

Magnetic structure analysis and refinement with FULLPROF

Lecture notes for the International School of Crystallography: Magnetic Crystallography

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Abstract

Contrary to the high impact of most common structural problems - symmetry and structure determination - in large fields of Science, the study of magnetic structures, from a crystallographic point of view, is still limited to the field of Physical Crystallography and microscopic magnetism. The description of magnetic structures has never attained the degree of standardisation of common Crystallography, or even Superspace Crystallography. The reasons are related to the relatively small community in this field. The situation is changing and, from 2011, the *Commission on Magnetic Structures* of the IUCr is making a development effort in order to improve the current situation. In these notes I summarize the most broadly used descriptions of magnetic structures and the ways existing in the FULLPROF SUITE to handle the analysis of magnetic neutron diffraction data. These notes are complemented with other documents distributed separately in the tutorial sessions.

Introduction

In conventional Crystallography an extremely useful simplification for describing the electron and nuclei density is the concept of *atomicity* that reduces the scattering density to well defined object - the atoms - represented as mass points (or spheres) characterised by their chemical nature, their positions within the unit cell and their displacement parameters describing the dynamic (static) spread-out around the equilibrium (average) positions. The symmetry properties of periodic arrangement of atoms/points are well described by the 230 space group types in three dimensions (3D) [1]. More complex spatial arrangements of atoms may need to be described by periodicity in higher dimensions (superspace approach), so that the atoms become *atomic surfaces* [2]. Incommensurate, composite and quasi-crystal structures represent a small part of the huge amount of materials that can be described by conventional 3D Crystallography. The success of Crystallography has been enhanced by the fact that atoms are effectively *visible* (as small balls) using modern electron/atomic force/tunnel microscopy.

Under the term *Magnetic Crystallography* we group a special subfield of Crystallography concerned with the description and determination of the *magnetisation density* or, in quantum mechanical terms, the *spin density* in solids. The corresponding classical objects, useful to describe the magnetic scattering density, are vectors, represented by arrows, defining the elemental magnetic moments (dipoles) of the magnetic atoms (those having unpaired electrons). A magnetic structure corresponds to a particular, nearly static, spatial arrangement of magnetic moments (*solid* phase) that sets up below the ordering temperature. Above the ordering temperature the system is in the paramagnetic state (*liquid*

phase). The magnetic structures are commonly represented as a set of arrows, associated to the magnetic atoms, with magnitudes and orientations characteristics of the particular structure. There is no hope *to visualise*, in a near future, the elemental magnetic moments using a special kind of magnetic microscope. Notice that magnetic imaging, using the effect of magnetic fields created by matter, is only possible for ferromagnets, or ferrimagnets, at a mesoscopic level. Contrary to crystal structures, many magnetic structures are non-commensurate: the periodicity of the orientation of the magnetic moments is not commensurate with the underlying crystal structure. This is a consequence of the competition of the exchange interactions giving rise to a kind of frustration in many compounds.

The symmetry properties of *commensurate* magnetic structures are currently described using two different approaches: the magnetic Shubnikov groups [3, 4] and the group representation analysis [5-7]. For *incommensurate* magnetic structures the representation analysis can also be used but the most complete way of working with this class of magnetic structures is the use of the concepts of superspace crystallography [2], including now spin reversal as additional operator, to work with magnetic superspace groups [8]. General documents concerned with magnetic structures and their mathematical description are gathered in references [9-11]. Here we will concentrate on how to work with the programs of the FULLPROF SUITE using the minimum strict formulae for facilitating the reading.

The programs of the FULLPROF SUITE have been developed by the current author and collaborators from the beginning of the nineties. The first published description of features available in FULLPROF for incommensurate magnetic structures was done in [12]. In that article there was also the first description of the program MAGSAN for determining commensurate magnetic structures using Simulated Annealing, later included in the program FULLPROF for general crystal and magnetic structures. By the middle-end of the nineties three programs, MODY, SARAH and BASIREPS [13, 14, 15] (this last included within the FULLPROF SUITE), for helping to determine magnetic structures. These programs use the representation analysis popularized by Bertaut [5] for generating the basis vectors of the irreducible representations (*irreps*) and were distributed and used by the community. The FULLPROF SUITE is being developed permanently and it is currently the most used set of program for handling magnetic structures using powder or single crystal neutron diffraction data. The most recent version includes the possibility to work with magnetic superspace groups.

