Introduction to Rietveld refinements

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The Rietveld method

- **1964-1966** - Need to refine crystal structures from powder. Peaks too much overlapped:
  - Groups of overlapping peaks introduced. Not sufficient.
  - Peak separation by least squares fitting (gaussian profiles). Not for severe overlapping.


- **1969** - First complete program with structures and profile parameters. Distributed 27 copies (ALGOL).


- **1977** - Wide acceptance. Extended to X-ray data.

- **Today**: the Rietveld method is widely used for different kind of analyses, not only structural refinements.

- “If the fit of the assumed model is not adequate, the precision and accuracy of the parameters cannot be validly assessed by statistical methods”. Prince.
Principles of the Rietveld method

• To minimize the residual function:

\[ WSS = \sum_i w_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2, w_i = \frac{1}{I_i^{\text{exp}}} \]

• where:

\[ I_i^{\text{calc}} = S_F \sum_k |F_k|^2 S(2\theta_i - 2\theta_k) P_k A + bkg_i \]

\( P_k \) = preferred orientation function
\( S(2\theta_i - 2\theta_k) \) = profile shape function

(PV : \( \eta, \text{HWHM} \))

\[ \text{HWHM}^2 = U \tan^2 \theta + V \tan \theta + W \]

\[ P_k = \left( r^2 \cos^2 \alpha + \frac{\sin^2 \alpha}{r} \right)^{-3/2} \]
Non classical Rietveld applications

• Quantitative analysis of crystalline phases (Hill & Howard, J. Appl. Cryst. 20, 467, 1987)

\[
I_i^{\text{calc}} = \sum_{n=1}^{N_{\text{phases}}} S_n \sum_{k} L_k |F_{k,n}|^2 S(2\theta_i - 2\theta_{k,n}) P_{k,n} A + bkg_i
\]

\[
W_p = \frac{S_p(ZMV)_p}{\sum_{n=1}^{N_{\text{phases}}} (ZMV)_n}
\]

Z = number of formula units
M = mass of the formula unit
V = cell volume

• Non crystalline phases (Lutterotti et al, 1997)
  • Using Le Bail model for amorphous (need a pseudo crystal structure)
Non classical Rietveld applications

• Microstructure:
  • Le Bail, 1985. Profile shape parameters computed from the crystallite size and microstrain values \(<M>\) and \(<\epsilon^2>^{1/2}\)
    • More stable than Caglioti formula
    • Instrumental function needed
Rietveld Stress and Texture Analysis (RiTA)

- Characteristics of Texture Analysis:
  - Powder Diffraction
  - Quantitative Texture Analysis needs single peaks for pole figure meas.
  - Less symmetries -> too much overlapped peaks
  - Solutions: Groups of peaks (WIMV, done), peak separation (done)

- What else we can do? -> Rietveld like analysis?
  - 1997. GSAS got the harmonic method (wide acceptance?).
Non classical applications: Texture

Orientation Distribution Function (ODF)

From pole figures
From spectra
Non classical applications: strains & stresses

- Macro elastic strain tensor (I kind)
- Crystal anisotropic strains (II kind)

Macro and micro stresses
Applied macro stresses
The classical Rietveld method

- The function to minimize by a least squares method (non linear):
  \[ WSS = \sum_i w_i \left( I_i^{\text{exp}} - I_i^{\text{calc}} \right)^2, w_i = \frac{1}{I_i^{\text{exp}}} \]

- The spectrum is calculated by the classical intensity equation:
  \[ I_i^{\text{calc}} = S_F \sum_{j=1}^{N\text{phases}} \frac{f_j}{\sqrt{V_j}} \sum_{k=1}^{N\text{peaks}} L_k \left| F_{k,j} \right|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + \text{bkg}_i \]

- The spectrum depends on
  - phases: crystal structure, microstructure, quantity, cell volume, texture, stress, chemistry etc.
  - instrument geometry characteristics: beam intensity, Lorentz-Polarization, background, resolution, aberrations, radiation etc.
  - sample: position, shape and dimensions, orientation.

- Each of the quantity can be written in term of parameters that can be refined (optimized).
The spectrum (at a 2θ point i) is determined by:
• a background value
• some reflection peaks that can be described by different terms:
  • Diffraction intensity (determines the “height” of the peaks)
  • Line broadening (determines the shape of the peaks)
  • Number and positions of the peaks

\[ I_{i}^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j \left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i \]
The classical Rietveld method

\[ I_{i\text{ calc}} = S_F \sum_{j=1}^{N\text{peaks}} \frac{f_j}{V_j^2} \sum_{k=1}^{N\text{phases}} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + b_{kg_i} \]

- The more used background in Rietveld refinements is a polynomial function in \(2\theta\):

\[ b_{kg}(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n \]

- \(N_b\) is the polynomial degree
- \(a_n\) the polynomial coefficients

- For more complex backgrounds specific formulas are availables
- It is possible to incorporate also the TDS in the background
The classical Rietveld method

$$I_{i}^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- Starting with the “Diffraction Intensities”, the factors are:
  - A scale factor for each phase
  - A Lorentz-Polarization factor
  - The multiplicity
  - The structure factor
  - The temperature factor
  - The absorption
  - The texture
  - Problems: extinctions, absorption contrast, graininess, sample volume and beam size, inhomogeneity, etc.
The classical Rietveld method

\[ I_{i}^{\text{calc}} = S_F \sum_{j=1}^{N\text{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N\text{peaks}} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i \]

