JOURNAL OF SOLID STATE CHEMISTRY 87, 237–240 (1990)

BRIEF COMMUNICATION

Spin Glass-Type Behavior in Iron Antimonate: The Identification of Unusual Phenomena at Low Temperatures in Low Magnetic Fields

FRANK J. BERRY AND MEGAN I. SARSON

School of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, United Kingdom

JAVIER TEJADA, AMILCAR LABARTA, AND RAUL RODRIGUEZ

Facultat de Fisica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

AND XAVIER OBRADORS

Institut de Ciencia de Materials de Barcelona, Marti i Franques s/u, 08028 Barcelona, Spain

Received January 12, 1990

We recently showed that iron antimonate of composition $FeSbO_4$ undergoes a spin glass transition at ca. 20 K. New magnetic susceptibility measurements which we have subsequently recorded in low magnetic fields of 50 and 100 Oe show that the magnetic behavior at temperatures below ca. 80 K is more complex than was initially observed. Two peaks in the zero field cooled magnetic susceptibility data have been determined at temperatures of ca. 70 and 25 K. Neutron powder diffraction patterns recorded at temperatures below 160 K show a peak of magnetic origin which can be indexed as (100). The absence of a magnetic contribution associated with the (001) peak is indicative of a highly anisotropic spin structure. Analysis of the linewidth of the (100) reflection indicates a finite antiferromagnetic spin correlation within the (001) plane which increases in length to a maximum of ca. 30 Å with decreasing temperature until ca. 70 K when saturation occurs. The low field magnetic susceptibility data and the neutron diffraction results may be associated with an inhibited antiferromagnetic transition. The processes may be associated with the formation at ca. 70 K of clusters of ca. 30 Å of imperfectly antiferromagnetically ordered Fe^{3+} ions and the subsequent onset at ca. 25 K of magnetic interactions between the clusters. © 1990 Academic Press, Inc.

Introduction

We recently described (*1*) how the zero field cooled magnetic susceptibility data recorded between 4.2 and 900 K from rutile-related iron antimonate of formula $FeSbO_4$ in an external magnetic field of 1 KOe shows that the material undergoes a spin glass transition at ca. 20 K. The data, together with results from ^{57}Fe and ^{121}Sb Mössbauer spectroscopy, were interpreted in terms of the formation at low temperatures of imperfectly antiferromagnetically ordered clusters of Fe^{3+} ions.

0022-4596/90 $3.00
Copyright © 1990 by Academic Press, Inc.
All rights of reproduction in any form reserved.

We have now recorded data in smaller applied magnetic fields which, together with neutron diffraction results, show that the magnetic behavior at temperatures below ca. 80 K is more complex than that which we initially described. We report in this communication on the interpretation of the new results in terms of low-temperature magnetic freezing phenomena and emphasize the importance of recording low field magnetic measurements from these types of materials. A definitive account of all aspects of the work, including an examination of the dynamic properties of the system, will appear later.

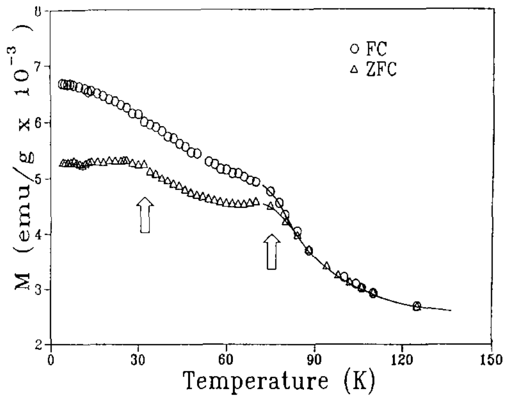

FIG. 1. Temperature dependence of the low field (H = 100 Oe) zero field cooled (ZFC) and field coded (FC) magnetization of iron antimonate. The peak positions are indicated by the arrows.

Experimental

Iron antimonate was prepared by methods similar to those described previously (*1*).

The magnetization measurements 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 several temperatures between 4.2 and 600 K at the Institute Laue-Langevin with the high-resolution D2B two-axes diffractometer using an incident beam of wavelength λ = 1.5945 Å. Diffraction patterns were also accumulated in 2 min with the sample temperature increasing at a rate of 0.7°C/min using the high flux multidetector D1B powder diffractometer with an incident beam wavelength λ = 2.52 Å. All the diffraction data were analyzed by using programs in the STRAP package (*2*).

