FullProf School

Neutron Powder diffraction for studying magnetic structures

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Outline

1. The calculated profile in neutron powder diffraction (NPD).
2. Components of the general expression for calculating powder diffraction patterns
3. Structure Factors and free parameters of crystal and magnetic structures
4. Neutron powder diffraction profile functions for CW and TOF
5. The Rietveld Method
6. R-Factors
7. Steps to solve and refine a magnetic structure using NPD

Experimental powder diffraction pattern

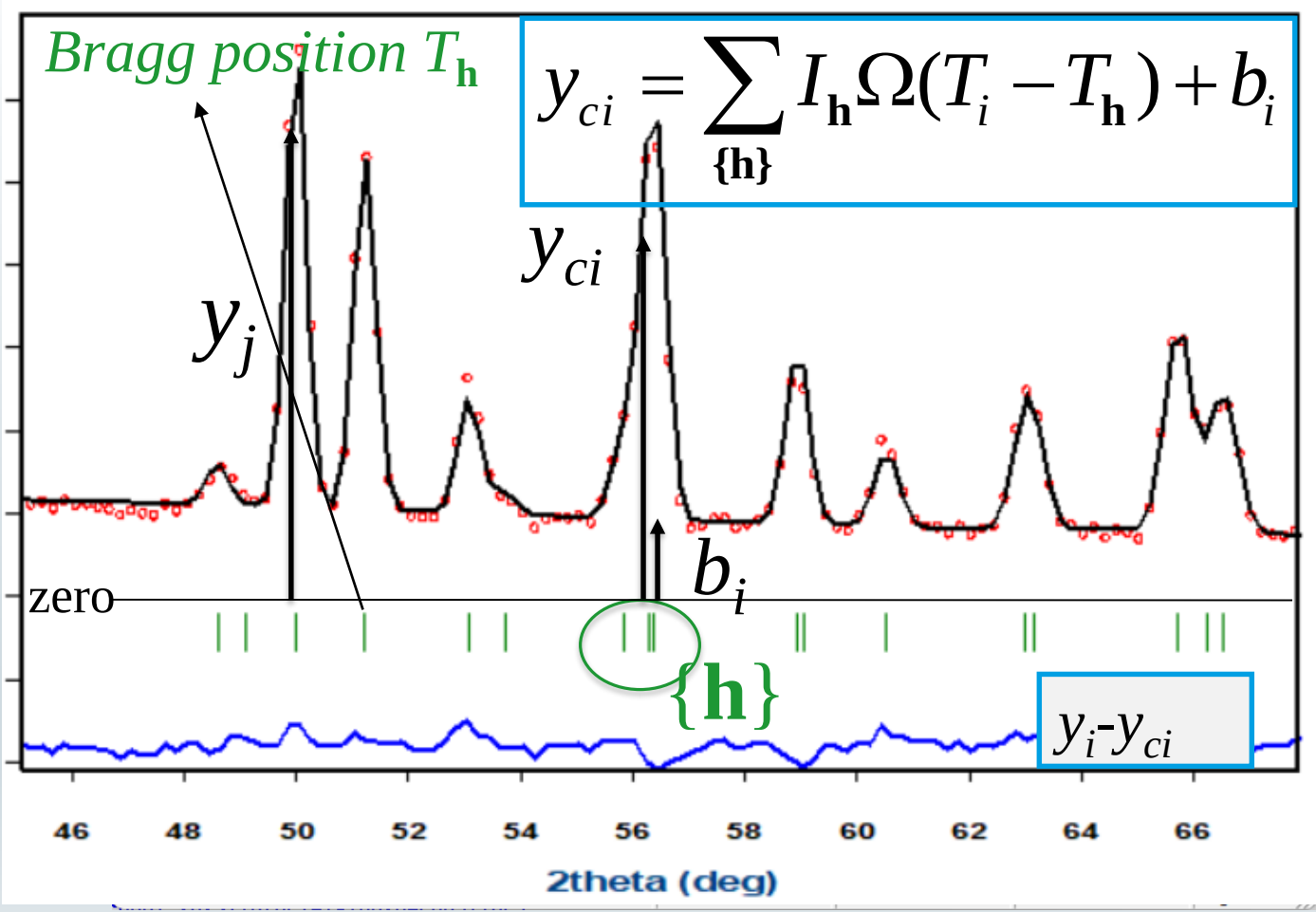
A powder diffraction pattern can be recorded in numerical form for a discrete set of scattering angles, times of flight or energies. We will refer to this scattering variable as : *T*.
The experimental powder diffraction pattern is usually given as three arrays :

