MSAE E8235x - Selected Topics In Materials Science: X-ray Powder Diffraction

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<th>Lecturer</th>
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My Bio

Education:
• University of Paris, PhD, 1987
• Research Associate, Synchrotron Radiation Source, Daresbury, UK, 88-89

Professional Experience:
• Assoc. Scientist, Res. Center with Ions and Lasers France, 90-95
• Scientist, European Synchrotron Radiation Facility, France, 96-00
• Scientist, Neel Institute, CNRS Grenoble, France, 2001-09
• Scientist, beamline lead, Brookhaven National Lab., NSLS II, 2009-

Background: Materials Science, Irradiation Physics, PD, SR
Current position: ‘Diffraction & In Situ Scattering’ Program Manager
Outline

1. Applications for Powder Diffraction
2. Experimental Methods for collecting PD data
3. PD for Quantitative Analysis and Crystallography
   Peak Profile Analysis for Microstructural Studies
4. Advanced PD techniques
Short History of Powder Diffraction

- **1895** Discovery of X-rays by Roentgen
- **1912** von Laue demonstrates that X-rays can be diffracted by crystals
- **1935** Le Galley constructs the first X-ray powder diffractometer
- **1947** Phillips introduces the first commercial powder diffractometer
- **1950-60’s** Powder diffraction used primarily to study structural imperfections, phase identification, ... largely by metallurgists and mineralogists
- **1969** Hugo Rietveld develops a method for whole pattern analysis of neutron powder diffraction data
- **1977** Cox, Young, Thomas and others first apply Rietveld method to synchrotron and conventional X-ray data
Examples of Powders

- Wood fiber board
- Glass ware
- Metal parts
- Powdered milk
- Cosmetic powder
- Gunpowder
- Powdered sugar
- Potassium bromate
- Pharmaceuticals
- Polymers
- Potassium bromate
- Zymin
- Brightening agent
- Ground coffee
- Flour
- Fine snow
- Ceramics
- Polycrystalline Materials
Uses of Powder Diffraction

Single Crystal Diffraction is preferred in most cases BUT:

• the product naturally occurs as a powder
• the functionalized form of the product is a powder
• because a single crystal of sufficient size or quality cannot be synthesized
Uses of Powder Diffraction

- **Qualitative Analysis**
  - Phase ID

- **Quantitative Analysis**
  - Lattice parameters (indexing)
  - Phase mass fraction (mixture)

- **Structure Determination**
  - Reciprocal Space Methods (*ab initio*)
  - Real Space Methods

- **Structure Refinement**
  - Rietveld Method (whole pattern)

- **Peak Shape Analysis**
  - Crystallite Size Distribution
  - Microstrain (metallurgy)
  - Anti-phase domains, stacking faults,...
Uses of Powder Diffraction

A versatile and powerful technique that can be used to study complex materials.

- Kinetics and mechanism of how structures form during reversible or irreversible chemical reactions.
- How materials work in devices under real working conditions. Ex: batteries, fuel cells.
- Functioning of catalyst during reactions.
- Phase transitions.
- Phase quantification (mixture of phases).

Monoclinic - Cubic phase transition at ~405 K
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry, ...

- Structure determination (crystallography)

MgCu$_2$ (cubic system, space group is $Fd\ 3m$)
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,...

- Structure determination (crystallography)
- Phase identification (mineralogy)
- Quantitative analysis (phase content)

\[ A + B \rightarrow A + C + D \text{ (kinetics: mass fractions } f(t) \text{)} \]

\hspace{1cm} e.g., Natural Granodiorite: Major Quartz, Feldspar, Albite, Biotite; lesser Clinochlore, Hornblende; traces of Zircon.

Pharmaceutical: Mannitol, Sucrose, DL-Valine, Starch, Nizatidine.
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,...

Texture (orientation) of polycrystalline materials

Crystallite orientations are not random
Texture is found in many engineered materials, and can have a great influence on materials properties (anisotropy)
e.g., geologic rocks show texture due to their thermo-mechanic history of formation processes
HT superconductor thin films deposited on metallic ribbons (critical currents in YBa$_2$Cu$_3$O$_7$)
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,...

