FullProf School

Introduction to the FullProf Suite. Options to Treat magnetic structures in FullProf

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OUTLINE

1: PRESENTATION OF THE FULLPROF SUITE

2: SHORT DESCRIPTIONS OF MAGNETIC STRUCTURES

3: MAGNETIC STRUCTURE FACTORS

4: DIFFERENT OPTIONS EXISTING IN FULLPROF

PRESENTATION OF THE FULLPROF SUITE

FullProf (may be run in console mode using scripts for thousands of patterns)

- **A program for :**

  Simulation of powder diffraction patterns

  Pattern decomposition⇨ integrated intensities

  Structure refinement

  Powder and single crystal data
- **Crystal and magnetic structures: special form factors, rigid bodies, symmetry adapted modes, incommensurate magnetic structures, restraints, microstructure effects, superspace for magnetic structures, etc.**
- **Multiple data sets: simultaneous treatment of several powder diffraction patterns (CW X-rays & neutrons, Energy dispersive X-rays, TOF neutron diffraction)**
- **Combined treatment of single crystal and powder data**
- **Crystal and magnetic Structure determination capabilities:**

  simulated annealing on integrated intensity and profile data
- **Polarized neutrons: Flipping ratio analysis**
- **Single crystal electron diffraction (kinematic only)**

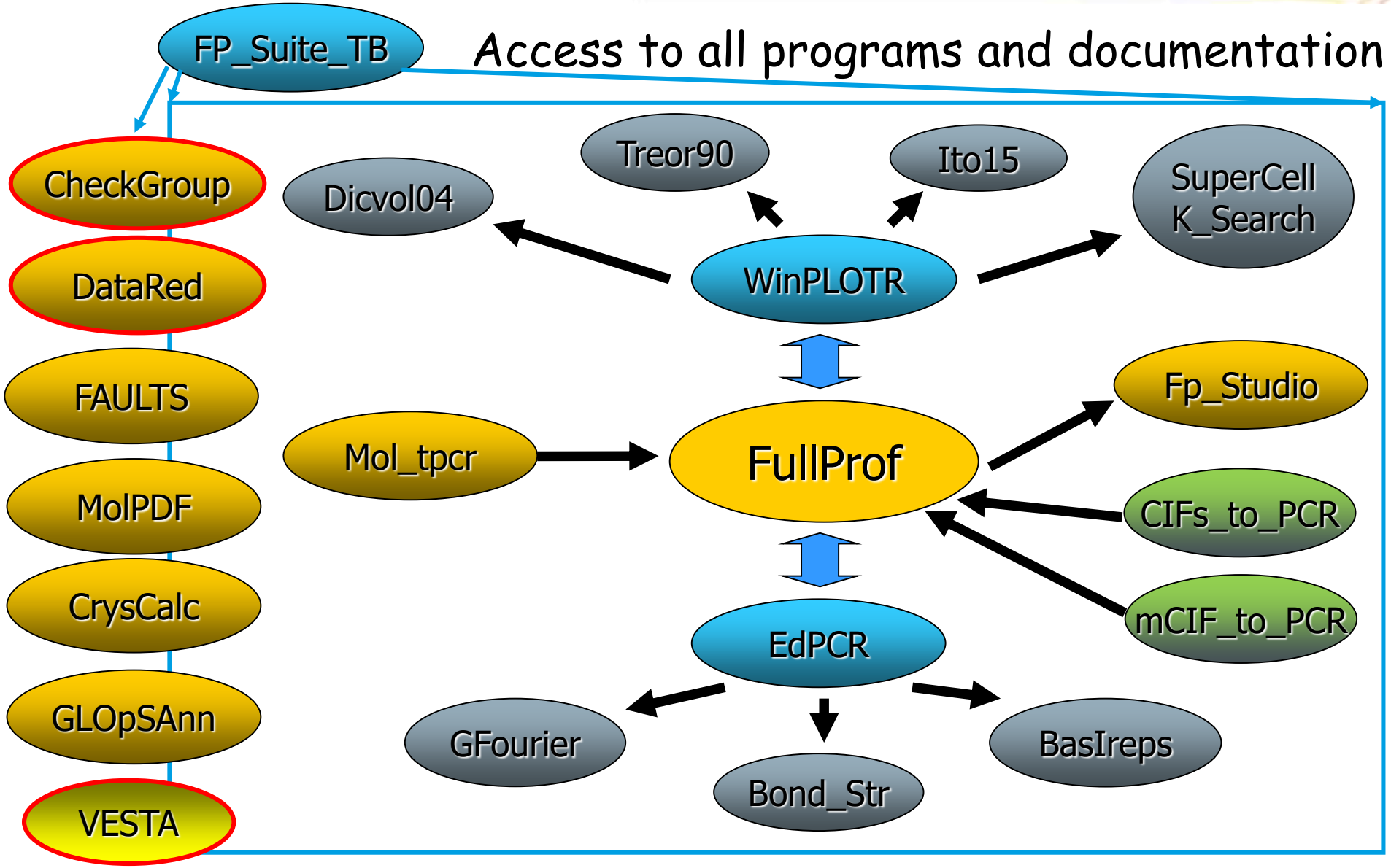
The PCR file

It is a text file containing all instructions for running **FullProf**. A good text editor is needed for using the most advanced options

The PCR file may be produced automatically for combining different patterns and phases using the utilities: **CIFs_to_PCR** or **mCIF_to_PCR**