$$\{T_i, y_i, \sigma_i\}_{i=1,2,\ldots n}$$

The profile can be modelled using the calculated counts: y_{ci} at the *i*th step by summing the contribution from neighbouring Bragg reflections plus the background. The standard deviation of the observed counts at *i* is σ_i

Powder diffraction profile:
scattering variable *T*:
2θ, TOF, Energy

The calculated and the observed profiles of powder diffraction patterns



The calculated profile of powder diffraction patterns

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

$$I_{\mathbf{h}} = I_{\mathbf{h}}\left(\boldsymbol{\beta}_{\mathbf{I}}\right)$$

Contains structural information: atom positions, magnetic moments, etc

$$\Omega = \Omega(x_{\mathbf{h}i}, \boldsymbol{\beta}_{\mathbf{P}})$$

Contains micro-structura
instr. resolution, defects,

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

Background: noise, incoh

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

Multiple phases contributing to the powder diffraction pattern

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

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

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

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

Components of the general expression for calculating powder diffraction patterns

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

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

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*)

Magnetic Bragg Scattering

Intensity (non-polarised neutrons)

$$I_{\mathbf{h}} = N_{\mathbf{h}} N_{\mathbf{h}}^{*} + \mathbf{M}_{\perp\mathbf{h}} \cdot \mathbf{M}_{\perp\mathbf{h}}^{*}$$

Magnetic interaction vector

$$\mathbf{M}_{\perp\mathbf{h}} = \mathbf{e} \times \mathbf{M}(\mathbf{h}) \times \mathbf{e} = \mathbf{M}(\mathbf{h}) - \mathbf{e}\,(\mathbf{e} \cdot \mathbf{M}(\mathbf{h}))$$

$$\mathbf{h} = \mathbf{H} + \mathbf{k} \quad \Leftarrow \text{Scattering vector} \qquad \mathbf{e} = \frac{\mathbf{h}}{h}$$

Structure Factors and free parameters of crystal and magnetic structures (isotropic case)

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

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

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

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

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

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

$g_j(\mathbf{h}_s)$

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

Structure Factors and free parameters of crystal and magnetic structures

The use of Shubnikov groups implies the use of the **magnetic unit cell** for indexing the Bragg reflections

$$\mathbf{M}_{\perp} = \mathbf{e}\times\mathbf{M}\times\mathbf{e} = \mathbf{M} - \mathbf{e}\,(\mathbf{e}\cdot\mathbf{M}) \qquad I \propto \mathbf{M}_{\perp}^{*}\mathbf{M}_{\perp}$$

Magnetic structure factor (without symmetry):

$$\mathbf{M}(\mathbf{H}) = p\sum_{m=1}^{N_{mag}} \mathbf{m}_m f_m(H)\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_m)$$

Using magnetic space group symmetry, we consider n independent magnetic sites labelled with the index j. The index s labels the representative symmetry operators of the Shubnikov group: $\mathbf{m}_{js} = \det(h_s)\,\delta_s\, h_s\,\mathbf{m}_j$ is the magnetic moment of the atom sited at the sublattice s of site j.

$$\boxed{\mathbf{M}(\mathbf{H}) = p\sum_{j=1}^{n} O_j f_j(H) T_j \sum_{s} \det(h_s)\,\delta_s\, h_s\,\mathbf{m}_j exp\{2\pi i[(\mathbf{H}\{h|\mathbf{t}\}_s\mathbf{r}_j]\}}$$

The maximum number of magnetic parameters n_p is, in general, equal to $3n$ magnetic moment components. Special positions make $n_p < 3n$.