We assume the reader has a good knowledge of crystallography and experience in working with single crystals or powder diffraction data. The program FULLPROF was developed motivated by the needs of the author and later made available to the community. This means that it is not a black-box program guiding the user through the data analysis imposing a unique way of working. The user can manage completely the input model provided he (or her) knows the rules of the input control file (called hereafter PCR file), so the learning curve may be steeper than for other computer programs.

Some facilities have been developed in the course of the years to make simpler the use of the program. In particular the graphic user interface (GUI) program EDPCR is able to handle the major part of options of FULLPROF without needing an explicit edition of the raw PCR file. This interface allows a combined way of working because the user may edit

manually the text of the PCR file within the GUI, make a change by hand and then reload the modified PCR file. EDPCR will detect automatically that a change has been produced and ask the user to reload the file.

Elementary description of Magnetic Structures in the *magnetic* unit cell

In crystallography the independent atoms are described by their chemical nature, the position in the unit cell, which is repeated in three directions giving rise to a periodic structure, and a set of symmetry operators (common to all atoms) constituting one of the 230 space group types. The symmetry operators generate the rest of atoms in the unit cell.

Ignoring symmetry (except the translation symmetry), a list of all the atoms, with their fractional coordinates, thermal displacement parameters and occupation probabilities, describes completely the crystal structure. We will ignore in the following thermal and occupation parameters. This list of chemical composition and coordinates is equivalent to a description in the space group number 1: *P1*.

Symmetry is extremely important because the number of free parameters to be obtained from experimental data is minimized. The extraction of all the coordinates when the description of the crystal structure is done in *P1* is usually hampered by the limited number of observations and correlations between the parameters in the refinement.

The description of a magnetic structure in *P1* means that, in addition to the coordinates of the atoms we need the list of magnetic moments attached to each atom. Notice that the magnetic cell of a commensurate structure is, in general, a multiple of the crystallographic cell or may coincide with it. The components of the magnetic moments are given in Bohr magnetons with respect to a basis formed by unitary vectors along the conventional crystal basis $U=(\mathbf{a}/a, \mathbf{b}/b, \mathbf{c}/c) = (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$. This simple way of describing a magnetic structure is a particular case of whatever of the options given below.

Concept of propagation vector(s) for describing magnetic structures within the crystallographic unit cell

Whatever class of magnetic structure can be represented by the Fourier series:

$$\mathbf{m}_{lj} = \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \exp[-2\pi i \mathbf{k} \mathbf{R}_l] \quad (1)$$

This defines the magnetic moment of the atom numbered *j* in the unit cell having as origin the lattice vector \mathbf{R}_l , the atom position in the crystal is $\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$. The \mathbf{k} -vectors are defined in reciprocal space and are called propagation vectors of the magnetic structure. They are restricted to the first Brillouin Zone (BZ) because adding a reciprocal lattice vector \mathbf{H} does not change the sum. Two propagation vectors are equivalent ($\mathbf{k} \equiv \mathbf{k}'$) if they differ in a reciprocal lattice vector.

We may have defined (1) in a slightly different manner also usual in literature (common convention in superspace approach). Instead of writing \mathbf{R}_l in the argument of the exponential function, one can write $\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$:

$$\mathbf{m}_{lj} = \sum_{\mathbf{k}} \mathbf{T}_{kj} \exp[-2\pi i \mathbf{k} \mathbf{R}_{lj}] = \sum_{\mathbf{k}} \mathbf{T}_{kj} \exp[-2\pi i \mathbf{k} (\mathbf{R}_l + \mathbf{r}_j)] \quad (2)$$

