FullProf School

Neutron Powder diffraction for studying magnetic structures

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THE EUROPEAN NEUTRON SOURCE

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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
8. Different options existing in FullProf for working with magnetic structures

Experimental powder diffraction pattern

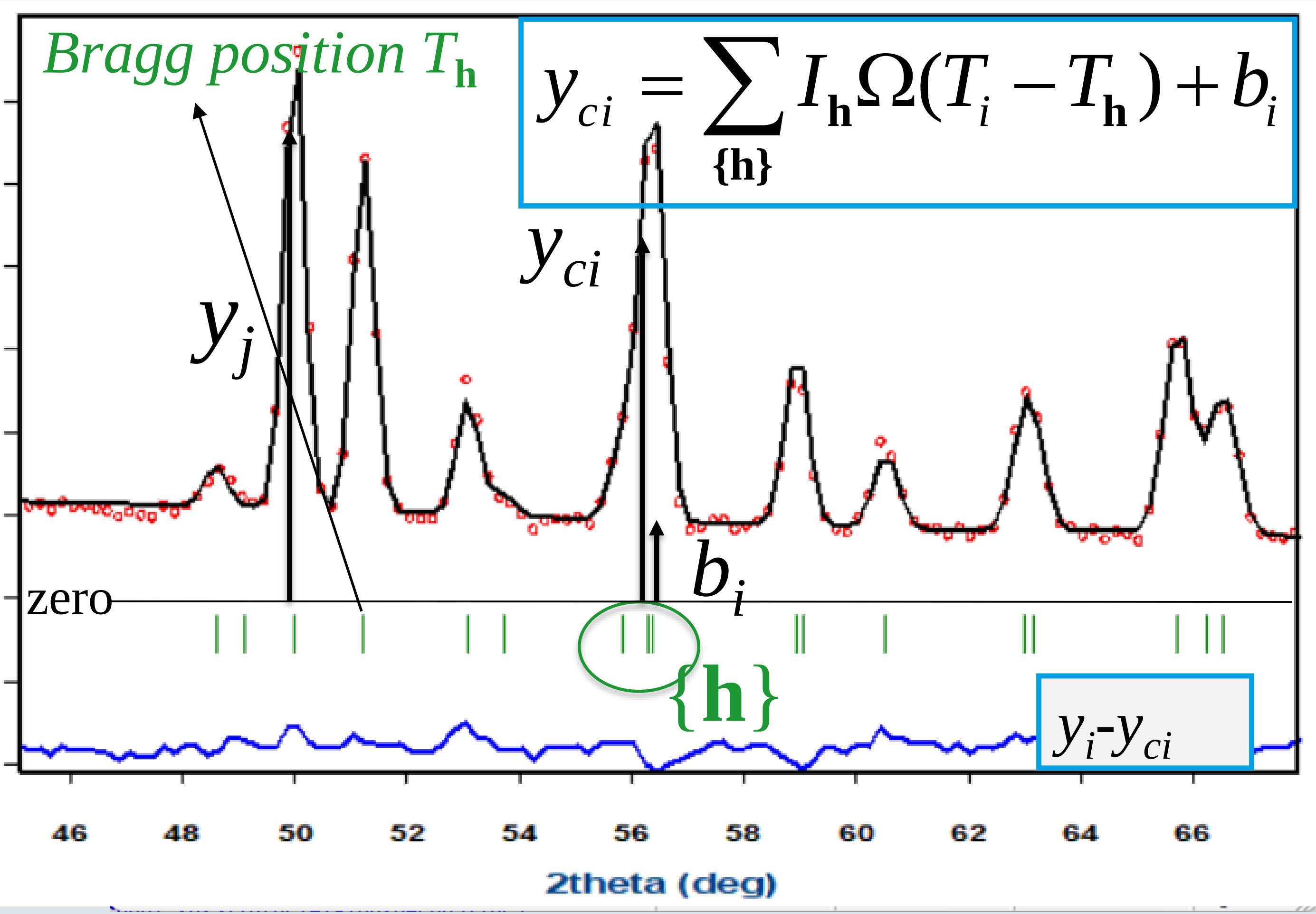
A powder diffraction pattern can be recorded in numerical form for a discrete set of scattering angles, times of flight or energies. We will refer to this scattering variable as : *T*.
The experimental powder diffraction pattern is usually given as three arrays :

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

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

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

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

Contains structural information:
atom positions, magnetic moments, etc

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

Contains micro-structura
instr. resolution, defects,

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

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

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

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

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

Components of the general expression for calculating powder diffraction patterns

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

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

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

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

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

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

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

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

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

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

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

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

$g_j(\mathbf{h}_s)$

Complex form factor of object j
Anisotropic DPs
Anharmonic DPs

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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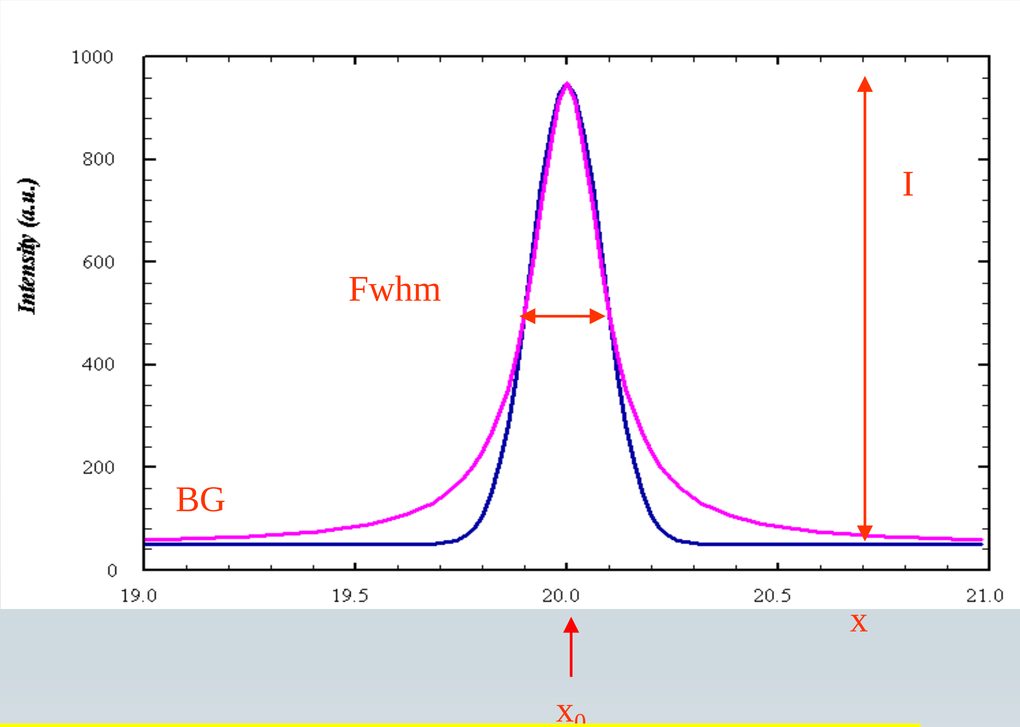
Constant wavelength neutron powder diffraction profiles

