# MAGNETIC STRUCTURE DETERMINATION FROM POWDER DIFFRACTION USING THE PROGRAM *FullProf*

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In this paper the techniques for magnetic structure determination from neutron powder diffraction (NPD) data as implemented in the program *FullProf* are reviewed. In the general case the magnetic moment of an atom in the crystal is given as a Fourier series. The Fourier coefficients are complex vectors constituting the "unknowns" to be determined. These vectors define the magnetic structure and they correspond to the "atom positions" of an unknown crystal structure. The use of group theoretical methods for the symmetry analysis is needed to find the smallest set of free parameters. In general the Fourier coefficients are linear combinations of the basis functions of the irreducible representations of the wave vector group. The coefficients of the linear combinations can be determined by the simulated annealing (SA) technique comparing the calculated versus the observed magnetic intensities. The SA method has been improved and extended to the case of incommensurate magnetic structures within *FullProf*.

## 1   Introduction

In the last years the Rietveld Method (RM) has allowed great progress in the analysis of powder diffraction data. The RM is not designed for structure determination, it is just a least squares optimisation of an initial model of the crystal and magnetic structure supposed to describe approximately the experimental powder diffraction pattern. It is important to start with a "good" initial model in order to succeed the refinement procedure. In this paper we shall be concerned with the problem of getting the initial model of a magnetic structure in order to refine it from powder diffraction data. We shall describe the basis of the technique and the way the magnetic structure determination is implemented in the program *FullProf*.

## 2   The formalism of propagation vectors for describing magnetic structures.

The reader interested in the basis of the elastic magnetic scattering in relation with magnetic structures may consult the references [1, 2]. Here we will follow the reference [3] but using a different convention for the sign of phases and a somewhat different notation. The intensity of a Bragg reflection (we neglect here the geometrical factors) for non polarised neutrons is given by:

$$I_{\mathbf{h}} = N_{\mathbf{h}} N_{\mathbf{h}}^* + \mathbf{M}_{\perp\mathbf{h}} \cdot \mathbf{M}_{\perp\mathbf{h}}^* \tag{1}$$

where $N_{\mathbf{h}}$ is the nuclear structure factor and the magnetic interaction vector $\mathbf{M}_{\perp\mathbf{h}}$ is defined as:

$$\mathbf{M}_{\perp\mathbf{h}} = \mathbf{e} \times (\mathbf{M}(\mathbf{h}) \times \mathbf{e}) = \mathbf{M}(\mathbf{h}) - \mathbf{e}(\mathbf{e} \cdot \mathbf{M}(\mathbf{h})) \tag{2}$$

$\mathbf{M}(\mathbf{h})$ is the magnetic structure factor, and $\mathbf{e}$ is the unit vector along the scattering vector $\mathbf{h} = \mathbf{H} + \mathbf{k}$, where $\mathbf{H}$ is a reciprocal lattice vector of the crystal structure and $\mathbf{k}$ the propagation vector corresponding to the current magnetic reflection. The magnetic structures that we are considering have a distribution of magnetic moments that can be expanded as a Fourier series:

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j}\, exp\{-2\pi i\mathbf{k}\mathbf{R}_l\} \tag{3}$$

The sum is extended to all propagation vectors that could belong to different stars. The Fourier coefficients $\mathbf{S}_{\mathbf{k}j}$ are, in general, complex vectors. The magnetic structure factor corresponding to such a magnetic structure can be written as:

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j^{iso} \sum_s M_{js}\mathbf{S}_{\mathbf{k}j} exp\left\{2\pi i\left[(\mathbf{H}+\mathbf{k})\{S|\mathbf{t}\}_s\, \mathbf{r}_j - \psi_{\mathbf{k}js}\right]\right\} \tag{4}$$

The sum over $j$ concerns the atoms of the magnetic asymmetric unit for the wave vector $\mathbf{k}$. We are concerned only with magnetic atoms within the crystallographic unit cell, so that $j$ label different sites: $f_j(\mathbf{h})$ is the magnetic form factor and $\mathbf{r}_j$ is the vector position of atom $j$. The constant $p = r_e\, \gamma/2 = 0.2695$ allows the conversion of the Fourier components of magnetic moments, given in Bohr magnetons to scattering lengths units of $10^{-12}$ cm. The sum over $s$ concerns the different symmetry operators of the crystal space group that belong to the wave vector group $G_{\mathbf{k}}$ (subgroup of the crystallographic space group formed by the operators leaving invariant the propagation vector). The matrix $M_{js}$ transform the components of the Fourier term $\mathbf{S}_{\mathbf{k}j}$ of the starting atom $j$ to that numbered as $js$ in the orbit of $j$. The phase factor $\psi_{\mathbf{k}js}$ has two components:

$$\psi_{\mathbf{k}js} = \Phi_{\mathbf{k}j} + \phi_{\mathbf{k}js} \tag{5}$$

$\Phi_{\mathbf{k}j}$ is a phase factor that is not determined by symmetry. It is a free parameter and it is significant only for an independent set of magnetic atoms (one orbit) which respect to another one. $\phi_{\mathbf{k}js}$ is a phase factor determined by symmetry. The Fourier component $\mathbf{S}_{\mathbf{k}j}$ of the representative starting atom $j$ is transformed to

$$\mathbf{S}_{\mathbf{k}js} = M_{js}\mathbf{S}_{\mathbf{k}j}\, exp\{-2\pi i\phi_{\mathbf{k}js}\} \tag{6}$$

The matrices $M_{js}$ and phases $\phi_{\mathbf{k}js}$ can be deduced from the atomic basis functions, obtained by applying projection operator formulas, corresponding to the active representation(s) participating in the definition of the actual magnetic structure. The sign of $\phi_{\mathbf{k}js}$ changes for $-\mathbf{k}$. In the general case $\mathbf{S}_{\mathbf{k}j}$ is a complex vector with six components. These six components per magnetic orbit constitute the parameters that have to be refined from the diffraction data. Symmetry reduces the number of free parameters to be refined. In some cases, transformations like expression (6) cannot be obtained from the basis functions of the irreducible representations of the propagation vector group; for those cases an alternative expression of the magnetic structure factor can be written as a function of "mixing coefficients" (parameters to be refined) and the atomic components of the basis functions of the relevant representation [4]. The expression of the Fourier coefficients in terms of the atomic components of the basis functions is given as:

$$\mathbf{S}_{\mathbf{k}js} = \sum_{m\lambda} C_{jm\lambda}^{\nu}\mathbf{S}_{m\lambda}^{\mathbf{k}\,\nu}(js) \tag{7}$$

The formula of the magnetic structure factor is then transformed to:

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j^{iso} \sum_{m\lambda} C_{jm\lambda}^{\nu} \sum_s \mathbf{S}_{m\lambda}^{\mathbf{k}\,\nu}(js) exp\left\{2\pi i\left[\mathbf{h}_s\mathbf{r}_j - \Phi_{\mathbf{k}j}\right]\right\} \tag{8}$$

In the above expressions, $\nu$ labels the active irreducible representation, $\Gamma_\nu$, of the of the propagation vector group $G_{\mathbf{k}}$, $\lambda$ labels the component corresponding to the dimension of the representation $\Gamma_\nu$, $m$ is an index running between one and the number of times the representation $\Gamma_\nu$ is contained in the global magnetic representation $\Gamma_M$. Finally $\mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$

are constant vectors obtained by the application of the projection operator formula to unit vectors along the directions of the unit cell basis. An addition sum over $\nu$ is sometimes necessary when more than one irreducible representation is involved in the magnetic phase transition. See reference [4] for details.

If the magnetic structure has several propagation vectors $\mathbf{k}$, it is not possible in general to determine unambiguously the spin configuration, because the phase between the different Fourier components cannot be determined. Fortunately, nature often selects simple solutions and many magnetic structures have a single propagation vector, or display some symmetry constraints that reduce the complexity of the periodic magnetic structure given by Eq.3. Solving a magnetic structure consist of finding a set of propagation vectors indexing the whole set of magnetic reflections and a set of "mixing coefficients" (or, equivalently, the components of the Fourier coefficients and phases) providing a good agreement between the intensities of the observed and calculated (using the above expressions) magnetic reflections. In some cases the search for a good starting model may be formulated in terms of other set of parameters. For instance, in cases of conical/helical structures involving magnetic atoms with a common cone-axis, the magnetic structure factor can be written in terms of the module of the magnetic moments, the angle between the moments and the cone-axis, and phases between the different atoms. This description in real space gives a more intuitive picture of the magnetic structure.

## 3    The search for the propagation vector and symmetry analysis.

The first problem to be solved before attempting the resolution of the magnetic structure is the determination of the propagation vector(s), i.e. its "periodicity". To find $\mathbf{k}$ is necessary to index the magnetic reflections appearing below the ordering temperature. With a single crystal the task is somewhat easy, but is tedious for a powder because only the module of reciprocal vectors is available. We have developed a method for searching the propagation vector of a commensurate or incommensurate structure implemented in the program *SuperCell* [5]. Once an approximate propagation vector is obtained the symmetry analysis according to references [4] can be started. The program *BasIreps* may be used for obtaining the vectors $\mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$ in Eq.7 for each crystallographic site occupied by magnetic atoms.

