

Recent advances in magnetic structure determination by neutron powder diffraction

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In spite of intrinsic limitations, neutron powder diffraction is, and will still be in the future, the primary and most straightforward technique for magnetic structure determination. In this paper some recent improvements in the analysis of magnetic neutron powder diffraction data are discussed. After an introduction to the subject, the main formulas governing the analysis of the Bragg magnetic scattering are summarized and shortly discussed. Next, we discuss the method of profile fitting without a structural model to get precise integrated intensities and refine the propagation vector(s) of the magnetic structure. The simulated annealing approach for magnetic structure determination is briefly discussed and, finally, some features of the program FullProf concerning the magnetic structure refinement are presented and discussed. The different themes are illustrated with simple examples.

1. Introduction

In a conference concerned with the usefulness of X-ray and neutron scattering in the study of magnetism, the topic of the 'oldest technique' (neutron powder diffraction) cannot be absent. Besides and before the 'high physics' concerning new phenomena and new sophisticated techniques in the study of microscopic magnetism, the powder method is, and will be, the primary and simpler tool in obtaining information on the arrangement of magnetic moments in crystals.

In the last twenty years the Rietveld method, added to the increased performance of powder diffractometers, has allowed great progress in the analysis of powder diffraction data. More recently, the multiphase refinement of incommensurate structures, with the possibility of varying peak shape parameters depending on a particular class of reflections, constitutes a new analytical tool that can give information not only on the magnetic structure, but also on the correlation lengths along particular directions in

reciprocal space. This allows a rough characterization of the 'defects' occurring in the magnetic structure. In the past, a list of the observed and calculated integrated intensities (with or without overlap) was the only means of showing agreement between the model and the data. Nowadays, the analysis taking into account all the details of the full profile should be the usual way of reporting magnetic structure refinements from powder data.

In this paper we shall review some methods used in the resolution of magnetic structures from powder data and discuss new procedures of tackling the problem. The methods based in the symmetry analysis, in the two versions of Shubnikov groups and representation analysis, will not be directly treated here but some comments and references will be given. Throughout the paper we use, on many occasions, the term 'spin' as synonymous of 'magnetic moment'.

2. Summary of useful magnetic scattering formulas: symmetry constraints

In this paragraph we shall give some important

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formulas, relating the magnetic structure with the observed magnetic reflection positions and intensities. The reader interested in more details on the elastic magnetic scattering in relation with magnetic structures can consult the references [1,2,3]. The interaction of neutrons with the magnetic moments of atoms is of dipolar origin through the magnetic moment of the neutron. The scattering amplitude vector, for a single atom, is given by

$$a_M(\mathbf{Q}) = pf(\mathbf{Q})\mathbf{m}_\perp = \frac{1}{2}r_e\gamma f(\mathbf{Q})\left\{\mathbf{m} - \frac{\mathbf{Q}(\mathbf{m} \cdot \mathbf{Q})}{Q^2}\right\} \quad (1)$$

where $r_e = e^2/mc^2 = 2.81776 \times 10^{-13}$ cm, $\gamma (=1.9132)$ is the gyromagnetic factor, $f(\mathbf{Q})$ is the atomic magnetic form-factor (Fourier transform of the unpaired electron density, normalized as $f(0) = 1$) and $\mathbf{m}_\perp$ is the perpendicular component of the atomic moment, $\mathbf{m}$, to the scattering vector $\mathbf{Q}$. The vectorial character of the interaction allows to determine the magnetic moment direction.

For unpolarized neutrons the nuclear and magnetic intensities are simply additive. The elastic scattered intensity by a crystal, as a function of $\mathbf{Q}$, is proportional to the square of the total amplitude (also called 'magnetic interaction vector'):

$$\mathbf{F}_\perp(\mathbf{Q}) = \sum_{\text{all atoms}} a_M(\mathbf{Q}), \quad (2)$$

$$I(\mathbf{Q}) = K(\mathbf{Q})\mathbf{F}_\perp(\mathbf{Q}) \cdot \mathbf{F}_\perp^*(\mathbf{Q}) \\ = K(\mathbf{Q})\left\{|\mathbf{F}(\mathbf{Q})|^2 - \left|\frac{\mathbf{Q} \cdot \mathbf{F}(\mathbf{Q})}{Q}\right|^2\right\}, \quad (3)$$

where $K(\mathbf{Q})$ includes geometrical terms (e.g., Lorentz factor), and the magnetic structure factor of the whole crystal, $\mathbf{F}(\mathbf{Q})$, is given by

$$\mathbf{F}(\mathbf{Q}) = p \sum_{ns} f_s(\mathbf{Q}) \sum_j \mathbf{m}_{nj}(s) W_{sj}(\mathbf{Q}) \\ \times \exp\{i\mathbf{Q} \cdot \mathbf{R}_{nj}(s)\}. \quad (4)$$

Here $\mathbf{R}_{nj}(s) = \mathbf{R}_n + \mathbf{r}_j(s)$. The index n labels the cell at $\mathbf{R}_n$ from the origin of the $n=0$ cell, (s) labels the Wyckoff position $\{W_r(s)\}$ (s -site) of multiplicity r and the index j ($1, 2, \dots, r$) labels

the r equivalent Bravais sublattices constituting $\{W_r(s)\}$. The term $W_{sj}(\mathbf{Q})$ is the Debye-Waller factor of atom sj and $f_s(\mathbf{Q})$ is the form factor of the chemical species at site s . We shall consider that there are n_s magnetic, 'symmetry-independent' sites in the crystal.

In this paper we shall be concerned only with 'periodic' spin-configurations. The following Fourier series defines the values of $\mathbf{m}$ at whatever atom position in the crystal:

$$\mathbf{m}_{nj}(s) = \sum_{\{\mathbf{k}\}} S_{kj}(s) \exp\{-2\pi i \mathbf{k} \mathbf{R}_n\} \\ = \sum_{\{\mathbf{k}\}} T_{kj}(s) \exp\{-2\pi i \mathbf{k} \mathbf{R}_{nj}(s)\} \quad (5)$$

where the vectors $\{\mathbf{k}\}$ are restricted to the first Brillouin Zone (BZ) and can be constituted by several (nonrelated) stars. From eq. (5) we deduce the following equation:

$$S_{kj}(s) = T_{kj}(s) \exp\{-2\pi i \mathbf{k} \mathbf{r}_j(s)\}. \quad (6)$$

The magnetic moments of the atoms in the zero-cell (reference cell, $\mathbf{R}_n = (000)$) are obtained from eq. (5) and are given by the expression

$$\mathbf{m}_{oj}(s) = \sum_{\{\mathbf{k}\}} S_{kj}(s) = \sum_{\{\mathbf{k}\}} T_{kj}(s) \exp\{-2\pi i \mathbf{k} \mathbf{r}_j(s)\}. \quad (7)$$

The above general expressions are complex but in real cases the number of terms in eq. (5) is small, and usually contain, at most, the terms of a single $\mathbf{k}$ -star. Substituting eq. (5) in eq. (4) it is easily found that $\mathbf{F} = 0$ unless $\mathbf{Q} = 2\pi(\mathbf{H} + \mathbf{k})$, where $\mathbf{H}$ is a vector of the reciprocal lattice. The magnetic reflections corresponding to $\mathbf{k} \neq 0$ are usually called 'satellites' because they appear distributed symmetrically in the reciprocal space around the 'fundamental' nuclear reflections ($\mathbf{Q} = 2\pi\mathbf{H}$). Except a constant factor, the formula (3) holds for the integrated intensity of a magnetic reflection if $\mathbf{F}$ is replaced by $\mathbf{F}_m$, the magnetic structure factor of the crystallographic unit cell. The expression for $\mathbf{F}_m$ is

$$\mathbf{F}_m(\mathbf{H} + \mathbf{k}) = p \sum_s f_s(\mathbf{Q}) \sum_j S_{kj}(s) W_{sj}(\mathbf{Q}) \\ \times \exp\{2\pi i(\mathbf{H} + \mathbf{k}) \mathbf{r}_j(s)\} \quad (8)$$

$$= p \sum_s f_s(Q) \sum_j T_{kj}(s) W_{sj}(Q) \exp\{2\pi i \mathbf{H} \mathbf{r}_j(s)\}. \quad (8')$$

From the expressions (8), (8') and (3) one can conclude that only the Fourier components of the magnetic structure are accessible from a neutron diffraction experiment. It is worth remarking that the Fourier components S_{kj} (a complex vector) contribute only to the set of reflections labeled with $\mathbf{k}$. If the magnetic structure has several propagation vectors $\mathbf{k}$, it is not possible 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. (5).