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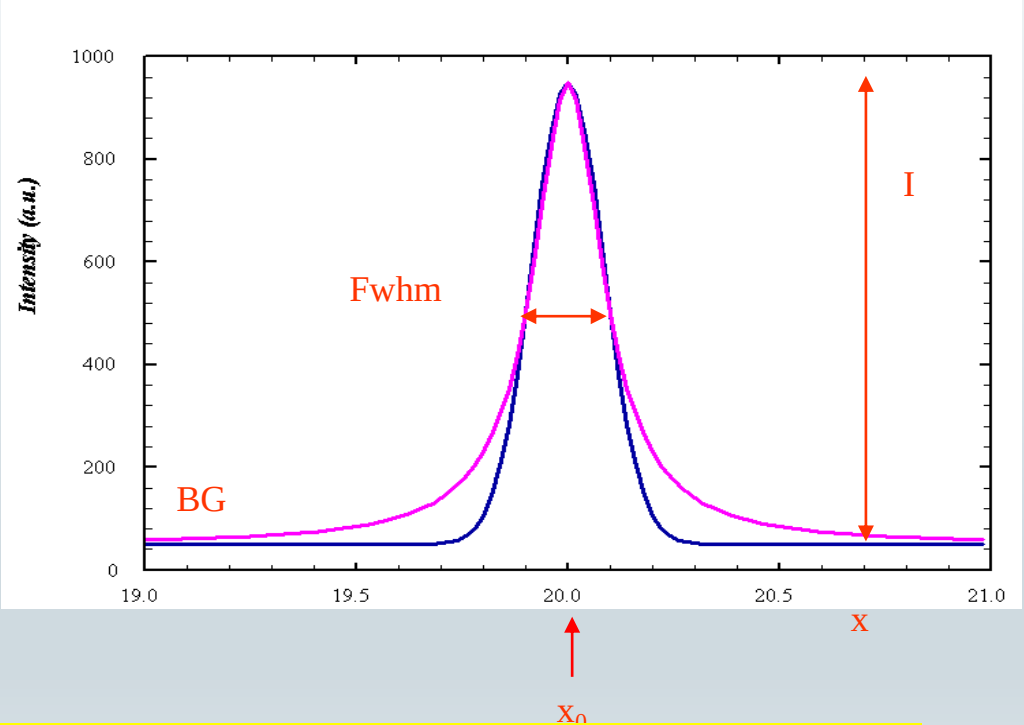
Constant wavelength neutron powder diffraction profiles

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

Comparison of Gaussian and Lorentzian peak shapes of the same peak height "I" and same width "Fwhm"



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

Convolution properties of Gaussian and Lorentzian functions

$$L(x,H_1)\otimes L(x,H_2)=L(x,H_1+H_2)$$

$$G(x,H_1)\otimes G(x,H_2)=G(x,\sqrt{H_1^2+H_2^2})$$

$$L(x,H_L)\otimes G(x,H_G)=V(x,H_L,H_G)$$

The Voigt function

$$V(x) = L(x) \otimes G(x) = \int_{-\infty}^{+\infty} L(x-u)G(u)du$$

$$V(x) = V(x, H_L, H_G) = V(x, \beta_L, \beta_G)$$

The pseudo-Voigt function

$$pV(x) = \eta L'(x) + (1-\eta)G'(x)$$

$$pV(x) = pV(x, \eta, H)$$

Properties of the Voigt function

$$V(x) = V_1(x) \otimes V_2(x)$$

The Voigt function has proven to be a very good experimental approximation in many cases

$$\beta_L = \beta_{1L} + \beta_{2L}$$

Lorentzian breadths simply have to be summed

$$\beta_G^2 = \beta_{1G}^2 + \beta_{2G}^2$$

Gaussian breadths have to be summed quadratically

$$\beta_{fL} = \beta_{hL} - \beta_{gL}$$

$$\beta_{fG}^2 = \beta_{hG}^2 - \beta_{gG}^2$$

Correction for instrumental broadening

Instrument and sample contribution to broadening

$$H_{hG}^2 = U_f \tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + H_{gG}^2$$

$$H_{hL} = X_f \tan\theta + \frac{Y_f}{\cos\theta} + H_{gL}$$

Sample **Instrument**

The Gaussian and Lorentzian contributions of the instrument must be determined experimentally with a size/strain-free sample

Modeling the Gaussian and Lorentzian components for the general anisotropic case in FullProf