• The scale factor (for each phase) is written in classical Rietveld programs as:

\[ S_j = S_F \frac{f_j}{V_j^2} \]

- \( S_j \) = phase scale factor (the overall Rietveld generic scale factor)
- \( S_F \) = beam intensity (it depends on the measurement)
- \( f_j \) = phase volume fraction
- \( V_j \) = phase cell volume (in some programs it goes in the F factor)

• In Maud the last three terms are kept separated.
The classical Rietveld method

\[ I_{i,\text{calc}} = S_F \sum_{j=1}^{N\text{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N\text{peaks}} L_{k,j} \left| F_{k,j} \right|^2 S_j \left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i \]

- The Lorentz-Polarization factor:
  - it depends on the instrument
    - geometry
    - monochromator (angle \( \alpha \))
    - detector
    - beam size/sample volume
    - sample positioning (angular)
  - For a Bragg-Brentano instrument:

\[ L_p = \frac{1 + P_h \cos^2(2\theta)}{2(1 + P_h)\sin^2\theta\cos\theta} \quad P_h = \cos^2(2\alpha) \]
The classical Rietveld method

\[ I_{i}^{\text{calc}} = S_{F} \sum_{j=1}^{N_{\text{phases}}} \frac{f_{j}}{V_{j}} \sum_{k=1}^{N_{\text{peaks}}} L_{k} \left| F_{k,j} \right|^{2} S_{j} \left( 2\theta_{i} - 2\theta_{k,j} \right) P_{k,j} A_{j} + bkg_{i} \]

- Under a generalized structure factor we include:
  - The multiplicity of the k reflection (with h, k, l Miller indices): \( m_{k} \)
  - The structure factor
  - The temperature factor: \( B_{n} \)

\[ \left| F_{k,j} \right|^{2} = m_{k} \sum_{n=1}^{N} f_{n} e^{-B_{n} \frac{\sin^{2} \theta}{\lambda^{2}}} \left( e^{2\pi i(hx_{n} + ky_{n} + lz_{n})} \right)^{2} \]

- \( N \) = number of atoms
- \( x_{n}, y_{n}, z_{n} \) coordinates of the \( n^{\text{th}} \) atom
- \( f_{n} \) atomic scattering factor
Atomic scattering factor and Debye-Waller

- The atomic scattering factor for X-ray decreases with the diffraction angle and is proportional to the number of electrons. For neutron it is not correlated to the atomic number.
- The temperature factor (Debye-Waller) accelerate the decreases.
Neutron scattering factors

- For light atoms neutron scattering has some advantages.
- For atoms very close in the periodic table, neutron scattering may help distinguish them.
The classical Rietveld method

\[ I_{i}^{\text{calc}} = S_F \sum_{j=1}^{N_{\text{phases}}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{\text{peaks}}} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i \]

- The absorption factor:
  - in the Bragg-Brentano case (thick sample):
    \[ A_j = \frac{1}{2\mu} , \quad \mu \text{ is the linear absorption coefficient of the sample} \]
  - For the thin sample or films the absorption depends on \(2\theta\)
  - For Debye-Scherrer geometry the absorption is also not constant

- There could be problems for microabsorption (absorption contrast)
The classical Rietveld method

\[ I_{i}^{\text{calc}} = SF \sum_{j=1}^{N\text{phases}} \frac{f_j}{V_j^{1/2}} \sum_{k=1}^{N\text{peaks}} L_k \left| F_{k,j} \right|^2 S_j \left(2\theta_i - 2\theta_{k,j}\right) \left(P_{k,j} A_j + bkg_i\right) \]

- The texture (or preferred orientations):
  - The March-Dollase formula is used:
    \[ P_{k,j} = \frac{1}{m_k} \sum_{n=1}^{m_k} \left( P_{MD}^2 \cos^2 \alpha_n + \frac{\sin^2 \alpha_n}{P_{MD}} \right)^{-3/2} \]
    - \( P_{MD} \) is the March-Dollase parameter
    - Summation is done over all equivalent hkl reflections (\( m_k \))
    - \( \alpha_n \) is the angle between the preferred orientation vector and the crystallographic plane hkl (in the crystallographic cell coordinate system)
  - The formula is intended for a cylindrical texture symmetry (observable in B-B geometry or spinning the sample)
The classical Rietveld method

\[ I_i^{\text{calc}} = S_F \sum_{j=1}^{\text{Nphases}} \sum_{k=1}^{\text{Npeaks}} \frac{f_j}{V_j^2} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i \]