• Structure determination (crystallography)
• Phase identification (mineralogy)
• Quantitative analysis (phase content)
• Texture (orientation) of polycrystalline materials

• Residual stress analysis
  created during the manufacturing process, or it may accumulate in a structure over many years in operation.
  stress can have a serious negative effect on a product's quality, durability and lifetime (QA, service)
  e.g., laser peening in aircraft engine blades
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,...

Peening is a working process to produce a compressive stress at the surface to overcome failure due to metal fatigue, stress corrosion cracking, fretting,...

- Residual stress analysis
  created during the manufacturing process, or it may accumulate in a structure over many years in operation.
  stress can have a serious negative effect on a product's quality, durability and lifetime (QA, service)
e.g., laser peening in aircraft engine blades
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,...

- Structure determination (crystallography)
- Phase identification (mineralogy)
- Quantitative analysis (phase content)
- Texture (orientation) of polycrystalline materials
- Residual stress analysis
- Microstructure: crystallite size and defects
- Structural behavior under complex environments
1. Applications for Powder Diffraction

2. Experimental Methods for collecting PD data

3. PD for Quantitative Analysis and Crystallography
   Peak Profile Analysis for Microstructural Studies

4. Advanced PD techniques
Single Crystal vs. Powder Diffraction

**Single Crystal Diffraction**
- Incident Beam
- Diffracted Beam

**Powder Diffraction**
- Incident Beam
- Diffracted Beam

In powder diffraction only a small fraction of the crystals (shown in blue) are correctly oriented to diffract.
Scheme of a One-Axis Diffractometer

- X-ray source (tube, rotating anode)
- Powder sample (flat plate, capillary)
- X-ray detector (a variety of technologies: direct counting or conversion)
- Diffraction plane (contains the incident and the diffracted beam)
Scheme of a Two-Axis Diffractometer

Optics:
- Para-focusing optics (Bragg-Brentano: sample rotates by $\theta$, detector rotates by $2\theta \rightarrow$ to keep detector on focusing (Rowland) circle
- Slits before the sample (divergence) and after (angle resolution $\Delta 2\theta$)
- Parallel optics (pre-sample mirror)
1. **Reflection**: low energy X-rays, thick or absorbing sample, surface
2. **Transmission**: high energy X-ray or transparent sample, bulk

**Bragg-Brentano parafocusing geometry**

**Debye Scherrer geometry**
Monochromation:
• ON: **Angle Dispersive** (detector is scanned to measure at all possible $2\theta$ angles)
• OFF (white beam case): **Energy Dispersive** (detector is fixed)
Spinning sample (in many cases):
- Average: as many crystallites (grains) in the beam as possible
- Randomize: eliminates preferred orientation
- Not a powder (texture, poor sampling) → intensities are affected
Parameters determining resolution and intensity:

• Source (flux output, divergence)
• Monochromator (ΔE)
• Mirror (focusing, parallel)
• Analyzer (discrimination, error immune)
From 0-D Powder Diffraction...

- 0-D (point) detector: scanning (slow and accurate)
- 1-D (strip) detector: intercepts all 2θ angle (fast but lower res)
• 2-D (large-area) detector: Debye-Scherrer cones (large field of view in one single shot, background high, lousy resolution)
• Non-random orientation (preferred orientation) generates non-uniform rings (texture, pole figures)
Nov. 2014
"Superconducting Order from Disorder in 2H-TaSe2-xSx" to Nature Materials
Coll. BNL, APAM Columbia, Rutgers U (NJ), Institute of Solid State Phys. in China.
First Publication at NSLS-II

- 48 keV
- 60 sec acquisition per frame

Title: "Enhanced Thermoelectric Power and Electronic Correlations in RuSe2"
Diffraction pattern (not a spectrum): elastic process no photon energy change
Today’s challenge is to reproduce this resolution and signal-to-noise discrimination from sample inside a HP vessel.