Instrument resolution function characterized by: $(U, V, W, X, Y)_g$

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

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

$$D_{fST}^2(\boldsymbol{\alpha}_D) = 10^{-8}\ 8\mathrm{Ln}2 \left(\frac{180}{\pi}\right)^2 \frac{\sigma^2(M_{hkl})}{M_{hkl}^2}$$

Time of Flight neutron powder diffraction profiles

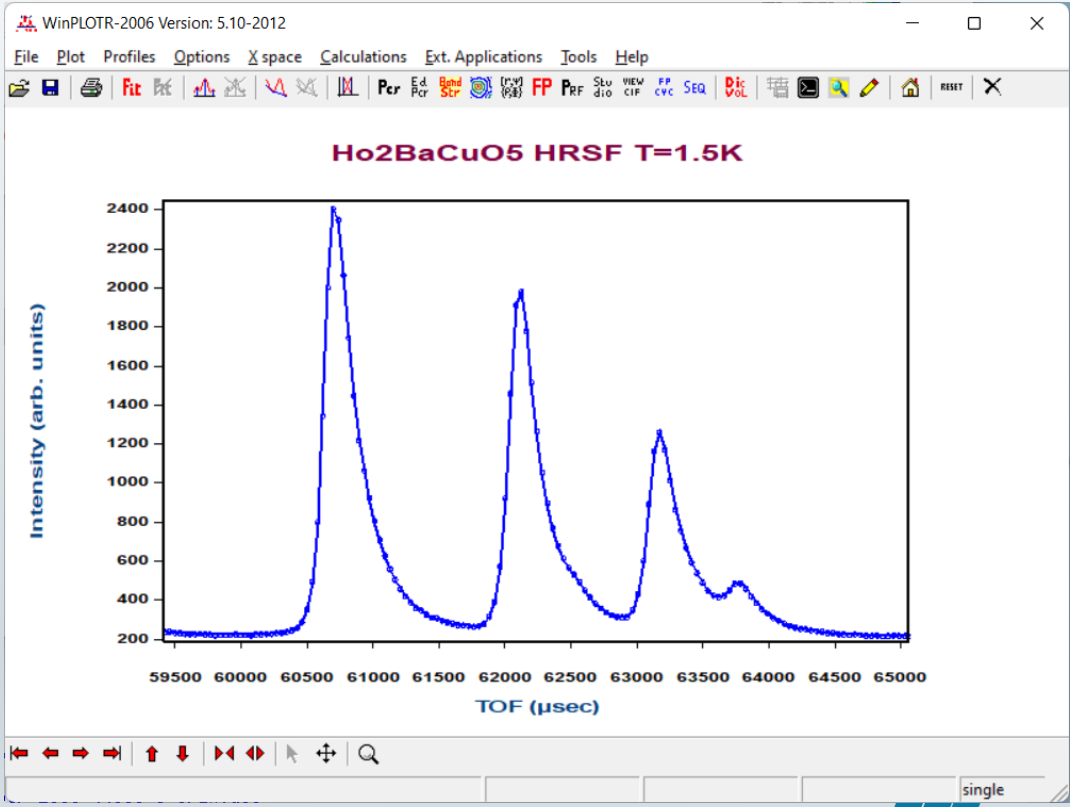
Convolution of back-to-back exponentials with a Voigt function

$$\Omega(x) = pV(x) \otimes E(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt$$

$$E(t) = 2Ne^{\alpha t} \qquad t \le 0$$

$$E(t) = 2Ne^{-\beta t} \qquad t > 0$$

$$N = \frac{\alpha\beta}{2(\alpha+\beta)}$$



More details in another talk. Consult the document TOF_FullProf.pdf

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:

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

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)

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

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 '$I_{obs,k}$'

Steps for determining magnetic structures with NPD (1)

1: Collect a NPD pattern of the sample in the paramagnetic state ($T > T_N$ or T_C). Refine the crystal structure using the collected data and get all the relevant structural and profile parameters. Use FULLPROF and WINPLOTR for doing this task.

2: Collect a NPD pattern below the ordering temperature. Normally additional magnetic peaks appear in the diffraction pattern. It is important to make a refinement by fixing all the structural parameters, without putting a magnetic model in the PCR file, in order to see clearly the magnetic contributions to the diffraction pattern. Get the peak positions of the additional peaks using WINPLOTR-2006 and save them in a format adequate to the program K-SEARCH.