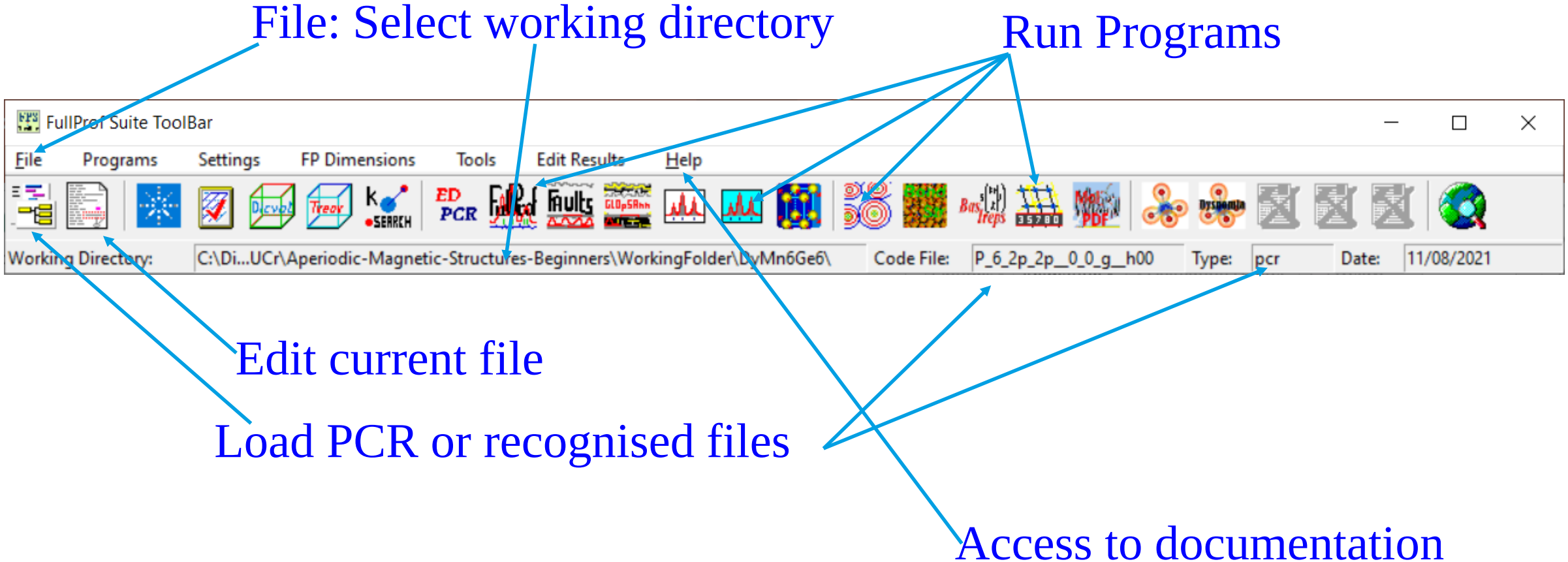
It may be produced from the scratch by using **EdPCR**

PRESENTATION OF THE FULLPROF SUITE

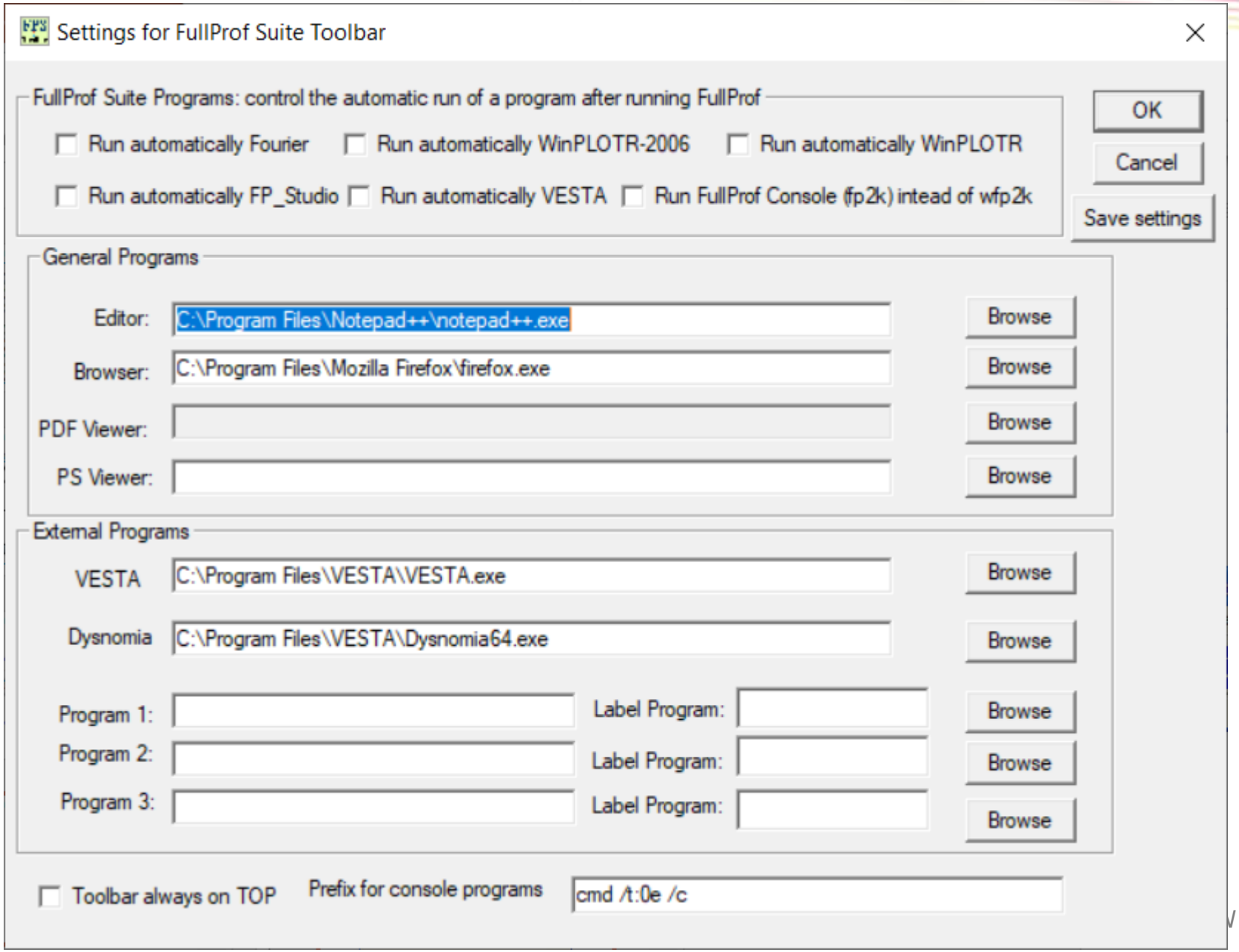


Other utilities:
MHall
TOF_fit_LM
. . .