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

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

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

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

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

Sample

Instrument

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

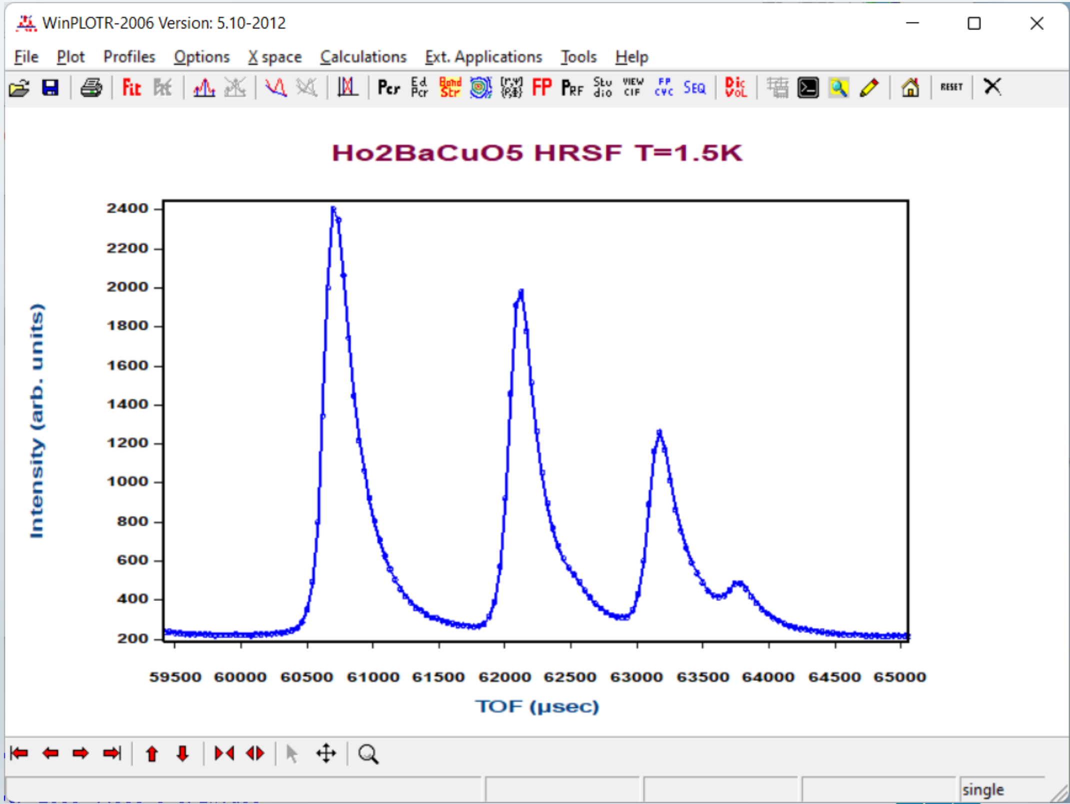
Convolution of back-to-back exponentials with a Voigt function

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

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

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

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



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)

$$\boxed{\begin{gathered} \mathbf{A}\boldsymbol{\delta}_{\boldsymbol{\beta}_0} = \mathbf{b} \\ A_{kl} = \sum_i w_i \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k} \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_l} \\ b_k = \sum_i w_i (y_i - y_{ic}) \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k} \end{gathered}}$$

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)

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

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 ‘$I_{obs,k}$’

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.

Different options existing in FullProf for working with magnetic structures

See the article:

Rodríguez-Carvajal, J., González-Platas, J., Katcho, N.A. (2025). *Magnetic structure determination and refinement using FullProf.* Acta Cryst **B**, 81(3), 302-317.

https://doi.org/10.1107/S2052520625003944

Different options for describing the magnetic model

(1) Standard Fourier (all kind of structures) coefficients refinement with $\mathbf{S}_\mathbf{k}$ described with components along {**a**/a, **b**/b, **c**/c} (`Jbt = 1,10`), or in spherical coordinates with respect to a Cartesian frame attached to the unit cell (`Jbt = -1, -10`).

(2) Time reversal operators, presently only for **k**=(0,0,0) (`Jbt = 10 + Magnetic symmetry` keyword after the symbol of the SPG) (obsolete)

(3) Shubnikov Groups in BNS formulation (`Jbt = 10 + Isy=2`). Whatever magnetic space group in any setting. The PCR file may be generated from an mCIF file.

