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# Short-range antiferromagnetic correlations in spin-glass-like iron antimonate of composition $FeSbO_4$

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**Abstract.** The magnetic susceptibility data recorded from rutile-related iron antimonate of composition $FeSbO_4$ in low applied magnetic fields show features such as susceptibility peaks and irreversibility which are characteristic of spin-glass-like behaviour. A small peak at ~70 K and a broad peak at ~25 K were observed in the zero-field-cooled (ZFC) magnetic susceptibility data. Neutron powder diffraction patterns recorded at temperatures between 160 and 80 K show that antiferromagnetic correlations develop within the (001) plane. The correlation length of the spins increases to a maximum of ~30 Å with decreasing temperature within this temperature range. A saturation of the antiferromagnetic correlation length is observed at temperatures below ~70 K. The results show that the magnetic behaviour of iron antimonate is considerably more complex than the canonic examples of random field Ising systems such as $Mn_{1-x}Zn_xF_2$ or canonic insulator spin-glasses such as $Eu_{1-x}Sr_xS$.

We suggest here that the peak in the ZFC magnetic susceptibility data at ~70 K may be associated with an inhibited antiferromagnetic transition which may be related to the thermally activated dynamics recently observed in different kinds of random magnetic systems. The broad peak at ~25 K may be associated with the dynamic crossover of the magnetic moments without a modification of the antiferromagnetic correlations.

## 1. Introduction

Dilute magnetic insulators of general formula $M_{1-x}Zn_xF_2$ (M = Fe, Mn) have attracted significant attention in recent years because the simplicity of the rutile-related structure renders them suitable as model systems for the examination of fundamental phenomena such as percolation theory [1] or random field distributions [2]. It is also relevant to note that dilute antiferromagnetic oxides have been shown to exhibit spin-glass behaviour [3–5] and, in structures of low symmetry such as the pseudobrookite $Fe_2TiO_5$, have been found to be suitable systems for the study of anisotropic spin-glasses [6].

In this context, the magnetic behaviour of the rutile-related iron antimonate of composition $FeSbO_4$ is interesting because it has magnetic characteristics similar to those of other anisotropic spin-glasses [6] such as $Fe_2TiO_5$ as well as the dilute antiferromagnetic fluorides [2]. Furthermore, we have recently shown [7] the existence of

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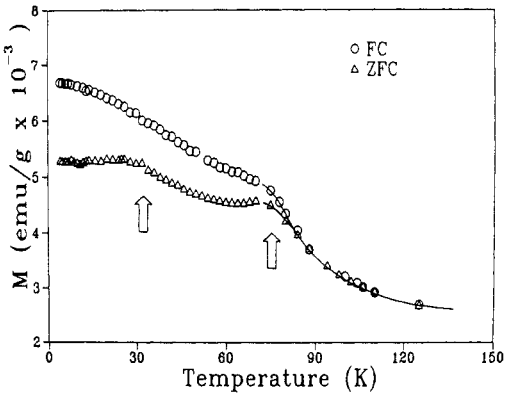


**Figure 1.** Low field ($H$ = 100 Oe) ZFC and FC magnetisation of iron antimonate. The peaks are indicated by arrows.

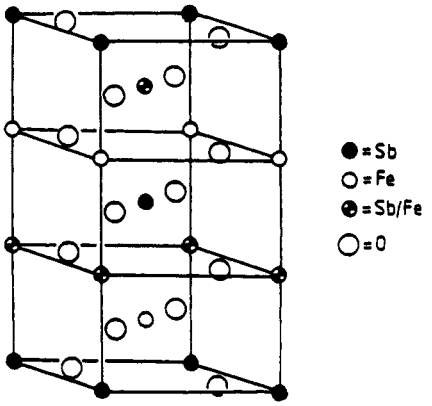


**Figure 2.** Diagram illustrating the positions of the iron, antimony and oxygen atoms in the tripled unit cell of ordered iron antimonate.

antiferromagnetic-like correlations in iron antimonate at temperatures below ~300 K and, at temperatures below ~70 K, a magnetic susceptibility cusp and irreversibility which is characteristic of spin-glass behaviour [3, 5]. However, Mössbauer spectroscopy has shown [8] that at temperatures of ~80 K the spin relaxation time is similar to that of the Mössbauer timescale of ~$10^{-8}$ s. In this paper we present new low-field magnetic susceptibility data recorded from iron antimonate which, together with neutron diffraction results, demonstrate that more complex behaviour occurs in the system than was originally supposed.