To solve the magnetic structure, the integrated intensities of the magnetic reflections may be obtained using the method of "profile matching", simultaneously with the Rietveld method, implemented in the program *FullProf* [3, 5]. This mixed procedure has to be used with caution: no structural parameter of the known phase must be refined. This is the usual case of neutron diffraction patterns of magnetically ordered compounds, where the nuclear reflections coexist with the magnetic reflections. For illustration purposes we show in Fig.1 the plot of the observed versus calculated pattern of a portion of the simulated diffraction pattern of $DyMn_6Ge_6$ at low temperature after performing the extraction procedure. The magnetic structure has two propagation vectors $\mathbf{k}_1=(0,0,0)$ and $\mathbf{k}_2=(0,0,\delta)$, with $\delta \approx 0.165$ with respect to the reciprocal lattice of the crystallographic unit cell. All satellite reflections are indexed with $\mathbf{h}=\mathbf{H}\pm\mathbf{k}_2$. There are also contributions to the same positions of the nuclear reflections, $\mathbf{h}=\mathbf{H}$ ($\mathbf{k}_1=0$), accounting for a ferromagnetic component. The spin arrangement corresponds to a double cone magnetic structure.
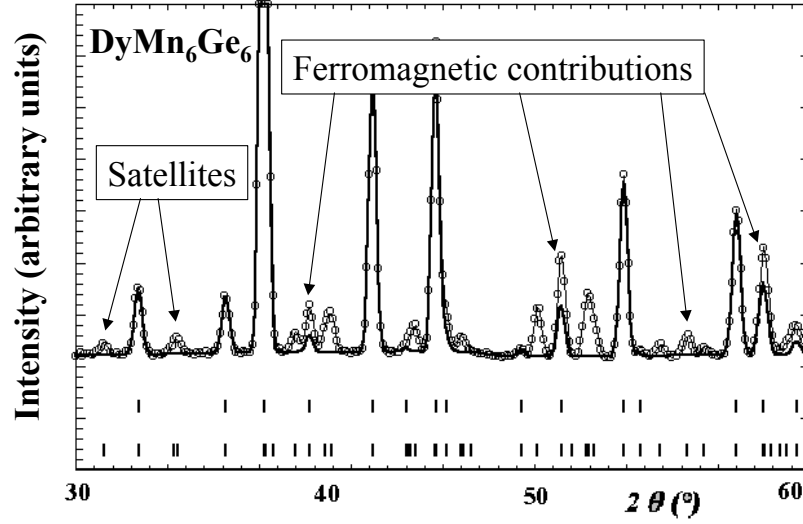
**Figure 1**. Profile matching refinement of the $DyMn_6Ge_6$ neutron diffraction pattern at low temperature. The profile of the calculated nuclear contribution (upper reflection marks) is also displayed as a thick continuous line. The second set of reflection markers corresponds to the magnetic peaks. Markers at the same positions as the nuclear (first set) reflections correspond to $k_1=(0,0,0)$, the extra markers are the position of the satellites corresponding to $k_2=(0,0,\delta)$.

## 4 The resolution of magnetic structures from powder data: the simulated annealing method

We shall describe the Simulated Annealing (SA) technique to solve the magnetic structure using clusters of overlapped reflections as single observations. The merging of clusters is automatically performed using the option "profile matching" of the program *FullProf* [5]. The SA method described below is also valid for the analysis of single crystal data where, except for domains, there is no reflection overlap.

The SA algorithm is a general-purpose optimisation technique for large combinatorial problems introduced in 1983 by Kirpatrick, Gelatt and Vecchi [6]. The function, $E(\omega)$ to be optimised with respect to the configuration described by the vector state $\omega$ is called the "cost" function. In the context of magnetic structures the configuration $\omega$ is the list of all the components of the Fourier coefficients of magnetic atoms existing in the chemical unit cell and this list is obtained from the independent parameters $\beta$ that are those really participating in the annealing procedure. The most general case of parameters constituting the vector $\beta$ corresponds to the set of mixing coefficients of the linear combination given by Eq.8, but, as stated above, another set of parameters in real space (moment amplitudes, angles, …) may also be used. First we select an initial configuration, $\omega_{old}$, then each step of SA method consists of a slight change of the old configuration to a new one, $\omega_{new}$. If $\Delta=E(\omega_{new})-E(\omega_{old}) \le 0$ the new configuration serves as old configuration for the next step. If $\Delta$ is positive, $\omega_{new}$ is accepted as current configuration only with certain probability that depends on the so-called "temperature", T, parameter and $\Delta$. The probability, given by the Boltzman factor $\exp(-\Delta/T)$, that a worse configuration is accepted is slowly decreased on "cooling".