(4) Real space description of uniaxial conical structures (`Jbt = 5`) (symmetry is ignored)

Daily Telegraph

Different options for describing the magnetic model

(5) Real space description of multi-axial helical structures with elliptic envelope

`(Jbt = -1, -10 + (More=1 & Hel = 2))`

(6) Refinement of $C_{n\lambda}^{\nu}$ coefficients in the expression:

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$$

`Jbt = 1 and Isy=-2`

(7) Refinement of the magnetic structure using symmetry modes (commensurate):

`Jbt = -6 and Isy=2`

(8) Refinement of the magnetic structure using superspace groups:

`Jbt = 7 and Isy=2`

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Standard Fourier coefficients (Jbt = +/-1, +/-10)

The Fourier component **k** of the magnetic moment of atom $j1$, that transforms to the atom js when the symmetry operator $g_s=\{S|t\}_s$ of $G_{\mathbf{k}}$ is applied ($\mathbf{r}^j{}_s=g_s\mathbf{r}^j{}_1=S_s\mathbf{r}^j{}_1+\mathbf{t}_s$), is transformed as:

$$\mathbf{S}_{\mathbf{k}js} = M_{js}\mathbf{S}_{\mathbf{k}j1} exp\{-2\pi i\phi_{\mathbf{k}js}\}$$

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{s} \mathbf{S}_{\mathbf{k}js} exp\ \{2\pi i[(\mathbf{H}+\mathbf{k})\{S|\mathbf{t}\}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}]\}$$

The matrices M_{js} and phases $\phi_{\mathbf{k}js}$ can be deduced from the relations between the Fourier coefficients and atomic basis functions. The matrices M_{js} correspond, in the case of commensurate magnetic structures, to the rotational parts of the magnetic Shubnikov group acting on magnetic moments.

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Standard Fourier coefficients (Jbt = +/-1, +/-10)

```
Ho2BaNiO5
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ     Nvk Npr More
   2   0   0 0.0 0.0 1.0   1  -1  -1   0    0       0.000     1   5    0
I -1                       <-- Space group symbol for hkl generation
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM  x,y,z
MSYM  u,v,w, 0.0
SYMM  -x,y,-z
MSYM  u,v,w, 0.0
SYMM  -x,-y,-z
MSYM  u,v,w, 0.0
SYMM   x,-y, z
MSYM  u,v,w, 0.0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ      Rx      Ry      Rz
!     Ix     Iy      Iz     beta11  beta22  beta33  MagPh
Ho   JHO3  1  0  0.50000 0.00000 0.20245 0.00000 0.50000   0.131   0.000   8.995
                    0.00    0.00   81.00    0.00    0.00  191.00    0.00  181.00
. . . . . . . . . . . . .
!     a          b          c         alpha      beta       gamma
   3.756032   5.734157  11.277159  90.000000  89.925171  90.000000
. . . . . . . . . . . . .
! Propagation vectors:
   0.5000000    0.0000000    0.5000000          Propagation Vector  1
    0.000000     0.000000     0.000000
```

(1) Standard Fourier coefficients

The symbol of the space group is used for the generation of the parent reflections. In this case half reciprocal lattice is generated

MSGs in BNS formulation (Jbt = 10 + Isy=2)

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
  18   0   0 0.0 0.0 1.0  10   0   2   0   0      1992.773   0   7   0
!
C_ac  number:"9.41"     <--Magnetic Space group symbol (BNS symbol & number)
! Nsym   Cen  N_Clat N_Ant
     2     0      1     2
! Centring vectors
   0.00000   0.50000   0.50000
! Anti-Centring vectors
   0.00000   0.00000   0.50000
   0.00000   0.50000   0.00000
! Symmetry operators
  1 x,y,z,+1
  2 x+1/2,-y+1/4,z,+1
!
!Atom   Typ     Mag Vek      X          Y          Z        Biso       Occ     N_type
!        Rx       Ry        Rz         Ix         Iy         Iz        MagPh
!      beta11   beta22    beta33     beta12     beta13    beta23
Dy_1   JDY3        1   0    0.62500  -0.04238    0.12500   0.44667    1.00000     1     0   #
                               0.00       0.00       0.00      0.00       0.00
     5.10000    2.00000    1.00000    0.00000    0.00000   0.00000    0.00000 <-MagPar
              0.00       0.00      0.00       0.00
Fe_1   MFE2        1   0    0.62500   0.86347   -0.00391   0.74386    1.00000     1     0   #
                               0.00       0.00       0.00      0.00       0.00
     1.00000    3.00000    1.00000    0.00000    0.00000   0.00000    0.00000 <-MagPar
             0.00       0.00      0.00       0.00
```

Real space description of multi-axial helical structures with elliptic envelope (Jbt = -1,-10 + More=1 & Hel = 2)

Same as **(1)**, but the Fourier component **k** of the magnetic moment of atom $j1$, is explicitly represented as:

$$\mathbf{S}_{\mathbf{k}j1} = \frac{1}{2}[m_{uj}\mathbf{u}_j + i m_{vj}\mathbf{v}_j]exp(-2\pi i\phi_{\mathbf{k}j})$$

With $\mathbf{u}_j$, $\mathbf{v}_j$ orthogonal unit vectors forming with $\mathbf{w}_j = \mathbf{u}_j$ x $\mathbf{v}_j$ a direct Cartesian frame.

Refinable parameters: m_{uj}, m_{vj}, $\phi_{\mathbf{k}j}$
plus the Euler angles of the Cartesian frame $\{\mathbf{u}, \mathbf{v}, \mathbf{w}\}_j$

Real space description of multi-axial helical structures with elliptic envelope (Jbt = -1,-10 + More=1 & Hel = 2)

```
Jbt=-1
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   3   0   0 0.0 0.0 1.0  -1   4  -1   0   0          0.000  -1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc    Jtyp  Nsp_Ref Ph_Shift
   3   0   2   0   0   0  1.0000  1.0000  0.0000  0.0000    1      0       0
!
P -1                        <--Space group symbol
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM   x, y, z
MSYM   u, v, w, 0.00
.....

