Analysis of powder neutron diffraction data

- The Rietveld method
- Examples

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Analysis of powder (neutron) powder diffraction data.

The Rietveld method

- Introduced by Hugo Rietveld in 1967
  H. M. Rietveld, Acta Cryst. 22 (1967) 151

- Revolutionized analysis of powder diffraction data. Cited 6516 times.

- Developed as a technique for *structure refinement*. 
The Rietveld method

• Developed as a technique for *structure refinement*.

The pre-Rietveld life

<table>
<thead>
<tr>
<th>hkl</th>
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<tbody>
<tr>
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<td>310</td>
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VD$_{0.8}$
a = 3.16 Å
The Rietveld method

- Developed as a technique for structure refinement.

### The pre-Rietveld life

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\[
I_{hkl} \propto \left| \sum b_i e^{2\pi i(hx_i+kl_i+lz_i)} \right|^2
\]

VD_{0.8}  
\(a = 3.16\ \text{Å} \)
The Rietveld method

- Developed as a technique for structure refinement.

The pre-Rietveld life

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<td>110</td>
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<tr>
<td>002</td>
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<td>121</td>
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<td>112+220</td>
<td>450</td>
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<tr>
<td>022+130</td>
<td>1000</td>
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</table>
The Rietveld method

- Developed as a technique for structure refinement.

Rietveld’s idea: Why not fit the entire calculated profile from the model to the data, instead of just the integrated intensities?
The Rietveld method
The Rietveld method

![Graph showing intensity vs. 2θ](image-url)
The Rietveld method

![Graph showing the Rietveld method](image)
The Rietveld method
The Rietveld method

The Rietveld method is a technique used in X-ray crystallography to refine the structural parameters of a crystal. The method combines a least-squares refinement of the structure factors with a Fourier synthesis of the electron density to refine the atomic positions, bond lengths, and other structural parameters. The Rietveld method is particularly useful for analyzing the structure of complex materials where the unit cell is not known a priori.
The Rietveld method

Intensity

$\theta$
The Rietveld method

![Graph showing the Rietveld method](image)
The Rietveld method
The Rietveld method
The Rietveld method

The calculated profile

\[ y_i^{\text{calc}} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K)P_K A + y_i^{\text{background}} \]
The Rietveld method

The calculated profile

\[ y_{i}^{\text{calc}} = s \sum_{K} L_{K} |F_{K}|^2 \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{\text{background}} \]

calculated intensity in point \( i \)
The Rietveld method

The calculated profile

\[ y_i^{calc} = S \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background} \]

scale factor

calculated intensity in point \( i \)
The Rietveld method

The calculated profile

\[ y_{i}^{\text{calc}} = S \left( \sum_{K} L_{K} |F_{K}|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{\text{background}} \right) \]

- **Scale factor**
- **Calculated intensity in point** \( i \)
- **Sum over all Bragg peaks,** \( K \), that contribute with intensity to point \( i \)
The Rietveld method

The calculated profile

\[ y_{i}^{calc} = S \sum_{K} L_{K} |F_{K}|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{background} \]

- Lorentz factor and multiplicity
- Scale factor
- Sum over all Bragg peaks, K, that contribute with intensity to point i
- Calculated intensity in point i
- Background intensity

\[ \phi = \frac{1}{\sin \theta \sin 2\theta} \] for powders
The Rietveld method

The calculated profile

\[ y_{i}^{\text{calc}} = S \sum_{K} L_K |F_K|^2 \phi(2\theta_i - 2\theta_K)P_K A + y_{i}^{\text{background}} \]

- \( y_{i}^{\text{calc}} \): calculated intensity in point \( i \)
- \( S \sum_{K} L_K |F_K|^2 \phi(2\theta_i - 2\theta_K)P_K A \): Lorentz factor and multiplicity
- \( F_K \): The square modulus of the structure factor for Bragg peak \( K \)
- \( P_K \): Scale factor and multiplicity
- \( \phi(2\theta_i - 2\theta_K) \): Sum over all Bragg peaks, \( K \), that contribute with intensity to point \( i \)
The Rietveld method