In such a case the Fourier coefficients, \mathbf{T}_{kj} , are related to \mathbf{S}_{kj} by a phase factor, $\mathbf{S}_{kj} = \mathbf{T}_{kj} \exp(-2\pi i \mathbf{k} \mathbf{r}_j)$, that depends on the atom positions inside the unit cell. In the following we will use the convention (1) that has some advantages for commensurate structures and the convention (2) for the case of using magnetic superspace group symmetry. The general expression of the Fourier coefficients used in FULLPROF is given by:

$$\mathbf{S}_{kj} = \frac{1}{2} \{ \mathbf{R}_{kj} + i \mathbf{I}_{kj} \} \exp(-2\pi i \phi_{kj}) = \frac{1}{2} \{ R_{kj}^x \mathbf{e}_1 + R_{kj}^y \mathbf{e}_2 + R_{kj}^z \mathbf{e}_3 + i(I_{kj}^x \mathbf{e}_1 + I_{kj}^y \mathbf{e}_2 + I_{kj}^z \mathbf{e}_3) \} \exp(-2\pi i \phi_{kj}) \quad (3)$$

In the case of using superspace approach for a single pair $(\mathbf{k}, -\mathbf{k})$ the convention (2) is used and the Fourier coefficients \mathbf{T}_{kj} are written as:

$$\mathbf{T}_{kj} = \frac{1}{2} \{ \mathbf{M}_{kj}^{\cos} + i \mathbf{M}_{kj}^{\sin} \} = \frac{1}{2} \{ M_{kj,x}^{\cos} \mathbf{e}_1 + M_{kj,y}^{\cos} \mathbf{e}_2 + M_{kj,y}^{\cos} + i(M_{kj,x}^{\sin} \mathbf{e}_1 + M_{kj,y}^{\sin} \mathbf{e}_2 + M_{kj,y}^{\sin} \mathbf{e}_3) \} \quad (4)$$

The magnetic Bragg reflections are indexed by diffraction vectors $\mathbf{h} = \mathbf{H} + \mathbf{k}$. Reflections having $\mathbf{k} \neq 0$ are called *satellite* reflections and those having $\mathbf{h} = \mathbf{H}$ are *fundamental* reflections.

Using the convention (1), the Fourier coefficients are identical to magnetic moments when there is a single term in the sum and $\mathbf{k} = 1/2\mathbf{H}$.

Working with Magnetic Structures in FULLPROF

In usual neutron powder and single crystal diffraction the incident beam is non-polarized so that interference terms in the scattering cross section do not play a role. The intensity of a Bragg reflections is the sum of the magnetic and nuclear contribution. This allows to treat the magnetic contribution as a separated *phase* in addition to the normal nuclear contribution.

There is a phase-dependent parameter in FULLPROF noted **Jbt** that informs the program what kind of intensity calculation is to be done with the information provided in the PCR file for the current phase. The format of the file and the provided information depends on the value of **Jbt** (see the manual). There are several ways of working with FULLPROF to analyse magnetic structures. A magnetic phase treated independently of the nuclear structure can have the following values:

Jbt=1. Normal way of working with magnetic structures using the formalism of propagation vectors. Refinable parameters are the components of \mathbf{R} and \mathbf{I} or the coefficients of the basis vectors of irreducible representations.

Jbt=-1. As above but the amplitudes of Fourier coefficients \mathbf{R} and \mathbf{I} are given in spherical components.

Jbt= 5. P1 real space description of incommensurate magnetic structures of conical type with a common cone axis oriented in an arbitrary direction.

Jbt=± 10. In this case the nuclear and magnetic phase are combined in a single phase. One can use directly Shubnikov groups or standard Fourier coefficients as is **Jbt=±1**.

Jbt=-6. Nuclear and magnetic contributions are treated in a single phase using symmetry modes of a higher symmetry phase (e.g. the paramagnetic phase). Only for commensurate structures.

Jbt=7. Magnetic structure described using magnetic superspace groups. The current version treats only incommensurate magnetic structures within a commensurate crystal structures: all displacement amplitudes of atom positions are zero.

Moreover there are other four phase-dependent parameters relevant for magnetic structures:

Nvk: Informs the program of the number of propagation vectors describing the magnetic structures. When $\mathbf{k}=-\mathbf{k}$, **Nvk** is given a negative value. For **Jbt=7**, **Nvk** is always positive.

Irf: Informs the program how to generate reflections. **Irf=0** generates all reflections using the symbol of the space group symbol or from the provided list of symmetry operators; **Irf=2** reads reflections and multiplicities from a file; **Irf=-1** generates only satellite reflections. If **Irf=4** experimental integrated intensities are provided (mandatory for single crystals).