PRESENTATION OF THE FULLPROF SUITE



PRESENTATION OF THE FULLPROF SUITE



Select a text Editor

Select a Browser

Locate VESTA exe

Locate External programs

PRESENTATION OF THE FULLPROF SUITE

WinPLOTR

0: Visualizing multiple powder patterns (superimposed or 3D)
1: Automatic peak search for indexing
2: Saving peaks as DICVOL04, Treor90, etc
3: Running indexing programs
4: Automatic generation of PCR file for cell refinement and integrated intensity extraction (Le Bail fit)
5: Making individual peak fits
6: Exporting background files
7: Invoking other programs

EdPCR

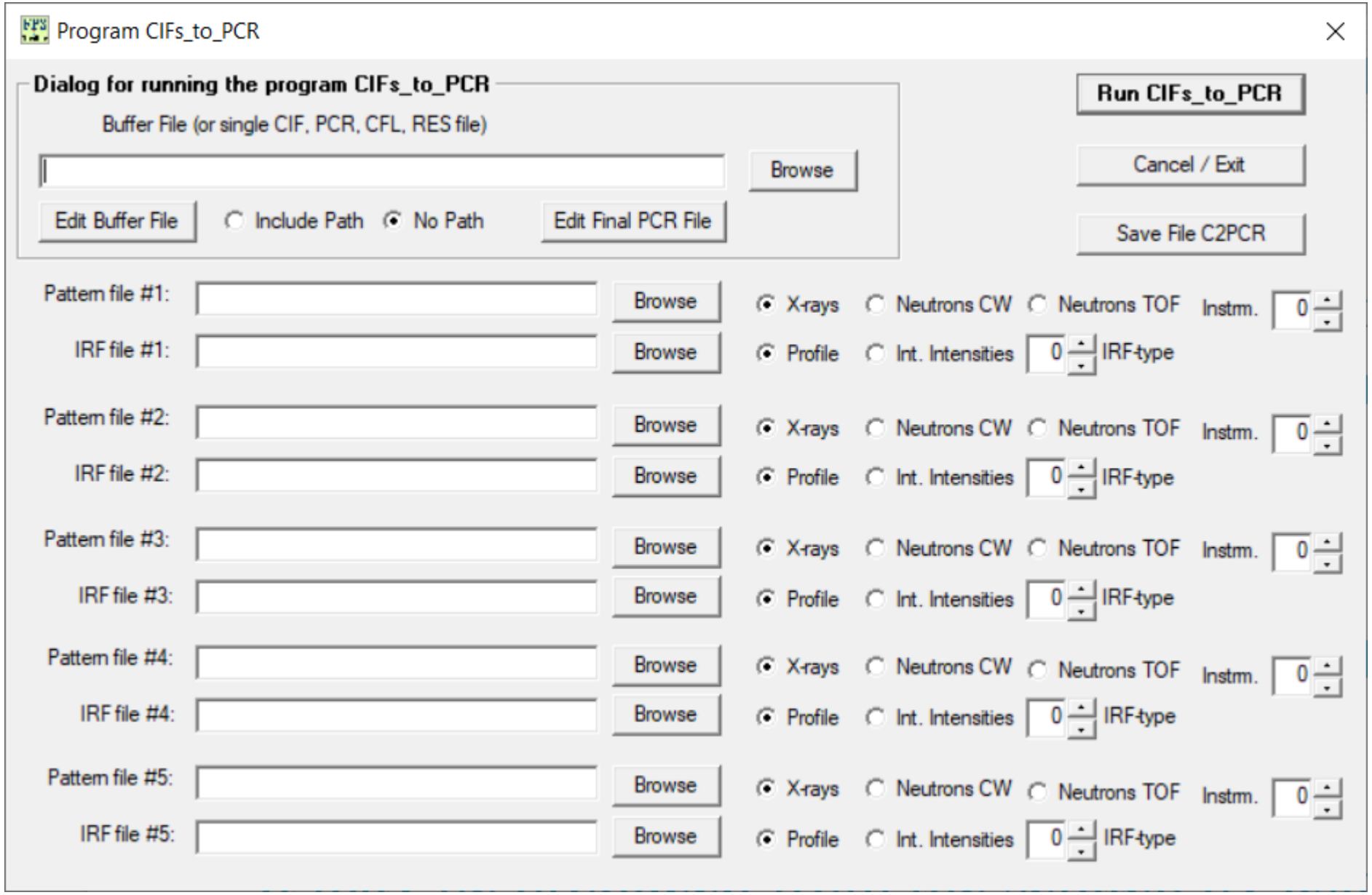
GUI for editing PCR files
Only limited number of options
Shubnikov and superspace groups are not currently available within EdPCR

PRESENTATION OF THE FULLPROF SUITE: CIFS_TO_PCR

Select input files with information of the different phases: e.g. a list of CIF files

Select data files containing diffraction patterns and the corresponding features

Select the IRF file of each pattern (radio buttons)



PRESENTATION OF THE FULLPROF SUITE

FAULTS Program to refine powder diffraction patterns (X-rays and neutrons) of crystal systems with any type of coherent planar defect. Based on DIFFaX and CrysFML

MolPDF Program to refine Pair Distribution Function specialized for Molecular systems

GLOpSAnn Global optimization by simulated annealing of crystal structures using a variety of cost functions: R-factors, BVS, distances, torsion angles, etc.

PRESENTATION OF THE FULLPROF SUITE

The programs of the **FullProf Suite** are not black-box-like with a single way of doing the things.

The GUIs are mere help utilities for handling the input control files.

The learning curve for the use of the programs may be steeper than for other programs, however understanding the content of the input files and making manual changes is much faster, once the user is becoming expert, than using the GUIs.