!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ       Mr       Mi      Chi
!   Phi    Theta  unused  beta11  beta22  beta33   MagPh
Fe   MFE3  1   0  0.12340 0.02210 0.25000 0.00000 0.50000   3.450    3.450    0.000
                     0.00    0.00    0.00    0.00    0.00    0.00     0.00     0.00
  15.000  25.000    0.000   0.000   0.000   0.000 0.00000
     0.00     .00    0.00    0.00    0.00    0.00    0.00
.....
```

Real space description of multi-axial helical structures with elliptic envelope (Jbt = -1,-10 + More=1 & Hel = 2)

```
Jbt=-10
....
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   3   0   0 0.0 0.0 1.0 -10   4  -1   0   0       492.121  -1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift
   3  -1   2   0   0   0 1.0000  1.0000  0.0000  0.0000    1       0       0
!
P -1                        <--Space group symbol
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM   x, y, z
MSYM   u, v, w, 0.00
...
!Atom Typ     Mag Vek      X          Y          Z         Biso       Occ     N_type
!      Mr         Mi       Chi        Phi       Theta    unused       MagPh
!     beta11    beta22    beta33    beta12    beta13    beta23   / Line below:Codes
Fe    MFE3        1   0   0.12340   0.02210   0.25000   0.00000   0.50000    1    0
                             0.00       0.00       0.00       0.00       0.00
   4.46000    4.46000   0.00000  10.00000  25.00169   0.00000   0.12110 <-MagPar
      0.00       0.00      0.00       0.00       .00       0.00       0.00
....
```

Coefficients of basis functions refinement

A magnetic phase has **`Jbt = 1 and Isy=-2`**

$$\boxed{\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j\, f_j(\mathbf{h})\, T_j \sum_{n\lambda} C_{n\lambda}^{\nu} \sum_{s} \mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)\, exp\left\{2\pi\, i\left[\mathbf{h}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}\right]\right\}}$$

The basis functions of the Irreps (in numerical form) are introduced together with explicit symmetry operators of the crystal structure.

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$$

The refined variables are directly the coefficients C1, C2, C3, ….

$$C_{n\lambda}^{\nu}$$

Coefficients of basis functions refinement

```
Ho2BaNiO5     (Irep 3 from BasIreps)
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ     Nvk Npr More
   2   0   0 0.0 0.0 1.0   1  -1  -2   0   0          0.000    1   5   0
I -1                     <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
     2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM x,y,z
BASR   1  0  0    0  0  1
BASI   0  0  0    0  0  0
SYMM  -x,y,-z
BASR   1  0  0    0  0  1
BASI   0  0  0    0  0  0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ       C1      C2      C3
!     C4     C5     C6      C7      C8      C9      MagPh
Ho    JHO3  1  0  0.50000 0.00000 0.20250 0.00000 1.00000   0.127   8.993   0.000
                     0.00    0.00   81.00    0.00    0.00   71.00  181.00    0.00
. . . . . . . . . . . . . . . .
!      a          b          c         alpha       beta        gamma
   3.754163   5.729964  11.269387  90.000000  90.000000  90.000000
. . . . . . . . . . . . . . . . . .
! Propagation vectors:
   0.5000000    0.0000000    0.5000000          Propagation Vector  1
```

Refinement of the magnetic structure using symmetry modes (commensurate): Jbt = -6 and Isy=2

The preparation of the PCR file for this option is done with the help of ISODISTORT that generates directly a PCR template adapted to this option.

Illustrated with the example 3: $DyFeWO_6$

Open ISOTROPY software suite on the web page and click on ISODISTORT. Here we can upload the CIF file and CLICK on OK. (https://stokes.byu.edu/iso/isotropy.php)

In the first box "Types of distortions to be considered" include the displacive distortions for all the atoms (Dy, Fe, W and O). In the occupation distortion, we don't need to add any atom. The magnetic modes correspond only to Dy and Fe, the magnetic atoms. After that we have to CLICK on Change.
We use the "Method 2: General method - search over specific k points", here we have to specify the *k*-point, in this particular case that labelled T, K23, which corresponds to the propagation vector **k** = (0, ½, ½). After that we click on OK.

Refinement of the magnetic structure using symmetry modes (commensurate): Jbt = -6 and Isy=2

ISODISTORT: search

Space Group: 33 Pna2_1 C2v-9, Lattice parameters: a=10.97235, b=5.18323, c=7.33724, alpha=90.00000, beta=90.00000, gamma=90.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Dy 4a (x,y,z), x=0.04249, y=0.45725, z=0.25000, Fe 4a (x,y,z), x=0.13660, y=-0.03500, z=-0.00640, W 4a (x,y,z), x=0.35220, y=0.45370, z=0.00890, O1 4a (x,y,z), x=-0.02760, y=-0.23340, z=0.04410, O2 4a (x,y,z), x=-0.476
z=-0.06590, O5 4a (x,y,z), x=0.14370, y=0.06010, z=0.25740, O6 4a (x,y,z), x=0.11990, y=-0.17080, z=-0.25290
Include displacive ALL, magnetic Dy Fe distortions

Types of distortions to be considered Change ?

strain: ☐
Displacive: all ☐ none ☐ Dy ☑ Fe ☑ W ☑ O ☑
Occupational: all ☐ none ☐ Dy ☐ Fe ☐ W ☐ O ☐
Magnetic: all ☐ none ☐ Dy ☑ Fe ☑ W ☐ O ☐
Rotational: all ☐ none ☐ Dy ☐ Fe ☐ W ☐ O ☐

Important: You must click on Change to implement any changes in the above type of distortions to be considered.

Selecting Displacive and Magnetic distortions
All atoms experience displacive modes and only Dy and Fe have magnetic moments

Method 1: Search over all special *k* points OK ?

Crystal system(s): triclinic ☐ monoclinic ☐ orthorhombic ☐ tetragonal ☐ trigonal ☐ hexagonal ☐ cubic ☐
Space-group symmetry: no choice ▾ Conventional lattice: no choice ▾ Primitive lattice: no choice ▾ Maximal subgroups only ☐ ?

Method 2: General method - search over specific *k* points OK ?

Specify *k* point: T, k23 (0,1/2,1/2) ▾ a= b= g= # of independent incommensurate modulations= 0

Change number of superposed IRs: 1 Change ?

Important: You must click on Change to implement any changes in the number of superposed IRs.

Selecting the propagation vector
Search for the Brillouin Zone point and set independent incommensurate modulations to zero

Refinement of the magnetic structure using symmetry modes (commensurate): Jbt = -6 and Isy=2

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:    1  ==> Current R_Bragg for Pattern#  1:     4.28
!-------------------------------------------------------------------------------
AMPLIMODES for FullProf        FIX xyz
! The nuclear structrure should be fixed and only the
! amplitudes are refinables. The crystal structure described below correspond to the parent in the setting of the subgroup.
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
  18   0   0 0.0 0.0 1.0  -6   0   2   0   66      31884.371   0   7   0 !code to symmetry modes
!
C_ac  number:  9.41   <--Magnetic Space Group Symbol (BNS symbol and number
Transform to standard:  a,b,c;0,0,0  <--Basis transformation from alt setting to standard BNS
Parent space group:  Pna2_1  IT_number:   33  <--Nonmagnetic Parent Group
Transform from Parent:  2c,-2b,a;0,-3/4,3/4  <--Basis transformation from parent to current
!Atom    Typ     Mag Vek      X         Y         Z        Biso      Occ     N_type  Spc/Fftype /Line below:Codes
!        Rx        Ry         Rz        Ix        Iy        Iz       MagPh   / Line below:Codes
!       beta11    beta22    beta33    beta12    beta13    beta23   / Line below:Codes
Dy_1    JDY3       1  0    0.75000   0.39637   0.04249   0.50000   1.00000    1    1
                              0.00      0.00      0.00      0.00      0.00
     0.00000   0.00000   0.00000   0.00000   0.00000   0.00000   0.00000 <-MagPar
        0.00      0.00      0.00      0.00      0.00      0.00      0.00
Dy_2    JDY3       1  0    0.00000   0.35363   0.95751   0.50000   1.00000    1    1
                              0.00      0.00      0.00      0.00      0.00
     0.00000   0.00000   0.00000   0.00000   0.00000   0.00000   1.00000 <-MagPar
        0.00      0.00      0.00      0.00      0.00      0.00      0.00
Fe_1    MFE3       1  0    0.62180   0.14250   0.13660   0.50000   1.00000    1    2
                              0.00      0.00      0.00      0.00      0.00
     0.00000   0.00000   0.00000   0.00000   0.00000   0.00000   0.00000 <-MagPar
        0.00      0.00      0.00      0.00      0.00      0.00      0.00
Fe_2    MFE3       1  0    0.87180   0.10750   0.86340   0.50000   1.00000    1    2
                              0.00      0.00      0.00      0.00      0.00
     0.00000   0.00000   0.00000   0.00000   0.00000   0.00000   0.00000 <-MagPar
        0.00      0.00      0.00      0.00      0.00      0.00      0.00
W_1     W          0  0    0.62945   0.39815   0.35220   0.50000   1.00000    0    3
                              0.00      0.00      0.00      0.00      0.00
```

