First FullProf School 2025:

Diffraction data analysis of energy materials

NEUTRONS
FOR SOCIETY

The Rietveld Method

Juan Rodríguez-Carvajal

Institut Laue Langevin

Outline

Structural models: the expressions of structure factors in the case of conventional description of crystal structures.

Brief introduction to the Rietveld method. R-factors. Strategy for setting up a refinement process.

Quantitative phase analysis.

The calculated profile of powder diffraction patterns

$$\boxed{y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i}$$

$$I_{\mathbf{h}} = I_{\mathbf{h}}(\beta_{\mathrm{I}})$$

Contains structural information:
atom positions, magnetic moments, etc

$$\Omega = \Omega(x_{\mathbf{h}i}, \beta_{\mathrm{P}})$$

Contains micro-structura
instr. resolution, defects,

$$\int_{-\infty}^{+\infty} \Omega(x)dx = 1$$

$$b = b(\beta)$$

Background: noise, incoh

$$\Omega(x) = g(x) \otimes f(x) = instrumental \otimes intrinsic\,profile$$

$$\boxed{y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i}$$

$$I_{\mathbf{h}} = S\left\{L p O A C F^2\right\}_{\mathbf{h}}$$

Integrated intensities are proportional to the square of the structure factor *F*. The factors are:
Scale Factor (S), Lorentz-polarization (*Lp*), preferred orientation (*O*), absorption (*A*), other “corrections” (*C*)

The Structure Factor contains the structural parameters (isotropic case)

$$F(\mathbf{h}) = \sum_{j=1}^{n} O_j f_j(h) T_j \sum_s exp\left\{2\pi i\left[\mathbf{h}\left\{S|\mathbf{t}\right\}_s \mathbf{r}_j\right]\right\}$$

$$\mathbf{r}_j = (x_j, y_j, z_j) \qquad (j = 1, 2, \ldots n)$$

$$T_j = \exp(-B_j \frac{\sin^2\theta}{\lambda^2})$$

Structural Parameters (simplest case)

$$\mathbf{r}_j = (x_j, y_j, z_j)$$

Atom positions (up to *3n* parameters)

$$O_j = k\frac{m_j}{M}$$

Occupation factors (up to *n-1* parameters)

$$B_j$$

Isotropic displacement (temperature) factors (up to *n* parameters)

Structural Parameters (complex cases)

As in the simplest case plus additional (or alternative) parameters:

- Anisotropic temperature (displacement) factors
- Anharmonic temperature factors
- Special form-factors (Symmetry adapted spherical harmonics), TLS for rigid molecules, etc.
- Magnetic moments, coefficients of Fourier components of magnetic moments , basis functions, etc.

The Structure Factor in complex cases

$$\boxed{F(\mathbf{h}) = \sum_{j=1}^{n} O_j f_j(h) T_j \sum_{s} g_j(\mathbf{h}_s)\, exp\left\{2\pi i\left[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j\right]\right\}}$$

$$\mathbf{h}_s = \begin{pmatrix} h \\ k \\ l \end{pmatrix}_s = S_s^T \begin{pmatrix} h \\ k \\ l \end{pmatrix} \qquad (s = 1, 2, \ldots N_G)$$

$$g_j(\mathbf{h}_s)$$

Complex form factor of object *j*
Anisotropic DPs
Anharmonic DPs

Example: General 2θ dependence of the instrumental broadening (determined by a standard sample)

$$H_{hG}^2 = (U_f + (1-\xi_f)^2 D_{fST}^2(\boldsymbol{\alpha}_D))\tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + \boxed{H_{gG}^2}$$

$$H_{hL} = (X_f + \xi_f D_{fST}(\boldsymbol{\alpha}_D))\tan\theta + \frac{[Y_f + F_f(\boldsymbol{\alpha}_S)]}{\cos\theta} + \boxed{H_{gL}}$$

The Gaussian and Lorentzian components of the instrumental Voigt function are interpolated between empirically determined values.

If needed, axial divergence is convoluted numerically with the resulting profile.

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The Rietveld Method

The Rietveld Method consist of refining a crystal (and/or magnetic) structure by minimising the weighted squared difference between the observed and the calculated pattern against the parameter vector: β

$$\boxed{\chi^2 = \sum_{i=1}^{n} w_i \left\{ y_i - y_{ci}(\beta) \right\}^2}$$

$$\boxed{w_i = \frac{1}{\sigma_i^2}}$$

σ_i^2 : **is the variance of the "observation"** y_i

Least squares: Gauss-Newton (1)

Minimum necessary condition: $\dfrac{\partial \chi^2}{\partial \boldsymbol{\beta}} = 0$