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2: SHORT DESCRIPTIONS OF MAGNETIC STRUCTURES

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The most elementary way of describing a commensurate magnetic structure

Ignoring symmetry (except the translation symmetry), a list of all the atoms within the unit cell, with their fractional coordinates, thermal displacement parameters and occupation probabilities, as well as the attached magnetic moments describes completely the crystal and magnetic structure. This is a description in *P*1

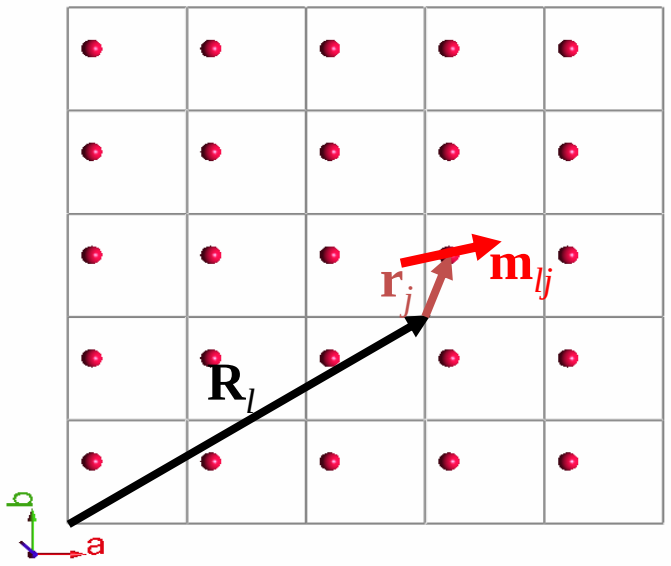
Unit cell: *a*, *b*, *c*, α, β, γ

$$\{\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c} \quad B_j, O_j \quad j = 1, 2, \ldots n\} \qquad \textit{crystal} \quad +$$

$$\{\mathbf{m}_j = m_{xj}\mathbf{a}/a + m_{yj}\mathbf{b}/b + m_{zj}\mathbf{c}/c \quad j = 1, 2, \ldots n\} \quad \textit{magnetic structure}$$

Notice that the magnetic moments in Bohr magnetons are referred to the frame:
U=(**a**/a, **b**/b, **c**/c) = ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$)

FORMALISM OF PROPAGATION VECTORS



This formalism allows the description of magnetic structures (commensurate and incommensurate) using the crystallographic unit cell of the paramagnetic state

$$\boxed{\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j}\ exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}}$$

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c} + x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

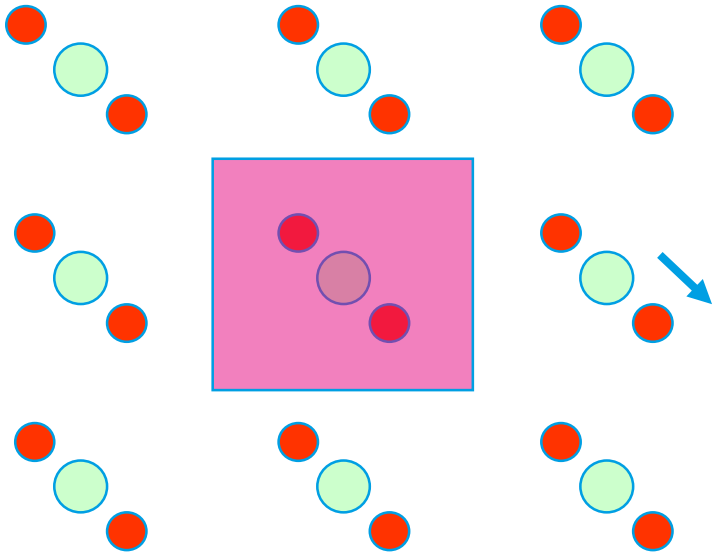
Necessary condition for real $\mathbf{m}_{lj}$ $\quad \boxed{\mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^{*}}$

General expression used in **FullProf** $\quad \mathbf{S}_{\mathbf{k}j} = \frac{1}{2}(\mathbf{R}_{\mathbf{k}j} + i\mathbf{I}_{\mathbf{k}j})\exp\{-2\pi i\phi_{\mathbf{k}j}\}$

Only six parameters are independent. The writing above is convenient when relations between the vectors **R** and **I** are established (e.g. when |**R**|=|**I**|, or **R . I** =0)

FORMALISM OF PROPAGATION VECTORS

Portion of reciprocal space



Magnetic reflections

Nuclear reflections

h = H+k

Magnetic reflections: indexed by a set of propagation vectors {**k**}

H is a reciprocal vector of the crystallographic structure

k is one of the propagation vectors of the magnetic structure (**k** is reduced to the Brillouin zone)

FORMALISM OF PROPAGATION VECTORS

Another convention (Used in Superspace formalism)

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{T}_{\mathbf{k}j} \; exp\left\{-2\pi\, i\mathbf{k}\mathbf{R}_{lj}\right\}$$

$$\mathbf{T}_{\mathbf{k}j} = \frac{1}{2}(\mathbf{M}_{\mathbf{k}j}^{\cos} + i\mathbf{M}_{\mathbf{k}j}^{\sin})$$

For a single pair (k,-k) and its harmonics:

$$\mathbf{m}_{lj} = \sum_{n} \mathbf{M}_{n\mathbf{k}j}^{\sin} \sin(2\pi\, n\mathbf{k}\mathbf{R}_{lj}) + \mathbf{M}_{n\mathbf{k}j}^{\cos} \cos(2\pi\, n\mathbf{k}\mathbf{R}_{lj})$$

$$\mathbf{m}_{lj} = \mathbf{m}(x_4) = \sum_{n} \mathbf{M}_{n\mathbf{k}j}^{\sin} \sin(2\pi\, nx_4) + \mathbf{M}_{n\mathbf{k}j}^{\cos} \cos(2\pi\, nx_4)$$

