Rietveld refinement

Method of refining powder diffraction data to find the crystal structure, developed by Hugo M. Rietveld

Seminal papers

Overview of Rietveld refinement guidelines
Practical reasons to perform a Rietveld refinement

- solving an unknown crystal structure
- calculating the amount disorder or mixing on a Wyckoff site
- quantitatively determining the percentages of different phases in your sample
- determining the crystallite sizes in your samples
Rietveld refinement

fits the whole pattern at once and refines:

• atomic positions

• disorder or mixing between atomic sites

• lattice parameters

• profile parameters (i.e., the peak shape)

• background parameters
Factors affecting peak intensities

1. Structure factors (form factors)
2. Multiplicity
3. Lorentz factor  }  LP factor
4. Polarization factor  }
5. Temperature factor or atomic displacement
6. Absorption
7. Preferred orientation
8. Extinction coefficients
Scattering considerations

incident beam

absorbing substance

fluorescent x-rays

transmitted beam

heat

electrons

scattered x-rays
(coherent & incoherent)

Scattering considerations

- Thompson/elastic scattering by electrons
  \[ I = I_0 \left( \frac{K}{r^2} \right) \sin^2 \alpha \]

- Form factor, \( f \): scattering by an atom over the scattering power of an electron.

- At \( \theta = 0 \), \( f = \) atomic number, but drops off as \( \sin \theta / \lambda \)

- Compton/inelastic scattering increases as atomic # decreases

Figure from Cullity & Stock, 2001.
Structure Factors

amplitude of the wave scattered by all the atoms in a unit cell

$$|\mathbf{F}_{hkl}| = \text{amplitude of the wave scattered by one electron}$$

$$\mathbf{F}_{hkl} = \sum f_n \exp [2\pi i (hu + kv + lw)]$$

It describes how the atom arrangement \((u, v, w)\) affects the scattered beam. \(f_n\) is the atomic scattering factor. The intensity of a diffracted beam is proportional to \(|\mathbf{F}|^2\).

Note: \(\exp(\pi i) = -1\)
\(\exp(2\pi i) = +1\)
\(\exp(n\pi i) = \exp(-n\pi i)\)
Structure Factors: example 1

\[ F_{hkl} = \sum f_n \exp [2\pi i (hu + kv + lw)] \]

A primitive cell with only one atom at the origin (0,0,0).

\[ F_{hkl} = f \exp [2\pi i (0)] \]
\[ F_{hkl} = f \]

The intensity of the diffracted beam \( F^2 \) depends only on \( f^2 \).
Structure Factors: example 2

NaCl, \textit{Fm}-3m, Cl is on the 4a site, and Na is on the 4b site.

Cl
(0,0,0)
(\frac{1}{2},\frac{1}{2},0)
(\frac{1}{2},0,\frac{1}{2})
(0,\frac{1}{2},\frac{1}{2})

Na
(\frac{1}{2},\frac{1}{2},\frac{1}{2})
(0,0,\frac{1}{2})
(0,\frac{1}{2},0)
(\frac{1}{2},0,0)
Structure Factors: example 2

Cl \hspace{1cm} (0,0,0) \hspace{1cm} (\frac{1}{2},\frac{1}{2},0) \hspace{1cm} (\frac{1}{2},0,\frac{1}{2}) \hspace{1cm} (0,\frac{1}{2},\frac{1}{2})

Na \hspace{1cm} (\frac{1}{2},\frac{1}{2},\frac{1}{2}) \hspace{1cm} (0,0,\frac{1}{2}) \hspace{1cm} (0,\frac{1}{2},0) \hspace{1cm} (\frac{1}{2},0,0)

\begin{align*}
F_{hkl} &= f_{Cl} e^{2\pi i(0)} + f_{Cl} e^{2\pi i(h/2+k/2)} + f_{Cl} e^{2\pi i(h/2+l/2)} + f_{Cl} e^{2\pi i(k/2+l/2)} \\
&\quad + f_{Na} e^{2\pi i(h/2+k/2+l/2)} + f_{Na} e^{2\pi i(l/2)} + f_{Na} e^{2\pi i(k/2)} + f_{Na} e^{2\pi i(h/2)}
\end{align*}