Use of superspace in FullProf

Refinement of the magnetic structure using **superspace groups**:

`Jbt = ±7 and Isy=2`

We illustrate the procedure with the magnetic structure of $DyMn_6Ge_6$ (Exercise 4) for which we know the crystal structure summarized in a CIF file.

Use ISODISTORT to create mcif files

a. Open ISOTROPY software suite on the web page and click on ISODISTORT. (https://stokes.byu.edu/iso/isotropy.php)

b. Upload into the system the structural CIF file and click on OK.

c. In the first box "Types of distortions to be considered" select only the magnetic modes for the magnetic atoms (Dy and Mn). After that we can CLICK on Change.

Use of superspace in FullProf

After uploading the CIF file with the crystal structure of $DyMn_6Ge_6$
One has to select magnetic "distortions" for Dy and Mn

ISODISTORT: search

Space Group: 191 P6/mmm D6h-1, Lattice parameters: a=5.20770, b=5.20770, c=8.15150, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Dy1 1a (0,0,0), Ge1 2d (1/3,2/3,1/2), Ge2 2c (1/3,2/3,0), Ge3 2e (0,0,z), z=0.34450, Mn1 6i (1/2,0,z), z=0.25030
Include magnetic Dy Mn distortions

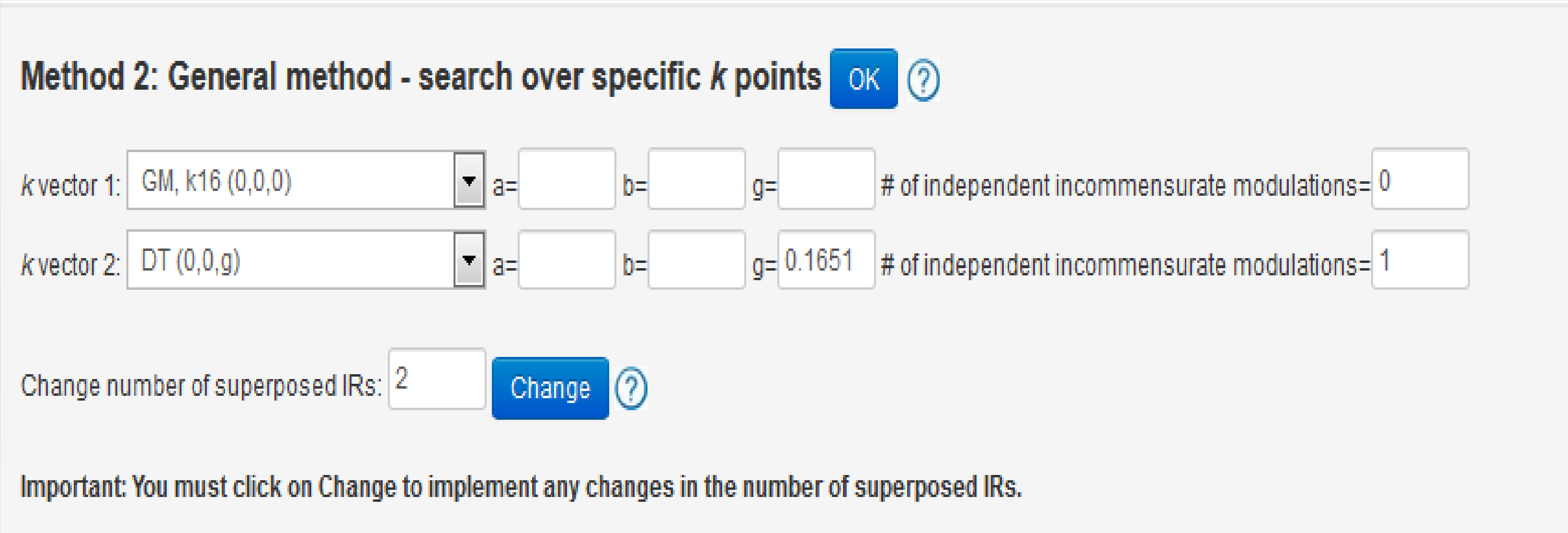
Types of distortions to be considered Change ?