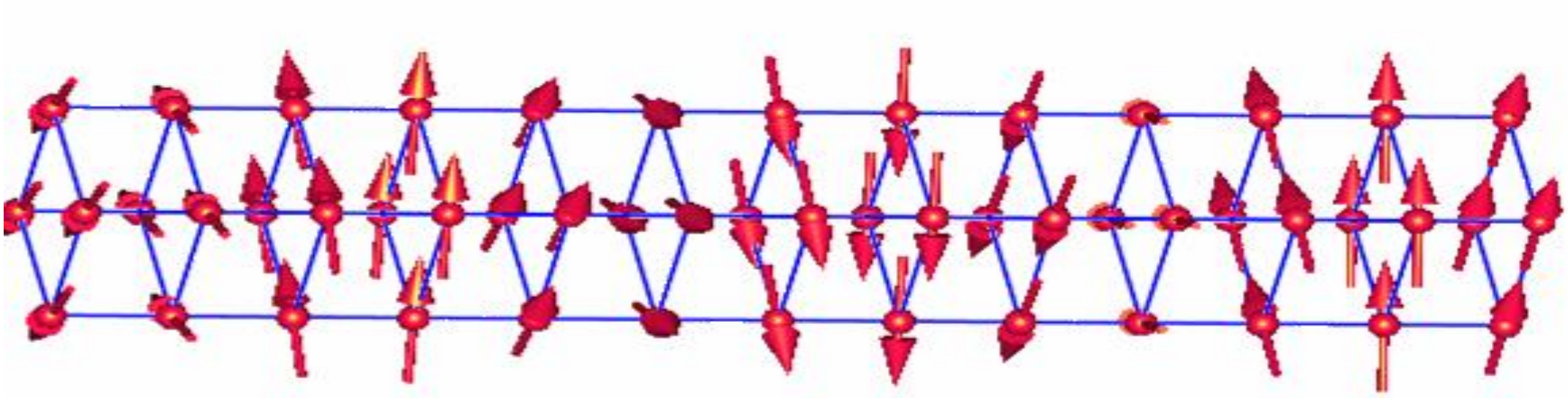
FORMALISM OF PROPAGATION VECTORS

A magnetic structure is fully described by:

i) Wave-vector(s) or propagation vector(s) $\{\mathbf{k}\}$.

ii) Fourier components $\mathbf{S}_{\mathbf{k}j}$ (6 components) for each magnetic atom j and wave-vector $\mathbf{k}$.

Or equivalently the vectors $\mathbf{T}_{\mathbf{k}j} = \frac{1}{2}(\mathbf{M}_{\mathbf{k}j}^{\cos} + i\mathbf{M}_{\mathbf{k}j}^{\sin})$



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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

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

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

Magnetic Structure Factor: Shubnikov Groups

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 $n_p < 3n$.

NEUTRONS FOR SOCIETY

Magnetic Structure Factor: k-vectors

We use of the **reciprocal unit cell of the paramagnetic state + k-vectors** for indexing the magnetic Bragg reflections

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

j : index running for all n magnetic atom sites in the magnetic asymmetric unit

s : index running for all atoms of the orbit corresponding to the magnetic site j (s=1,… p_j). Total number of atoms: N = Σ p_j

$\{S|\mathbf{t}\}_s$ Symmetry operators of the propagation vector group or a subgroup

If no symmetry constraints are applied to S_k, the maximum number of parameters for a general incommensurate structure is 6N (In practice 6N-1, because a global phase factor is irrelevant)

Magnetic Structure Factor: Basis Vectors of *irreps*

The fundamental hypothesis of the Representation Analysis of magnetic structures is that the Fourier coefficients of a magnetic structure are linear combinations of the basis functions of the irreducible representation of the propagation vector group $\mathbf{G_k}$ or the full group **G.**

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

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

Magnetic structure factor in terms of basis vectors of irreducible representations and refinable coefficients $C_{n\lambda}^{\nu}$

Magnetic Structure Factor: Symmetry Modes

Using the cell basis of the subgroup of the paramagnetic state group and considering displacive and magnetic modes from the representation analysis one can write the position of the atoms and the magnetic moments of the asymmetric unit as:

$$\mathbf{r}_{\mu} = \mathbf{r}_{0\mu} + \mathbf{u}_{\mu} = \mathbf{r}_{0\mu} + \sum_{\tau,m} A_{\tau,m}\ \boldsymbol{\varepsilon}_{(\tau,m|\mu)}$$

$$\mathbf{m}_{\mu} = \sum_{\tau,m} M_{\tau,m}\ \boldsymbol{\kappa}_{(\tau,m|\mu)}$$

The structure factor can be written in terms of the amplitudes of displacive and magnetic modes ($A_{\tau,m}, M_{\tau,m}$) through the (normalized) basis vector ($\boldsymbol{\varepsilon}_{(\tau,m|\mu)}, \boldsymbol{\kappa}_{(\tau,m|\mu)}$) of the irreducible representations (τ) contributing to the final symmetry

$$\mathbf{M}(\mathbf{H}) = p\sum_{\mu=1}^{n} O_{\mu} f_{\mu}(H) T_{\mu} \sum_{s} \det(h_s)\,\delta_s\, h_s \sum_{\tau,m} M_{\tau,m}\ \boldsymbol{\kappa}_{(\tau,m|\mu)} exp\{2\pi i[(\mathbf{H}\{h|\mathbf{t}\}_s(\mathbf{r}_{0\mu} + \sum_{\tau,m} A_{\tau,m}\ \boldsymbol{\varepsilon}_{(\tau,m|\mu)})]\}$$

The free parameters of the structure are the amplitudes: $A_{\tau,m}, M_{\tau,m}$

Magnetic Structure Factor: Superspace formalism

Let us consider a general case with d propagation vectors $\mathbf{k}_p$, a Bragg reflections is indexed like:

$$\mathbf{h} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* + \sum_{p=1}^{d} m_p\mathbf{k}_p$$

The integer indices (h_1, h_2, h_3, m_1, … m_d) = (h_1, h_2, … h_{3+d}) may be considered as the coordinates in the reciprocal space of a (3+d)D superspace.