\begin{align*}
F_{hkl} &= f_{Cl} \{ 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \} \\
&\quad + f_{Na} \{ e^{\pi i(h+k+l)} + e^{\pi il} + e^{\pi ik} + e^{\pi ih} \}
\end{align*}

\begin{align*}
F_{hkl} &= f_{Cl} \{ 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \} \\
&\quad + f_{Na} e^{\pi i(h+k+l)} \{ 1 + e^{\pi i(-h-k)} + e^{\pi i(-h-l)} + e^{\pi i(-k-l)} \}
\end{align*}

\begin{align*}
F_{hkl} &= \{ 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \} \{ f_{Cl} + f_{Na} e^{\pi i(h+k+l)} \}
\end{align*}

recall: \( \exp(n\pi i) = \exp(-n\pi i) \)
Structure Factors: example 2

\[
F_{hkl} = \left\{ 1 + e^{\pi i (h+k)} + e^{\pi i (h+l)} + e^{\pi i (k+l)} \right\} \left\{ f_{Cl} + f_{Na} e^{\pi i (h+k+l)} \right\}
\]

If \( h+k+l \) is odd-odd-even or odd-even-even

\[
\left\{ 1 + e^{\pi i (h+k)} + e^{\pi i (h+l)} + e^{\pi i (k+l)} \right\} = 0
\]

If \( h+k+l \) is all even, \( \left\{ f_{Cl} + f_{Na} e^{\pi i (h+k+l)} \right\} = f_{Cl} + f_{Na} \)

\[
F_{hkl} = 4 \left( f_{Cl} + f_{Na} \right) = 4 \left( 18 e^- + 10 e^- \right) = 112 e^- \\
F^2 = 12544
\]

If \( h+k+l \) is all odd, \( \left\{ f_{Cl} + f_{Na} e^{\pi i (h+k+l)} \right\} = f_{Cl} - f_{Na} \)

\[
F_{hkl} = 4 \left( f_{Cl} - f_{Na} \right) = 4 \left( 18 e^- - 10 e^- \right) = 32 e^- \\
F^2 = 1024
\]

Note: atomic scattering factor is the number of electrons in the ions
Structure Factors: example 2

If \( h+k+l \) is odd-odd-even or odd-even-even, \( F^2 = 0 \)

If \( h+k+l \) is all even, \( F^2 = 12544 \)

If \( h+k+l \) is all odd, \( F^2 = 1024 \)

<table>
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<th>( d )</th>
<th>( 2\theta )</th>
<th>( I )</th>
<th>( hkl )</th>
</tr>
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<tr>
<td>3.258</td>
<td>27.36</td>
<td>13</td>
<td>111</td>
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<td>2.821</td>
<td>31.70</td>
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<td>200</td>
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<td>1.994</td>
<td>45.45</td>
<td>55</td>
<td>220</td>
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<td>15</td>
<td>222</td>
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<td>1.410</td>
<td>66.23</td>
<td>6</td>
<td>400</td>
</tr>
<tr>
<td>1.294</td>
<td>73.07</td>
<td>1</td>
<td>331</td>
</tr>
</tbody>
</table>
Multiplicity (M)

In a cubic structure ($a = b = c$)

\{100\} is (100), (010), (001), (-100), (0-10), (001) so $M = 6$

\{110\} is (110), (-110), (1-10), (-1-10) so $M = 12$

The \{110\} peak is expected to be TWICE as strong as the \{100\}
How distortions affect multiplicity

From cubic \((a = b = c)\) → tetragonal \((a = b \neq c)\)

\[
\begin{align*}
(100) & \quad M = 6 \\
& \quad \rightarrow (100), (-100), (010), (0-10) \quad M = 4 \\
& \quad (001), (00-1) \quad M = 2 \\
(110) & \quad M = 12 \\
& \quad \rightarrow (110) \quad M = 4 \\
& \quad (101) \quad M = 8 \\
(111) & \quad M = 8 \\
& \quad \rightarrow (111) \quad M = 8
\end{align*}
\]
Lorentz factor

The Lorentz factor is a measure of the amount of time that a point of reciprocal lattice remains on the sphere of reflection during the measuring process.

