Structural Analysis

Apurva Mehta

SSRL
Physics of Diffraction

X-ray Lens not very good

Mathematically

Intersection of Ewald sphere with Reci Lattice
outline

- Information in a Diffraction pattern
- Structure Solution
- Refinement Methods
- Pointers for Refinement quality data
What does a diffraction pattern tell us?

- **Peak Shape & Width:**
  - crystallite size
  - Strain gradient

- **Peak Positions:**
  - Phase identification
  - Lattice symmetry
  - Lattice expansion

- **Peak Intensity:**
  - Structure solution
  - Crystallite orientation
Sample ↔ Diffraction

Diffraction Pattern ~ \{\text{FT(sample)}\} \{\text{FT(sample)}\}

Sample size (S) = \text{Sample} \times \text{Infinite Periodic Lattice (P)}

Motif (M)
**Sample ↔ Diffraction**

\[ \text{FT(Sample)} = \text{FT}((S \times P)\times M) \]

Convolution theorem

\[ \text{FT(Sample)} = \text{FT}(S \times P) \times \text{FT}(M) \]

\[ \text{FT(Sample)} = (\text{FT}(S) \times \text{FT}(P)) \times \text{FT}(M) \]
FT(P)
\[ \text{FT} (S \times P) = \text{FT}(S) \times \text{FT}(P) \]
FT(M)
$\text{FT(sample)} = \text{FT}(S \times P) \times \text{FT}(M)$

Along X direction
What does a diffraction pattern tell us?

- **Peak Shape & Width:**
  - crystallite size
  - Strain gradient

- **Peak Positions:**
  - Phase identification
  - Lattice symmetry
  - Lattice expansion

- **Peak Intensity:**
  - Structure solution
  - Crystallite orientation
Structure Solution

- **Single Crystal**
  - Protein Structure
  - Sample with heavy Z problems Due to
    - Absorption/extinction effects
  - Mostly used in Resonance mode
    - Site specific valence
    - Orbital ordering.

- **Powder**
  - Due to small crystallite size
    - kinematic equations valid
  - Many small molecule structures obtained via synchrotron diffraction
  - Peak overlap a problem – high resolution setup helps
  - Much lower intensity – loss on super lattice peaks from small symmetry breaks. (Fourier difference helps)
Diffraction from Crystalline Solid

- Long range order ----> diffraction pattern periodic
- crystal rotates ----> diffraction pattern rotates

Pink beam laue pattern
Or intersection of a large Ewald Sphere with RL
From 4 crystallites
From Powder
Powder Pattern

- Loss of angular information
- Not a problem as peak position = \( fn(a, b \& \alpha) \)

- Peak Overlap :: A problem
- But can be useful for precise lattice parameter measurements
Peak Broadening

- ∼ (invers.) “size” of the sample
  - Crystallite size
  - Domain size

- Strain & strain gradient

- Diffractometer resolution should be better than Peak broadening But not much better.
\[ W_d^2 = M^2 \times \phi_b^2 + \phi_s^2 \]

\[ M = \left( \frac{2 \tan \theta}{\tan \theta_m} - \frac{\tan \theta_a}{\tan \theta_m} - 1 \right) \]

Where

- \( \phi \) = divergence of the incident beam,
- \( \phi_b \) = cumulative divergences due to slits and apertures
- \( \phi_s \) = cumulative divergences due to slits and apertures
- \( \theta \), \( \theta_a \) and \( \theta_m \) = Bragg angle for the sample, analyzer and the monochromator
Powder Average

Single crystal – no intensity
Even if Bragg angle right,
But the incident angle wrong

\[ \Theta +/- \delta(\Theta) = \theta +/- \delta(\theta) \]

\[ \delta(\theta) = \text{Mosaic width} \sim 0.001 - 0.01 \text{ deg} \]
\[ \delta(\Theta) = \text{beam dvg} \sim >0.1 \text{ deg for sealed tubes} \]
\[ \sim 0.01 \text{ deg for synchrotron} \]

For Powder Avg

Need <3600 rnd crystallites – sealed tube
Need \sim 30000 rnd crystallites - synchrotron

Powder samples must be prepared carefully
And data must be collected while rocking the sample
Physics of Diffraction

No X-ray Lens

Mathematically

radiation: light electrons x-rays neutrons
Phase Problem

\[ \rho_{xyz} = \sum_{hkl} F_{hkl} \exp(-2\pi i \{hx + ky + lz\}) \]
\[ F_{hkl} \text{ is a Complex quantity} \]
\[ F_{hkl}(f_i, r_i): (F_{hkl})^2 = I_{hkl}/(K*Lp*Abs) \]
\[ \rho_{xyz} = \sum_{hkl} C\sqrt{I_{hkl}} \exp(-(\phi + \Delta\phi)) \]
\[ \Delta\phi = \text{phase unknown} \]
\[ \text{Hence Inverse Modeling} \]
Solution to Phase Problem

- Must be guessed
  - And then refined.