Only in some simpler cases (single propagation vector) can the Fourier components be identified with the magnetic moments: for $\mathbf{k} = 0$, or $\mathbf{k} = \frac{1}{2}\mathbf{H}$. One can verify that the expression (8), taking into account eq. (7), is more suitable for computing purposes than expression (8'). The reason is that the phase factor $\exp\{-2\pi i \mathbf{k} \mathbf{r}_j(s)\}$, in eqs. (6) and (7), precludes the identification of T_{kj} with the real magnetic moment as happens for S_{kj} . In the following we shall refer only to S_{kj} as Fourier components.

For $\mathbf{k}$ in special points of the BZ, the symmetry analysis can be performed following two procedures: the first one is based in the 'classification' of the magnetic structure within the Shubnikov groups, and the second is based on the analysis of the irreducible representations of the propagation vector group and their associated basis functions. For incommensurate structures only the second procedure can be applied¹. The subject is too large to be treated here. The interested reader can consult ref. [4] for the magnetic groups and refs. [5,6] for the representation analysis. Whatever the symmetry ap-

proach followed, one can arrive to a set of relations between the magnetic moments (commensurate structures described in the magnetic cell), or their Fourier components, of the atoms belonging to equivalent sublattices. It is worth mentioning that a crystallographic Wyckoff site may split in two or more orbits in the ordered magnetic state. For simplicity we shall consider that the group of the propagation vector $\mathbf{k}$, $G_{\mathbf{k}}$, does not split the sublattices of $\{W_j(s)\}$, then all $S_{kj}(s)$ can be written as a linear function of $S_{k1}(s)$ (the reference atom of the site s at $\mathbf{r}_1(s)$):

$$S_{kj}(s) = M_j(s) S_{k1}(s) \exp\{2\pi i \phi_j(s)\} \quad (9)$$

where M is a real rotation matrix and $\phi_j(s)$ is a phase parameter fixed by symmetry (normally involving products of $\mathbf{k}$ by the translation part of symmetry operators of $G_{\mathbf{k}}$ and/or 'returning translations', see the first article of ref. [6]). The structure factor can be written in such cases as

$$F_{\mathbf{m}}(\mathbf{H} + \mathbf{k}) = p \sum_s f_s(Q) o_s \sum_j M_j(s) S_{k1}(s) W_{sj}(Q) \times \exp\{2\pi i [(\mathbf{H} + \mathbf{k})(g|\mathbf{t})_j \mathbf{r}_1(s) + \psi_j(s)]\}. \quad (10)$$

Here o_s is the occupation factor of site (s). The symmetry operation $(g|\mathbf{t})_j$ belongs to $G_{\mathbf{k}}$, and the phase $\psi_j(s) = \phi_j(s) + \Phi(s)$ contains a term that is not fixed by symmetry, $\Phi(s)$, which depends on the coupling between sublattices belonging to different sites. The relevant magnetic parameters to be determined from the experiment are the real and imaginary parts of the Fourier components $S_{k1}(s)_\alpha$ ($\alpha = x, y, z$, $s = 1, \dots, n_s$) and the phases $\Phi(s)$ ($s = 2, \dots, n_s$, one can always take $\Phi(1) = 0$ as phase reference), in general $N_p = 7n_s - 1$. For simpler cases, sinusoidal and helical spin configurations for instance, additional restrictions arise between the Fourier components [2,7].

3. The search for the propagation vector(s): the profile matching method in getting precise integrated intensities

The resolution of magnetic structures needs as prerequisite the knowledge of the crystal struc-

¹ As in incommensurate crystal structures, symmetry analysis in higher dimensions could also be used, but, to the knowledge of the author, no detailed work in this sense has been done yet.

ture. The symmetry analysis allows to classify systematically the different kinds of probable (possible) structures according to the crystallographic space group. The result of this analysis is a set of possible models that can be tested successively to select the model giving the best agreement between the observed and calculated diffraction pattern. This 'trial-and-error' method is usually enough to solve a magnetic structure, but in cases with many magnetic atoms in the unit cell other techniques have to be used. In some cases a Patterson-function-like analysis has been employed [3]. In the next paragraph we shall discuss the approach of the so-called 'simulated annealing' to explore the space of possible solutions.

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 k it is necessary to index the magnetic reflections appearing below the ordering temperature (T_C or T_N). With a single crystal the task is somewhat easy, but is tedious for a powder because only the module of reciprocal vectors is available. Graphic or numerical procedures can be used. In refs. [8,9] the reader can find a method to determine the propagation vector of a simple spiral or sinusoidal structures.

Once an approximate propagation vector is obtained, the integrated intensities are needed to solve the magnetic structure. We shall discuss a method, which is of general applicability, of fitting the full profile with the constraints imposed by the instrumental resolution function, the cell parameters and propagation vectors.

The model used for describing the powder pattern profile is based on the following expression:

$$y_{i\text{ cal}} = \sum_{\phi} S_{\phi} \sum_{\mathbf{h}} I_{\phi\mathbf{h}} \Omega(T_i - T_{\phi\mathbf{h}}) + B_i \quad (11)$$

where $\mathbf{h}$ (H or $H + k$) labels the Bragg reflections, the subscript ϕ labels the 'phase' and vary from 1 up to the number of 'phases' existing in the model. Here the name 'phase' is synonymous of a 'same procedure for calculating the inte-

grated intensities $I_{\phi\mathbf{h}}$ '. The presence of several phases in the model does not mean necessarily that impurities exist in the sample. $\Omega(T_i - T_{\phi\mathbf{h}})$ is the value of the function $\Omega(x)$, normalized to unit area, selected to describe the peak shape, at the position T_i due to the reflection centered at $T_{\phi\mathbf{h}}$. Finally, S_{ϕ} is a scale factor and B_i is the background at T_i . In the Rietveld method [10], the functions I , Ω and B are calculated using a model that depends on a series of parameters. The structural information is contained in the integrated intensities ($I_{\phi\mathbf{h}} \approx |F_{\perp m}|^2$ for a magnetic 'phase') and the peak positions (through the cell parameters and propagation vectors), while the instrumental and microstructural effects are included in the peak shape function. If the set of model parameters is $\beta = (\beta_1, \beta_2, \dots, \beta_p)$, the Rietveld method tries to optimize the chi-square function:

$$\chi_p^2 = \sum_i w_i \{y_{i\text{ obs}} - y_{i\text{ cal}}(\beta)\}^2 \quad (12)$$