For magnetic structure determination, the cost function can be chosen as the conventional crystallographic R-factor, or some function related to it. In the new version of *FullProf* [5] the following expression is used:

$$E[\omega(\beta)] = R[\omega(\beta)] = c \sum_k \left| I_{obs}(k) - S\sum_{j(k)} I_{calc}(j)[\omega(\beta)] \right|$$

The sum over $k$ is extended for all the "observations" (clusters of overlapped reflections), and that over $j(k)$ for all the reflections contributing to the observation $k$. The constant factor $c$ is given by: $1/c = I_T = \Sigma_k I_{obs}(k)$. $S$ is a scale factor.
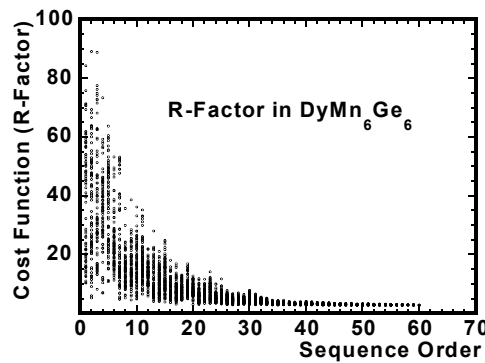


**Figure 2**. Evolution of the cost function for accepted configuration in the resolution of the magnetic structure of DyMn$_6$Ge$_6$ by simulated annealing as a function of the sequential order of temperatures. For a single temperature on can see the dispersion of the R-factor, corresponding to the different configurations, that is reducing as temperature decreases.

To start solving a magnetic structure with the SA method one has to create the intensity file where the indices of each reflection and its intensity are written. This is performed automatically within *FullProf* by using profile matching modes and the option that outputs the overlapped reflection clusters in a file that can be used as input for the SA method. The usual PCR file [5] of *FullProf* is then used for controlling the algorithm. A pseudo-code describing the SA procedure was given in reference [3]. The SA parameters are those defining the limits of loops in the algorithm described in [3]: $T\_ini$ = initial temperature, $N$ = maximum number of temperatures, $NcyclM$ = number of Montecarlo cycles per temperature, $Accept$=Minimum percentage of accepted configurations; and the "cooling" schedule $T(t+1)=qT(t)$ ($q<1$, $q \approx 0.9$). The user may select either a fixed step for each variable (that are defined within a simulation box of hard or periodic limits) or a variable step (Corana's algorithm) that is dynamically adapted in order to have an adequate rate of accepted configurations for each temperature [7].

The starting point may be an arbitrary configuration or a given one. At variance with least-squares optimisation methods, the SA algorithm never diverges. Always the algorithm proceeds roughly in two steps. The first step, at high temperatures, the algorithm is searching for the "basin of attraction" of the minimum in the configuration space, this part constitutes the "magnetic structure determination". Once the region is attained, a more or less sharp drop in the average "energy" (R-factor) occurs. Then, the second step starts when the average R-factor is low enough, the algorithm enters in its phase of "refinement", where the good configuration has already been found, and performs a progressive improvement of the solution. This is clearly seen in the behaviour of the cost function versus the ordinal number of the temperature parameter in Fig.2, illustrating the case of DyMn$_6$Ge$_6$. In figure 3 it is shown the behavior of the amplitude of the magnetic moments of Dy and Mn atoms. The plot shows that there are a large

dispersion at the stage of "magnetic structure solution" (starting phase of the algorithm) and a progress toward definite values within the "refinement" region.

For a given set of constraints the final average R–factor should be reasonably good (below 20%) except for contradictory or fals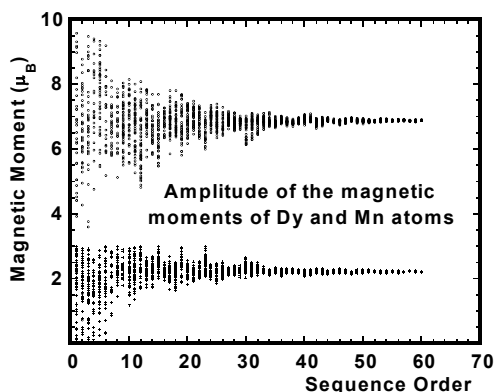e constraints. False minima are encountered when the number of free parameters is of the same order of magnitude than the number of observations and/or the observations are of bad quality (very weak magnetic reflections and large errors associated to them). Ambiguities can be easily discovered. When the intensity data do not depend on a parameter, this shows an anomalous behaviour: in a plot similar to that of Fig. 3, large oscillations persist even at low temperature.



**Figure 3**. Evolution of the magnetic moment of Dy and Mn versus the number of sequential temperature. Similar plots can be observed for other magnetic parameters (cone angles and magnetic phase angles).

In conclusion, we have shown that the SA algorithm can be used for the magnetic structure determination even in the case of complex incommensurate magnetic structures. The method is straightforward and is fully implemented in the program *FullProf* that is publicly available [5].

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