Isy: Informs the program how read and use symmetry in the magnetic phase. We have the following cases (details and examples will be provided in the tutorials):

Isy=0. The symmetry operators are generated from the symbol of the space group or obtained from the database of Shubnikov groups (in this case other considerations should be complied)

Isy=1. The symmetry operators are provided as numerical matrices and vectors.

Isy=-1. The symmetry operators are provided as SYMM (e.g. x,-y+1/2, z) and MSYM symbolic operators. The MSYM operator representing a rotation matrix M and a phase ϕ in units of 2π (M, ϕ) (e.g. -u, v,-w, ϕ). The MSYM operators act on the Fourier coefficients as: $\mathbf{S}_{\mathbf{k}_s} = M_s \mathbf{S}_{\mathbf{k}_l} \exp\{-2\pi i \phi_{\mathbf{k}_s}\}$. The phase factor ϕ for commensurate $\mathbf{k}=1/2\mathbf{H}$ magnetic structures is normally zero because the Fourier coefficients are real vectors coinciding with the magnetic moments.

Isy=-2. The symmetry operators acting on atom positions are given as SYMM symbols and the calculation of the Fourier components are performed as linear combination of basis vectors of irreducible representations.

Isy=2. The symmetry operators are given like SYMM symbols complemented with +1 or -1 for unprimed and primed elements respectively (e.g. x, y+1/2, -

$z, -1$). For superspace approach only the generators of the group are needed in the form: $x, y+1/2, -z, t+1/2, -1$ or as described in magnetic CIF files as $x1, -x2, x3, -x4+1/2, 1$.

Hel=2: In combination with **Jbt=-1** (or **Jbt=-10**) and **Isy=-1** indicates to the program to use a direct space formulation of incommensurate multi-helical magnetic structures.

Commensurate Magnetic Structures in FULLPROF

In the case of commensurate magnetic structures one can use the formalism of propagation vectors in spite of the existence of a magnetic unit cell. The symmetry constraints can be obtained easily from the calculation of the basis vector of the irreducible representations of the propagation vector group G_k . One can use the program BASIREPS or SARAh to partially construct the PCR file if one prefers to use this method instead of the crystallographic magnetic groups. For *irreps* of dimension 1 there is a one-to-one correspondence with a Shubnikov group and for $k=0$ the symbol of the magnetic group can be easily be obtained from the character table of the *irreps*. The basis vectors for each particular crystallographic site provide directly the constraints to be applied to the component of the magnetic moments. In the case of irreps of dimension higher than one there are several options for the possible magnetic groups depending on the direction of the order parameter. Using the propagation vector formalism ($Jbt=\pm 1$) and the option $Isy=-1$ the magnetic structure factor calculated by is given by:

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) e^{-B_j |\mathbf{h}/2|^2} \sum_s M_s \mathbf{S}_{kj} \exp\{2\pi i [(\mathbf{H} + \mathbf{k}) \{S|\mathbf{t}\}_s \mathbf{r}_j] - \phi_s\} \quad (4)$$

The index j running for all magnetic atom sites in the magnetic asymmetric unit ($j=1, \dots, n$) and the second sum over the symmetry operators, indexed by s , described by the SYMM ($\{S|\mathbf{t}\}_s$) and MSYM ($(M, \phi)_s$) items in the PCR file. For $k=1/2\mathbf{H}$ the phase factors $\phi_s=0$ and the M_s matrices corresponds to the magnetic group operators $M_s = \delta_s \det(S_s) S_s$, described in the Opechowski-Guccione setting (see [11] for details). In such a case, the Fourier coefficients correspond directly to the magnetic moments: $\mathbf{S}_{kj} = \mathbf{m}_j$

If one wants to use directly the basis vectors of the *irreps* the expression of the Fourier coefficients (in this case they are real) is given by the linear combination:

$$\mathbf{S}_{kjs} = \sum_{n\lambda} C_{n\lambda}^{\mathbf{k}\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js) \quad (5)$$

Where the vectors $\mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)$ correspond to the atomic components of the basis vectors or the *irrep* Γ_ν ; n is an index running from 1 up to n_ν , being n_ν the number of times the *irrep* Γ_ν is contained in the reducible magnetic representation Γ_{mag} and λ runs from 1 to the $\dim(\Gamma_\nu)$; and they are calculated using the program BASIREPS. The coefficients $C_{n\lambda}^{\mathbf{k}\nu}$ are the free parameters of the magnetic structure.