## 2. Experimental procedure

Iron antimonate was prepared by methods previously described [7].

Magnetisation measurements involving both ZFC and field-cooled (FC) procedures were performed with a Quantum Design SQUID magnetometer at temperatures between 4.2 and 130 K in applied magnetic fields of 50 and 100 Oe.

Neutron powder diffraction patterns were recorded at the Institut Laue–Langevin with the high-resolution D2B two-axis diffractometer using an incident beam of wavelength $\lambda = 1.5945$ Å and also with the high-flux multidetector D1B powder diffractometer using an incident beam wavelength of $\lambda = 2.52$ Å. The data were collected at several temperatures between 4.2 and 600 K with the D2B diffractometer to complement the magnetic susceptibility data. The diffraction patterns recorded by the D1B diffractometer were accumulated in two minutes with the sample temperature increasing at a rate of 0.7 °C $min^{-1}$. All the diffraction data were analysed by using programs in the STRAP package [9].

## 3. Results and discussion

The temperature dependence of the zero-field-cooled and field-cooled magnetisation of iron antimonate at 100 Oe in the temperature range 4.2 to 130 K is shown in figure 1.

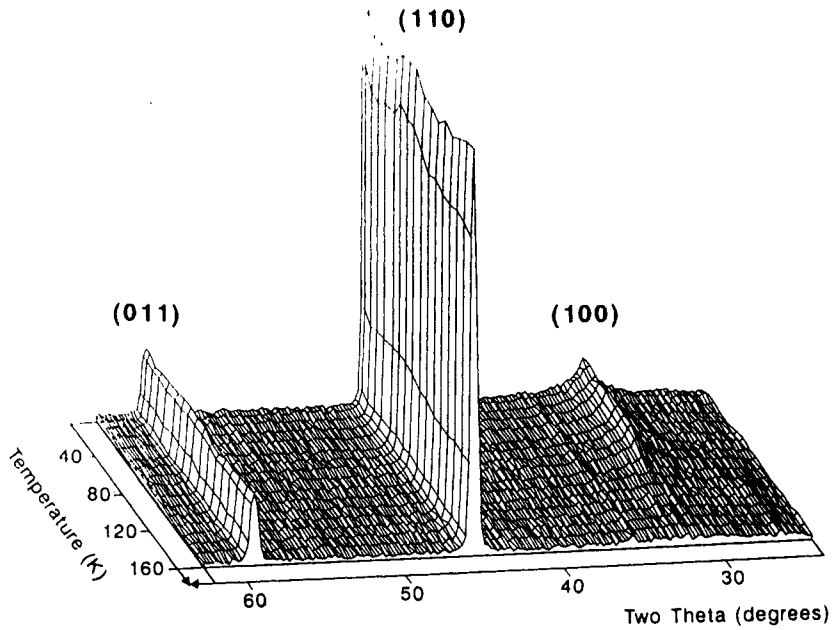


**Figure 3.** Neutron diffraction patterns recorded from iron antimonate between 4.8 and 160 K.

The temperature dependence of the ZFC magnetisation data shows two peaks at ~70 and 25 K. The onset of magnetic irreversibility occurs at a temperature very near to 80 K. The results contrast with those recorded in high-magnetic fields (1 kOe) which showed [10] only a broad maximum at low temperature and clearly demonstrate the high sensitivity of the magnetic susceptibility of iron antimonate to the strength of the applied magnetic field.

