample consists of many crystallites with random orientations
  - we get many overlapping reciprocal lattices, resulting in a “sphere” of reciprocal lattice points that fulfill the Bragg condition at a given $2\theta$ 
  - the sphere will intersect the Ewald sphere in a circle
  - we will observe “powder rings”

Cullity; “Elements of X-ray Diffraction”
Anything from “several single crystals” to “almost homogeneous” is possible! Often referred to as “graininess problem” (e.g., not enough grains in the beam). Can result in non-random integrated intensities.
Powder Data Display

\[ Q = 4\pi \sin \theta / \lambda \]
Why Use Powder Diffraction?

- Originally, powder diffraction was mainly used for phase identification

- Advantages over single crystal methods: Can be used on ANY sample
  - If you can mount it, you can measure it!

- For some materials, single crystal growth is difficult or impossible
  - Powder methods are the only option

- “Real life samples” rarely come as single crystals: Engineering materials, formulations etc.
  - Powder diffraction can be used on mixtures of compounds
  - Peak shape analysis gives insights into size, stress and defects
Powder crystallography before Rietveld

- Primary strategy: AVOID when it comes to structure determination!
  - There was no straightforward way to deal with data
  - Had to manually integrate intensities
  - Overlapping reflections were a big problem
    - Usually discarded
    - Alternative: Rewriting of single crystal software to refine using sums of overlapped reflections

- Powder pattern simulation was more common
  - Relatively straightforward
  - Conclusions drawn based on similarities between patterns (e.g., isostructural compounds)
    - Visual comparison

- Main use of powder diffraction was for phase identification
Modern Use: What Information Can We Get From Powder Diffraction Data?

◆ Phase identification (qualitative phase analysis)
  – Most important/frequent use of PXRD
  – Qualitative analysis tool
  – Search pattern against database to identify phases present
    – Starting materials, known target compounds, likely impurities
    – Assumption: The material, or an isostructural material, is in the database

◆ Phase fraction analysis (quantitative phase analysis)
  – Applied to mixtures of two or more crystalline phases
  – Compare intensities of selected peaks of all phases
    – Theoretically only requires one peak/phase, but better with multiple peaks
  – Accurate analysis requires standardization
    – Mix known quantities of two phases in several different ratios
  – Caution: Possibility of amorphous components
What Information Can We Get From Powder Diffraction Data? (Cont’d)

◆ Lattice parameters
  – Two modes of analysis:
    – Accurate lattice parameters for a compound of known structure
    – Unit cell determination for an unknown compound through indexing
  – ACCURATE peak positions are crucial!

◆ Rietveld refinement (structural analysis)
  – Least squares based minimization algorithm to obtain the best fit between a structural model and a powder pattern
  – Starting model necessary to apply this method
  – Applicable to simple and complicated structures, single phase and multi-phase samples
  – Automatically gives phase fractions and lattice parameters from ALL peaks
  – Requires good data for meaningful results
What Information Can We Get From Powder Diffraction Data? (Cont’d)

♦ Structure Determination from Powder Data (SDPD)
  – Powder diffraction is subject to the same laws of physics as single crystal diffraction, but data overlap
  – Careful analysis can allow determination of unknown structures
  – Usually done with high quality synchrotron and/or neutron data
  – Requires excellent data and sound crystallographic knowledge!

♦ Phase transition behavior
  – *In situ* diffraction experiments
    – Temperature-induced phase transitions
    – Pressure-induced phase transitions
    – Kinetic studies
    – Requires specialized setups
What Information Can We Get From Powder Diffraction Data? (Cont’d)

◆ Line shape analysis
  – Width of Bragg peaks is inversely related to crystallite size
  – Often used for crystallite size estimates for nanoparticles
  – Requires use of a standard to determine instrument contribution first
  – Microstrain (nonuniform strain) also results in peak broadening
    – Due to atomic disorder, dislocations, vacancies etc.
    – Different angular dependence than size effects
    – Residual stress can be determined
  – Defects like stacking faults and antiphase boundaries also affect line shape

◆ Texture analysis
  – Epitaxial growth in thin films
  – Preferred orientation
    – Qualitative and quantitative measurements possible
Extracting Information from the Diffractogram

- All diffractograms contain three pieces of information:
  - Peak positions
  - Peak intensities
  - Peak shapes

- Each of these can be used to extract qualitative or quantitative information from the data

- Single crystal experiments are only concerned with peak positions and intensities, whereas powder diffraction also analyzes peak shapes to extract microstructural information from samples
  - Often not important to get crystal structure, but can be crucial to understand behavior of “real life materials”!
Peak Positions