The magnetic structure factor in this case is:

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^{n_a} O_j f_j(\mathbf{h}) e^{-B_j |\mathbf{h}/2|^2} \sum_{n\lambda} C_{n\lambda}^{\mathbf{k}\nu} \sum_s \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js) \exp\{2\pi i(\mathbf{h}_s \mathbf{x}_j + \mathbf{h} \cdot \mathbf{t}_s)\} \quad (6)$$

Where we have written $\mathbf{h}_s = S_s^T \mathbf{h}$ (superscript T stands for transpose of matrix S_s).

Notice that this formalism can also be applied to incommensurate magnetic structures.

Commensurate structures have a magnetic space group with a magnetic unit cell. One can use the Shubnikov group of Type 4 using the Belov-Neronova-Smirnova setting (see [11]) for describing the symmetry operators in the magnetic unit cell. There are programs in the Bilbao Crystallographic Server (BCS) [16-18] or ISODISTORT [19] that are able to produce directly a magnetic CIF file or a template of PCR file with the appropriate list of operators for the case discussed above. The Shubnikov description in FULLPROF is accessible if one uses `Jbt=±10`, `Isy=2` and `Nvk=0`. The program can read the list of operators included in the PCR file by the user or generated by one of the program MAXMAGN or k-SUBGROUPSMAG as a magnetic CIF file. There is a utility in the FULLPROF SUITE that is able to convert a magnetic CIF file to a PCR template. The utility program is called MCIF_TO_PCR and is directly accessible from the `TOOLS` menu of the FULLPROF SUITE toolbar, the same utility is also available at the BCS. The magnetic structure factor in this case uses only magnetic moments and no Fourier coefficients nor propagation vectors:

$$\mathbf{M}(\mathbf{H}) = p \sum_{j=1}^n O_j f_j(H) e^{-B_j |\mathbf{H}/2|^2} \sum_s \delta_s \det(h_s) S_s \mathbf{m}_j \exp\{2\pi i[(\mathbf{H}\{S|\mathbf{t}\}_s \mathbf{r}_j)]\} \quad (7)$$

This expression of the magnetic structure factor is quite close to that for calculating the nuclear intensities of crystal structures except for the vectorial character. Examples of the use of this options will be presented during the tutorials.

Incommensurate Magnetic Structures in FULLPROF

Calculations ignoring symmetry

The option `Jbt=5` allows to introduce the description of a conical magnetic structure in terms of magnitudes of magnetic moments, half-angle of the cone, orientation of the common axis and phases. The reason for this kind of option is that conical structures with a common axis is predicted by theoretical calculations in important class of materials [20, 21]. The formula used for calculating the magnetic structure factor for fundamental and satellite reflections is that provided by Hasting and Corliss [22].

In case of difficulties for determining a magnetic structure that shows macroscopic net magnetization, and satellite reflections, this option is quite useful in combination with simulated annealing. Examples of this approach will be discussed during the tutorials.

Calculations using $\mathbf{S}_{\mathbf{k}}$ Fourier coefficients or basis vectors $\mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)$ of irreps

These options corresponding to $Jbt=\pm 1$, $Nkv<0$ and $Isy=-1$ or $Isy=-2$. The expressions of the structure factor is formally equivalent to the expressions (4) and (6), but now the phase ϕ is not zero and the C-coefficients in (6) may be complex. The user can apply symmetry constraints and determine the phase factors as deduced from the analysis of the basis vectors of the *irreps* but this has to be done carefully. In particular the program BASIREPS calculates only the representations and basis vectors of the little group $G_{\mathbf{k}}$ from which the full representation of the star of \mathbf{k} can be calculated using the induction formula [11]. Moreover, the basis vectors are calculated in the general case (arbitrary direction of the order parameter, lowest symmetry!). The selection of the order parameter and the application of the induction formula has to be done, presently, by the user. In the most simple case of a single pair $(\mathbf{k}, -\mathbf{k})$ both arms of the star have to be considered and the *irreps* are at least of dimension 2. The symmetry operators existing in the paramagnetic group transforming \mathbf{k} into $-\mathbf{k}$ should be added to the list of relevant operators (extended little group: $G_{\mathbf{k},-\mathbf{k}}$) otherwise symmetry can be neglected introducing artificially more parameters than needed for describing the magnetic structure. This approach is able to handle whatever kind of magnetic structure but it is cumbersome for the non-specialist user.