The neutron powder diffraction patterns recorded at temperatures exceeding 600 K, where the magnetic susceptibility data showed [7] the absence of antiferromagnetic correlations between the $Fe^{3+}$ ions, displayed no evidence of magnetic interactions. The data could be refined in the space group $P4_2/mnm$ in terms of the rutile-related structure of iron antimonate, $a = b = 4.6370$ Å, $c = 3.0743$ Å, with a disordered distribution of iron and antimony in the octahedral sites. A broad low-angle peak in the neutron diffraction data is consistent with the existence of short-range atomic order in iron antimonate. The result is consistent with evidence recorded by electron diffraction techniques [10] which have shown iron antimonate to contain a superlattice involving the tripling of the unit cell along the $c$ axis (figure 2).

The neutron diffraction patterns recorded at temperatures lower than 160 K were significantly different in that they showed a new broad peak of magnetic origin which could be indexed as (100) in a material with identical lattice parameters to those determined from the neutron diffraction patterns recorded at higher temperatures. The absence of a magnetic contribution associated with the (001) peak (figure 3) is indicative of a highly anisotropic spin structure and resembles results observed in the dilute rutile Ising antiferromagnets of composition $MnF_2$ [11] and $FeF_2$ [12].

The variation of the linewidth of the (100) reflection of magnetic origin with temperature is shown in figure 4. The (100) magnetic peak displayed, even at 4.2 K, a

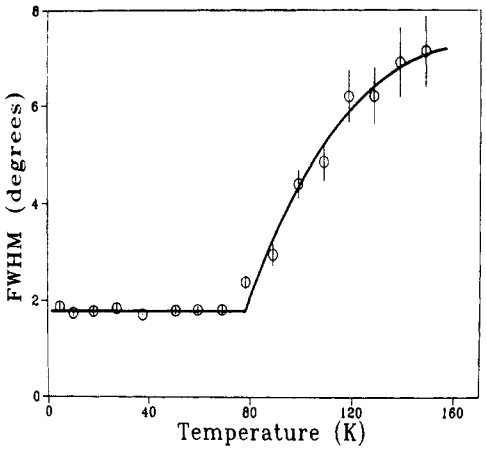


**Figure 4.** Temperature dependence of the experimental full width at half maximum of the (100) peak of magnetic origin.

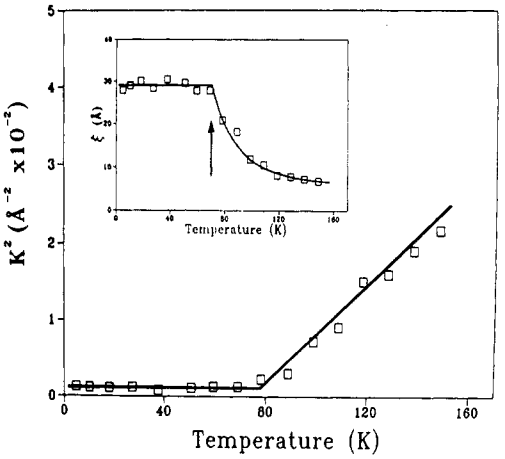


**Figure 5.** Temperature dependence of the squared inverse correlation length showing the validity of the mean-field exponent $\nu = \frac{1}{2}$. The inset depicts the variation of the correlation as a function of the temperature showing the saturation to $\xi = 30$ Å.

linewidth which exceeded the intrinsic experimental resolution of the D2B diffractometer. The result is indicative of a finite antiferromagnetic spin correlation over a short distance within the (001) plane and thereby shows that the magnetic structure of iron antimonate is not amenable to description in terms of long-range antiferromagnetic order. A quantitative estimate of the length of the spin correlation within the (001) plane was achieved by fitting the magnetic peak to a Lorentzian shape convoluted with the Gaussian resolution function, and in figure 5 the spin correlation length as deduced from our fitting procedure as a function of temperature is depicted. The results indicate that a progressive increase of the spin correlation length with decreasing temperature occurs at temperatures above ~70 K whilst, at lower temperatures where irreversibility is observed in the magnetic susceptibility data, the correlation length within the (001) plane saturates to ~30 Å and does not change with decreasing temperature. The temperature dependence of the spin correlation length follows a standard mean-field law [13] $\xi^{-1}\alpha[(T - T_c)/T]^{1/2}$ such that the value of $T_c$ of 70 K agrees with the value deduced from low-field magnetic susceptibility measurements.

