Applications of Powder Diffraction Methods

Jim Rhyne
Lujan Neutron Scattering Center, LANL
Los Alamos, NM 87545

- Scattering sources, instruments, line shapes, resolution
- Rietveld Structure Refinement Analysis
- Magnetic Structures and Diffraction
- Example Refinement Ho$_6$Fe$_{23}$D$_x$
What do we need to do neutron scattering?

- **Neutron Source** – produces neutrons
- **Diffractometer or Spectrometer**
  - Allows neutrons to interact with sample
  - Sorts out discrete wavelengths by monochromator (reactor) or by time of flight (pulse source)
  - Detectors pick up neutrons scattered from sample
- **Analysis methods to determine material properties**
- **Brain power to interpret results**
Powder Diffraction
Experimental View

◆ Two types of diffractometers
  – Fixed Wavelength Diffraction (x rays, neutrons at a Reactor [HFIR, NCNR])
  – Variable wavelength (white beam neutrons) [beam may be pulsed (LANSCE [20 Hz], ISIS [50 Hz], SNS [60 Hz]) or continuous (PNS, Geneva)]

◆ Objective (determine “d” or “2θ”)
  Bragg Law $\lambda = 2d \sin \theta$
  – $d = \lambda / (2 \sin \theta)$
    » pulse neutron source - vary $\lambda$, keep $\theta$ fixed
    » x-ray or reactor neutron source -- vary $\theta$, keep $\lambda$ fixed
Neutron sources – steady state (Reactors) and pulsed (Spallation)

- **Reactor**
  - Fission of U\(^{235}\) produces neutrons
  - Fission spectrum moderated (slowed down) by either D\(_2\)O or H\(_2\)O (less good moderator) and neutrons are extracted through beam tubes for spectrometers – fixed wavelength used

- **Spallation source**
  - High E protons (e.g., 800 MeV) impinge on target (W, Hg or U)
  - Nucleus of target is raised to excited state and subsequent decay produces neutrons (+ \(\gamma\)s, nucleons and neutrinos) – 15 – 25 neutrons produced per proton with average E = 55 MeV
  - Neutrons moderated by liquid H, H\(_2\)O or methane
  - Spallation sources generally operate in pulse mode – 20 Hz at LANSCE, 60 Hz at new SNS

Time of flight is used to sort out wavelengths
COMPARISON OF POWDER DIFFRACTION INSTRUMENTS

*** Bragg Scattering: \( \lambda = 2d \sin \theta \) [we need “d”] ***

*Reactor Source* -- Monochromator selects near mono-energetic neutrons, detector moves \((2\theta)\) to collect discrete diffraction data

\[(\lambda \text{ fixed, vary } \theta)\]

*Pulse Source* -- White beam of moderated neutrons used, neutron time-of-flight selects wavelength, detectors grouped in banks, no moving parts

\[(\theta \text{ fixed, vary } \lambda)\]

\[\lambda = f(t) \text{ so } d = \frac{\lambda}{2 \sin \theta} = \frac{f(t)}{2 \sin \theta}\]

short \(t\) \(\rightarrow\) short \(\lambda\) \(\rightarrow\) small \(d\); long \(t\) \(\rightarrow\) long \(\lambda\) \(\rightarrow\) large \(d^5\)
Using Powder Diffraction

Input Information -- Structure Determination

◆ **Know instrument-dependent scattering line-shape**
  - Gaussian for λ fixed
  - Sample distortions (pseudo Voigt) linear comb. of Lorentzian and Gaussian
  - Convolution of rising and falling exponentials with Gaussian for TOF

◆ **Dependence of resolution on “d”** [or Q] varies widely with instrument design
  - For pulse sources Δd/d near constant
  - For reactor – resolution has minimum

\[ R(Q) = \sqrt{\frac{4 \ln 2}{\pi \Gamma^2}} e^{-\frac{4 \ln 2 (Q - Q_o)^2}{\Gamma^2}} \]

\[ R(T) = N \left[ e^{\alpha T} \text{erfc}(y) + e^{\beta T} \text{erfc}(z) \right] \]

(VonDreele, Jorgensen & Windsor)
Rietveld Profile Refinement
Least Squares Fitting Procedure for Powder Data

◆ Input Data
  – Powder scattering pattern data
  – Trial structure space group and approximate lattice parameters and atomic positions [coordinates of atoms in cell - may be variables x,y,z]
  – Line shape function and Q-dependence of resolution

◆ Output Results
  – Lattice Parameters
  – Refined atomic positions and occupancies
  – Thermal parameters (Debye Waller) for each atom site
  – Line shape parameters (may reflect sample strains, etc.)
  – Background parameters
  – R factors of fit (and other measures of fit precision)
  – Preferential orientation, absorption, etc.