where w_i is the inverse of the variance associated to the observation i ($\sigma^2(y_{i\text{ obs}})$). If there is no model for the structural problem (crystal and/or magnetic structure) the Rietveld method is not applicable. Pawley [11] proposed a method to obtain integrated intensities (for a single 'phase') by refinement of the whole profile using $I_{\mathbf{h}}$ in expression (11) as least squares (LS) parameters. The matrix of the normal LS-equations is usually singular, due to the reflection overlap. Pawley solved the problem by using 'slack constraints' [11]. However, there is an intrinsic indetermination causing an infinite number of solutions. When the reflections $\mathbf{h}_1$ and $\mathbf{h}_2$ are accidentally at the same position $T_{\mathbf{h}_1} = T_{\mathbf{h}_2}$ the global intensity $I(\mathbf{h}_1, \mathbf{h}_2)$ can be decomposed, $I_{\mathbf{h}_1} + I_{\mathbf{h}_2}$, in an infinite number of ways. Usually the a priori bayesian guess, $I_{\mathbf{h}_1} = I_{\mathbf{h}_2}$, is chosen. This uncertainty is the fundamental point limiting the capability of getting a structural solution from powder data. The LS approach proposed by Pawley has the drawback of needing the inversion of a matrix that can be of considerable size even if it is sparse. An alternative procedure is to iterate the calculated profile up to 'match' the

observed pattern. For doing that a criterion to approach the observed pattern must be defined. The problem can be formulated, for a single phase, as follow. Let $y_{\text{obs}} = \{y_{i \text{ obs}}\}_{i=1, \dots, N}$ (N : number of points in the profile) be the observed diffraction pattern. This set of values can be calculated if the integrated intensities $I^0 = \{I_j^0\}_{j=1, \dots, n}$ (n : number of reflections), the cell parameters and the peak shape are known. In that case the expression (11) can be rewritten as

$$y_{i \text{ obs}} = y_{i \text{ cal}} + e_i = \sum_{\{j\}} I_j^0 \Omega_{i,j} + B_i + e_i \quad (13)$$

where e_i is a statistic fluctuation of the order of $\sigma(y_{i \text{ obs}})$, and eq. (12) is a minimum by definition. In practice, the set I^0 is not known and the cell and profile parameters are known approximately. The set I^0 can be considered as a *fixed point* of the n -dimensional space, R_+^n (positive components), associated with the diffractogram y_{obs} . If we start from an arbitrary point I^1 , of R_+^n , we have to find an operator Γ that, acting on that point, transforms it into another one closer to I^0 . The term ‘closer’ means that the distance $d(I^0, \Gamma[I^1])$ is smaller than $d(I^0, I^1)$. Any formal definition of distance is good. Actually, due to the degeneracy discussed above, I^0 is not a single point but belongs to an extended region: $V(I^0) \subset R_+^n$. A good operator must verify

$$I^k = \Gamma[I^{k-1}] = \Gamma^{k-1}[I^1], \quad (14)$$

$$\lim_{k \rightarrow \infty} I^k = \lim_{k \rightarrow \infty} \Gamma^{k-1}[I^1] = I^\infty \in V(I^0). \quad (14')$$

The expression provided by Rietveld [10] to estimate the ‘observed’ integrated intensity in order to mimic the classical crystallographic R -factor (now called R -Bragg), defined as expression (15), is an excellent Γ -operator:

$$R_B = \frac{\sum_j |I_j(\text{obs}) - I_j(\text{calc})|}{\sum_j I_j(\text{obs})}. \quad (15)$$

The R_B provides the natural definition of distance in the space R_+^n . Rietveld’s formula for $I_j(\text{obs})$ with a notation slightly modified was

$$I_j(\text{obs}) = \sum_i I_j(\text{calc}) \Omega_{i,j} \frac{y_{i \text{ obs}} - B_i}{y_{i \text{ cal}} - B_i}. \quad (16)$$

This formula can be written in the same form as eq. (14):

$$I_j^k = \sum_i \frac{y_{i \text{ obs}} - B_i}{y_{i \text{ cal}} - B_i} \Omega_{i,j} I_j^{k-1}. \quad (17)$$

Any Rietveld program can be easily modified to include the possibility of ‘fitting’ the whole profile without structural model using the expression (17) for iterative calculation of the integrated intensities. Of course, the rest of the profile parameters, including the propagation vector(s) of the magnetic structure, can be refined simultaneously with the usual LS procedure. The method of ‘profile matching’ is extremely efficient and fast. This procedure has been used first by Taylor [12] and Le Bail et al. [13] and it is implemented in the program FullProf [14] developed at the ILL. This program allows the mixture of the Rietveld and ‘profile matching’ methods for the analysis of a diffraction pattern. This mixed procedure has to be used with caution: the use of both methods simultaneously is necessary when one tries to get the integrated intensities of an unknown structure in presence of another, already known, phase. Thus, 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.

As an example of propagation vector refinement, we present the case of the spinel-like oxide Co_5TeO_8 showing the following magnetic behaviour. Below 60 K strong diffuse scattering develops around the reflection (111). The diffuse scattering ‘condenses’ in incommensurate reflections appearing as satellites around the nuclear reflections that, in turn, receive the contribution of magnetic reflections characterized by a propagation vector $\mathbf{k}_1 = [000]$. The satellites can be indexed with a propagation vector $\mathbf{k}_2 = [00\delta]$ with $\delta \approx 0.08$ at $T \approx 30$ K. As shown in fig. 1, where a plot of the full profile refinement without structural model is pre-

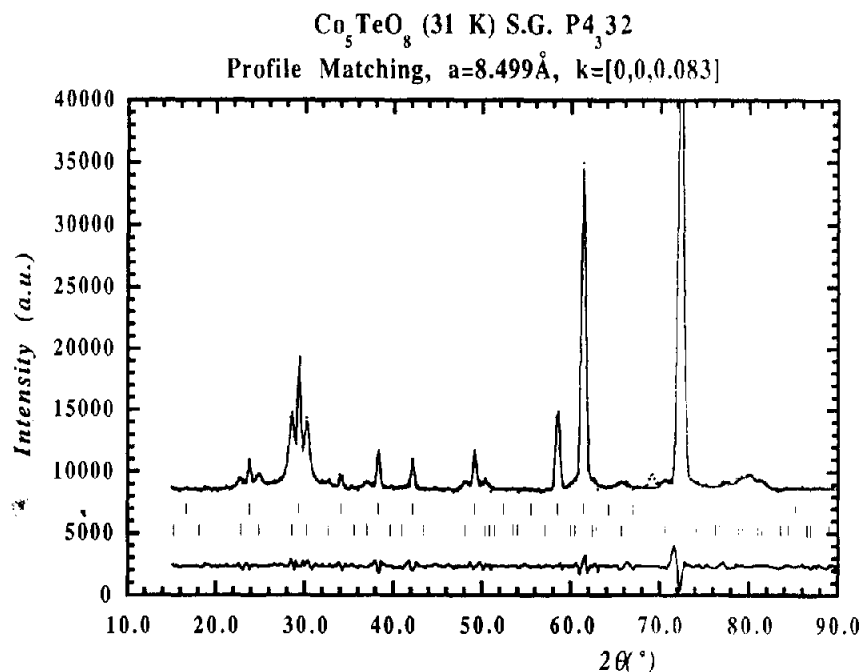


Fig. 1. Plot of the profile matching result, refinement without structural model, obtained for the oxide Co_5TeO_8 . The satellites (second row of reflection markers) are broadened and have a Lorentzian shape with a propagation vector $[0\ 0\ \delta]$ with $\delta \approx 0.08$ (see text).

sented, the shape of the $H + k_2$ peaks is Lorentzian, while that of the fundamental reflections is nearly Gaussian. This is due to the short correlation length (broadening $\sim 1/\cos\theta$) of the conical spiral constituting the magnetic structure. On cooling, δ becomes smaller and the correlation length increases (reflection sharpening). At low temperature ($\sim 4.2\text{ K}$) the classical Néel ferromagnetic state is a good approximation to the magnetic structure [16].