- Peak positions can be used to obtain the following pieces of information:
  - Unit cell dimensions
    - d-spacing is related to unit cell constants
    - Could be a refinement of a know starting cell or a determination “from scratch” by indexing
  - Possible space groups
    - Look at systematic absences – “no peak” is information, too!
  - Qualitative phase analysis
    - What’s in the sample?
    - Approximate peak positions sometimes suffice for this
Standards

✦ A standard can be used to check the alignment of a diffractometer
  – Many different materials commercially available
    – SiO$_2$, Si, CeO$_2$, Al$_2$O$_3$…
    – Sold through independent vendors (e.g., NIST) or provided by diffractometer company

✦ Easiest to use standards come as pressed solids
  – No sample preparation, for Bragg Brentano: Sample height is predefined

✦ Experimentally determine peak positions of the standard, then compare to certified values to construct a calibration curve
  – Allows for correction of data collected under same conditions
  – Also used to determine instrument constants/wavelength at beamlines
Internal Standards

- A standard can also be mixed with your powder sample
  - Called internal standard

- You can use any material that is available as a powder and has well-established lattice constants

- If you are planning to refine a model for your data, a model for your internal standard can be refined at the same time
  - Constrain standard to known lattice constants, refine sources of peak position errors, which also apply to your sample

- Choose a standard with similar absorption properties as your sample
  - This allows you to account best for ALL sources of error
    - E.g., sample transparency, absorption
Peak Intensities

- Peak intensities contain information about the following:
  - Positions and types of atoms
  - Site occupancy of atoms
  - Atomic displacement parameters
    - Often referred to as “temperature factors”

- Accurate intensities are necessary for:
  - Quantitative phase analysis
  - Rietveld (structural) refinement
  - Structure solution from powder data

- Use integrated peak intensities to eliminate line broadening effects!

- Experimental setup also influences peak intensities
  - Lorentz-Polarization factor, absorption…

- So does the sample itself
Preferred Orientation

- Some samples do not show random intensities
  - Some orientations are over- or underrepresented
- In severe cases, only some lines are observed, others are absent
- Preferred orientation can be desired
  - E.g., epitaxial film
- Generally problematic and undesirable for powder data analysis
Surface Roughness Effects (Microabsorption Problem)

This is problematic for Bragg-Brentano setups; e.g., most of your lab diffractometers

http://www.osti.gov/bridge/servlets/purl/5062229-1CKCM6/5062229.PDF
Peak Shapes

- Peak shapes are affected by the following:
  - Crystallite size
    - Significant effects for crystallites below 100 nm
  - Microstrain
    - Microstrain can lead to a “range” of lattice parameters due to strain
  - Ordered defects
    - Stacking faults, antiphase boundaries
  - Instrument
    - Finite source size
    - Axial divergence
    - Slits
    - Detector resolution

- Isotropic or anisotropic peak broadening can result
- For quantitative analysis, a standard with no crystallite size or strain broadening must be used to determine the instrumental contribution
Examples of Peak Shapes

Gaussian peak shape

\[ G(t, \Gamma_g) = \frac{1}{\sqrt{2\pi\Gamma_g^2}} \exp\left(\frac{-t^2}{2\Gamma_g^2}\right) \]

Lorentzian peak shape

\[ L(t, \Gamma_L) = \frac{\Gamma_L}{2\pi \left(\frac{\Gamma_L}{2}\right)^2 + t^2} \]

Pseudo-Voigt peak shape

\[ P(t) = \eta \cdot L(t, \Gamma) + (1 - \eta) \cdot G(t, \sigma) \]
Sample Related Peak Broadening

- **Crystallite size:**
  - Diffraction from an infinite crystal would give infinitely sharp peaks (delta function)
  - Finite repeat leads to broadening
  - Can be used to calculate crystallite size (Scherrer equation), \( B = \text{FWHM} \) in radians
    - For lab instrument: \( B_{\text{size}} = 0.9 \ \lambda / (t \cos(\theta)) \)
  - Instrument broadening must be accounted for to get meaningful, qualitative results!
    - \( B^2_{\text{measured}} = B^2_{\text{instrument}} + B^2_{\text{size}} \)

- **Strain broadening:**
  - Results in distribution of lattice constants
    - More shift at higher angles – proportional to \( \tan(\theta) \)

- Both effects can be isotropic or anisotropic!
  - Anisotropic effects are generally hkl dependent
Sample related peak broadening
Powder Diffraction Detector Options

- Powder X-ray diffraction can use 1D or 2D detectors
  - Area (2D) detectors allow for very fast data collection
    - On high intensity synchrotron beamlines, a dataset can be collected in a fraction of a second!
    - Tradeoff with respect to resolution
    - Often used for parametric studies when speed of data collection is most important
  - Point detectors (1D) allow for very high resolution data
    - A single crystal analyzer can be mounted between the sample and the detector
    - Data collection speed can be improved by using multiple detectors
    - Example: 11-BM high resolution diffractometer at APS
Powder Diffraction Detector Options