strain: ☐
Displacive: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐
Occupational: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐
Magnetic: all ☐ none ☐ Dy ☑ Ge ☐ Mn ☑
Rotational: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐

Important: You must click on Change to implement any changes in the above type of distortions to be considered.

Different options for describing the magnetic model

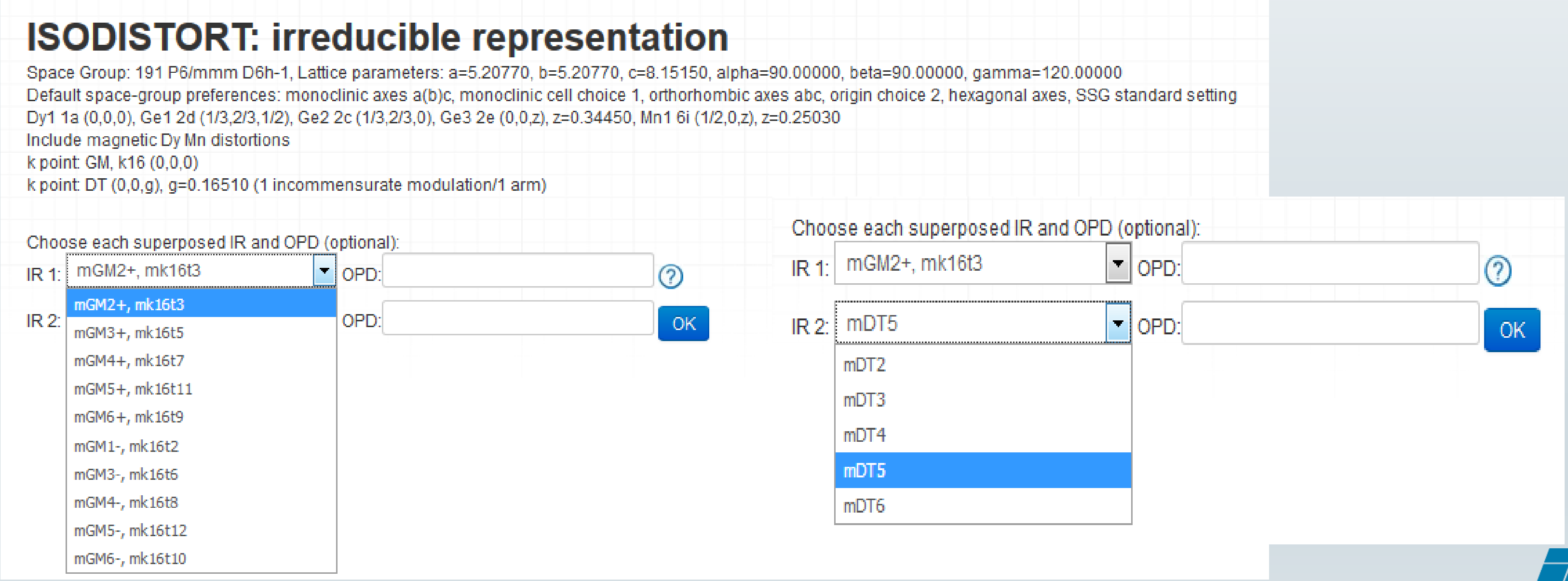
a. We should use the “Method 2: General method - search over specific k points”, here on “Change number of superposed IRs” we should increase the number from 1 to 2, as we have to two propagation vectors. Click on Change. After that, the program shows two set of propagation vectors.
b. For the k-vector 1 we select the **k** = (0, 0, 0), and the number of incommensurate modulations is fixed to 0.
c. For the k-vector 2 we select the **k** = (0, 0, 0.1651) [DT (0, 0, g)], and change the number of incommensurate modulations to 1. After that we click on OK.



Use of superspace in FullProf

In the next menu we can combine the *irreps* obtained from each propagation vector. In the case of **k** = 0, there are 10 possible magnetic *irreps*. While for the incommensurate vector the number of solutions are only 5.

Now we need to combine the possible *irreps* and sort the magnetic superspace groups from high to low symmetry.



Creating a PCR file compatible with magnetic superspace groups.

1. A template PCR file compatible with the magnetic super-space group can be created in a similar way that was shown on the example 1 using the mCIF_to_PCR utility from the FullProf toolbar.
2. Alternatively you can use a previous created template and modify it according with the new magnetic superspace group.

To do the procedure by hand you should only modify the block of the sample data. You can start from the previous PCR file with only the structural phase. Here below there is a description of the PCR file for magnetic super-space formalism.

