SPIN-GLASS BEHAVIOUR IN IRON SPINELS
J. Soubeyroux, D. Fiorani, E. Agostinelli, S. Bhargava, J. Dormann

To cite this version:
J. Soubeyroux, D. Fiorani, E. Agostinelli, S. Bhargava, J. Dormann. SPIN-GLASS BEHAVIOUR IN IRON SPINELS. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-1117-C8-1118. <10.1051/jphyscol:19888513>. <jpa-00228720>

HAL Id: jpa-00228720
https://hal.archives-ouvertes.fr/jpa-00228720
Submitted on 1 Jan 1988
SPIN-GLASS BEHAVIOUR IN IRON SPINELS

J. L. Soubeyroux (1), D. Fiorani (2), E. Agostinelli (2), S. C. Bhargava (3) and J. L. Dormann (3)

(1) Institut Laue Langevin, 156X, 38042 Grenoble Cedex, France
(2) Istituto di tecnica, Struttura Elettronica e Comportamento, Spettrochimico dei Composti di Coordination.
Via Salaria 29.5 km, P. O. Box 10, 00016 Monterotondo Stazione, Roma, Italy
(3) Laboratoire de Magnétisme, CNRS, 92196 Meudon, France

Abstract. – The magnetic properties of FeGa2O4, FeAl2O4 and FeIn2S4 have been studied by neutron diffraction, low field susceptibility and Mössbauer measurements. A strong spin-glass character is observed for the sulfide compound while less pronounced for the oxide compounds.

1. Introduction

Systems with spinel structure are good candidates for spin-glass behaviour [1], as different types and degrees of disorder and frustration may be present in the lattice. The disorder may be due to a random magnetic dilution in one of the two sublattices, tetrahedral (A) and octahedral (B), as well as to a random distribution of magnetic ions between the two sublattices. The frustration may be topological in type, as in the antiferromagnetic B-sublattice, like in ZnCr2Ga2-xO4 [2], or due to the existence of competing ferromagnetic and antiferromagnetic interactions, like in ZnCr2In2-xS4 [3].

In the framework of our systematic investigation of the magnetic phase diagram of the spinels [2, 4, 5], we have studied the magnetic properties of three iron spinels, FeGa2O4, FeAl2O4 and FeIn2S4, where the iron ions are differently distributed between the two sublattices, leading to the concomitant occurrence of competing A-A, B-B and A-B interactions.

We have performed neutron diffraction experiments, Mössbauer spectroscopy and susceptibility experiments (DC and AC), which all give evidence of spin-glass like behaviour in the three spinels.

2. Results and discussion

2.1 Neutron diffraction experiments. – Neutron diffraction experiments were performed between 1.5 and 300 K on the multidetector D1B at the ILL, Grenoble. The wavelength used (2.52 Å) allowed a Q range 0.17 – 3.35 Å⁻¹ to be explored without moving the detector.

2.1.1 Crystallographic study. – Allowing for the importance of cation site occupancy on the magnetic interactions we have refined the nuclear structure of the different compounds. The degree of site inversion of cations in a spinel is defined by λ in the formula:

\[
\left( C_{1-2\lambda}^{+2} C_{2\lambda}^{-3} \right)_{A} \left( C_{2-2\lambda}^{+2} C_{2\lambda}^{-3} \right)_{B} O_{4},
\]

where C and C' represent two different types of cations. In table I we have reported the crystallographic results so obtained. The values of λ shows that these compounds have partial inversion with 54 %, 17 % and 95 % of iron atoms on the B site for FeGa2O4, FeAl2O4 and FeIn2S4 respectively.

Table I. – Crystallographic parameters calculated in space group F d-3 m at 5 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>FeGa2O4</th>
<th>FeAl2O4</th>
<th>FeIn2S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.388(1)</td>
<td>8.166(1)</td>
<td>10.616</td>
</tr>
<tr>
<td>u (O or S)</td>
<td>0.2586(4)</td>
<td>0.2649(4)</td>
<td>0.2598(5)</td>
</tr>
<tr>
<td>λ₁</td>
<td>0.268(8)</td>
<td>0.074(9)</td>
<td>0.477(8)</td>
</tr>
<tr>
<td>λ₂</td>
<td>0.258(8)</td>
<td>0.096(9)</td>
<td>0.473(8)</td>
</tr>
<tr>
<td>Average λ</td>
<td>0.263</td>
<td>0.086</td>
<td>0.475</td>
</tr>
</tbody>
</table>