- small deviations from Bragg’s Law – depends on $1/(\sin 2\theta)$
- orientation of crystals – depends on $\cos \theta$
- fraction of the diffraction cone that intercepts the detector – depends on $1/(\sin 2\theta)$

$Lorentz \ factor = 1/(4 \sin^2 \theta \cos \theta)$
Polarization factor

\[ \text{Polarization factor} = \frac{1}{2} (1 + \cos^2 2\theta) \]

\[ \text{LP factor} = \frac{(1+\cos^2 2\theta)}{\sin^2 \theta \cos \theta} \]

Note 1. If a monochromator is used, then the polarization factor is \( \frac{1}{2} (1 + \cos^2 2\theta \cos^2 2\theta_M) \) where \( \theta_M \) is the Bragg angle for the monochromator.

Note 2. For neutron diffraction, polarization is a constant.

LP vs \( \theta \) figure from Cullity & Stock, 2001.
Temperature factor

Thermal vibrations
1. Unit cell expansion causes changes in the 2θ positions.
2. Decrease in the intensities of diffracted lines.
3. Increase in the intensity of background scattering.

Figure from Cullity & Stock, 2001.
Temperature factor or atomic displacement

\[
\text{temperature factor} = \exp(-2M) \\
\quad f = f_0 \exp(-M) \\
\quad M = 8\pi^2 \bar{u}^2 \left(\frac{\sin\theta}{\lambda}\right)^2 \\
\quad M = B \left(\frac{\sin\theta}{\lambda}\right)^2 
\]

\(\bar{u}\) is the mean square displacement of the atom in a direction normal to the diffracting plane

Debye-Waller temperature factor

\[ B = 8\pi^2 \bar{u}^2 \]

Isotropic factor \quad B or \bar{u}

Anisotropic factor \quad B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23} \\
\quad \bar{u}_{11}, \bar{u}_{22}, \bar{u}_{33}, \bar{u}_{12}, \bar{u}_{13}, \bar{u}_{23} \]
Absorption

\[ I_{\text{diffracted}} = I_{\text{incident}} \exp(-\mu t) \]

\( \mu \) is the linear absorption coefficient, and \( t \) is the thickness of the sample.
Preferred orientation

- crystals are not randomly oriented
- examples: plate-like crystals or needle-shaped crystals

March-Dollase function

\[ P(\alpha) = \frac{r^2 \cos^2 \alpha + \sin^2 \alpha}{r} \]

- \( P(\alpha) \) pole distribution
- \( \alpha \) angle between hkl & PO vector
- \( r \) adjustable parameter

Spherical harmonic function

- measurement of the pole density distributions of a number of diffraction planes
- more complex and thus more powerful
Extinction

Destructive interference from re-reflections within the crystals. The strong peaks appear weaker. The solution is to grind the powdered sample more.
Lorentzian vs Gaussian: peak profile shape functions

Gaussian

\[ I_{i,k} = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}H_k} \exp \left\{ -\frac{4\ln 2}{H_k^2} \left( 2\theta_i - 2\theta_k \right)^2 \right\} \]

Lorentzian

\[ I_{i,k} = \frac{2}{\pi H_k} \left\{ 1 + \frac{4}{H_k^2} \left( 2\theta_i - 2\theta_k \right)^2 \right\}^{-1} \]

psuedo-Voigt

\[ I_{i,k} = \eta L_{i,k} + (1 - \eta) G_{i,k} \]
Crystallite Size ($\tau$)

Scherrer equation \[ \tau = 0.9 \lambda \frac{B}{\cos \theta_B} \]

If Lorentzian \[ B_{\text{exp}} = B_{\text{size}} + B_{\text{inst}} \]

If Gaussian \[ B_{\text{exp}}^2 = B_{\text{size}}^2 + B_{\text{inst}}^2 \]

