SPIN GLASS BEHAVIOUR OF $FeSbO_4$ STUDIED BY MOSSBAUER AND MAGNETOMETRY

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Abstract

In this paper evidence of a spin glass behaviour in $FeSbO_4$ rutile from susceptibility and hysteresis loop measurements are presented.

The spin glass transition has as a precursor effect a strong deviation of the Curie-Weiss law at $T \leq 20$ T_g which indicates that strong antiferromagnetic spin correlations develop. It is argued that antisite Fe-Sb atomic ordering makes possible that nearest neighbours interactions compete with higher order magnetic interactions.

Introduction

The experimental evidence for a true phase transition in spin glasses seems now fairly convincing[1]. It is apparent, however, that further research of the microscopic mechanisms leading to the spin glass behaviour is very important.

Dilute insulator magnets having different crystallographic and magnetic interactions bear an undeniable interest as a well defined arena for the analysis of the frustration effects leading to the spin glass transition[2].

For instance, previous experimental studies of insulator systems with short range magnetic interactions have shown that magnetic frustration may arise from two different microscopic mechanism: a) competition among ferromagnetic and antiferromagnetic interactions[3,4] or a competition among antiferromagnetic interactions in lattices with a degenerate ground state[5,6]. There are, however, some evidences that a spin glass transition may also occur in dilute antiferromagnetic systems with lattices having a non-degenerate ground state[7,8]. In this paper we present evidence for the spin glass behaviour in a rutile with magnetic and non-magnetic ions, $FeSbO_4$, which must be related to the nearly Heisenberg random dilute antiferromagnetic system $Mn_xZn_{1-x}F_2$[9].

Experimental

The synthesis of the iron antimoniate $FeSbO_4$ was performed by calcination in air at T=1273°K of a precipitate formed by the addition of concentrated ammonia to a mixture of iron(III) nitrate and antimony(V) chloride in nitric acid.

Room temperature powder X-ray diffraction patterns showed a rutile-type crystal lattice (S.G. $P4_2/mnm$) with lattice parameters a=4.63(1) Å and c=3.07(1) Å.

^{57}Fe and ^{121}Sb Mössbauer spectra were obtained with conventional spectrometers in view of characterizing the cationic valences.

The magnetic susceptibility was measured in the temperature range of $4.2 \leq T \leq 900$ °K by using a Faraday balance and a vibrating sample magnetometer in an external magnetic field of H=1 KOe. Zero field cooled (ZFC) and field cooled (FC) processes were investigated in which the magnetic field remains constant while increasing (ZFC) and decreasing the temperature (FC). Hysteresis loop measurements were performed as well after a field cooling (FC) process in the VSM.

Results and discussion

Recent convergent beam electron diffraction studies of the same $FeSbO_4$ sample have shown the existence of superlattice diffraction spots attributed to a Fe-Sb antisite atomic ordering[10]. The new crystal lattice has tripled the c-axis, c=9.23 Å of the original disordered rutile structure and so a tentative model for the atomic ordering has been given in which successive layers of octahedra are obtained (Figure 1).

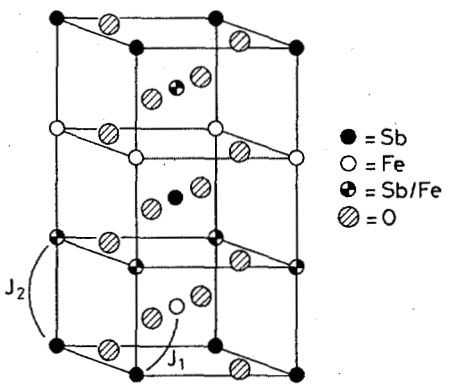

Figure 1: Atomic ordering in $FeSbO_4$ rutile as proposed from convergent beam electron diffraction[10]. Nearest neighbour (J_1) and next nearest neighbour (J_2) exchange interactions are indicated.

As we shall see, the consequences of this atomic ordering on the magnetic properties are straighforward.

The cationic valences of Fe and Sb ions have been determined from ^{57}Fe and ^{121}Sb Mössbauer spectra which show that high spin Fe^{3+} and diamagnetic Sb^{5+} ions coexist in the $FeSbO_4$ rutile. A full account of the Mössbauer spectroscopy analysis will be reported elsewhere.

The temperature dependence of the inverse of the ZFC magnetic susceptibility of $FeSbO_4$ is shown in Figure 2.

In the inset of the Figure 2 the most characteristi "elements" of the spin glass behaviour are observed: a maximun in the ZFC susceptibility at $T_g \simeq 20$ K together with the magnetic irreversibility at a temperature near the freezing temperature. It is apparent that a continous increase of the ZFC susceptibility below T_g does exist. This is a quite typical phenomenon in systems with short range interactions and may be attributed to uncoupled spins or to a randon anisotropy effect[11,12].