2.1.2 Spin-correlation determination. – The neutron diffraction patterns at 1.5 K do not exhibit any additional Bragg lines. An important modulation of the background is present from 1.5 to 150 K. It has been interpreted on the model of Burlet [6] for spin-spin correlations (SSC) and the different scattering intensities have been analysed as in reference [4, 7]. The parameters cγi obtained from experiments are the product of the number of surrounding i atoms (with spin Si) about a given origin atom (So) with γi, the SSC function in an isotropic model:

\[
γ_i = (3/2) (S_0.S_i) / S (S + 1).
\]

When performing the Fourier transform of the observed difference patterns we found maxima and minima at τi values corresponding to radius vectors between the spin So and the spin Si. Absolute values of the product cγi are obtained by fitting the observed difference cross section with its Fourier transform. The τi values are fixed to radii obtained from the nuclear refinements. The parameters so calculated are given in table II. The variation of these parameters with decreasing temperature leads to a plateau at temperatures close to Tg as determined by the susceptibility measurements. It is interesting to note than for FeGa2O4, 3 parameters only have been used to describe the SSC, that means that SSC are very weak and that explains
Table II. - Interatomic distances and coefficients $c_i \gamma_i$ calculated at 1.5 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>A-A</th>
<th>A-B</th>
<th>B-B</th>
<th>$r_i$ (Å)</th>
<th>$c_i \gamma_i$ (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeGa$_2$O$_4$</td>
<td>3.48</td>
<td>5.14</td>
<td>5.93</td>
<td>6.87</td>
<td></td>
</tr>
<tr>
<td>FeAl$_2$O$_4$</td>
<td>3.39</td>
<td>5.00</td>
<td>5.77</td>
<td>6.69</td>
<td></td>
</tr>
<tr>
<td>FeIn$_2$S$_4$</td>
<td>4.00</td>
<td>6.50</td>
<td>7.50</td>
<td>8.40</td>
<td></td>
</tr>
<tr>
<td>n=6</td>
<td>7.84</td>
<td>8.16</td>
<td>8.80</td>
<td>9.93</td>
<td></td>
</tr>
</tbody>
</table>

The AC measurements at $\nu = 116$ Hz show a maximum at $T_m = 12.2$ K, 13.2 K and 12.05 K for FeGa$_2$O$_4$, FeAl$_2$O$_4$ and FeIn$_2$S$_4$ respectively. In the limited frequency range examined, the frequency dependence of $T_m$ is satisfactory fitted by a Fulcher law, with $\gamma_0 = 10^{-13}$ and $T_0 = 7.4$ K, 8.1 K and 8.4 K for FeGa$_2$O$_4$, FeAl$_2$O$_4$ and FeIn$_2$S$_4$ respectively. The corresponding Fulcher ratios $(T_m-T_0)/T_m$ are 0.39, 0.38 and 0.30 respectively. The static susceptibility measurements show at low temperature a splitting between FC and ZFC curves. A different behaviour is observed for the FC susceptibility, which increases with decreasing temperature for FeGa$_2$O$_4$, remains almost constant for FeAl$_2$O$_4$ and decreases after a maximum for FeIn$_2$S$_4$ (Fig. 1). These differences should reflect a different extent of magnetic correlations in the three spinels.

2.3 Mössbauer measurements. - Mössbauer spectroscopy measurements have been performed between 1.4 and 300 K. The iron populations of the B site determined from 300 K spectra are 0.48±0.02, 0.20±0.05 and 0.97±0.02, for FeGa$_2$O$_4$, FeAl$_2$O$_4$ and FeIn$_2$S$_4$ respectively, in agreement with the neutron diffraction results. A large distribution of the A site quadrupole interaction $\varepsilon_A$ occurs due to the local distortion of the site caused by the random substitution of Fe in the B site. In the case of FeAl$_2$O$_4$, the $\varepsilon_A$ distribution recovers the $\varepsilon_B$ value and then the determination of the B population is less accurate. At low temperature, magnetic enlarged hyperfine spectra appear revealing a hyperfine field $H_{hyp}$ distribution coherent with a disordered magnetic structure. The transition temperature $T_c$ is near 18, 19 and 16 K for FeGa$_2$O$_4$, FeAl$_2$O$_4$ and FeIn$_2$S$_4$ respectively. We have noted an interesting feature for FeAl$_2$O$_4$ where the $H_{hyp}$ variation is not the same with decreasing and increasing temperatures around 12-18 K. This property should be in favour of a weak phase transition near 12 K.