Figure from Cullity & Stock, 2001.
Putting it all together:
the calculated diffraction pattern

\[ y_{ci} = s \sum L_k |F_k|^2 \varphi (2\theta_i - \theta_k) P_k A + y_{bi} \]

- \( y_{ci} \): calculated intensity at the \( i^{th} \) step
- \( s \): scale factor
- \( k \): the Miller indices, \( h, k, l \), for a Bragg reflection
- \( L_k \): multiplicity, Lorentz and polarization factor
- \( F_k \): structure factor for the \( k^{th} \) Bragg reflection
- \( \varphi \): reflection profile function
- \( P_k \): Preferred orientation
- \( A \): absorption factor
- \( y_{bi} \): background intensity at the \( i^{th} \) step
Rietveld Method in Practice

Basic requirements

1. Accurate diffraction data

2. A reasonable starting structural model
   a. Space group symmetry
   b. Approximate atomic positions
   c. Model may be from: isostructural materials, theoretical simulations, high-resolution atomic imaging

3. A Rietveld refinement program
   a. GSAS (Larson and von Dreele)
   b. Fullprof (Rodriguez – Carvajal)
   c. Others: BGMN (Bergmann), DBW (Wiles and Young), LHPM-Rietica (Hunter), MAUD (Lutterotti), Rietan (Izumi), Simref (Ritter)
GSAS: General Structure Analysis System
EXP-GUI suite (Brian Toby)
Rietveld refinement
Quick overview of refinement method

1. Le Bail or model-biased fit
   a. Intensities are assumed to be correct
   b. Fit the background
   c. Refine the lattice parameters (including zero point or sample displacement)
   d. Refine the peak shape

2. Rietveld refinement
   a. First keep the above fixed, refine atomic positions, displacements, and fractional occupancies
   b. Slowly re-refine the lattice parameters and the peak shapes. Sometimes you are near shallow minima, so you must turn off previous parameters.
Example of Rietveld refinement

(time permitting)
Beware of false minimas
Goodness of fit: R’s and $\chi^2$

$$R_F = \frac{\sum |I_K('obs')^{1/2} - I_K('calc')^{1/2}|}{\sum I_K('obs')^{1/2}}$$  \hspace{0.5cm} \text{R-structure factor}

$$R_B = \frac{\sum |I_K('obs') - I_K('calc')|}{\sum I_K('obs')^{1/2}}$$  \hspace{0.5cm} \text{R-Bragg factor}

$$R_p = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)}$$  \hspace{0.5cm} \text{R-pattern}

$$R_{wp} = \left\{ \frac{\sum w_i(y_i(obs) - y_i(calc))^2}{\sum w_i(y_i(obs))^2} \right\}^{1/2}$$  \hspace{0.5cm} \text{R-weighted pattern}

$$\chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2$$  \hspace{0.5cm} \text{Reduced Chi-squared}

Which R should you believe?
How do you know if a refinement is good/done?

The difference pattern will tell you!

- bad peak position
- poor peak shape
- peak intensities are off
Some common problems

• Wrong symmetry

• Wrong impurity peaks

• Missed peak

• High background

• Can’t find O (or some other light element) in a compound containing heavy elements.
Example 1: amorphous background

$R_{wp} \ 1.95\% \ \text{and} \ \chi^2 \ 0.3518$
Web resources

www.ccp14.ac.uk
Collaborative computational project number 14: freely available software for analysis of single crystal and powder diffraction data

www.iucr.ac.uk/iucr-top/comm/cpd/rietveld.html
IUCr Commission on powder diffraction: Rietveld and Related Software

www.iucr.org/cww-top/edu.index.html
IUCr Crystallographic education online

www.boulder.nist.gov/div853/balzar
Davor Balzar’s NIST Web page. Information on size/strain analysis

www.ill.fr/dif
ILL’s diffraction group home page

www.icdd.com
International Centre for Diffraction Data

www.hwi.buffalo.edu/ACA
American Crystallographic Association
Books on Rietveld/X-ray diffraction


Journal articles on Rietveld