- The profile shape function:
  - different profile shape function are available:
    - Gaussian (the original Rietveld function for neutrons)
    - Cauchy
    - Voigt and Pseudo-Voigt (PV)
    - Pearson VII, etc.
  - For example the PV:
    \[ PV(2\theta_i - 2\theta_k) = I_n \left[ \eta_k \left( \frac{1}{1 + S_{i,k}^2} \right) + (1 - \eta_k) e^{-S_{i,k} \ln 2} \right] \]
    \[ S_{i,k} = \frac{2\theta_i - 2\theta_k}{\omega_k} \]
    - the shape parameters are:
      - Caglioti formula: \[ \omega^2 = W + V \tan \theta + U \tan^2 \theta \]
      - Gaussianity: \[ \eta = \sum_{n=0}^{N_g} c_n (2\theta)^n \]
The classical Rietveld method

\[ I_{i}^{\text{calc}} = S_F \sum_{j=1}^{N_{\text{phases}}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{\text{peaks}}} L_k |F_{k,j}|^2 S_j \left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i \]

- The number of peaks is determined by the symmetry and space group of the phase.
- One peak is composed by all equivalent reflections \( m_k \)
- The position is computed from the d-spacing of the hkl reflection (using the reciprocal lattice matrix):

\[ d_{hkl} = \sqrt{\frac{V_C}{s_{11}h^2 + s_{22}k^2 + s_{33}l^2 + 2s_{12}hk + 2s_{13}hl + 2s_{23}kl}} \]

\[ S = \begin{pmatrix} a^2 & a^* b^* \cos \gamma^* & a^* c^* \cos \beta^* \\ a^* b^* \cos \gamma^* & b^2 & b^* c^* \cos \alpha^* \\ a^* c^* \cos \beta^* & b^* c^* \cos \alpha^* & c^2 \end{pmatrix} \]
Quality of the refinement

- Weighted Sum of Squares:
  \[ WSS = \sum_{i=1}^{N} \left[ w_i (I_{i}^{\text{exp}} - I_{i}^{\text{calc}}) \right]^2, \quad w_i = \frac{1}{\sqrt{I_{i}^{\text{exp}}}} \]

- R indices (N=number of points, P=number of parameters):
  \[ R_{wp} = \sqrt{\frac{\sum_{i=1}^{N} \left[ w_i (I_{i}^{\text{exp}} - I_{i}^{\text{calc}}) \right]^2}{\sum_{i=1}^{N} [w_i I_{i}^{\text{exp}}]^2}}, \quad w_i = \frac{1}{\sqrt{I_{i}^{\text{exp}}}} \]
  \[ R_{exp} = \sqrt{\frac{(N - P)}{\sum_{i=1}^{N} [w_i I_{i}^{\text{exp}}]^2}}, \quad w_i = \frac{1}{\sqrt{I_{i}^{\text{exp}}}} \]

- The goodness of fit:
  \[ GofF = \frac{R_{wp}}{R_{exp}} \]
The R indices

- The $R_{wp}$ factor is the more valuable. Its absolute value does not depend on the absolute value of the intensities. But it depends on the background. With a high background it is more easy to reach very low values. Increasing the number of peaks (sharp peaks) is more difficult to get a good value.
  - $R_{wp} < 0.1$ correspond to an acceptable refinement with a medium complex phase
  - For a complex phase (monoclinic to triclinic) a value $< 0.15$ is good
  - For a highly symmetric compound (cubic) with few peaks a value $< 0.08$ start to be acceptable
- With high background better to look at the $R_{wp}$ background subtracted.
- The $R_{exp}$ is the minimum $R_{wp}$ value reachable using a certain number of refineable parameters. It needs a valid weighting scheme to be reliable.
WSS and GofF (or sigma)

- The weighted sum of squares is only used for the minimization routines. Its absolute value depends on the intensities and number of points.

- The goodness of fit is the ratio between the $R_{\text{wp}}$ and $R_{\text{exp}}$ and cannot be lower than 1 (unless the weighting scheme is not correctly valuable: for example in the case of detectors not recording exactly the number of photons or neutrons).

- A good refinement gives GofF values lower than 2.

- The goodness of fit is not a very good index to look at as with a noisy pattern it is quite easy to reach a value near 1.

- With very high intensities and low noise patterns it is difficult to reach a value of 2.

- The GofF is sensible to model inaccuracies.
Why the Rietveld refinement is widely used?

• Pro
  • It uses directly the measured intensities points
  • It uses the entire spectrum (as wide as possible)
  • Less sensible to model errors
  • Less sensible to experimental errors

• Cons
  • It requires a model
  • It needs a wide spectrum
  • Rietveld programs are not easy to use
  • Rietveld refinements require some experience (1-2 years?)

• Can be enhanced by:
  • More automatic/expert mode of operation
  • Better easy to use programs
Expert tricks/suggestion

- First get a good experiment/spectrum
- Know your sample as much as possible
- Do not refine too many parameters
- Always try first to manually fit the spectrum as much as possible
- Never stop at the first result
- Look carefully and constantly to the visual fit/plot and residuals during refinement process (no “blind” refinement)
- Zoom in the plot and look at the residuals. Try to understand what is causing a bad fit.
- Do not plot absolute intensities; plot at iso-statistical errors. Small peaks are important like big peaks.
- Use all the indices and check parameter errors.
- First get a good experiment/spectrum