Another example is presented in fig. 2, where the mixed Rietveld-profile matching method is used to obtain the integrated intensities of the magnetic reflections of $\text{Er}_2\text{Cu}_2\text{O}_5$. The crystal structure belongs to the space group $\text{Pna}2_1$ and the propagation vector is $[0\ 0\ 0]$. There are four independent sites and a total of 16 magnetic atoms in the unit cell. We present this case because the obtained integrated intensities have been used as input data for an example of the

'simulated annealing' method developed in the next paragraph.

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

The set of integrated intensities obtained with whatever full profile refinement method, must be analysed (and eventually modified) to tackle the problem of structure determination. A procedure, rooted in the ideas of 'maximum entropy', has been proposed by David [15] in the context of crystal structure determination from powder data. To use the simulated annealing (SA) technique it is not necessary to seek sophisticated treatments of the reflection overlap. One can just add the dubious reflections treating the sum as one observation to which one or more independent reflections contribute. The method

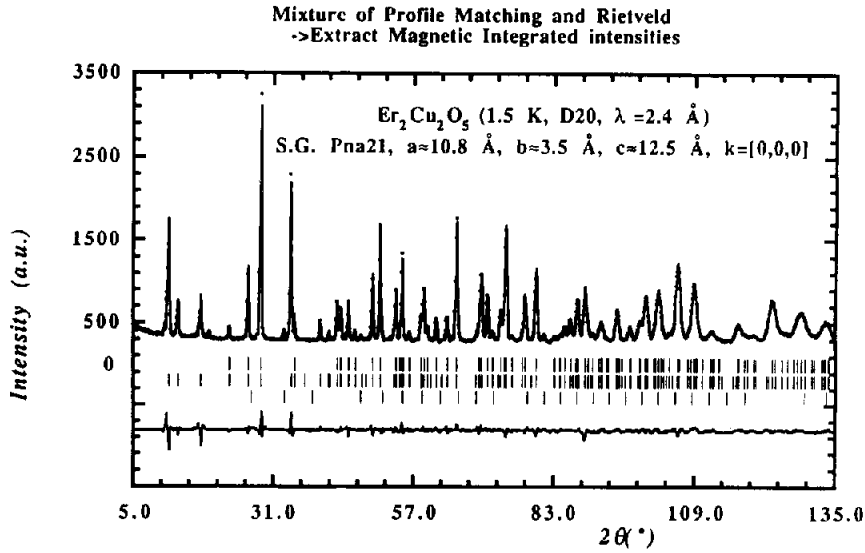


Fig. 2. Mixed Rietveld-profile matching refinement applied to $\text{Er}_2\text{Cu}_2\text{O}_5$, to obtain the integrated intensities of the magnetic reflections marked in the second row. The first and third rows correspond to the reflections of the nuclear structure of $\text{Er}_2\text{Cu}_2\text{O}_5$ and Er_2O_3 , that are treated with the conventional Rietveld method (intensities calculated from the structural model).

described below is, of course, valid for the analysis of single crystal data.

The SA is a general purpose optimization technique for large combinatorial problems introduced in 1983 by Kirkpatrick, Gelatt and Vecchi [17]. An introductory review of SA applied to structural problems in condensed matter physics can be found in ref. [18]. Here we need only a qualitative explanation of the SA optimization procedure. The function, $E(\Omega)$, to be optimized with respect to the configuration described by the vector state Ω is called the 'cost' function. First we select an initial configuration, Ω_{old} , then each step of SA method consists of a slight change of the old configuration to a new one, Ω_{new} . If $\Delta = E(\Omega_{\text{new}}) - E(\Omega_{\text{old}}) \leq 0$ the new configuration serves as old configuration for the new step. If Δ is positive, Ω_{new} is accepted as current configuration only with certain probability that depends on the so-called 'temperature' parameter T and Δ . The probability that a worse configuration is accepted is slowly decreased on 'cooling'. The following pseudo-code, adapted

from ref. [18], summarizes the SA algorithm, and shows the simplicity to implement it:

```
begin
  Initialize (set to zero useful quantities, do preliminary
    calculations)
   $\tau = 1$ 
  do
    do
      Perturb the system:
       $\Omega_{\text{old}} \rightarrow \Omega_{\text{new}}, \Delta = E(\Omega_{\text{new}}) - E(\Omega_{\text{old}})$ 
      if  $\Delta \leq 0$  then accept, else
        if  $\exp(-\Delta/T_\tau) > \text{random}[0,1]$  then accept
        if accept then Update (replace  $\Omega_{\text{old}}$  by  $\Omega_{\text{new}}$ )
      until equilibrium is approached closely enough (Ncyc)
       $T_{\tau+1} = f(T_\tau)$  (decrease temperature, usually  $T_{\tau+1} = qT_\tau$ ,
         $q \approx 0.9$ )
       $\tau = \tau + 1$ 
    until stop criterion is true (maximum  $\tau$ , convergence, low
      % accepted...)
end
```

During the development of the algorithm several statistical quantities, evaluated for each temperature, are saved for a later analysis. Between these quantities some are of special interest: the

average value of the energy, the ‘heat capacity’ and the percentage number of accepted jumps [18].

This method has been used, in the context of magnetism, to obtain the ground state configuration of classical magnetic models compatible with an a priori magnetic unit cell [19]. The classical quadratic hamiltonian governing the spin arrangements in crystals is given by

$$E[\mathbf{\Omega}] = \sum_{(i,j)} \mathbf{S}_i^T [\mathbf{J}]_{ij} \mathbf{S}_j + \sum_i \{ D_i (\mathbf{u}_i \mathbf{S}_i)^2 - \mathbf{H}^T \cdot \mathbf{S}_i \} \quad (18)$$

here $\mathbf{S}_i$ is the classical spin, attached to the atom i , written as a column matrix, ^{T} denotes transposed, $\mathbf{H}$ is the applied magnetic field and $\mathbf{u}$ is a unit vector defining the direction of the single ion anisotropy. Applying the SA technique, provided that one knows the values of the generalized exchange parameters defined by the tensor $[\mathbf{J}]_{ij}$ and D_i , it is possible to get the ground state configuration $\mathbf{\Omega}_0$: list of all $\mathbf{S}_i$ minimizing eq. (18) within the simulation box.