In real space the magnetic moments can be written as a very general Fourier series as:

$$\mathbf{m}_{jl} = \mathbf{m}_j(\bar{x}_4, \bar{x}_5, .., \bar{x}_{3+d}) = \sum_{n_1=-m_1}^{m_1} \dots \sum_{n_d=-m_d}^{m_d} \mathbf{T}_j^{(n_1,..,n_d)} \exp[-2\pi i\{n_1, n_2 ... n_d\}\cdot \mathbf{r}_I^j]$$

$$\mathbf{m}_j(\bar{x}_4, \bar{x}_5, .., \bar{x}_{3+d}) = \sum_{n_1=0}^{\infty} .. \sum_{n_d=0}^{\infty} \mathbf{M}_{\cos j}^{(n_1,..,n_d)} \cos[2\pi(n_1\bar{x}_4 + .. + n_d\bar{x}_{3+d})] + \mathbf{M}_{\sin j}^{(n_1,..,n_d)} \sin[2\pi(n_1\bar{x}_4 + .. + n_d\bar{x}_{3+d})]$$

Where $\bar{x}_{3+p} = t_p + \mathbf{k}_p\bar{\mathbf{r}}_{jl} = t_p + \mathbf{k}_p(\mathbf{R}_l + \mathbf{r}_j^0) = t_p + \boldsymbol{\sigma}_{1p}\bar{x}_1 + \boldsymbol{\sigma}_{2p}\bar{x}_2 + \boldsymbol{\sigma}_{3p}\bar{x}_3$

are the components of the vector $\mathbf{r}_I^j$. The initial phase t_p is arbitrary and may be taken as zero.

A point in superspace has coordinates: $\mathbf{r}_S^j = (x_{S1}^j, x_{S2}^j, ... x_{S3+d}^j) = (\mathbf{r}_E^j, \mathbf{r}_I^j)$

Magnetic Structure Factor: Superspace formalism

An operator in superspace has the form:

$$\hat{g}_S = \{g_S, \delta \,|\, \mathbf{t}_S\} \quad \Rightarrow \quad g_S = \begin{pmatrix} \mathbf{g} & \mathbf{0} \\ \mathbf{H}_g & \mathbf{E}_g \end{pmatrix} \qquad \mathbf{t}_S = (t_1, t_2, \ldots t_{3+d}) = (\mathbf{t}, t_4, \ldots, t_{3+d}) = (\mathbf{t}, \mathbf{t}_I)$$

Where $\mathbf{g}$ is the 3×3 rotational part of the parent 3D operator, $\mathbf{H}_g$ is a d×3 matrix and $\mathbf{E}_g$ is a d×d integer matrix with zeros and ones, verifying the relations:

$$\boldsymbol{\sigma}\mathbf{g} = \mathbf{E}_g \boldsymbol{\sigma} + \mathbf{H}_g$$

where $\boldsymbol{\sigma}$ is a d×3 matrix containing as rows the components of the propagation vectors. The parameter δ is equal to 1 if the operator is un-primed and -1 if it is primed. These matrices are determined by the action of the 3D operators of the parent paramagnetic space group on the propagation vectors.

The action of the symmetry operators in the magnetic moment of an atom with internal coordinates $\mathbf{r}_I^j$ is given by the equation:

$$\mathbf{m}_k[\mathbf{r}_I^k] = \mathbf{m}_k[\mathbf{H}_g \mathbf{r}_0^j + \mathbf{E}_g \mathbf{r}_I^j + \mathbf{t}_I] = \delta det(\mathbf{g}) \mathbf{g}\, \mathbf{m}_j[\mathbf{r}_I^j]$$

This equation is the basis for obtaining the constraints on the amplitudes $\mathbf{M}_{\cos j}^{(n_1,..,n_d)}, \mathbf{M}_{\sin j}^{(n_1,..,n_d)}$ for the site j. The program **FullProf** calculates the magnetic structure factor applying these equations when the complete list of operators are obtained from the provided generators.

Magnetic Structure Factor: Superspace formalism

Writing $\mathbf{T}_j^{(n_1,..,n_d)} = \mathbf{T}_j^{[n]} = \frac{1}{2}(\mathbf{M}_{\cos j}^{[n]} + i\mathbf{M}_{\sin j}^{[n]})$

The general expression of the magnetic structure factor in 3D when the underlying crystal structure is not modulated is:

$$\mathbf{M}(\mathbf{h}_s) = p\sum_j O_j f_j(\mathbf{h}) e^{-B_j|h/2|^2} \sum_{\hat{g}} \delta det(\mathbf{g})\mathbf{g}\mathbf{T}_j^{[n]\mathbf{E}_g} \exp\{2\pi i(\mathbf{H}(\mathbf{g}\mathbf{r}_0^j + \mathbf{t}_g) + [n](\mathbf{H}_g\mathbf{r}_0^j + \mathbf{t}_I))\}$$

In which $\mathbf{h}_s = (\mathbf{H},[n])$ are the integer indices of the reflection; $\mathbf{g}$, $\mathbf{H}_g$ and $\mathbf{E}_g$ are the submatrices of a general superspace operator and $\mathbf{t}_s = (\mathbf{t}_g, \mathbf{t}_I)$ is the translational part of the operator.

We have used the notation $[n] = (n_1, n_2 \ldots n_d)$ as a d-dimensional vector characterizing the satellite reflections. The application of the submatrix $\mathbf{E}_g$ transforms $[n]$ into another set of indices $[n']$ that are equal, or opposite, to a provided set of $\mathbf{T}^{[m]}$, and we can apply the constraint $\mathbf{T}^{[-m]} = \mathbf{T}^{[m]*}$. For calculating the symmetry constraints on $\mathbf{T}^{[m]}$ for a particular atom in position one has to apply the equations:

$$\mathbf{T}_j^{[n]\mathbf{E}_g} = \sum_{\hat{g}} \exp\{2\pi i(\mathbf{H}(\mathbf{g}\mathbf{r}_0^j + \mathbf{t}_g) + [n](\mathbf{H}_g\mathbf{r}_0^j + \mathbf{t}_I))\}\delta det(\mathbf{g})\mathbf{g}\,\mathbf{T}_j^{[n]\mathbf{E}_g}$$

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Different options for describing the magnetic model

(1) Standard Fourier (all kind of structures) coefficients refinement with $\mathbf{S_k}$ 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)

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

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

The Fourier component **k** of the magnetic moment of atom *j*1, 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.