\( \text{M + B + 2H}_2 \rightarrow \text{MBH}_4 \) (M = Li, Na, ½Mg, etc)

550 - 700° C; 3 - 15 MPa (≈ 200 atm H2)


“Low Temperature” phase of Mg(BH4)2

This is not noise

\( \lambda \sim 0.7\text{Å} \)
From Laboratory Powder Diffraction...

- Flux (weak scatterer, diluted, time-dependent)
- Energy tunability (less absorption, anomalous, white beam)
- Optics (resolution, small beam size)
• X-ray source: $ value and photon flux $ \times 1,000,000$
• Capacity of NSLS-2: 60 beamlines
• Each beamline has its own support staff, its specific techniques, its research program, its user communities
Source and Front End

Front End (shutter, masks, slits)

Damping Wiggler
POWDER DIFFRACTION BEAMLINE (XPD)

Optical Enclosure

Beam size = 0.56 x 0.12 mm² (no slits)

3 endstations

5 years from design to start of operations
XPD OPTICAL ENCLOSURE

Filter array

Diamond filters

Vertical mirror

Double Laue Monochromator
VERTICALLY FOCUSING MIRROR

Slope Error:
0.36 microrad
(0.02 mdeg)

Roughness
0.3nm rms

Bending 10kms
Other Powder Diffraction machines

Melbourne

Oxford

Chicago

Japan
Off the shelf systems: LN2 Cryostream, Cyberstar hot air blower, Linkam furnaces, Flat plate heater

Capabilities:
- Temperature Range: 80K, Ambient - 1500°C
- Sample holder Type: Capillary (compatible with Robotic sample changer), Flat Plate
Sample Environments

**User-custom:** flat plate and capillary furnaces, He cryostats, Flow cells, Hydrothermal cells and functional devices (poach cells, coin cells)

**Capabilities:**
- Temperature Range: 4K - 1200°C
- Sample holder Type: Capillary, flat plate
- Gas Flow, gas/liquid Pressure
Neutrons vs. Synchrotron

**Synchrotron X-rays**

![Synchrotron X-ray graph]

**TbBaFe$_2$O$_5$ - 300 K Synchrotron X-ray**

**Neutrons**

![Neutron data graph]

**TbBaFe$_2$O$_5$ - 70 K Neutron Data**

The peak intensities drop off at high angles in an X-ray diffraction pattern because the form factor decreases.

Neutrons are scattered from the nucleus and the form factor is not angle dependent. Intensities do not drop off at high angle.
Neutrons vs. Synchrotron

**Synchrotron X-rays**
- Extremely high resolution
- Subtle distortions
- Indexing and Structure determination
- Anomalous scattering
- Texture effects

**Neutrons**
- Scattering length contrast
- More sensitive to light elements (H, N, O, F, C, etc.) and isotope distributions
- Low absorption: large samples, easy sample environments
- Magnetic structures
- Structure refinement
- Moderate resolution
Outline

1. Applications for Powder Diffraction
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The crystal structure of a material (the packing of atoms within the crystal) can be described by a discrete set of lattice planes \((hkl)\). Lattice planes have specific inter-spacings \(d(hkl)\).
Bragg diffraction: constructive interference occurs when the path length difference is equal to an integer multiple of the wavelength of the incident radiation.

- Translational symmetry and unit cell defines the diffraction peak positions
- Atomic distribution (atom locations) defines the intensities

**Bragg Law**

\[ 2d \sin(\theta) = \lambda_0 \]

where:
- \( d \) = lattice interplanar spacing of the crystal
- \( \theta \) = x-ray incidence angle (Bragg angle)
- \( \lambda \) = wavelength of the characteristic x-rays
Powder Diffraction Pattern

A series of intensity values (detector photon counts) vs. diffraction angle
Qualitative Analysis

Any powder pattern can be used like a fingerprint to see if it matches the powder pattern of an already known compound. The International Centre for Diffraction Data (ICDD) (PA) maintains a database of known powder diffraction patterns (www.icdd.com)