There is another option, in which MSYM operators can be used and the parameters to refine are simple geometrical parameters and magnitudes of magnetic moments. This corresponds to the option $Hel=2$ mentioned above. In this case we use a particular form of the Fourier coefficients for the first representative of atom at site j :

$$\mathbf{S}_{\mathbf{k}_j} = \frac{1}{2} [m_{uj} \mathbf{u}_j + im_{vj} \mathbf{v}_j] \exp(-2\pi i \phi_{\mathbf{k}_j}) \quad (8)$$

In which the unitary vectors \mathbf{u}_j and \mathbf{v}_j are orthogonal and form a plane in which the magnetic moments lay. The normal to this plane $\mathbf{w}_j = \mathbf{u}_j \times \mathbf{v}_j$ completes a Cartesian frame attached to the atom. Depending of the orientation of the propagation vector \mathbf{k} with respect to the plane $(\mathbf{u}_j, \mathbf{v}_j)$ the structure may be a normal spiral or helix (\mathbf{k} parallel to \mathbf{w}_j) or a cycloid (\mathbf{k} perpendicular to \mathbf{w}_j). The free parameters per independent atom are the three Euler angles of the Cartesian frame attached to the atom with respect to the Cartesian frame of the crystal, the moment components m_{uj} , m_{vj} and the phase factor. Of course if symmetry constraints some particular orientation the number of free parameters is smaller. If $m_{uj} = m_{vj}$ the envelope of the helix is circular otherwise is elliptical.

Calculations using superspace operators and $\mathbf{T}_{\mathbf{k}}$ Fourier coefficients

This option is the most recent capability included in FULLPROF it corresponds to $Jbt=7$. 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 $(h_1, h_2, h_3, m_1, \dots, m_d) = (h_1, h_2, \dots, h_{3+d})$ may be considered as the coordinates in the reciprocal space of a $(3+d)$ D superspace. For details the reader can consult the reference [23]. The superspace has a 3D section which is the real physical space (called also *external* space) and an internal part of dimension d corresponding to phase

shifts of the modulation functions in the external space. In real space the magnetic moments can be written as a very general Fourier series as:

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

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

Where $\bar{x}_{3+p} = t_p + \mathbf{k}_p \bar{\mathbf{r}}_{jl} = t_p + \mathbf{k}_p (\mathbf{R}_l + \mathbf{r}_j^0) = t_p + \sigma_{1p}\bar{x}_1 + \sigma_{2p}\bar{x}_2 + \sigma_{3p}\bar{x}_3$ are the components of the vector \mathbf{r}_l^j . The initial phase t_p is arbitrary and may be taken as zero. A point in superspace has coordinates:

$$\mathbf{r}_S^j = (x_{S1}^j, x_{S2}^j, \dots, x_{S3+d}^j) = (\mathbf{r}_E^j, \mathbf{r}_I^j)$$

An operator in superspace has the form:

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

The inverse operator is needed for the action in modulation functions, it is obtained as extended matrix like:

$$\hat{g}_S^{-1} = \begin{pmatrix} \mathbf{g}^{-1} & \mathbf{0} & -\mathbf{g}^{-1}\mathbf{t} \\ -\mathbf{E}_g^{-1}\mathbf{H}_g\mathbf{g}^{-1} & \mathbf{E}_g^{-1} & \mathbf{E}_g^{-1}\mathbf{H}_g\mathbf{g}^{-1}\mathbf{t} - \mathbf{E}_g^{-1}\mathbf{t}_I \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \mathbf{g}^{-1} & \mathbf{0} & -\mathbf{g}^{-1}\mathbf{t} \\ \mathbf{N}_g & \mathbf{E}_g^{-1} & -\mathbf{N}_g\mathbf{t} - \mathbf{E}_g^{-1}\mathbf{t}_I \\ 0 & 0 & 1 \end{pmatrix}$$