A Taylor expansion of $y_{ic}(\boldsymbol{\beta})$ **around** $\boldsymbol{\beta}_0$ **allows the application of an iterative process. The shifts to be applied to the parameters at each cycle for improving** χ^2 **are obtained by solving a linear system of equations (normal equations)**

$$\mathbf{A}\boldsymbol{\delta}_{\boldsymbol{\beta}_0} = \mathbf{b}$$

$$A_{kl} = \sum_i w_i \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k} \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_l}$$

$$b_k = \sum_i w_i (y_i - y_{ic}) \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k}$$

Least squares: Gauss-Newton (2)

The shifts of the parameters obtained by solving the normal equations are added to the starting parameters giving rise to a new set

$$\beta_1 = \beta_0 + m.\delta_{\beta_0}$$

The new parameters are considered as the starting ones in the next cycle and the process is repeated until a convergence criterion is satisfied. The variances of the adjusted parameters are calculated by the expression:

$$\boxed{\begin{gathered}\sigma^2(\beta_k) = (\mathbf{A}^{-1})_{kk}\,\chi_\nu^2 \\ \chi_\nu^2 = \frac{\chi^2}{N - P + C}\end{gathered}}$$

Least squares: a local optimisation method

- **The least squares procedure provides (when it converges) the value of the parameters constituting the local minimum closest to the starting point**

- **A set of good starting values for all parameters is needed**

- **If the initial model is bad for some reasons the LSQ procedure will not converge, it may diverge.**

R-factors and Rietveld Refinement (1)

$$R_p = 100\frac{\sum_i \left|y_{obs,i} - y_{calc,i}\right|}{\sum_i \left|y_{obs,i}\right|}$$

R-pattern

$$R_{wp} = 100\left[\frac{\sum_i w_i \left|y_{obs,i} - y_{calc,i}\right|^2}{\sum_i w_i \left|y_{obs,i}\right|^2}\right]^{1/2}$$

R-weighted pattern

$$R_{exp} = 100\left[\frac{(N - P + C)}{\sum_i w_i y_{obs,i}^2}\right]^{1/2}$$

Expected R-weighted pattern

R-factors and Rietveld Refinement (2)

$$\chi_{\nu}^{2} = \left[\frac{R_{wp}}{R_{exp}} \right]^{2}$$

Reduced Chi-square

$$S = \frac{R_{wp}}{R_{exp}}$$

Goodness of Fit indicator

R-factors and Rietveld Refinement (3)

Two important things:

- **The sums over “*i*” may be extended only to the regions where Bragg reflections contribute**
- **The denominators in R_P and R_{WP} may or not contain the background contribution**

Crystallographic R-factors used in Rietveld Refinement

$$R_B = 100 \frac{\sum_k \left| 'I_{obs,k}' - I_{calc,k} \right|}{\sum_k \left| 'I_{obs,k}' \right|}$$

Bragg R-factor

$$R_F = 100 \frac{\sum_k \left| 'F_{obs,k}' - F_{calc,k} \right|}{\sum_k \left| 'F_{obs,k}' \right|}$$

Crystallographic R_F-factor.

Crystallographic R-factors used in Rietveld Refinement

$$'I_{obs,k}' = I_{calc,k} \sum_i \left\{ \frac{\Omega(T_i - T_k)(y_{obs,i} - B_i)}{(y_{calc,i} - B_i)} \right\}$$

Provides ‘observed’ integrates intensities for calculating Bragg R-factor

$$'F_{obs,k}' = \sqrt{\frac{'I_{obs,k}'}{jLp}}$$

In some programs the crystallographic R_F-factor is calculated using just the square root of ‘$I_{obs,k}$’

Strategy for setting up a Rietveld refinement (1)

Use the best possible starting model: this can be easily done for background parameters and lattice constants

Collect all the information available both on your sample (approximate cell parameters and atomic positions) and on the diffractometer and experimental conditions

Do not start by refining all structural parameters at the same time. Some of them affect strongly the residuals (they must be refined first) while others produce only little improvement.

Strategy for setting up a Rietveld refinement (2)

A sensible sequence for the refinement of a crystal structure:

Scale factor

Zero point, background parameters (if appropriate) and lattice constants.

Atomic positions and displacement parameters

Peak shape and asymmetry parameters.

Atom occupancies (if required).

Microstructural parameters: size and strain effects.

It is essential to plot frequently the observed and experimental patterns.

The examination of the difference pattern is a quick and efficient method to detect blunders in the model or in the input file controlling the refinement process. I may also provide useful hints on the best sequence to refine the whole set of model parameters for each particular case.