- 365,900 standardized entries
- 42,800 Minerals
- 502,000 Organics
## Crystal Structure

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<tr>
<th>Crystal System</th>
<th>Parameters</th>
<th>Lattice Symmetry</th>
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<tbody>
<tr>
<td>Triclinic</td>
<td>(a \neq b \neq c; \alpha \neq \beta \neq \gamma)</td>
<td>(\bar{1})</td>
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<tr>
<td>Monoclinic</td>
<td>(a \neq b \neq c; \alpha = \gamma = 90^\circ; \beta &gt; 90^\circ)</td>
<td>(2/m)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ)</td>
<td>(mmm)</td>
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<tr>
<td>Tetragonal</td>
<td>(a = b \neq c; \alpha = \beta = \gamma = 90^\circ)</td>
<td>(4/mmm)</td>
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<tr>
<td>Rhombohedral (Trigonal(^*))</td>
<td>(a = b = c; \alpha = \beta = \gamma \neq 90^\circ)</td>
<td>(\overline{3}m)</td>
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<tr>
<td>Hexagonal</td>
<td>(a = b \neq c; \alpha = \beta = 90^\circ; \gamma \neq 120^\circ)</td>
<td>(6/mmm)</td>
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<tr>
<td>Cubic</td>
<td>(a = b = c; \alpha = \beta = \gamma = 90^\circ)</td>
<td>(m\overline{3}m)</td>
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**Diagrams:**
- **Isometric (Cubic)**
- **Hexagonal**
- **Tetragonal**
- **Orthorhombic**
- **Monoclinic**
- **Triclinic**
Crystal Structure

the unit cell
the space group
the asymmetric unit

Crystal data

- Formula: O2 Ti
- Crystal system: tetragonal
- Space group: P 42/m n m (no. 136)
- Unit cell dimensions: $a = 4.5937 \, \text{Å}$, $c = 2.9587 \, \text{Å}$
- Cell volume: 62.40 Å³
- Z: 2

Atomic coordinates

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<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>0</td>
<td>0</td>
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<tr>
<td>O</td>
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<td>4f</td>
<td>0.30469</td>
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Selected geometric parameters (Å, °)

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<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
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<td>Ti—Ti</td>
<td>2.959</td>
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<tr>
<td>O—O</td>
<td>2.959</td>
<td>Ti—Ti</td>
<td>3.569</td>
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Crystal Scattering Amplitude

A crystal = convolution of an atomic motif $M(\vec{r})$ and a lattice $R(\vec{r})$

$$C(\vec{r}) = R(\vec{r}) \ast M(\vec{r})$$

The scattered amplitude corresponds to the Fourier transform of the scattering object

$$C(\vec{h}) = TF\{C(\vec{r})\} = TF\{R(\vec{r}) \ast M(\vec{r})\} = R(\vec{h})xF(\vec{h})$$

The Fourier space is called \textbf{reciprocal space}

$R(\vec{h}) = $ FT of the (direct) lattice: \textbf{Reciprocal Lattice}

$F(\vec{h}) = $ FT of the atomic motif: \textbf{Structure factor}

\textit{Knowing the reciprocal lattice and the structure factors is equivalent to knowing the structure in real space}
Crystal Structure Factor

Atomic form factor = scattering amplitude

\[ F(hkl) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \]

Structure factor is the Fourier transform of the electron density. It takes into account the individual scattering \( f \) of all \( j \) atoms contained in the crystal unit cell.
X-ray vs. neutron Scattering length
Crystal Structure Factor

\( F_{hkl} \): structure factor for reflection (hkl) = TF{ \( M(\vec{r}) \) }, atomic motif

\( F_{hkl} \): Fourier transform of the scattering density of the crystal

\[
F_{hkl} = \sum_{j \in \text{cell}} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))
\]

\( f_j \): scattering factor for atom j with coordinates \((x_j, y_j, z_j)\). FT of its scattering density

For x-rays, \( f_j \) is the atomic form factor,

For neutrons, \( f_j = b_j \) is the Fermi length.