Where \mathbf{g} is the 3×3 rotational part of the parent 3D operator, \mathbf{H}_g is a $d \times 3$ matrix and \mathbf{E}_g is a $d \times d$ integer matrix with zeros and ones, verifying the relations: $\sigma \mathbf{g} = \mathbf{E}_g \sigma + \mathbf{H}_g$, where σ is a $d \times 3$ matrix containing as rows the components of the propagation vectors. The parameter δ is equal to 1 if the operator is unprimed and -1 if it is primed. The other matrices are obtained by identification of the corresponding terms. These matrices are determined by the action of the 3D operators of the parent paramagnetic space group on the propagation vectors. In the crystal structure the atom k is obtained for the symmetry operator $\{g|\mathbf{t}\}$ applied to the atom j , and if the derived superspace operator is a symmetry of the magnetic structure superspace group, its action on the modulation function is given by:

$$\mathbf{m}_k[\mathbf{r}_l^k] = \hat{g} \mathbf{m}_j[\mathbf{r}_l^j] = \delta \det(\mathbf{g}) \mathbf{g} \mathbf{m}_j[\hat{g}^{-1} \mathbf{r}_l^j] = \delta \det(\mathbf{g}) \mathbf{g} \mathbf{m}_j[\mathbf{N}_g(\bar{\mathbf{r}}^j - \mathbf{t}) + \mathbf{E}_g^{-1}(\mathbf{r}_l^j - \mathbf{t}_I)]$$

Similarly we can write an equation a little bit simpler putting the argument of the transformed moment in terms of the internal coordinates of the source atom as:

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

This equation is the basis for obtaining the constraints on the amplitudes $\mathbf{M}_{\cos j}^{(n_1, \dots, n_d)}$, $\mathbf{M}_{\sin j}^{(n_1, \dots, n_d)}$ 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. Currently the determination of the magnetic superspace group is done by trial and error starting a process involving the group of the propagation vector and the

representations. It is more simple use ISODISTORT for getting the list of the possible groups and try the operators for calculating the diffraction pattern.

What is important is to determine how the amplitudes $\mathbf{T}_j^{(n_1, \dots, n_d)} = \mathbf{T}_j^{[n]} = \frac{1}{2}(\mathbf{M}_{\cos j}^{[n]} + i\mathbf{M}_{\sin j}^{[n]})$

transform under the symmetry operators of the superspace group and then write in a general form the expression of the magnetic structure factor in 3D when the underlying crystal structure is not modulated. The final result is given by the formula:

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

In which $\mathbf{h}_s = (\mathbf{H}, [n])$ are the integer indices of the reflection and \mathbf{g} , \mathbf{H}_g and \mathbf{E}_g are the submatrices of a general superspace operator and $\mathbf{t}_s = (\mathbf{t}_g, \mathbf{t}_l)$ is the translational part of the operator. We have used the notation $[n] = (n_1, n_2 \dots n_d)$ 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:

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

In the general case with a several of propagation vectors and set of indices $[n]$ these equations can be written in composite matrix form and the constraint relations can be obtained as the eigenvectors corresponding to eigenvalues equal to 1.

Determination of magnetic structures using the programs of the FULLPROF SUITE from Neutron Powder Diffraction

I will describe shortly how to work with the different programs of the relevant for magnetic structures and the steps needed for determining and refining a magnetic structure using Neutron Powder Diffraction (NPD).

Of course for determining a magnetic structure the paramagnetic crystal structure should be well known and its refinement is a pre-requisite before starting to determine the magnetic structure. The procedure for determining a magnetic structure using NPD is relatively simple. It can be summarised as follows:

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 $\mathbf{k} = (0, 0, 0)$.

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_k , see reference [11] for details). With the help of this program one can determine the Shubnikov group and the appropriate magnetic symmetry operators, or, alternatively, use directly the basis vectors of the *irreps*. If the propagation vector is rational, another option is to use the Bilbao Crystallographic Server or ISODISTORT to obtain templates of PCR files for the possible Shubnikov groups.

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.

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. This method will be explained during the tutorials in detail.

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.

The different steps described above and their order may be changed slightly depending on the previous knowledge the user has on the sample. We will illustrate these steps with a simple cases that may be useful for beginners in magnetic structure determination. We provide together with this document the data files and PCR files corresponding to the examples treated in the reference [11] and other cases.

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