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A new protocol for the determination of magnetic structures using simulated annealing and representational analysis (SARA*h*)

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Abstract

The determination of magnetic structures from neutron diffraction data is often carried out by trial and error. Much time is wasted in the examination of structures that are in fact symmetry forbidden. The technique of representation analysis (RA) uses simple matrix calculations to provide model magnetic structures that can arise from a second-order phase transition, but has fallen into misuse because of its tedious nature. New Windows-based code performs these calculations automatically. Integration with refinement packages based on simulated annealing (SA) algorithms allows these models to be fitted against diffraction data. Combination of simulated annealing and representation analysis creates a powerful new protocol for the determination of magnetic structures. © 2000 Elsevier Science B.V. All rights reserved.

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The determination of magnetic structures is a special topic in the research of magnetic phenomena. A large number of trial structures are fitted sequentially against experimental data. These trial structures are typically chosen in an accidental manner, rather than being based on theoretical expectations as a detailed knowledge of the exchange interactions are not generally available. For second-order phase transitions representational analysis [1–3] can be used to determine structures that can occur given a non-magnetic space group and propagation vector $\boldsymbol{k}$. This leads to a reduction in the number of trial structures and often also in the number of refinable parameters.

Representational analysis is based on the Landau thermodynamic theory of a second-order phase transition [4] and involves the systematic decomposition of a magnetic representation Γ of the little group $G_{\boldsymbol{k}}$ into irreducible representations. These calculations are based on the code of KAREP [5]. Basis vectors, ψ^{ν}, are then obtained using a projection operator. SARA*h* performs these calculations automatically given the crystallographic space group, $\boldsymbol{k}$ and the positions of the magnetic sites.

Within the first cell the magnetic phase relating a moment on site j with respect to a reference atom i is given by

$$\phi_{ji} = 2\pi \boldsymbol{k} \cdot (x_j - R x_i). \tag{1}$$

The atomic spin on a particular atom is given by the sum of basis vectors for a particular irreducible representation,

$$S_i^{\boldsymbol{k}} = \sum_{\nu} C_i^{\boldsymbol{k}\mu} \psi_i^{\boldsymbol{k}\mu}, \tag{2}$$

where $C_i^{\boldsymbol{k}\nu}$ is the mixing coefficient for atom i of the basis vector ν. When the basis vectors are complex, appropriate contributions of the basis vectors of the group $-\boldsymbol{k}$ must be included to make the atomic spins real. If we include the translation properties of the magnetic structures and omit the subscript of the atom, for the case of a two-arm channel the atomic vector for an atom in the nth cell related to that in the *zeroth* cell by translation t_n is

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given by

$$S_n^k = S_0^k e^{ikt_n} + S_0^{k*} e^{-ikt_n}. \quad (3)$$

Basis vectors and magnetic phases are calculated for each of the symmetry elements of the paramagnetic space group and given in a refinement file that acts as a summary of all symmetry allowed structures of the magnetic phase. A unique feature of SARA*h* is that refinement is carried out in terms of the basis vector coefficients and so the symmetry of G_k is implicitly taken into account.

An additional problem encountered with magnetic structure determination is the instability associated with least-squares (LS) algorithms. These provide an excellent method for the optimisation of a fit to experimental data, but due to the presence of false minima and susceptibility of the fit to diverge, which are most useful when one is already close to the final structure. To enable the more complete exploration of a trial model an integrated refinement package based on simulated annealing [6] has been written. This is a global search algorithm and samples all regions of phase space with an equal probability. Changes to the magnetic configuration follow a random Markov chain and are accepted on a statistical basis with the probability $e^{-\Delta\chi^2/T}$, where T is a criteria analogous to the temperature of an MC calculation. The related reverse-Monte Carlo (RMC) uses a constant T parameter.

In terms of solving long-range ordered structures reverse-Monte Carlo is widely used only in Full-Prof [7]. SARA*h* differs in that it allows simulated annealing cycles and also lists χ^2 versus model parameters. Thus SARA*h* examines the data rigorously in terms of *only* symmetry allowed structures. Separate minima found in the listing can be further examined by LS optimisation.

Notably, there is no increase in complexity when dealing with incommensurate and modulated structures, e.g. ellipses. Neutron scattering intensity is determined using the general formula of Halpern and Johnson:

$$F^2(\boldsymbol{Q}) = |\boldsymbol{F}_m(\boldsymbol{Q})|^2 - (\boldsymbol{e}\cdot\boldsymbol{F}_m(\boldsymbol{Q}))^2, \quad (4)$$

where $\boldsymbol{F}_M(\boldsymbol{Q})$ is the magnetic structure factor, and $\boldsymbol{e}$ is the unit vector along the scattering vector $\boldsymbol{Q}$.

The combination of simulated annealing and representation analysis techniques creates a powerful new protocol for the determination of the magnetic structures that can arise from a second-order phase transition. The Windows-based software package SARA*h* has been specifically written to perform these calculations automatically within an intuitive GUI environment. While the code is currently restricted to the cases where the groups of $\boldsymbol{k}$ and $-\boldsymbol{k}$ are equivalent, the inclusion of genetic algorithms into the simulated annealing code is being examined as a method for raising this limitation and increasing further the generality of the technique.

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