It is also notable that features observed here such as magnetic periodicity and magnetic anisotropy have also been observed [11] in the uniaxial antiferromagnet $MnF_2$. The uniaxial spin structure of iron antimonate restricts our knowledge of the spin correlations to the (001) plane and this precludes information about antiferromagnetic order along the *c* axis.

The complex magnetic behaviour of iron antimonate at low temperature is not easily explained in terms of current theories. In the absence of experimental results from single crystals of iron antimonate several interpretations of the magnetic properties of iron antimonate may be suggested. First, it is possible to relate the low-field magnetic susceptibility data and the neutron diffraction data to two- or three-dimensionally inhibited antiferromagnetism. In this situation the observation of magnetic contributions in the low-temperature neutron diffraction patterns only in the (100) reflection may be related to the Ising character of the $Fe^{3+}$ moments which develop antiferromagnetic

correlations either only within the (001) planes (quasi-bidimensional antiferromagnetism) or along all three dimensions. The peak at ~70 K in the ZFC magnetic susceptibility data may then be associated with the two-dimensional antiferromagnetic correlations within the (001) plane whilst the broad peak at ~25 K in the ZFC magnetic susceptibility data may be related to the freezing of the magnetic moments in the third dimension. This behaviour would be analogous to that observed in anisotropic spin-glasses. Given that magnetic scattering is only observed in the (100) reflection, the results suggest that any magnetic correlations perpendicular to the (001) planes would involve distances which are significantly shorter than 30 Å.

An alternative explanation of the magnetic susceptibility and neutron diffraction results can also be made in terms of three-dimensional magnetic cluster formation and can be directly associated with the magnetic susceptibility data recorded from iron antimonate in high magnetic fields which we reported previously [7]. The earlier results [7] showed three regions of magnetic susceptibility behaviour. In the first, which occurred at temperatures between 1000 and 300 K, the data followed a Curie–Weiss law with a magnetic moment of ~6.0 BM/ion and a Curie temperature of ~500 K. At temperatures between ~130 and 70 K a new Curie–Weiss law was obeyed in which the effective magnetic moment of 3.2 BM/ion can be associated with the formation of imperfectly antiferromagnetically ordered clusters of $Fe^{3+}$ ions. We would envisage that the antiferromagnetic interactions within the clusters extend over a maximum distance of ~30 Å. The peak at ~25 K may be associated with the onset of a dynamic crossover which may be related to magnetic interactions between clusters.

Hence, in conclusion, we suggest that the magnetic behaviour of iron antimonate is considerably more complex than that of random dilute antiferromagnets or the canonic examples of random field Ising systems such as $Mn_{1-x}Zn_xF_2$ [2] or canonic insulation spin-glasses such as $Eu_{1-x}Sr_xS$ [5]. The origin of the complex behaviour may be associated with the antisite atomic order which has been identified in iron antimonate by electron diffraction (figure 2) [10]. Such cationic order may result in the next-nearest-neighbour superexchange interactions being of comparable strength to the nearest-neighbour interactions and thereby destabilise the long-range antiferromagnetic ordering but with a magnetic frustration which is insufficient to produce a true spin-glass phase transition where the magnetic correlations are of much shorter range.

Finally, we note the absence of evidence for a true critical antiferromagnetic transition and suggest that this may be related to a dynamic inhibition of the magnetic correlation [14]. This is a feature which has been associated with thermally activated relaxation processes [15] which produce a fast divergence of the characteristic relaxation times and which thereby preclude the development of true infinite-range correlations within the finite experimental time scale. Such an interpretation requires an examination of the critical dynamics of iron antimonate.

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