3: Determine the propagation vector(s) of the magnetic structure by using the program K-SEARCH or by trial and error with an additional phase in the PCR file treated in Le Bail Fit (LBF) mode (no magnetic model). If there are no additional peaks and only an additional contribution to the nuclear peaks is observed, the magnetic structure has as propagation vector **k** = (0, 0, 0).

Steps for determining magnetic structures with NPD (2)

4: Once the propagation vector is determined, use the program BASIREPS in order to get the basis vectors of the *irreps* of the propagation vector group $G_{\mathbf{k}}$. In the case of *irreps* with dimensions higher than 1, the user has to select the appropriate combination of basis vectors because BASIREPS does not make an analysis of the isotropy groups as a function of the order parameters. For selecting the appropriate symmetry few options are available:

4-1: ***Commensurate structure***: With BASIREPS, one can determine the appropriate magnetic symmetry operators, or use directly the basis vectors of the *irreps*. Use the BCS to obtain mCIF files that can be converted to templates of PCR files. One can also use ISODISTORT to obtain directly a template of a PCR file for working with displacive and magnetic symmetry modes. (Warning: ISODISTORT uses the standard setting)

Steps for determining magnetic structures with NPD (3)

4-2: ***Incommensurate structure***: One can directly use the output of BASIREPS for constructing a model of incommensurate magnetic structure using the basis vectors or complex Fourier coefficients. Other options are those that allows working with particular forms of magnetic structures (conical structures, real space description of multi-helical structures, etc.)

4-3: ***Incommensurate structure in superspace***: If the superspace approach is preferred, the best option currently available for working with FULLPROF is to obtain from ISODISTORT a magnetic CIF files that can be converted to PCR by using the program MCIF_TO_PCR. The best way of working is to generate the superspace group using a setting related to the parent paramagnetic space group without changing the origin.

Steps for determining magnetic structures with NPD (4)

5: Solve the magnetic structure by using the symmetry information obtained in step 4 using trial and error methods (5-1) or the simulated annealing (SAnn) procedure (5-2) implemented in FULLPROF.

5-1: **In the first case one has to modify the PCR file used in step 2 by adding an additional magnetic phase** by putting `Jbt=1` (magnetic phase with Fourier coefficients/magnetic moments referred to the unitary basis along the unit cell axes), `Irf=-1` (only satellites will be generated). The best way to create such additional magnetic phase is to copy it from an already existing PCR file similar to that of the current case and modify it using the symmetry information obtained in step 4. Run FULLPROF fixing nearly all parameters, except the magnetic moments or the coefficients of the basis functions, and check in the plots if the calculated magnetic peaks have intensities close to the observed ones. If not, change the magnetic model (use another representation or other magnetic symmetry operators) and try again. In some cases this is enough to solve the magnetic structure. In case this does not work use the method described in 5-2.

Steps for determining magnetic structures with NPD (5)

5-2: **In the second case one has to modify the PCR file used in step 2 by adding an additional phase in LBF mode** (as for one of the options in step 3). This additional phase has no atoms and we have to put `Jbt`=2, `Irf`= -1 and `Jview`=11. The nuclear phase has to be treated with fixed scale factor and structural parameters. This allows getting the purely magnetic reflections in a separate file that can be used by FULLPROF in SAnn mode.

6: Refine the magnetic structure using the Rietveld method implemented in FULLPROF. Once the magnetic model gives a calculated powder diffraction pattern close enough to the observed one, we start the refinement phase. If we use the trial and error method (5-1) the refinement step is just the continuation of the previous step. If the simulated annealing method (5-2) was used we have to translate the final solution, stored in an automatically generated PCR file, to the file for treating directly the powder diffraction profile.

Strategy for setting up a Rietveld refinement

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.

Limits of NPD for magnetic structure determination and refinement

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.

How to perform a Rietveld refinement

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.

A sensible sequence for the refinement of a magnetic structure:

The above steps have been performed for the paramagnetic state
For magnetic structures: FIX structural parameters at first stages and refine components of magnetic moments (or coefficients of basis functions). Everything can be refined simultaneously if the model is correct and the quality of the data is enough.

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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THANK YOU!