The calculated profile

\[ y_{i}^{\text{calc}} = \sum_{K} L_{K} \left| F_{K} \right|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{\text{background}} \]

- \( y_{i}^{\text{calc}} \): Calculated intensity in point \( i \)
- Sum over all Bragg peaks, \( K \), that contribute with intensity to point \( i \)
- \( L_{K} \): Scale factor and multiplicity
- \( F_{K} \): Lorentz factor
- \( \phi(2\theta_{i} - 2\theta_{K}) \): The square modulus of the structure factor for Bragg peak \( K \)
- \( P_{K} \): The profile function
- \( A \): Background contribution
The Rietveld method

The calculated profile

\[ y_{i}^{\text{calc}} = s \sum_{K} L_{K} |F_{K}|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{\text{background}} \]

- **calculated intensity in point** \( i \)
- **scale factor**
- **Lorentz factor and multiplicity**
- **The profile function**
- **preferred orientation**
- **The square modulus of the structure factor for Bragg peak** \( K \)
- **Sum over all Bragg peaks,** \( K \), **that contribute with intensity to point** \( i \)
The Rietveld method

The calculated profile

\[ y_{i}^{calc} = S \sum_{K} L_{K} |F_{K}|^2 \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{background} \]

- Calculated intensity in point \( i \)
- Sum over all Bragg peaks, \( K \), that contribute with intensity to point \( i \)
- Lorentz factor and multiplicity
- The square modulus of the structure factor for Bragg peak \( K \)
- The profile function
- Absorption
- Preferred orientation
The calculated profile

\[ y_{i}^{\text{calc}} = S \sum_{K} L_{K} |F_{K}|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{i}^{\text{background}} \]

- calculated intensity in point \( i \)
- sum over all Bragg peaks, \( K \), that contribute with intensity to point \( i \)
- scale factor
- Lorentz factor and multiplicity
- The profile function
- absorption
- preferred orientation
- The square modulus of the structure factor for Bragg peak \( K \)
- background
The Rietveld method

Fitting the profile

\[ y_i^{\text{calc}} = s \sum_{K} L_K |F_K|^2 \phi(2\theta_i - 2\theta_K)P_K A + y_i^{\text{background}} \]

The parameters in \( y_i^{\text{calc}} \) undergo a least-square refinement to minimize \( R_{wp} \)

\[ R_{wp} = \sqrt{\frac{\sum_i w_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{\sum_i w_i (y_i^{\text{obs}})^2}} \]
The Rietveld method – structure refinement

The structure factor

\[ |F_K|^2 = \sum_i b_i \cdot e^{2\pi i (\mathbf{r}_i \cdot \mathbf{K})} \]

The displacement factor

\[ b(\theta) = b \cdot e^{-B \left( \frac{\sin \theta}{\lambda} \right)^2} \]

The square mean shift of the atom from its equilibrium position.

\[ B = 8\pi^2 \bar{U} \]
The Rietveld method – structure refinement

The profile function

\[ y_i^{\text{calc}} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{\text{background}} \]

Gaussian: \( \phi(2\theta_i - 2\theta_K)_{\text{gauss}} = A \cdot e^{-C \frac{(2\theta_i - 2\theta_K)^2}{H}} \propto e^{-x^2} \)

Lorentzian: \( \phi(2\theta_i - 2\theta_K)_{\text{Lorentz}} = D \frac{1}{1 + E \frac{(2\theta_i - 2\theta_K)^2}{H^2}} \propto \frac{1}{1 + x} \)

pseudo-Voigt: \( \phi(2\theta_i - 2\theta_K)_{\text{pseudo-Voigt}} = \eta \cdot \phi_{\text{lorentz}} + (1 - \eta) \cdot \phi_{\text{gauss}} \)
The Rietveld method – structure refinement

An example

Approximate model of Al₂O₃:
- Trigonal, space group R ~3 c
- a ~ 4.75 Å, c ~ 12.99 Å
- Al in 0 0 ~0.35
  O in ~0.30 0 ¼

We want a more accurate structure model!
The Rietveld method – structure refinement