\( T_j = \textbf{Debye-Waller} \) factor related to atomic displacements (thermal, positional,…).

In an isotropic, harmonic approximation one has :

\[
T_j = \exp\{-B_j (\sin^2 \theta) / \lambda^2 \}
\]

with \( B_j = 8\pi^2 \langle U_j^2 \rangle \)

\( \langle U_j^2 \rangle \) is the root mean square displacement of atom j.
If the crystal contains symmetry elements with translations, some categories of reflections have zero intensity by symmetry. One speaks of *systematic extinctions*.

**Example:** body centered lattice I: translation \( \frac{a + b + c}{2} \)

For every atom at \((x_j, y_j, z_j)\) there an equivalent atom at \((x_j + 1/2, y_j + 1/2, z_j + 1/2)\)

\[
F_{hkl} = \sum_{j \in \text{cell}} f_j \exp(2i\pi(hx_j + ky_j + lz_j))
\]

\[
F_{hkl} = \sum_{j \in 1/2 \text{cell}} f_j \exp(2i\pi(hx_j + ky_j + lz_j))\{1 + \exp(i\pi(h + k + l))\}
\]

=> The lattice is I \(\Leftrightarrow\) \(F_{hkl} = 0\) for every odd \((h+k+l)\)

This is used to detect symmetry-translation elements and restrict the space group choice.
The diffracted intensity is the quantity accessible in a diffraction experiment (proportional to the number of diffracted particles reaching the detector).

In the kinematic approximation (neglecting double diffraction), one has:

\[ I_{hkl} = S \cdot C_{hkl} \cdot |F_{hkl}|^2 \]

\[ F_{hkl} = \sum_{j \in \text{cell}} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j)) \]

\( F_{hkl} \) : complex number \( \Rightarrow \) phase of \( F_{hkl} \) not measured. Information is incomplete. To solve the structure, one must retrieve the phases of \( F_{hkl} \), one way or another…
1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more well adapted diffraction experiments
Optimize the data quality (low background, low peak overlapping,…)
(x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, etc…)

3) Find unit cell and index Bragg reflections (Dicvol, Treor, Ito, etc…). See www.ccp14.ac.uk/solution/indexing/

4) Obtain intensities of Bragg reflections and determine the space group
   (LeBail technique + CheckGroup)

5) Find approximate starting structural model of the atomic motif ab initio using Direct Methods (e.g., Expo - phases of strong reflections are obtained directly from the structure factor moduli) or Charge Flipping (Superflip)

6) Rietveld refinement and Fourier recycling to obtain a complete and accurate structure using Fullprof or GSAS-II
Ab Initio Structure Solving in Direct Space

Plausible structure models are randomly generated by moving atoms or groups of atoms in crystal coordinates. The calculated diagram is compared to the observed one.

- avoid a priori impossible configurations (too small distances, etc.)
- avoid to get blocked in a local minimum

**Example**: simulated annealing

For each configuration, one calculates a **cost function**, based on a pseudo-potential energy to minimize, and on the agreement between experiment and model:

\[ C = \alpha E_{pot} + (1-\alpha) R \]

*Epot* may depend on the bond type (ionic, covalent, intermetallic...), Lennard-Jones, Coulomb, ...

\[ R = 100 \sum_{2\theta} \left| I_{\exp}(2\theta) - I_{\text{calc}}(2\theta) \right| / \sum_{2\theta} I_{\exp}(2\theta) \]

One goes from config. Ci to Ci+1 following a **Monte-Carlo** type algorithm:

- If Ci+1 < Ci, move accepted
- If Ci+1 > Ci, move accepted with probability: \( \exp[-(Ci+1-Ci)/K] \)

\( K \approx \) temperature, decreases slowly during search.
The model to calculate a powder diffraction pattern is:

\[ y_{ci} = \sum_{h} I_h \Omega(T_i - T_h) + b_i \]

Profile function characterized by its full width at half maximum (FWHM=\(H\)) and shape parameters (\(\eta, m, \ldots\))

\[ \int_{-\infty}^{+\infty} \Omega(x)dx = 1 \]

\[ \Omega(x) = g(x) \otimes f(x) = \text{instrumental} \otimes \text{intrinsic profile} \]