- How to guess?
  - Heavy atom substitution, SAD or MAD
  - Similarity to homologous compounds

- Patterson function or pair distribution analysis.
Procedure for Refinement/Inverse Modeling

- Measure peak positions:
  - Obtain lattice symmetry and point group
    - Guess the space group.
    - Use all and compare via F-factor analysis
- Guess the motif and its placement
  - Phases for each hkl
- Measure the peak widths
  - Use an appropriate profile shape function
- Construct a full diff. pattern and compare with measurements
Inverse Modeling Method 1

- Reitveld Method

Model  →  Profile shape  →  Background  →  Data  →  Profile shape  →  Refined Structure
Inverse Modeling Method 2

Fourier Method

Model \rightarrow \text{Background} \rightarrow \text{Profile shape} \rightarrow \text{Data} \rightarrow \text{Refined Structure}

Integrated Intensities

phases
Inverse Modeling Methods

- Rietveld Method
  - More precise
  - Yields Statistically reliable uncertainties

- Fourier Method
  - Picture of the real space
  - Shows “missing” atoms, broken symmetry, positional disorder

- Should iterate between Rietveld and Fourier.
  - Be skeptical about the Fourier picture if Rietveld refinement does not significantly improve the fit with the “new” model.
Need for High Q

Many more reflections at higher Q.

Therefore, most of the structural information is at higher Q.
Profile Shape function

- Empirical
  - Voigt function modified for axial divergence (Finger, Jephcoat, Cox)
    - Refinable parameters – for crystallite size, strain gradient, etc…

- From Fundamental Principles
Collect data on Calibrant under the same conditions

- Obtain accurate wavelength and diffractometer misalignment parameters
- Obtain the initial values for the profile function (instrumental only parameters)
- Refine polarization factor
- Tells of other misalignment and problems
Selected list of Programs

- CCP14 for a more complete list
  http://www.ccp14.ac.uk/mirror/want_to_do.html
- GSAS
- Fullprof
- DBW
- MAUD

- Topaz – not free - Bruker – fundamental approach
Structure of MnO

\[ f_{\text{Mn}}(x,y,z,T,E) \]

\[ f_{\text{O}}(x,y,z,T,E) \]

Scattering density

\[ \text{structural fit} \]
Resonance Scattering

\[ F_{hkl} = \sum_{xyz} f_{xyz} \exp(2\pi i \{hx + ky + lz\}) \]

- \( f_{xyz} = \) scattering density
- Away from absorption edge
- \( \alpha \) electron density
Anomalous Scattering Factors

\[ f_{xyz} = f_e \left\{ f_i \xi_{xyzT} \right\} \]

\( f_e \) = Thomson scattering for an electron

\[ f_i = f_{i0}(q) + f_i'(E) + i f_i''(E) \]

\( \mu(E) = E \ast f_i''(E) \)

Kramers-Kronig :: \( f_i'(E) \leftrightarrow f_i''(E) \)

\[
f'(E_0) = \frac{2}{\pi} \int_{0}^{\infty} f''(E) \frac{E}{E^2 - E_0^2} dE
\]
Resonance Scattering vs Xanes

\[ \mu = \frac{f'}{E} \]

from KK transform of XANES

from resonance scattering
XANE Spectra of Mn Oxides

Energy (eV)

Absorption

Mn Valence

MnO

MnO₂

Mn₂O₃

Mn₃O₄

MnO

Mn

Mn(II)?

Mn(I)?

Avg.

Actual
F’ for Mn Oxides
Why Resonance Scattering?

- Sensitive to a specific crystallographic phase. (e.g., can investigate FeO layer growing on metallic Fe.)
- Sensitive to a specific crystallographic site in a phase. (e.g., can investigate the tetrahedral and the octahedral site of Mn$_3$O$_4$)
**Mn valences in Mn Oxides**

- Mn valence of the two sites in Mn$_2$O$_3$ very similar
- Valence of the two Mn sites in Mn$_3$O$_4$ different but not as different as expected.

![Graph showing Mn valences in Mn Oxides](attachment:image.png)

Mn$_3$O$_4$

A. Mehta, A. Lawson, and J. Arthur