◆ More than one phase can be separately refined

\[ \Gamma^2 = U \tan^2 \theta + V \tan \theta + W \]

Rice & Paoletti, Caglioti, e.g., Caglioti, Paoletti & Rice
Progress of a Refinement

First Cut -- Input data and basic info and refine scale factor, background.

Refining Atom Pos., Therm. Factrs, Occup.

Next Refine Lattice Parameters and Zero Point

Refine Resolution Parameters, Peak Asymmetry, More background coefficients
Cautions with Rietveld
(i.e. don’t blindly believe the results)

◆ Hazards

- Incorrect space group -- may only slightly degrade R factors, symptoms -- unrealistically large thermal factors, misfit on some peaks not others
- Parameter correlation and compensation -- e.g., absorption and thermal parameters may correlate -- look at variance-covariance matrix (if available from program)
- Refining multiple phases may be unrealistic -- get a better sample!
- Over parameterization -- Simultaneous refining of too many parameters may lead to lack of uniqueness
Profile Fitting Programs

- FULLPROF [good for magnetic structures] -- Juan Rodriguez-Carvajal, ILL
Magnetic Powder Diffraction

- Neutron has a magnetic moment -- will interact with any magnetic fields within a solid, e.g., exchange field

- Equivalent (to b) magnetic scattering amplitude for an atom

\[ p = \left( \frac{e^2 \gamma}{2mc^2} \right) f g J = 0.269 \times 10^{-12} \, f g J (cm) \]

where \( g \) = Lande “g” factor, \( J \) = total spin angular momentum, \( f \) = magnetic electrons form factor

- Magnetic scattering comes from polarized spins (e.g., 3d [Fe] or 4f [RE]) not from nucleus -- Therefore scattering amplitude is Q-dependent (like for x-rays) via \( f \)

- at \( Q = 0 \) for Fe \( \mu = g J = 2.2 \) Bohr magneton

\[ p = 0.6 \] (comparable to nuclear \( b = 0.954 \)) all in units of \( 10^{-12} \text{cm} \)
Magnetic Powder Diffraction II

- In diffraction with unpolarized neutrons (polarized scattering is a separate topic) the nuclear and magnetic cross sections are independent and additive:

\[
\frac{d\sigma}{d\Omega} \propto S(Q) = S_{\text{nucl}} + q^2 S_{\text{magn}} = S_{\text{nucl}} + (1 - \cos^2 \alpha) S_{\text{magn}}
\]

- \( q^2 \) is a “switch” reflecting fact that only the component of the magnetic moment \( \mu \perp \) scattering vector \( K \) (or \( Q \)) contributes to the scattering.
q² “switch” affects intensity on Bragg peaks in a polycrystal (powder)

- **Polycrystalline averaging** over \( q^2 = (1 - \cos^2\alpha) \) for various symmetries
  - Cubic: \( q^2 = 2/3 \) [no moment direction information]
  - Tetragonal: \( q^2 = 1 - d^2[1/2(h^2+k^2)a^*^2\sin^2\phi+l^2c^*^2\cos^2\phi] \)
    \( \phi = \) angle between \( \mu \) and \( c \) axis
  - Hexagonal: \( q^2 = 1 - d^2[1/2(h^2+k^2+hk)a^*^2\sin^2\phi+l^2c^*^2 \cos^2\phi] \)
  - ...
How is magnetism reflected in a scattering pattern?

- **Long-range ordered**
  - **Ferromagnet (Fe, Ni, Gd)**
  - Spins parallel on lattice
    - Ferrimagnet (TbFe$_2$, Fe$_3$O$_4$)
      - Spins parallel on each site
      - Sites can reverse spin direction
      - $\Sigma \mu \neq 0$ on each site, but overall $\Sigma \mu$ could = 0
  - **Antiferromagnet (MnO, MnF$_2$)**
    - Parallel spins with alternate sites reversed in direction

  ![Graph showing ferromagnetic scattering](image)

  ![Graph showing antiferromagnetic scattering](image)

  Scattering only at Bragg peak positions (adds to nuclear), but not necessarily all ($q^2$ switch)

  Net moment = 0
  Job security for neutron scatterers

  - Magnetic unit cell doubled wrt crystal cell
  - Purely magnetic scattering peaks at half Miller index positions
How is magnetism reflected in a powder pattern?