For structure determination, the cost function can be chosen as the conventional crystallographic R -factor, or some function related to it. In the program MagSan [20] the following expression is used:

$$E[\mathbf{\Omega}(\boldsymbol{\beta})] = \left\{ \sum_n \left| I_{\text{obs}}(n) - S \sum_{j(n)} I_{\text{calc}}(j) [\mathbf{\Omega}(\boldsymbol{\beta})] \right| \right\} / I_T.$$

The sum over n is extended for all the ‘observations’, and that over $j(n)$ for all the reflections contributing to the observation n . $I_T = \sum_n I_{\text{obs}}(n)$ and S is a scale factor. The configuration $\mathbf{\Omega}$ is the list of all the components of the magnetic moments existing in the chemical unit cell (the program is, for the moment, adapted to the analysis of commensurate structures) and this list is obtained from the independent parameters $\boldsymbol{\beta}$ (any symmetry constraint can be imposed) that are those really participating in the annealing procedure. In practice the vector $\boldsymbol{\beta}$ has the form

$$\begin{aligned} \boldsymbol{\beta} &= \langle \theta_1, \phi_1, S_1, \theta_2, \phi_2, S_2, \dots, \theta_{n_s}, \phi_{n_s}, S_{n_s} \rangle \\ &= \langle (\theta_s, \phi_s, S_s)_{s=1, \dots, n_s} \rangle \end{aligned}$$

where the index s labels the sites, θ_s and ϕ_s are the polar angles of the spin, and S_s is the modulus of the magnetic moment at site s .

To start solving a magnetic structure with the SA method one has to create two files: the first is the intensity file where the indices of each reflection and its intensity is written, in the second file the cell parameters, atom positions, symmetry constraints and SA parameters are given. The later parameters are those defining the limits of loops in the algorithm presented above (N_τ = maximum τ , Ncyc, Minacc%) and the ‘cooling’ schedule $T_{\tau+1} = f(T_\tau) = qT_\tau$ ($q < 1$, $q \approx 0.9$). The selection of these parameters is still empirical and there is no rule giving explicit values with the guarantee of working well in every particular problem.

The starting point is an arbitrary configuration. Always the algorithm proceeds roughly in two steps. The first step, at high temperatures, is a work 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 been found, and performs a progressive improvement of the solution.

To illustrate the use of the SA method we have chosen two cases where the magnetic structure was already known. A summary of the relevant information is collected in panels grouped in the appendix. The case of $\text{Ho}_2\text{BaNiO}_5$ crystallizing in the space group Immm [21], has a propagation vector $[\frac{1}{2} 0 \frac{1}{2}]$ and two sites, Ho and Ni, of two and one sublattice, respectively, in the primitive cell (panel I). The second case corresponds to the compound $\text{Er}_2\text{Cu}_2\text{O}_5$ [22], crystallizing in the space group Pna2₁, that has a propagation vector $[000]$, same magnetic and crystallographic unit cell, and four sites: Er(1), Er(2), Cu(1) and Cu(2), each of them of four sublattices (panel II). In panels I and II is presented the comparison between the known magnetic structure and the results obtained with SA for different conditions. In fig. 3

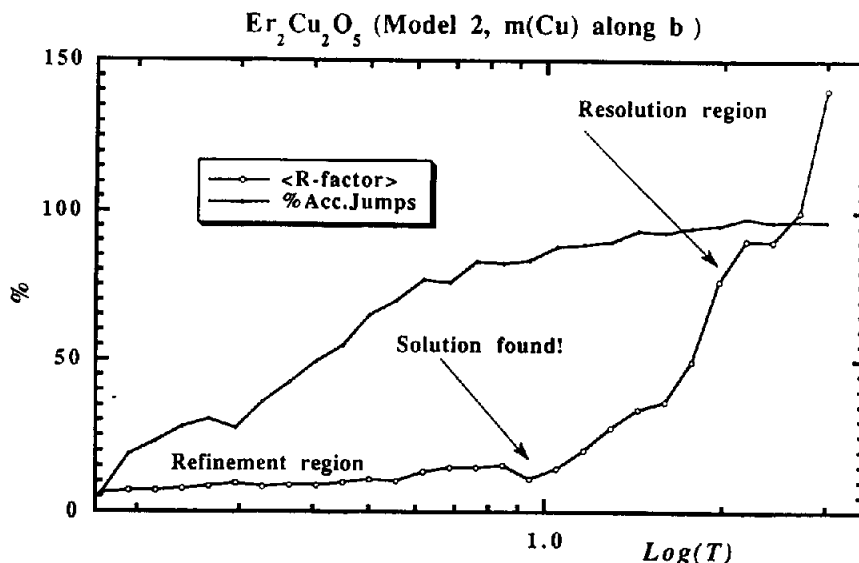


Fig. 3. Variation of the average R -factor and the percentage of accepted jumps for model 2 of panel II (see appendix) for $\text{Er}_2\text{Cu}_2\text{O}_5$ as a function of temperature.

is shown the variation of the R -factor and the percentage of accepted jumps for model 2 of panel II as a function of temperature. The

corresponding evolution of the average values of the first eight parameters is presented in fig. 4.

From a limited empirical experience on the

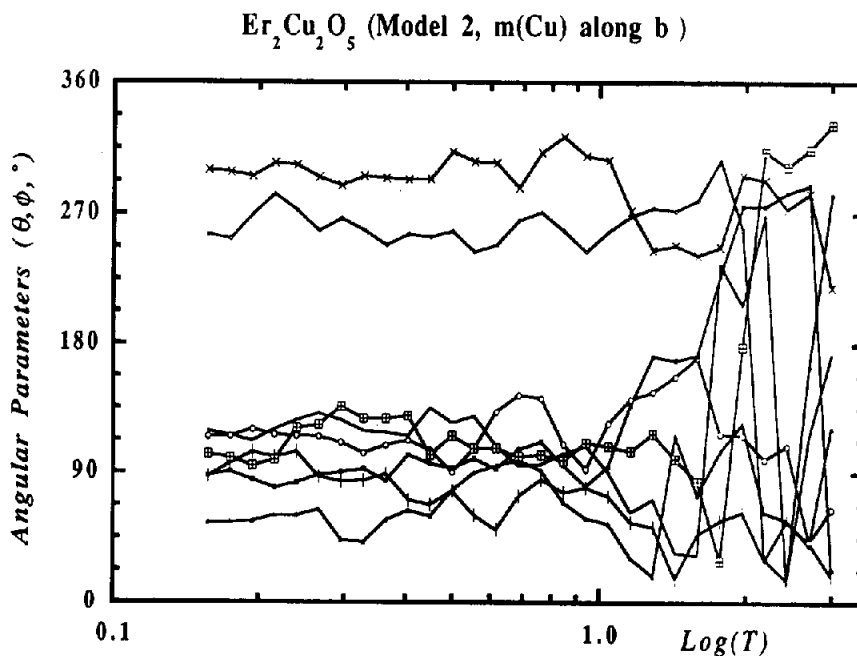


Fig. 4. Average values of 8 angular parameters as a function of temperature. Note that large fluctuations dominate at high temperature and the parameters change slowly in the 'refinement region' (model 2 of panel II).

use of the SA algorithm applied to magnetic structure determination, several points can be drawn.

1. The algorithm never diverges. For a given set of constraints the final average R -factor should be reasonably good (below 10%) except for contradictory or false constraints.
2. 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).
3. Ambiguities can be easily discovered. When the intensity data do not depend on a parameter, this one shows an anomalous behaviour. In a plot like in fig. 4, large oscillations persist even at low temperature.

The method is still being tested and a set of annealing parameters is being investigated to get empirical rules for improving its capability in providing a good starting model for later refinement.

5. Refinement of magnetic structures: some features of the program FullProf; examples

The analysis of magnetic structures in polycrystalline samples has some intrinsic limitations. In *collinear* structures it is not possible to determine the direction of the magnetic moments in compounds of high symmetry [23]. For crystallographic systems tetragonal, hexagonal and rhombohedral only the angle of the magnetic moments with the principal axis can be determined. In the cubic system only the sequence of + and - signs is accessible. For *noncollinear* structures other ambiguities can occur and one has to be careful in analyzing the configurations that give the same powder diffraction pattern. This is specially true for the case of the so-called 'multi- k ' structures, where several arms of the k -star participate in the Fourier sum (5); usually it is possible to find a single- k structure giving the same diffraction pattern. Powder diffraction is unable to solve the distinction between those structures. With single crystals the problem also

appears due to the usual presence K-domains [2]. With these limitations in mind, and taking the appropriate precautions, the refinement of a magnetic structure from powder data gives valuable information about the spin arrangements in crystalline solids.