An example

\[ y_i^{\text{calc}} = \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{\text{background}} \]

Refining:
- Scale factor
The Rietveld method – structure refinement

An example

$$y_i^{\text{calc}} = \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{\text{background}}$$

Refining:
- Scale factor
- Unit cell parameters
  - (a = 4.75 Å → 4.7587 Å)
  - (c = 12.99 Å → 12.988 Å)
The Rietveld method – structure refinement

An example

\[ y_{i\text{calc}} \equiv S \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K)P_K A + y_{i\text{background}} \]

Refining:
- Scale factor
- Unit cell parameters
  \((a = 4.75 \text{ Å} \rightarrow 4.7587 \text{ Å})\)
  \((c = 12.99 \text{ Å} \rightarrow 12.988 \text{ Å})\)
- Background (6 parameters)
The Rietveld method – structure refinement

An example

\[ y_i^{\text{calc}} = \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{\text{background}} \]

Refining:

- Scale factor
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  \((a = 4.75 \text{ Å} \rightarrow 4.7587 \text{ Å}) \quad (c = 12.99 \text{ Å} \rightarrow 12.988\text{Å})\)
- Background (6 parameters)
- Profile shape
The Rietveld method – structure refinement

An example

$$y_i^{\text{calc}} = S \sum_K L_K F_K \phi(2\theta_i - 2\theta_K) P_K A + y_i^{\text{background}}$$

Refining:
- Scale factor
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  - \(a = 4.75\ \text{Å} \rightarrow 4.7587\ \text{Å}\)
  - \(c = 12.99\ \text{Å} \rightarrow 12.988\ \text{Å}\)
- Background (6 parameters)
- Profile shape
- Atomic positions
  - \(z(\text{Al}) = 0.35 \rightarrow 0.3524\)
  - \(x(\text{O}) = 0.30 \rightarrow 0.3068\)
The Rietveld method – structure refinement

An example

\[ Y_i^{\text{calc}} = S \sum_K L_K F_K \phi(2\theta_i - 2\theta_K) P_K A + Y_i^{\text{background}} \]

Refining:
- Scale factor
- Unit cell parameters
  - (a = 4.75 Å → 4.7587 Å)
  - (c = 12.99 Å → 12.988 Å)
- Background (6 parameters)
- Profile shape
- Atomic positions
  - z(Al) = 0.35 → 0.3524
  - x(O) = 0.30 → 0.3068
- Displacement factors
Case 1: Titanium hydride

- What we know:
  - Ti absorb hydrogen (deuterium).
  - The product has a fcc lattice of Ti with $a = 4.44$ Å.

- What we want to know:
  - Where is the hydrogen (deuterium) located?
Case 1: Titanium hydride

X-ray diffraction
Case 1: Titanium hydride

Neutron diffraction
Case 2: $\text{Th}_2\text{AlD}_4$

- Very few metal hydrides with H-H distances below 2 Å are reported in the literature.
- $\text{Th}_2\text{AlD}_4$ is a rare exception.
Case 2: Th$_2$AlD$_4$

- Very few metal hydrides with H-H distances below 2 Å are reported in the literature.
- Th$_2$AlD$_4$ is a rare exception.

Structure data (Bergsma et al. 1961)

\[ a = 7.629 \, \text{Å} \quad c = 6.517 \, \text{Å} \quad \text{s.g. } I4/mcm \]

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<tr>
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<th>Th</th>
<th>Al</th>
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<tbody>
<tr>
<td>x</td>
<td>0.162</td>
<td>0.000</td>
<td>0.368</td>
</tr>
<tr>
<td>y</td>
<td>0.662</td>
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<tr>
<td>z</td>
<td>0.000</td>
<td>0.000</td>
<td>0.137</td>
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\[ D-D = 2z(D)c \]
Case 2: $\text{Th}_2\text{AlD}_4$

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PND anno 1961

PND anno 1999
Case 2: Th$_2$AlD$_4$

X-ray diffraction
Case 2: $\text{Th}_2\text{AlD}_4$

Neutron diffraction