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 *j*1, is explicitly represented as:

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

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`**

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

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

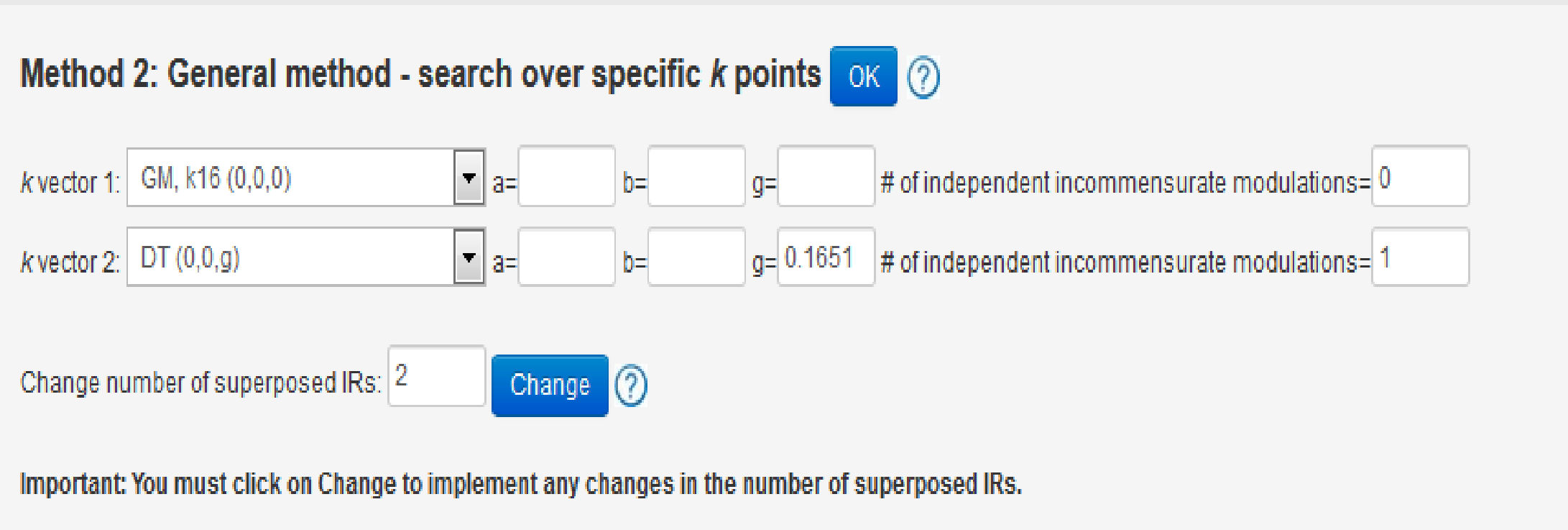
Types of distortions to be considered Change ?

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

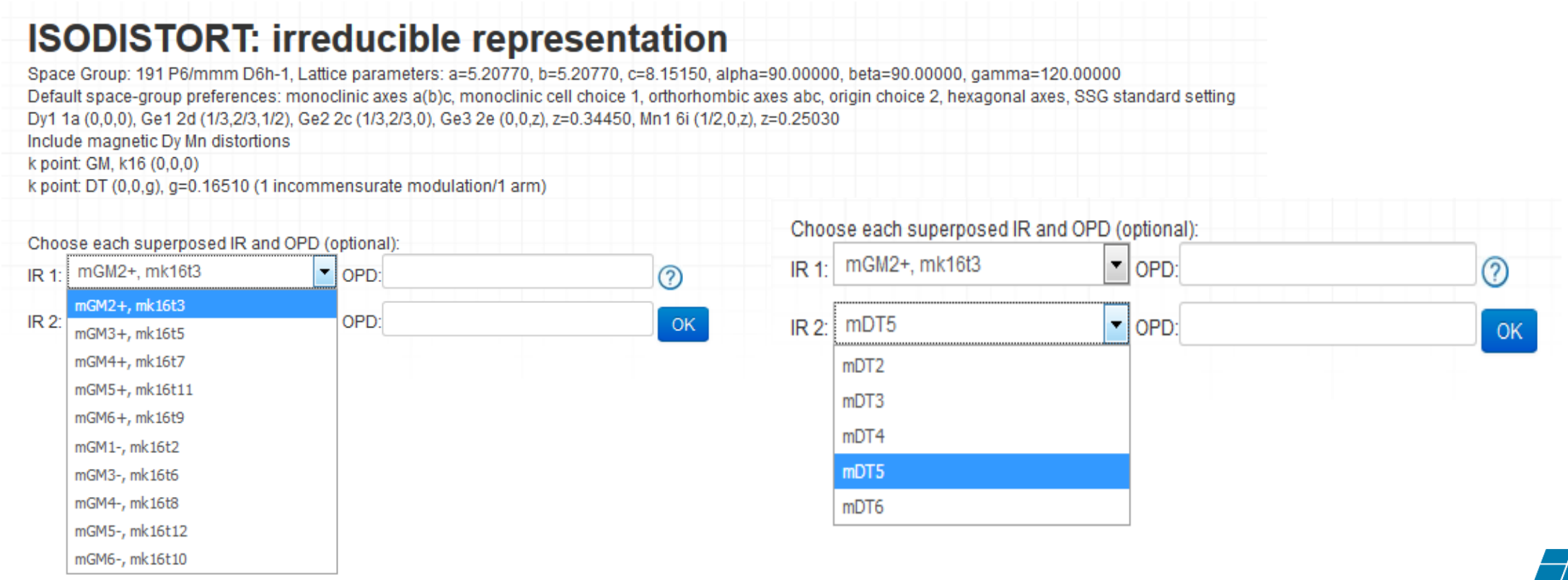
a. We should use the “Method 2: General method - search over specific k points”, here on “Change number of superposed IRs” we should increase the number from 1 to 2, as we have to two propagation vectors. Click on Change. After that, the program shows two set of propagation vectors.
b. For the k-vector 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.