- **Profile refinement**: modeling is constrained by peak positions (symmetry, unit cell) and peak profile
- **Rietveld refinement**: and intensities are constrained by the atomic model (atom coordinates in the unit cell)
The Rietveld Method consist of refining a crystal (and/or magnetic) structure by minimising the weighted squared difference between the observed and the calculated pattern against the parameter vector: $\beta$

$$\chi^2 = \sum_{i=1}^{n} w_i \{ y_i - y_{ci}(\beta) \}^2$$

$$w_i = \frac{1}{\sigma_i^2}$$

$\sigma_i^2$: is the variance of the "observation" $y_i$
Rietveld Refinement 3

1) Peak position fitting: **unit cell parameters** (thermal expansivity, macroscopic strain)

2) Intensity fitting of individual reflections to extract the structure factors: they contain the phase fractions (**quantitative analysis**) and the structural parameters (**crystal structure**: atomic positions)

3) Isotropic or anisotropic temperature or displacement factors

4) **Peak shape fitting** of individual from the perfect crystal
   - crystallite size
   - shape (needle, platelet,...)
   - microstrain

*Peak broadens when crystallite size decreases*
a = 6,5358 Å
b = 17,6040 Å
c = 19,7070 Å
P 2\textsubscript{1} 2\textsubscript{1} 2\textsubscript{1}
χ\textsuperscript{2} = 1,73

Hydrogen linked network
Rietveld Structure refinement

Cation sorption in a zeolite (filter, membrane, trap)

Formula: $\text{Si}_{110} \text{Al}_{84} \text{O}_{384}, n\text{H}_2\text{O}$

Space Group: Fd -3 m

Unit cell parameter: 25 Å
Peak Profile Fitting

• XRD Crystallite Size using the Scherrer Formula
  \[ D = \frac{K \lambda}{\beta \cos \theta} \]

\( \beta \) is the FWHM of the Bragg peak after correction for instrumental broadening

• Modeling the Gaussian and Lorentzian components of the Bragg profile function:
  \[ H_G^2 = (U + (1 - \xi)^2 D_{ST}^2) \tan^2 \theta + V \tan \theta + W + \frac{I_G}{\cos^2 \theta} \]
  \[ H_L = (X + \xi D_{ST}) \tan \theta + \frac{[Y + F(S_Z)]}{\cos \theta} \]

Size and Strain in Reciprocal Space

Williamson-Hull Plot

$$FWMHM \times \cos(\theta) = \frac{K \times \lambda}{Size} + Strain \times 4 \times \sin(\theta)$$

Grain size and strain broadening

Grain size broadening

Gaussian peak shape assumed

K = 0.94

grain (actual particle of matter) ≠ crystallite (coherent domain)
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Anomalous Powder Diffraction

\[ F_{hkl} = \sum_{i=1}^{n} f^i \cdot e^{2\pi i (hx_i + ky_i + lz_i)} \]

- **Electronic property of atom**
- **Structural property (position)**
- **Two terms**

Dispersive term
Absorption term

\[ f(\theta, \lambda) = f_0(\theta) + f'(\lambda) + if''(\lambda) \]

Se K edge = 0.9795 Å
Effect of Short Range Order

Simulation by T. Proffen at the SNS
Total Scattering

- “Traditional” powder diffraction data analysis is insufficient or fails in particular for non-crystalline materials (disorder, defects) and nanomaterials (short structural coherence length, broad Bragg peaks).

- PD patterns of complex materials often show diffuse scattering smeared in the reciprocal under the Bragg peaks.