1
Symmetry block

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   5   0   0 0.0 0.0 1.0   7   0   2   0   0      34495.781    1   7   0
!
P6/mm'm'(0,0,g)0000     <-- Magnetic  SuperSpace group symbol (not currently used)
genr x1,x2,x3,x4,+1     <-- List of symmetry operators or generators
genr x1-x2,x1,x3,x4,+1
....
genr x1,x1-x2,-x3,-x4,-1
...
genr  x2,x1,x3,x4,-1
N_qc  1                        <-- Number of Q_coeff (harmonics)
Q_coeff                        <-- List of Q_coeff, 1 coefficient per line
   1
!
```

2
Atoms
block

```
Dy      JDY3     -1          0.00000    0.00000    0.00000    0.00000    0.25000   1    0
                             0.00000    0.00000    0.00000    0.00000    0.00000
MagM0-Moment:      0.00000   0.00000   -5.63530   <- Homogeneous magnetic moment
                   0.00000   0.00000    0.00000
 Mcos-Msin-1:      0.00000   0.00000    0.97112  0.00000  0.00000   0.00000 <-Mom.Amplitudes
                   0.00000   0.00000   51.00000  0.00000  0.00000   0.00000
 Ucos-Usin-1:      0.00000   0.00000    0.00000  0.00000  0.00000   0.00000 <-Dis. Amplitudes
                   0.00000   0.00000    0.00000  0.00000  0.00000   0.00000
Mn      MMN2      1          0.50000    0.00000    0.25092    0.00000    1.63901   3    0
                             0.00000    0.00000    0.00000    0.00000   41.00000
MagM0-Moment:      0.00000    0.00000    0.70663   <- Homogeneous magnetic moment
                   0.00000    0.00000    0.00000
 Mcos-Msin-1:      0.00000    0.00000    3.01341  0.00000  0.00000   3.14535   <-Mom.Amplitudes
                   0.00000    0.00000   61.00000  0.00000  0.00000  71.00000
   Beta_0(i,j):    0.00000    0.00000    0.00000  0.00000  0.00000   0.00000   <-Betas
                   0.00000    0.00000    0.00000  0.00000  0.00000   0.00000
Ge1     GE        0          0.33333    0.66666    0.50000    0.00000    0.50000   0    0
                             0.00000    0.00000    0.00000    0.00000    0.00000
Ge2     GE        0          0.33333    0.66666    0.00000    0.00000    0.50000   0    0
                             0.00000    0.00000    0.00000    0.00000    0.00000
Ge3     GE        0          0.00000    0.00000    0.34741    0.00000    0.50000   2    0
                             0.00000    0.00000   31.00000    0.00000    0.00000
   Beta_0(i,j):    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000  <-Betas
                   0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
```

3
Propagation vector block

```
!   Pref1     Pref2      Asy1      Asy2      Asy3      Asy4       S_L       D_L
  1.00000   0.00000   0.00000   0.00000   0.00000   0.00000   0.02495   0.03168
     0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
! Propagation vectors:
   0.0000000    0.0000000    0.1647532   1 1.0000 <-- Prop. Vector, nharm, sintl_lim
   0.000000     0.000000     0.000000
!  2Th1/TOF1     2Th2/TOF2   Pattern to plot