- 2D detector (CHESS B2) and 1D detector array (APS 11-BM)
Neutron Diffraction: Reactor Sources

- Experimental setup very similar to lab X-ray diffraction
- Large samples needed
  - low intensity beams
- No form factor fall-off gives good quality data at small d-spacings
  - but $d_{\text{min}}$ is often similar to a lab X-ray experiment

Typical monochromator cut at $\sim 1.5$ Å for $T = 300$ K
Spallation Source – TOF Experiments

- Neutrons are particles with mass, so wavelength and speed are correlated (de Broglie)

\[ m \cdot v = \frac{h}{\lambda} \quad \text{with} \quad v = \frac{(L + L_1)}{t} \]

so \[ t = \frac{m(L + L_1)\lambda}{h} \]

- Data are plotted as a function of t (TOF)
- Detectors are combined in “banks” at fixed angles
  - Each detector bank collects an entire diffraction pattern
  - Accessible d-spacing range depends on angle of bank
Neutron TOF Powder Instruments

- Earlier TOF neutron instrument at IPNS (SEPD), and modern instrument at SNS (POWGEN)
Powder Pattern Analysis Beyond Search/Match

- As stated previously, early use of powder methods, and most common use today, was for phase ID

- 1966-1969: Hugo Rietveld\* introduced a whole pattern fitting approach for neutron data
  - Nowadays known as “Rietveld method”
  - Soon applied to X-ray data (1977)
  - Became more feasible with increasing computer power
  - “Routine” powder tool by now

- The Rietveld method can be used to verify structures, determine accurate lattice parameters, microstructural sample characteristics, phase fractions in mixtures etc.

\*It is with great sadness that we acknowledge the passing of Hugo Rietveld on July 16, 2016.
Major Breakthrough: Overlapped Reflections

- Rietveld witnessed the power of introducing computers into crystallography during his dissertation (1961-1964)
- He realized that computers can handle individual datapoint intensities, which allowed calculation of $|F_{hkl}|$ even for overlapped reflection!
What is the Rietveld Method?

◆ Least squares based minimization algorithm to obtain the best fit between a structural model and a powder pattern
   - Demanding, as the algorithm is non-linear
   - User decides which parts of the model can be varied

◆ Each point in the pattern can be regarded as an observation
   - “No Bragg intensity” tells you something about your material, too!

◆ Full pattern fitting
   - In contrast to single crystal data, “experiment dependent parameters” must be fitted as well: Background, peak shape – sample and instrument contributions, lattice constants, …

◆ Requires an approximate starting model

◆ Good data are needed!
Parameters in Rietveld Refinements

◆ Structural variables
  - Atom positions, fractional occupancies, atomic displacement parameters (ADPs)
  - Only these parameters are refinable in most single crystal software

◆ Profile parameters
  - Background
  - Peak shape, including width and asymmetry
  - Unit cell constants
  - Wavelength
  - Diffractometer zero point
  - Sample height and transparency

◆ Correction terms
  - Absorption
  - Extinction
  - Surface roughness
  - Preferred orientation
Possibilities

◆ Works for simple and complicated structures
  - Thanks to today’s computing power, fast even for complicated structures

◆ Can be used to refine several phases as well as mixed occupancies
  - Use of internal standard possible – excellent lattice constants!
  - Quantitative analysis of mixture or versus a standard (amorphous content, too)
  - Non-stoichiometry/partial occupancy can be refined

◆ Refinement of several data sets together
  - X-ray and neutron data
  - Several different wavelengths => changes scattering contrast between atoms

◆ Engineering properties
  - Residual strain
  - Preferred orientation
Limitations

- Determination of absolute structure from powder data is impossible due to precise overlap of hkl and -h-k-l reflections
- Parameters can sometimes be correlated
- For limited data, constraints or restraints can be necessary
  - Restrain bond distances or bond angles
  - Constrain composition if known
- The method only works if you have a good starting model!
  - Otherwise, divergence might be observed
  - A local instead of a global minimum may be found
  - YOU need to judge the refinement – no simple rules of thumb for R-values etc. or cif file and checkcif!
Useful Resources

◆ CCP14: Free software including tutorials and examples
  http://www.ccp14.ac.uk/
  – Unfortunately no longer maintained due to lack of funding

☐ Rietveld mailing list
  http://www.mail-archive.com/rietveld_l@ill.fr/
  – Not sure whether this website is accessible from here?

☐ GSAS tutorials
  http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/
  – Scroll down to “Software tutorials”

☐ R. A. Young; “The Rietveld method”
  – Comprehensive text including history, description of several Rietveld programs, as well as details about certain parameters (e.g. background modeling, peak shapes, pattern decomposition…)

☐ …and many more good books!