- FT of the total powder diffraction data (Bragg + diffuse) gives the PDF.
Pair distribution function (PDF) gives the probability of finding a neighbor atom at a distance “r” from a given atom.

\[ Q = 4\pi \sin(\theta)/\lambda \]
PDF Set-up at NSLS

FT of the signal \(\rightarrow\) far in reciprocal space
\(\rightarrow\) High photon energy (>60keV)
\(\rightarrow\) 2D detector close to the sample
PDF Analysis Examples

Graphene

Cu$_2$Se

Intensity (arbitrary units)

$G$(Å$^{-2}$)

$Q$(Å$^{-1}$)

$TTH$

$r$(Å)

SRO

LRO

Gruni, Diff, Gcalc
PDF Benchmarking NSLS-II (Columbia, BNL)

Measured (blue) and calculated (red) Pair Distribution Functions. Green curve shows the difference.

Ni Standard
Q\text{max} = 25 \text{ Å}^{-1}, R_w = 3.6\%

PbSe
Q\text{max} = 25 \text{ Å}^{-1}, R_w = 3.8\%

65.7 keV (300\text{µm})^2
1 \text{min} @ 25\text{mA}
Summary of the Scientific Scope

Powder Diffraction addresses a wide range of topics from Fundamental (incl. metallurgy, physics, chemistry, biology etc.) to Applied Research → controlling complexity (real devices, heterogeneous)

Crystallography

High resolution

Structure solving

Kinetics / time-resolved

High throughput

Extreme environments (T, P, gas, B, E)

In situ in Operando
Complex materials:

- Photovoltaics with improved efficiency – Nanoparticles in the light collecting layer
- High energy density batteries – Electrodes, Electrolytes
- Fuel cells – Electrodes, Electrolytes
- Catalysts – Higher-order oxides, graphitic carbon, nanoparticles
- Hydrogen storage – MOF’s
- Carbon sequestration – Functionalized mesoporous materials
- Strongly correlated materials – Materials doped with impurities

Complexity: Defects, Surfaces, Interfaces, Nano and multi-scale structures, heterogeneities, nanoscale disorder and surface relaxation etc.

Properties in relation with LRO (average) and SRO (deviations)
Powder Diffraction Resources


- [http://www.ccp14.ac.uk/mirror/mirror.htm](http://www.ccp14.ac.uk/mirror/mirror.htm) Collaborative Computational Project Number 14 Tutorials and Program Repository.

- [http://www.lightsources.org/](http://www.lightsources.org/) news and science highlights from each facility, as well as photos and videos, education and outreach resources, a calendar of conferences and events

International Tables for Crystallography

- Home page = [http://it.iucr.org/](http://it.iucr.org/)

A. Space-group symmetry
   Symmetry relations between space groups

B. Reciprocal space

C. Mathematical, physical and chemical tables

D. Physical properties of crystals

E. Subperiodic groups

F. Crystallography of biological macromolecules

G. Definition and exchange of crystallographic data

H. Powder Diffraction (new: 50 chapters, 800 pages)
   1. Introduction to the principles of powder diffraction.
   2. Instrumentation for laboratory X-ray studies, synchrotron, neutron and electron diffraction, 2D diffraction, and special environments (temperature, pressure, magnetic fields, reaction cells).
   3. Different methodologies used in powder diffraction.
   4. Structure determination and validation.
   5. Defects, texture and microstructure: stress and strain, grain size and thin films.
   6. Review of available software.
   7. Applications to: macromolecules, zeolites, mining, ceramics, cement, forensic science, archaeology and pharmaceuticals.

I. X-ray Absorption Spectroscopy (new)
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- Milinda Abeykoon (BNL)
- and ... google!
The crystal structure of SrTiO$_3$ is cubic, space group Pm3m with a unit cell edge $a = 3.90$ Å. Calculate the expected 2$\theta$ positions of the first three peaks ((100), (110) and (111)) in the diffraction pattern, if the radiation energy is 30 keV.

1) Use $1/d^2 = (h^2 + k^2 + l^2)/a^2$ and the Bragg’s Law

2) SrTiO$_3$ is a perovskite (see figure). Calculate the structure factor of the (100) reflection at $G = \sin(\theta)/\lambda = 5\text{Å}^{-1}$ (see slide 51, ignore Debye-Waller term, and use [lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactor)s/formfactors.php](lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactor)s/formfactors.php)