- **Paramagnetism ($T > T_C$)**
  - spins thermally disordered

- no coherent magnetic scattering
- Incoherent neutron scattering (weak) has form factor dependence
We can make life more complicated with magnetic structures

- Complex antiferromagnetic cells (multi-site, but on each site $\Sigma\mu = 0$)
- Periodic Moment Structures (e.g., Er, Au$_2$Mn)
  - $\Sigma\mu = 0$, but periodic spin arrangement gives rise to magnetic scattering satellites (+, -) of nuclear Bragg peaks

(111) FM Sheets

FM layers along (0001)

bcc site antiparallel to corners

AFM line along (111)
Magnetic structure refinement

- Nuclear and magnetic intensity are additive
  \[ \frac{d\sigma}{d\Omega} \propto S(Q) = S_{\text{nucl}} + q^2 S_{\text{magn}} = S_{\text{nucl}} + (1 - \cos^2 \alpha) S_{\text{magn}} \]

- Magnetic structure can be refined using GSAS as a separate “phase” alongside the atomic structure

- General magnetic structure factor depends on Shubnikov-Dehaas groups

- Magnetic scattering amplitude depends on moment and form factor
  \[ p = \left( \frac{e^2 \gamma}{2mc^2} \right) fgJ = 0.269 \times 10^{-12} \text{ fgJ(cm)} \]

- Form factors, f, are determined experimentally for most magnets (e.g., RE’s) -- can be calculated from electronic band structure and other techniques

- Refinement gives moment magnitudes on each site and x,y,z components (if symmetry permits)
Form Factors

◆ **Experimental**

Form Factor Curves for Various Elements:
- **Lu**
- **Mo**
- **Mn**
- **Fe**
- **Ho**

Legend:
- Less Localized Moment
- More Localized Moment

◆ **Calculated**

Magnetic Form Factor Curves for Different Ions:
1. **Nd^{3+}, 4f^{9/2}**
2. **Sm^{3+}, 5d^{5/2}**
3. **Ho^{3+}, 5f^{8}**
4. **Yb^{3+}, 2F^{7/2}**

Graphical representation showing the form factors as a function of $\sin \theta / \lambda$ and $\sin \theta / \lambda$ (in Å⁻¹).
Structure determination case study

Rare earth intermetallic compounds

$\text{Ho}_6\text{Fe}_{23}$ and $\text{Ho}_6\text{Fe}_{23}\text{D}_x$
Structure Refinement Example

$\text{Ho}_6\text{Fe}_{23}$ and $\text{Ho}_6\text{Fe}_{23}\text{D}_x$

- Rare Earth Intermetallic Compound
- fcc cell - Fm3m structure (space group)
- 4 Formula Units per Unit Cell
- Large Unit Cell -- $a = 12$ Å
- Absorbs H (or D) from 1 up to 16 atoms/FU -- forms stable hydride compounds
- Also magnetic (both Ho and Fe)
Ho$_6$Fe$_{23}$ and Ho$_6$Fe$_{23}$D$_x$ (Fm3m) Unit Cell

4 F.U./cell
16 metal atoms (4 sites - all full)

324 possible D atoms (5 sites)
– only 64 D atoms in fact
-- some sites are empty or
-- some sites are partially occupied

<table>
<thead>
<tr>
<th>ATOM</th>
<th>WYCOFF NOTATION</th>
<th>PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>(24E)</td>
<td>(x,0,0)</td>
</tr>
<tr>
<td>FE</td>
<td>(4b)</td>
<td>(0.5,0.5,0.5)</td>
</tr>
<tr>
<td>FE</td>
<td>(24d)</td>
<td>(0.25,0.25,0.25)</td>
</tr>
<tr>
<td>FE</td>
<td>(32f,1/2)</td>
<td>(x,x,x)</td>
</tr>
</tbody>
</table>

Ho$_6$ Octahedron

Fe - f$_2$
Fe - f$_1$
Fe - d
Fe - b (Behind center of square faces)
**Ho$_6$Fe$_{23}$D$_x$**

**Occupied Crystallographic Sites (13 allowed)**

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</tr>
<tr>
<td>Fe</td>
<td>24d</td>
<td>(0, 0.25, 0.25)</td>
</tr>
<tr>
<td>Fe</td>
<td>32f$_{1,2}$</td>
<td>(x, x, x)</td>
</tr>
<tr>
<td>D</td>
<td>4a</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>D</td>
<td>32f$_3$</td>
<td>(x, x, x)</td>
</tr>
<tr>
<td>D</td>
<td>96j$_{1,2}$</td>
<td>(0, y, z)$_{1,2}$</td>
</tr>
<tr>
<td>D</td>
<td>96k</td>
<td>(x, x, z)</td>
</tr>
</tbody>
</table>