The Rietveld method is applicable once a starting model is available. For simple structures the Rietveld-Hewatt program [24] and many others are perfectly adequate. For complex or incommensurate structures the use of a limited number of integrated intensities [25] or profile refinement programs [26,27] written for each particular case is still the common way of handling these cases.

The program FullProf [14], developed at the ILL starting from the code of the program of Wiles and Young [28], can handle the refinement of magnetic structures of arbitrary complexity (commensurate or incommensurate) with the possibility of taking advantage of any symmetry constraint. The formula for the magnetic structure factor (10), and its derivatives with respect to the parameters, has been programmed to have a general tool for magnetic structure calculation and refinement. The Fourier coefficients S_k can be represented either in crystallographic or spherical components. The program can generate automatically the satellite reflections up to 24 propagation vectors per phase, and refine their components (in reciprocal lattice units).

In some particular cases, the user can decide that it is easier writing a subroutine to calculate the magnetic intensity as a function of parameters defined in direct space. For instance, classical helical or conical structures can be described in terms of the magnetic moment, axis of the helix and relative phases between sublattices [7]. The subroutine can be linked with the FullProf library and the user generates a particular executable code.

The user can benefit from the implementation of a great variety of 'microstructural' effects responsible of modifying the shape and width of reflection profiles. That allows the treatment of very complicated situations.

As an illustration these capabilities we have chosen as an example CsMnF_4 that is still in

course of analysis from the point of view of the involved physics [29]. Here we shall be interested only in the problem of magnetic structure refinement. The compound was described as a planar ferromagnet [30] and belongs to the space group $P4/n$. The crystal structure is very simple [29,30] and has MnF_6 octahedra forming perovskite layers (of composition MnF_4) separated by Cs^+ ions. There is no Mn–F–Mn superexchange path between layers. Due to the Jahn–Teller effect of Mn^{3+} and the antiferrodistorsive orbital ordering within the perovskite layers, the in-plane Mn–F–Mn exchange is ferromagnetic and much more intense than the interaction between adjacent layers. The weakness of this later interaction and, probably, the existence of structural defects perturbs the ferromagnetic ground state causing a more complex magnetic structure. Two different prepared samples [29] have been studied. In fig. 5 a comparison between the low angle portions of their neutron diffraction patterns, at 1.5 K on D1B, is presented. One can observe that two symmetry-unrelated propagation vectors, $k_1 = [00\delta]$ and $k_2 = [00\frac{1}{2}]$, are present in both cases. From the figure it is deduced that $(k_1, -k_1)$ and k_2 are correlated.

The intensity of the reflection $(00\frac{1}{2})$ is higher when δ increases (sample B). Instead of the coexistence of two magnetic phases, both propagation vectors are defining the magnetic structure. In the limit $\delta \rightarrow 0$ the propagation vector k_2 disappears and a ferromagnetic ground state is obtained. Moreover the magnetic reflections $(00l)^\pm$ have a lorentzian character and are broadened, the reflections $(hk0)^\pm$ are gaussian and resolution limited. The rest of the magnetic reflections present an intermediate behaviour.

The magnetic structural model allowing the refinement of the magnetic intensities is given in panel III of the appendix. The particular peak-shape displayed by both samples can be modeled by a 'size effect'. The in-plane correlation lengths is infinity whereas along the c axis the magnetic structure has a finite correlation length. The angular lorentzian broadening of magnetic reflections, that is convoluted with the instrumental gaussian, is given by the expression of panel III.

In fig. 6 is presented the low-angle part of the profile refinement using the above models. The resulting magnetic structure corresponds to a perturbed helix described by the formula given

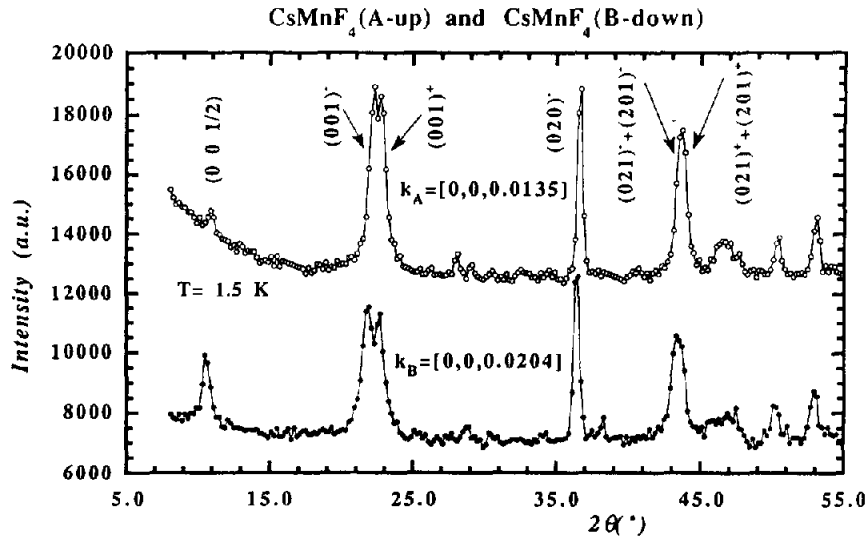


Fig. 5. Comparison between the low-angle portions of the neutron diffraction patterns, at 1.5 K on D1B, of two different samples of CsMnF_4 . Two symmetry-unrelated propagation vectors, $k_1 = [00\delta]$ and $k_2 = [00\frac{1}{2}]$, are present in both cases.