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Quantitative Phase analysis with the Rietveld Method

The scale factor used in the Rietveld method is proportional to the quantity of corresponding crystalline phase

$$y_i = \sum_{\phi} S_{\phi} \left(\sum_{\mathbf{h}} \mathbf{I}_{\mathbf{h}} \Omega(T_{\mathbf{h}} - T_i) \right)_{\phi} + b_i$$

$$S_{\phi} = \frac{C}{\bar{\mu}} \frac{W_{\phi}}{(\mathrm{ZMV})_{\phi}}$$

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Scale Factors

Experimental constant

Weight fraction of phase ϕ

$$S_\phi = \frac{C}{\bar{\mu}} \frac{W_\phi}{(ZMV)_\phi}$$

Average absorption coefficient

Unit cell volume of phase ϕ

Molecular weight of phase ϕ

Number of formula units of phase ϕ

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Quantitative Phase analysis with the Rietveld Method

If all phases are well crystallized one can constraint the sum of the weight fractions to 1, so that:

$$W_\phi = \frac{S_\phi (ZMV)_\phi}{\sum_{i=1,\ldots n} S_i (ZMV)_i}$$

$$W_\phi = \frac{S_\phi (ZMV)_\phi / \tau_\phi}{\left[\sum_{i=1,\ldots n} S_i (ZMV)_i / \tau_i \right]}$$

Micro-absorption
Brindley coefficients

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Quantitative Phase analysis with the Rietveld Method

Micro-absorption phenomena can be accounted through Brindley considerations:

Classification of powders according to the value of μr product
(m: linear absorption coefficient; r: linear size of particles)

. Fine powders: $\mu r < 0.01$
. Medium powders: $0.01 < \mu r < 0.1$
. Coarse powders: $0.1 < \mu r < 1.0$
. Very coarse powders: $\mu r > 1.0$

Brindley coefficients

The Brindley coefficients can be calculated iteratively by starting with the weight fractions obtained when all τ =1 and using the empirical formula:

$$\boxed{\tau_\phi = 1 - 1.450(\mu_\phi - \bar{\mu})r + 1.426\left[(\mu_\phi - \bar{\mu})r\right]^2}$$

Expression valid for low absorption contrast $-0.1 \leq (\mu_\phi - \bar{\mu})r \leq 0.1$

Mean Powders (Brindley): $0.01 \leq 2r\mu_\phi \leq 0.1$

r **is the mean crystallite radius and** μ_ϕ **the linear absorption coefficient**

G.W. Brindley, Philosophical Magazine. **36**, 347 (1945)

Quantitative Phase analysis with the Rietveld Method

with

$$\boxed{W_\phi = \frac{S_\phi (ZMV)_\phi . f_\phi^2 / \tau_\phi}{\sum_{i=1}^{N_\phi} S_i .(ZMV)_i . f_i^2 / \tau_i} = \frac{S_\phi ATZ_\phi . V_\phi}{\sum_{i=1}^{N_\phi} S_i ATZ_i . V_i}}$$

S_ϕ	Scale factor in FullProf (refinable variable)
$ATZ_i = Z_i M_i f_i^2 / \tau_i$	FullProf parameter
τ_i	Brindley factor (particle absorption contrast factor). τ is tabulated as a function of $(\mu_i - \mu).r$ FullProf parameter

Quantitative Phase analysis with the Rietveld Method

f_i Used to transform the site multiplicities in PCR FullProf input file, to their real values. For a stoichiometric phase, f = 1 if these multiplicities are calculated by dividing the Wyckoff multiplicity m of the site by the general multiplicity M of the space group. Otherwise, $f = occ.M/m$, where $occ.$ is the occupation number in the PCR file

☺ In order to GET PROPER VALUES OF WEIGHT FRACTIONS LET THE PROGRAM RE-CALCULATE **ATZ** by putting them to ZERO.

The correct **ATZ** value is rewritten in the PCR file.

Quantitative Phase analysis with the Rietveld Method

1. Crystal structure has to be refined:

   JBT=0 (**IRF**=0)

   ➔ Refine the structural parameters as usually

2. **Crystal structure is well known:**

   2.1 Create hkl file containing hkl list with corresponding F^2 (**JLKH**=5)

   2.2 Refine the pattern without entering atomic positions
   JBT=-3, **IRF**=2 (Le Bail fit mode with constant relative intensities for the current phase, but refinable scale factor)

Quantitative Phase analysis with the Rietveld Method

☺
- ✓ easy to operate (automatic analysis in FullProf)
- ✓ no internal standard
- ✓ non destructive method
- ✓ up to 16 phases in FullProf
- ✓ polymorphism, microstructure
- ✓ neutron case: large amounts of powder analysis (real samples)
- ✓ industrial applications (cements, clays …)

☹
- ✓ structure model dependent: $\{F_{hkl}\}$ have to be known
- ✓ beware of preferred orientation

Some references on Q.P.A.by Rietveld method

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  Quantitative phase analysis from neutron powder diffraction data using the Rietveld method

- G.W. Brindley, Phil. Mag. 36, 347-369 (1945)
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- D.L. Bish & S.A. Howard, J. Appl. Cryst. 21, 86-91 (1988)
  Quantitative phase analysis using the Rietveld method

- J.C. Taylor, Powder Diffraction 6, 2-9 (1991)
  Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile

- R.J. Hill, Powder Diffraction 6, 74-77 (1991)
  Expanded use of Rietveld method in studies of phase abundance in multiphase mixtures