- **Reitveld least squares refinement procedure determines**
  - Lattice parameters
  - Atomic position coordinates
  - Site occupation numbers vs. maximum
  - Thermal (Debye-Waller) factors for each atom
  - Instrumental parameters (background, peak shape parameters)

- Note: Ho, Fe sites all full 4x(6+23) – 116

- D sites not full – 324 allowed > max 4x16 = 64
Ho$_6$Fe$_{23}$D$_{15.7}$ Refinement Parameters I

Lattice Parameters, Volume Expansion
relative to Ho$_6$Fe$_{23}$,

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{T(K)} & a_0 & \Delta V/V_0 & R_e & R_{wp} & \chi \\
\hline
295 & 12.029 & 0 & 6.1 & 11.5 & 1.9 \\
4.2 & 12.000 & 0 & 8.9 & 18.0 & 2.0 \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{T(K)} & a_0 & \Delta V/V_0(\%) & R_e & R_{wp} & \chi \\
\hline
295 & 12.423 & 9.8 & 5.1 & 9.2 & 1.8 \\
4.2 & 12.406 & 10.2 & 3.1 & 9.8 & 3.2 \\
\hline
\end{array}
\]

$R_e$ = statistical variance for a perfect fit with taking into account the statistical precision of the data.

$R_{wp}$ = weighted profile variance of the fit (big pks. vs little pks.)

$\chi = \text{ratio of } R_{wp} / R_e$ (values near 2 are generally indicative of a good profile fit to the model structure)
**Ho$_6$Fe$_{23}$D$_{15.7}$ Refinement Parameters II**
Refined atomic coordinates, thermal factors, and occupancy factors
(D) – Values are per formula unit – 4 formula units/unit cell

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>N</th>
<th>X(or Y)</th>
<th>Z</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>$24c(x,0,0)$</td>
<td>6</td>
<td>0.205</td>
<td>(f)</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>$4b(0.5,0.5,0.5)$</td>
<td>1</td>
<td>(f)</td>
<td>(f)</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>$24d(0,0.25,0.25)$</td>
<td>6</td>
<td>(f)</td>
<td>(f)</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>$32f_1(x,x,x)$</td>
<td>8</td>
<td>0.177</td>
<td>=x</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>$32f_2(x,x,x)$</td>
<td>8</td>
<td>0.372</td>
<td>=x</td>
<td>--</td>
</tr>
<tr>
<td>D</td>
<td>$4a(0,0,0)$</td>
<td>0</td>
<td>(f)</td>
<td>(f)</td>
<td>n/a</td>
</tr>
<tr>
<td>D</td>
<td>$32f_3(x,x,x)$</td>
<td>7.2</td>
<td>0.096</td>
<td>=x</td>
<td>0.55</td>
</tr>
<tr>
<td>D</td>
<td>$96j_1(0,y,z)$</td>
<td>4.9</td>
<td>0.135</td>
<td>0.340</td>
<td>0.19</td>
</tr>
<tr>
<td>D</td>
<td>$96j_2(0,y,z)$</td>
<td>3.1</td>
<td>0.076</td>
<td>0.385</td>
<td>0.29</td>
</tr>
<tr>
<td>D</td>
<td>$96k(x,x,z)$</td>
<td>1.4</td>
<td>0.159</td>
<td>0.047</td>
<td>0.94</td>
</tr>
</tbody>
</table>

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**All sites full**

**Sites part full**
Ho$_6$Fe$_{23}$D$_{15.7}$ Magnetic Moments

- Refined magnetic structure confirms a colinear spin arrangement
- Ho moments (1 site – 24e) antiparallel to Fe moments (4 sites – 4b, 24d, 32f$_1$, 32f$_2$)
- Refinement produces site specific values of magnetic moment

[Note: Total magnetic moment may have large errors due to compounding of errors from each site.]

- Moments at 4.2 K:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>N</th>
<th>Mom. ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>24e</td>
<td>6</td>
<td>-10.2</td>
</tr>
<tr>
<td>Fe</td>
<td>4b</td>
<td>1</td>
<td>2.2</td>
</tr>
<tr>
<td>Fe</td>
<td>24d</td>
<td>6</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe</td>
<td>32f$_1$</td>
<td>8</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe</td>
<td>32f$_2$</td>
<td>8</td>
<td>2.2</td>
</tr>
</tbody>
</table>