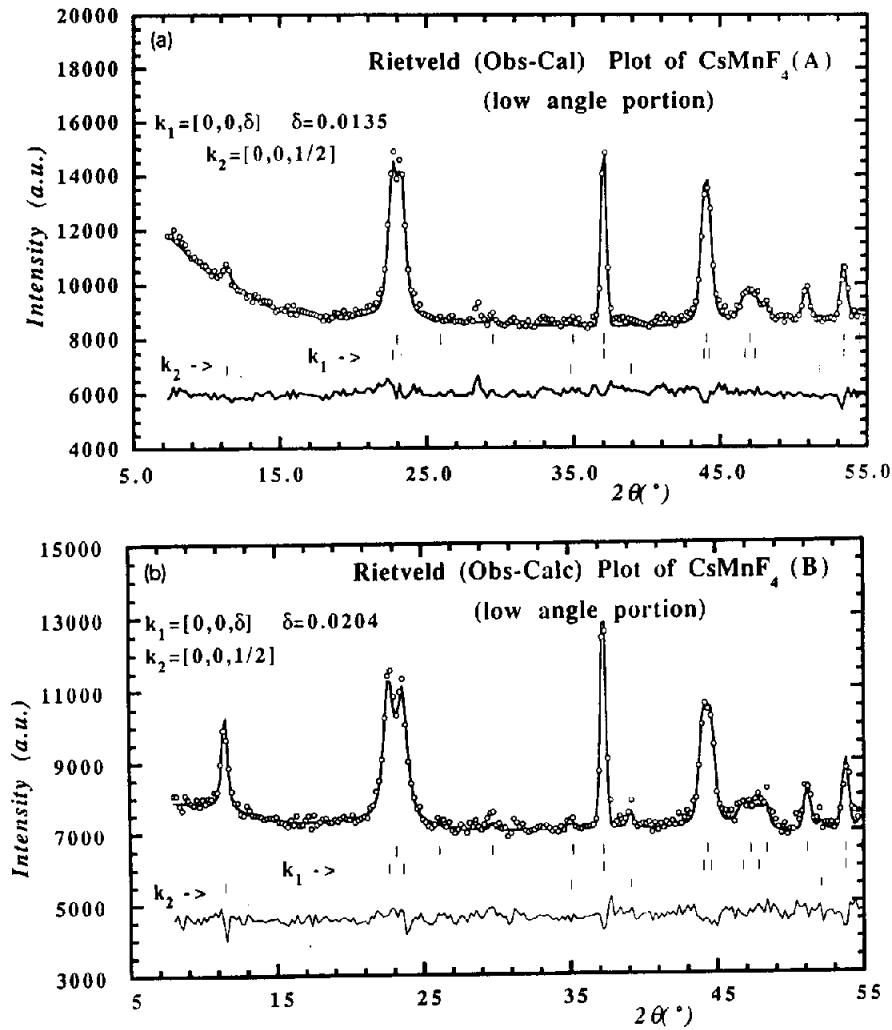


Fig. 6. Plots (a and b) of the observed and calculated patterns of the low-angle part for the two samples (A and B) of CsMnF₄. The fit is performed with the model discussed in the text and detailed in panel III of the appendix.

in panel III. The magnitude of the magnetic moment fluctuates between two values, $m_{\min}$ and $m_{\max}$, but is constant in each basal plane.

6. Conclusions

Several topics concerning the resolution of magnetic structures from powder data have been treated. The summary of magnetic scattering formulas has been presented in order to clarify

the formalism used for magnetic structure factor calculations for incommensurate structures. The selection of S_k in formula (5), instead of T_k , as Fourier components allows the treatment of the $k = \frac{1}{2}H$ structures with the same formalism and an easy identification of S_k with real magnetic moments. A powerful method for obtaining integrated intensities has been discussed. The method of SA appears as a very useful tool in solving magnetic structures. One has to be cautious and analyse critically the solutions au-

tomatically proposed. Ambiguities and false minima are frequent. The method should be used as a complement to group theoretical calculations. Some features of the program FullProf have been presented and some examples discussed. The author is really convinced that, nowadays, it is possible to get much more information from magnetic neutron powder diffraction than was possible only few years ago.

Acknowledgements

The author is indebted to Michel Bonnet for many interesting discussions about the symmetry analysis of magnetic structures and to Jean Pannetier for useful discussions about the simulated annealing technique.

Appendix

In this part, three panels summarizing the relevant information of three examples referenced in the text are presented. The panels I and II concern the SA technique. The reader unfamiliar with the notation used here for describing the magnetic structures, can consult the appropriate references. The given magnetic moment vectors refer to the first atom of the site, the rest of the magnetic moments are obtained according to the corresponding basis functions. In models 2 and 3 of panel II the atoms are independent and the basis functions given are only approximate. To simplify the presentation we have given only one (averaged) magnetic moment. The average components of the magnetic moment are calculated by summing the absolute value for each atom and dividing by the number of atoms. The aim of these panels is to show some typical values of the 'annealing parameters', the results obtained applying SA with different constraints and a rough comparison with the results obtained, once the solution is known, from Rietveld refinement.

Panel III summarizes the magnetic model, used in Rietveld refinements, for the two samples of CsMnF_4 described in the text.

Panel I

Summary of data and results obtained from the SA technique for $\text{Ho}_2\text{BaNiO}_5$. See ref. [21] for details of magnetic structure.

$\text{Ho}_2\text{BaNiO}_5$, Immm, $a \approx 3.75 \text{ \AA}$, $b \approx 5.73 \text{ \AA}$,
 $c \approx 11.27 \text{ \AA}$, $k = [\frac{1}{2}, 0, \frac{1}{2}]$.

Two magnetic sites: Ho (2 sublattices),

Ni (1 sublattice) in the primitive cell.

Results from Rietveld refinement [20]:

basis functions of the magnetic structure:

Ho $\{F_x, 0, F_z\}$ and Ni $\{S_x, 0, S_z\}$;

refined magnetic moments (in μ_B) of representative atoms:

$\{\text{Ho}\} \rightarrow \{F_x, 0, F_z\}$, $m(\text{Ho}) = [0.12(5), 0, 9.06(4)]$;
 $\{\text{Ni}\} \rightarrow \{S_x, 0, S_z\}$, $m(\text{Ni}) = [0.58(9), 0, -1.26(4)]$;
 $R_{\text{mag}} = 1.6\%$.

Results obtained from simulated annealing

Model 1

$N_{\text{cyc}} = 200$, $T_0 = 1.0$, $q = 0.9$, $\text{Minacc}\% = 5$, $N_r = 90$.

Correct symmetry constraints, $m(\text{Ho})$ fixed to $9\mu_B$.

Number of free parameters: 3;

number of observations: 30 (48 reflections).

Final $T = 0.01$, R -factor (average structure) = 2.3%:

$\{\text{Ho}\} \rightarrow \{F_x, 0, F_z\}$, $m(\text{Ho}) = [0.21, 0, 8.99]$;
 $\{\text{Ni}\} \rightarrow \{S_x, 0, S_z\}$, $m(\text{Ni}) = [0.81, 0, -1.30]$.

Model 2

$N_{\text{cyc}} = 200$, $T_0 = 1.0$, $q = 0.9$, $\text{Minacc}\% = 5$, $N_r = 90$.

Partially correct symmetry constraints

(F_y and S_y should be zero), $m(\text{Ho})$ fixed to $9\mu_B$.

Number of free parameters: 5;

number of observations: 30 (48 reflections).

Final $T = 0.01$, R -factor (average structure) = 2.3%:

$\{\text{Ho}\} \rightarrow \{F_x, F_y, F_z\}$, $m(\text{Ho}) = [-0.31, 0.33, 8.99]$;
 $\{\text{Ni}\} \rightarrow \{S_x, S_y, S_z\}$, $m(\text{Ni}) = [1.12, -0.30, -1.30]$.

Model 3

$N_{\text{cyc}} = 400$, $T_0 = 1.0$, $q = 0.95$, $\text{Minacc}\% = 1$, $N_r = 300$.

No symmetry constraints, $m(\text{Ho})$ fixed to $9\mu_B$.

Number of free parameters: 7;

number of observations: 30 (48 reflections).

Final $T = 0.014$, R -factor (average structure) = 2.3%:

$\text{Ho1} \rightarrow \{S_x, S_y, S_z\}$, $m(\text{Ho1}) = [-0.26, 0.49, 8.98]$;
 $\text{Ho2} \rightarrow \{S_x, S_y, S_z\}$, $m(\text{Ho2}) = [-0.33, 0.18, 8.99]$;
 $\{\text{Ni}\} \rightarrow \{S_x, S_y, S_z\}$, $m(\text{Ni}) = [1.12, -0.27, -1.32]$.

Panel II

Summary of data and results obtained from the SA technique for $\text{Er}_2\text{Cu}_2\text{O}_5$. See ref. [22] for details of magnetic structure.

$$\text{Er}_2\text{Cu}_2\text{O}_5, \text{Pna}2_1, \quad a \approx 10.78 \text{ \AA}, \quad b \approx 3.47 \text{ \AA}, \\ c \approx 12.45 \text{ \AA}, \quad \mathbf{k} = [0, 0, 0].$$

Four magnetic sites: Er(1), Er(2), Cu(1) and Cu(2) in the primitive cell.