Different options for describing the magnetic model

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 $P6/mm'm'(0,0,\gamma)0000$ magnetic superspace group, that is clearly incorrect

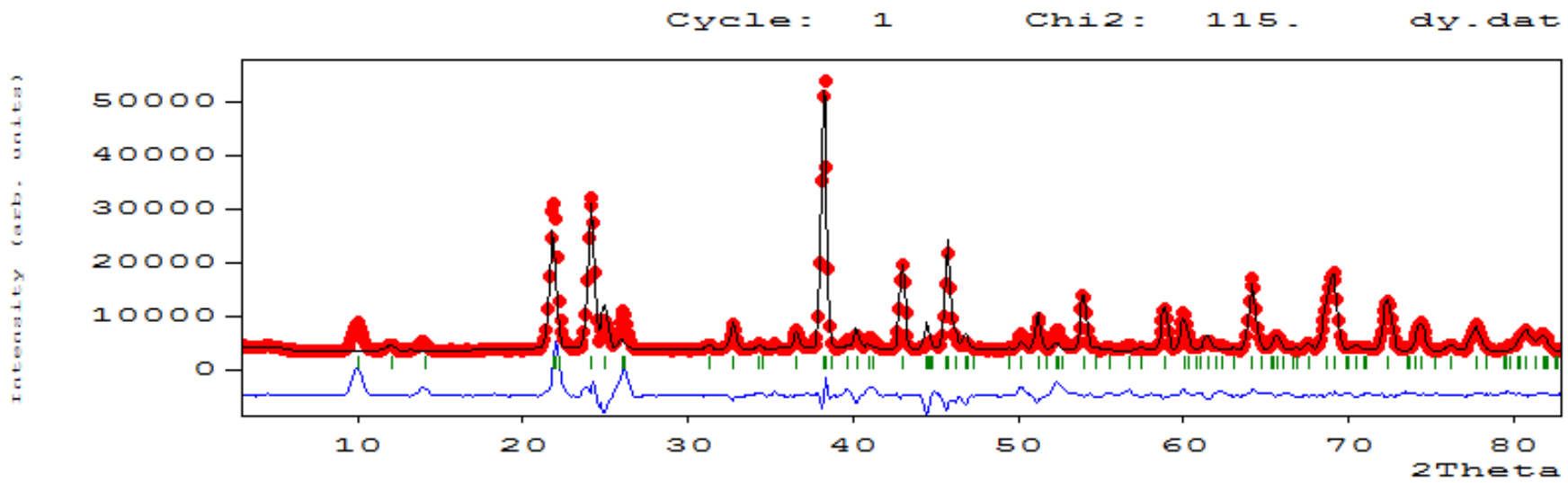
FullProf Program

Load Edit PCR Mode Run Exit

```
   => Phase:        1
   =>    Bragg R-factor:   22.32
   =>    RF-factor     :   16.01
   =>      Nuclear  R-factor:   22.32
   =>      Magnetic R-factor:   49.21
   => Pure Magnetic R-factor:   49.21
=> Normal end, final calculations and writing...


=> CPU Time:     1.875 seconds
=> 0.031 minutes

=> END   Date:28/05/2019  Time => 14:30:08.338
```



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

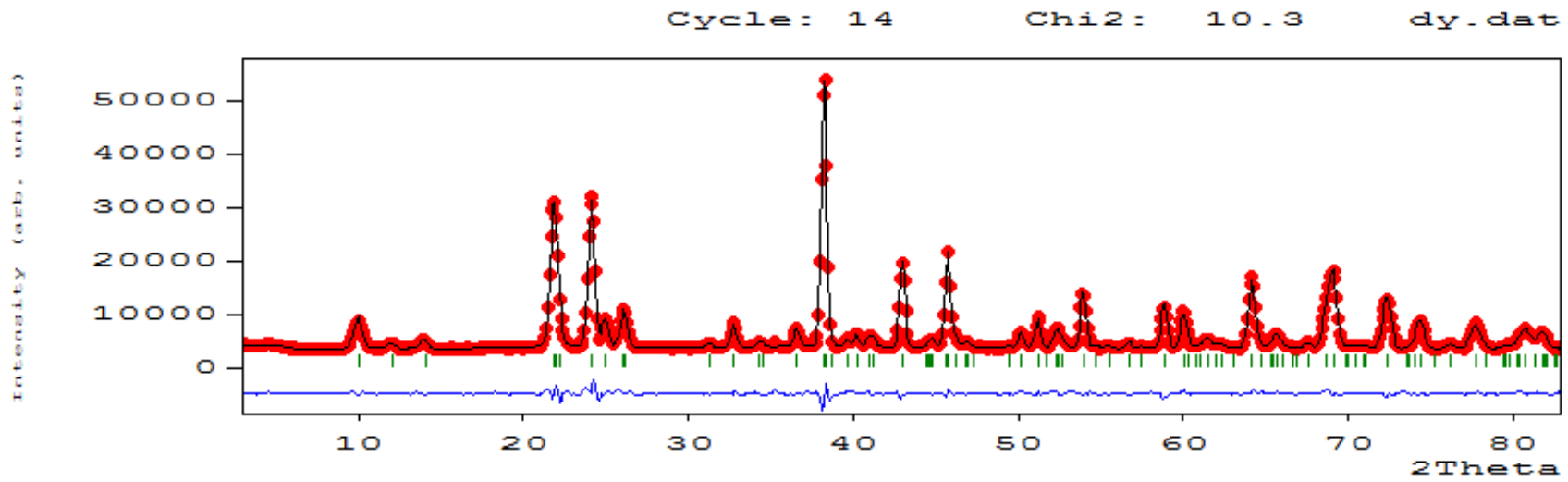
FullProf Program

Load Edit PCR Mode Run Exit

```
    => Phase:        1
    =>     Bragg R-factor:    3.030
    =>     RF-factor      :    2.844
    =>       Nuclear  R-factor:    3.024
    =>       Magnetic R-factor:    4.606
    => Pure Magnetic R-factor:    4.606
=> Normal end, final calculations and writing...


=> CPU Time:      4.469 seconds
=> 0.074 minutes

=> END    Date:28/05/2019  Time => 19:29:34.891
```



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


science
campus
THANK YOU!