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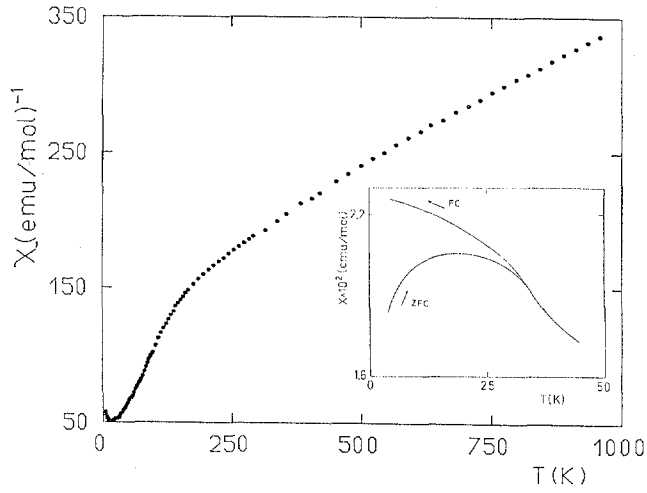

Figure 2: Inverse susceptibility versus temperature of $FeSbO_4$. The inset shows the irreversibility among ZFC and FC susceptibilities measured at 1 KOe.

A further verification of the spin glass behaviour in $FeSbO_4$ has been obtained from the observation of displaced hysteresis loops arising from induced uniaxial anisotropies below T_g after a field cooling process (Figure 3).

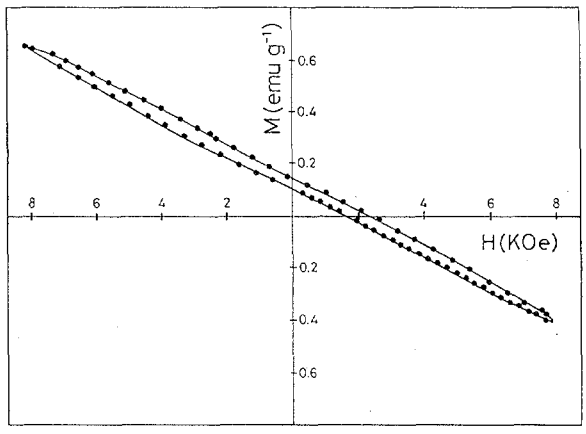

Figure 3: Hysteresis loop of $FeSbO_4$ measured at T=4.2 K after a FC process under H=8 KOe from room temperature.

This arises from the correlation among spin directions and local anisotropy fields which in $FeSbO_4$ are originated probably from dipolar interactions.

This is in fact the source of the Ising character of the rutile antiferromagnet MnF_2[18].

From the observation of the high temperature magnetic susceptibility (Figure 2), three different regions may be distinguished. In the high temperature region T> 600K a Curie-Weiss law $\chi = C/(T+\theta)$ is obeyed with an effective magnetic Fe^{3+} moment

$$\mu_{eff.} = g\mu_B (S(S+1))^{1/2} = 6.0(1)\ \mu_B/\text{ion}$$

corresponding to high spin Fe^{3+} ions and a Curie temperature of θ=580 K indicating very strong antiferromagnetic interactions.

The first nearest neighbour exchange integral value obtained for the MFA was $J_1/k = 25$ in the case of a random cationic distribution and $J_1/k = 50$ in the case of a perfect order as indicated in Figure 1. These values increase slightly if we assume that the antiferromagnetic n.n and ferromagnetic n.n.n. exchange integrals ratio observed in MnF_2 [14] is preserved in $FeSbO_4$. The value of J_1 deduced in the case of an ordered atomic arrangement seems rather large compared to typical exchange interactions in ferric oxides, hence it is very plausible that both, the atomic ordering is not perfect and the higher-order neighbour exchange interactions become non negligible. In this way the magnetic frustration of $FeSbO_4$ leading to the spin glass behaviour is associated with different sign competing interactions or to competing antiferromagnetic interactions.

It is remarkable, in any case, that the effect of the antisite atomic ordering is very important since only in this way do the n.n. and higher-order neighbours exchange interactions have a comparable weight. Furthermore, this is probably the reason for the different behaviour of $FeSbO_4$ as compared to the random antiferromagnet $Mn_xZn_{1-x}F_2$ where the site percolation model gives an accurate description of the magnetic properties[9].

Below T≃ 600K a progressive deviation of the high temperature Curie-Weiss behaviour is observed indicating the developpement of short range correlations among Fe^{3+} magnetic moments. Finally below T≃130K and up to T_g a new Curie-Weiss law is obeyed with $\mu_{eff.} \simeq 3.2\ \mu_B$/ion and θ'=31K. This low temperature paramagnetic-like behaviour has been previously observed in other spin glasses[4,7,15,16] and reflects the existence of relaxing rigid clusters which in our case have predominant antiferromagnetic moments as reflected by the decrease of the effective magnetic moment. The relaxation time of these clusters must be, in any case, much shorter than $\tau \simeq 10^{-8}$s as it is evidenced by ^{57}Fe Mössbauer spectroscopy where any sign of spin relaxation phenomena is seen in this temperature range.

The antiferromagnetic extrapolated Curie temperature θ' observed in this temperature range indicate that the residual exchange interactions among the rigid clusters is still negative and so it is probably a effect of higher-order neighbour antiferromagnetic interactions.

As a matter o fact, this residual magnetic interactions make possible that further magnetic correlation develops along the fractal structure of the exchange paths leading to a cooperative phase transition [17].

As a final conclusion we may state that the $FeSbO_4$ rutile exhibits a behaviour characteristic of the spin glass phase and this is induced by antisite atomic ordering which allows to make comparable the nearest-neighbour antiferromagnetic interaction with higher order neighbours exchange interactions.

We thanks the CAYCIT for finnancial support, contrac number 916/84.

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