Each site (in general position) has four sublattices.

Results from Rietveld refinement [22]:

basis functions of the magnetic structure: (G_x, A_y, C_z) ;

refined magnetic moments (in μ_B) of representative atoms:

$$\{\text{Er}(1), \text{Er}(2)\} \rightarrow \{G_x^{(1)} + G_x^{(2)}, A_y^{(1)} + A_y^{(2)}, C_z^{(1)} - C_z^{(2)}\},$$

$$\mathbf{m}(\text{Er}) = [0.7(1), -5.5(1), 2.9(1)];$$

$$\{\text{Cu}(1), \text{Cu}(2)\} \rightarrow \{\sim 0, A_y^{(1)} + A_y^{(2)}, \sim 0\},$$

$$\mathbf{m}(\text{Cu}) = [0, 1.2(1), 0];$$

$$R_{\text{Mag}} = 9.4\%.$$

*Results obtained from simulated annealing**Model 1*

$$N_{\text{cyc}} = 300, T_0 = 2.0, q = 0.9, \text{Minacc}\% = 1, N_r = 20.$$

Correct symmetry constraints, $\mathbf{m}(\text{Er})$ and $\mathbf{m}(\text{Cu})$ fixed to $6.2\mu_B$ and $1.0\mu_B$, respectively.

Number of free parameters: 4;

number of observations: 16 (20 reflections).

Final $T = 0.24$, R -factor (average structure) = 4.8%:

$$\{\text{Er}(1), \text{Er}(2)\} \rightarrow \{G_x^{(1)} + G_x^{(2)}, A_y^{(1)} + A_y^{(2)}, C_z^{(1)} - C_z^{(2)}\},$$

$$\mathbf{m}(\text{Er}) = [0.5, -5.4, 3.0];$$

$$\{\text{Cu}(1), \text{Cu}(2)\} \rightarrow \{\sim 0, A_y^{(1)} + A_y^{(2)}, \sim 0\},$$

$$\mathbf{m}(\text{Cu}) = [0.1, 0.99, -0.1].$$

Model 2

$$N_{\text{cyc}} = 300, T_0 = 3.0, q = 0.9, \text{Minacc}\% = 5, N_r = 30.$$

$\mathbf{m}(\text{Cu})$: constrained to be along $[010]$ with symmetry constraints, $\mathbf{m}(\text{Er})$ fixed to 6.2.

Number of free parameters: 17;

number of observations: 31 (38 reflections).

Final $T = 0.14$, R -factor (average structure) = 5.3%.

Local minimum (some atoms had wrong components).

Final (approximate) basis functions and moments (averaged components):

$$\{\text{Er}(1), \text{Er}(2)\} \rightarrow \{C_x^{(1)} - C_x^{(2)}, A_y^{(1)} + A_y^{(2)}, C_z^{(1)} - C_z^{(2)}\},$$

$$\mathbf{m}(\text{Er}) = [0.5, -5.22, -2.9];$$

$$\{\text{Cu}(1), \text{Cu}(2)\} \rightarrow \{0, A_y^{(1)} + A_y^{(2)}, 0\},$$

$$\mathbf{m}(\text{Cu}) = [0, 0.99, 0].$$

Model 3

$$N_{\text{cyc}} = 300, T_0 = 5.0, q = 0.9, \text{Minacc}\% = 10, N_r = 50.$$

No symmetry constraints, all the atoms are independent, $\mathbf{m}(\text{Er})$ fixed to 6.2.

Number of free parameters: 33;

number of observations: 54 (82 reflections).

Final $T = 0.24$, R -factor (average structure) = 10.7%.

Local Minimum (some atoms had wrong components).

Final (approximate) basis functions and moments (averaged components):

$$\{\text{Er}(1), \text{Er}(2)\} \rightarrow \{C_x^{(1)} + C_x^{(2)}, A_y^{(1)} + A_y^{(2)}, G_z^{(1)} - G_z^{(2)}\},$$

$$\mathbf{m}(\text{Er}) = [-0.9, 5.1, 3.0];$$

$$\{\text{Cu}(1), \text{Cu}(2)\} \rightarrow \{C_x^{(1)} + C_x^{(2)}, A_y^{(1)} + A_y^{(2)}, A_z^{(1)} - A_z^{(2)}\},$$

$$\mathbf{m}(\text{Cu}) = [0.3, -0.99, 0.4].$$

Panel III

Crystal and magnetic data for CsMnF_4 . Results obtained from Rietveld refinement of the magnetic structure [29,30].

$$\text{CsMnF}_4, \text{P}4/\text{n}, \quad a \approx 7.91 \text{ \AA}, \quad c \approx 6.31 \text{ \AA},$$

two propagation vectors

$$\mathbf{k}_1 = [0, 0, \delta] \text{ and } \mathbf{k}_2 = [0, 0, \frac{1}{2}].$$

One magnetic site of four sublattices in the primitive cell.

$$\text{Mn}(4d): \quad [1] (0, 0, 0), \quad [2] (0, \frac{1}{2}, 0), \\ [3] (\frac{1}{2}, \frac{1}{2}, 0), \quad [4] (\frac{1}{2}, 0, 0).$$

Magnetic model

Fourier components: $S_{kj} = S_{k1}$ ($j = 2, 3, 4$) for all $\mathbf{k}$.

$$\mathbf{k}_1 = [0, 0, \delta] \rightarrow S_{k1} = \frac{1}{2} m_1 (\mathbf{x} + i\mathbf{y}),$$

$$S_{-k1} = \frac{1}{2} m_1 (\mathbf{x} - i\mathbf{y});$$

$$\mathbf{k}_2 = [0, 0, \frac{1}{2}] \rightarrow S_{k1} = m_2 \mathbf{x} \text{ (or } m_2 \mathbf{y})$$

($\mathbf{x}, \mathbf{y}$ unit vectors along a and b axis).

The magnetic moment of Mn [1] in the cell labelled by the integers (p, q, r) is given by

$$\mathbf{m}_{pqr} = m_1 [\cos(2\pi\delta r), \sin(2\pi\delta r), 0] \\ + m_2 [(-1)^r, 0, 0].$$

The magnetic moment of the Mn varies between the values $m_{\min} = m_1 - m_2$ and $m_{\max} = m_1 + m_2$.

Peak shape model

Caused by an infinite correlation length within the (001) planes ($\xi_{xy} \rightarrow \infty$) and a finite correlation length, ξ_z , along [001]. The angular, lorentzian component, broadening of Bragg reflections is given by

$$\text{FWHM}_L = \lambda \cos \phi / \xi_z \cos \theta$$

where ϕ is the acute angle between the scattering vector and the c axis. The experimental peak shape is voigtian (convolution of gaussian and lorentzian shapes).

Results obtained for samples A and B

$$\begin{aligned} A \rightarrow m_1 &= 3.63(4)\mu_B, \quad m_2 = 0.43(6)\mu_B, \\ \delta &= 0.0135 \quad (\Lambda = 1/\delta \approx 74), \quad \xi_z \approx 400 \text{ \AA}; \\ B \rightarrow m_1 &= 3.57(6)\mu_B, \quad m_2 = 0.79(5)\mu_B, \\ \delta &= 0.0204 \quad (\Lambda = 1/\delta \approx 49), \quad \xi_z \approx 270 \text{ \AA}. \end{aligned}$$

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