.  .  .  .
```

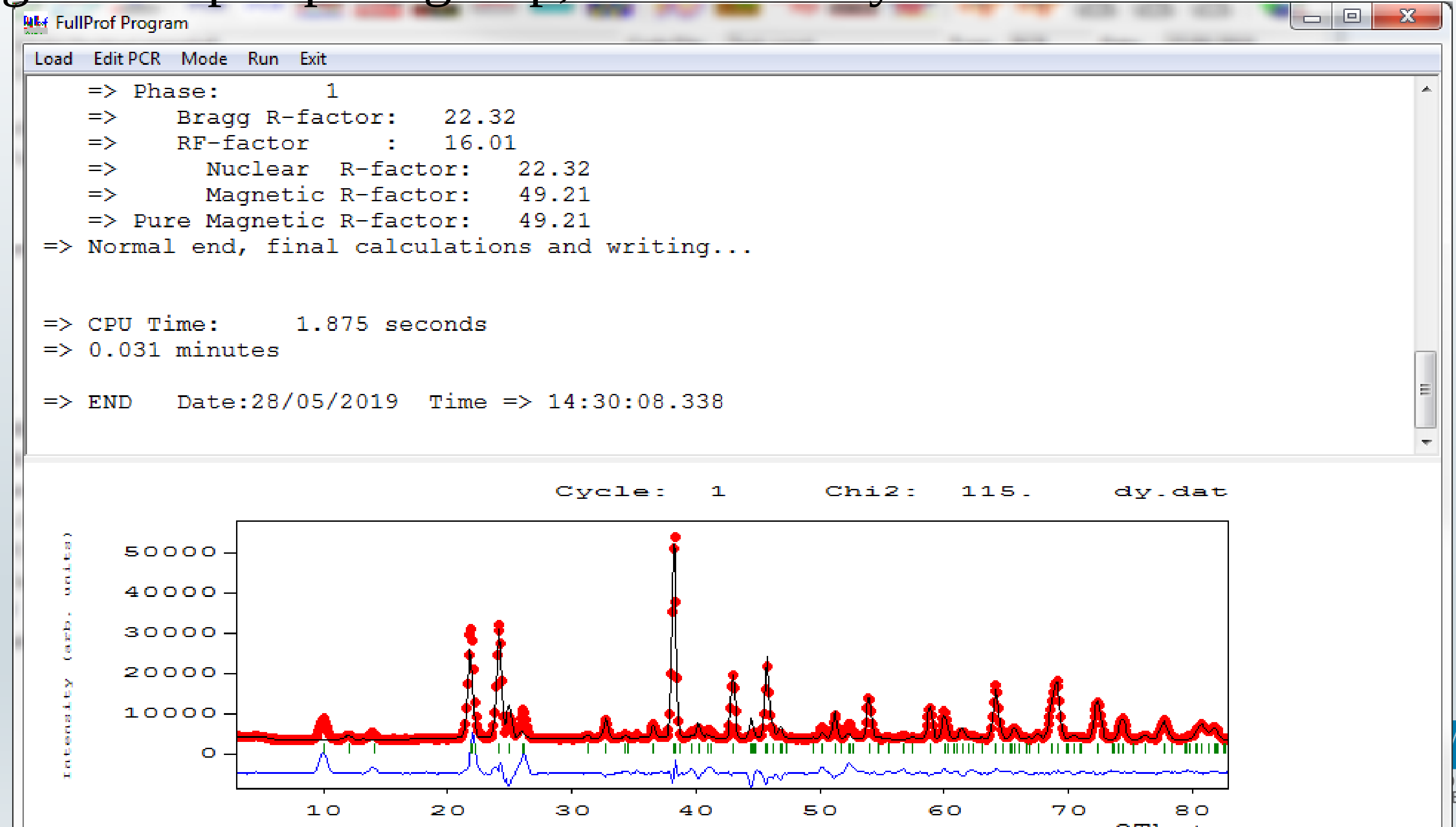
The red block correspond with the "homogeneous magnetic moment", the component described by the commensurate propagation vector **k**=0.

The green part corresponds to the modulations, the three first terms are the Cosine terms (x, y, z) and the last term are the Sine components (x, y, z).

FullProf apply automatically the symmetry constrains if the instructions **VARY mxmymz McosMsin** are included on the PCR file after the phase name. The generation of reflections in superspace takes into account automatically the possible systematic absences.

The mxmymz instruction allows to refine and apply symmetry constrains to the commensurate part while the McosMsin do the same with the cosine and sine amplitudes.

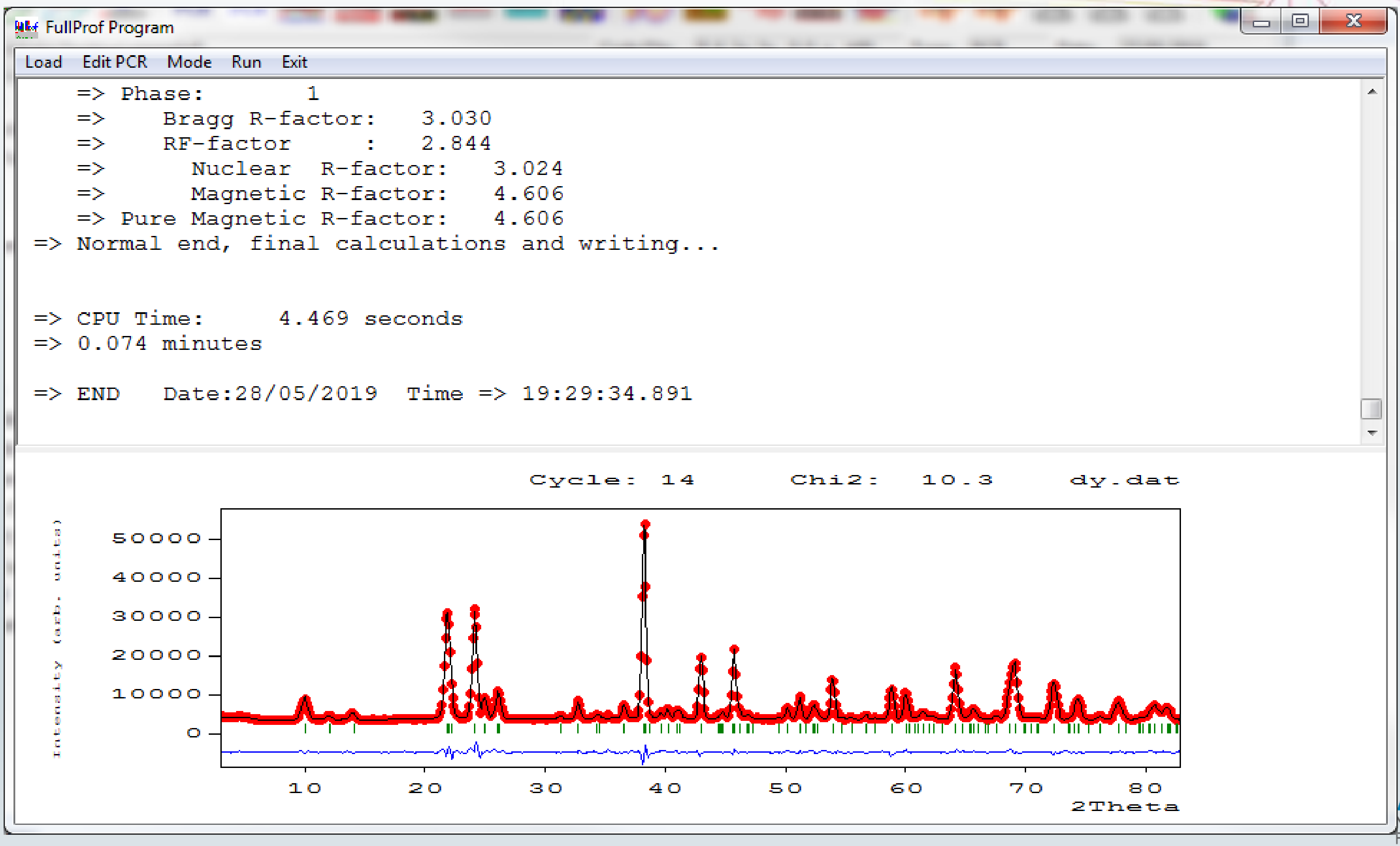
The PCR file was created using the *P*6/*mm*'*m*'(0,0,*γ*)0000 magnetic superspace group, that is clearly incorrect



1 In order to allow magnetic structures with magnetic moments out of a single axis we can try with magnetic superspace groups with lower symmetry. So we could decrease the symmetry exploring the P622 groups. The combination of mGM2+ with DT5 give rise to the P62'2'(0,0,g)t00 magnetic space group while if mGM2+ with DT6 the magnetic space group is P62'2'(0,0,g)h00. However, the first magnetic space group can be rejected as the amplitudes of modulated moments of the Dy atoms should be zero by symmetry. Therefore, let check if the P62'2'(0,0,g)h00 space group is able to fit the experimental data.

2 Create a PCR file including the symmetry operator of the P62'2'(0,0,g)h00 space group. Here below you can check the list obtained directly from the mcif generated by ISODISTORT.

The PCR file was created using the $P622'(0,0,\gamma)h00$ magnetic superspace group, that is clearly correct



Different options for describing the magnetic model

The documentation for using the different options in FULLPROF is scattered in the old manual and the document `fp2k.inf`

Se also the document:

Magnetic structure analysis and refinement with FullProf.pdf

Daily Telegraph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