Results and Discussion

The temperature dependence of the zero field cooled magnetization of iron antimonate, $FeSbO_4$, at 100 Oe in the temperature range 4.2 to 130 K is shown in Fig. 1. The data show two peaks at ca. 70 and 25 K. The onset of magnetic irreversibility occurs at a temperature very near to 70 K. The results contrast with those recorded in high magnetic fields (1 KOe) which showed only the maximum at low temperature (*1*) and clearly demonstrate the high sensitivity of the magnetic susceptibility of iron antimonate to the strength of the applied magnetic field.

The neutron diffraction patterns recorded at temperatures exceeding ca. 600 K where the magnetic susceptibility data showed 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. No evidence of the presence of impurity phases was observed.

The neutron diffraction patterns recorded at temperatures lower than 160 K were significantly different in that they showed a new broad peak which could be indexed as (100) in a material with identical lattice parameters to those determined from the neutron diffraction patterns recorded at higher

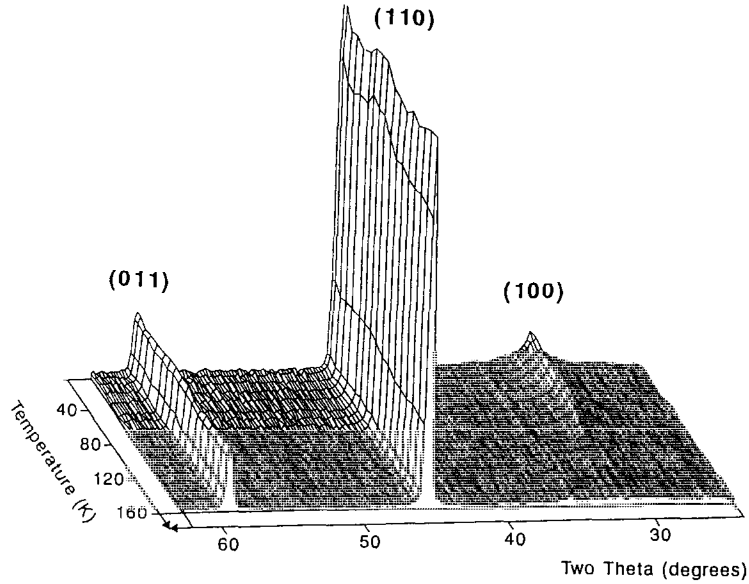

FIG. 2. Neutron powder diffraction patterns recorded from iron antimonate between 160 and 4.2 K.

temperatures (Fig. 2). The origin of this new peak may be associated with short-range atomic order, perhaps similar to that proposed for the cobalt- and manganese-aluminosilicate glasses (*3*), or to short-range magnetic correlations. It is difficult to distinguish between these two possibilities because either or both could produce the observed phenomenon. However, the magnetic susceptibility results reported here show a peak at ca. 70 K which can be associated with the new peak in the neutron diffraction data recorded at low temperature (see below). Hence we suggest that the new (100) peak in the neutron diffraction pattern is of magnetic origin. The absence of a magnetic contribution associated with the (001) peak is indicative of a highly anisotropic spin structure. The linewidth of the (100) reflection of magnetic origin exceeded the intrinsic experimental resolution of the D2B diffractometer even at 4.2 K. 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 antiferomagnetic 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 Fig. 3 the spin correla-

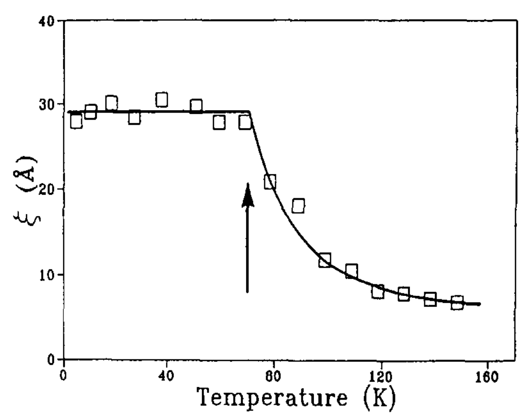

FIG. 3. Variation of the spin correlation length within the (001) plane as a function of temperature.

tion length as deduced from our fitting procedure as a function of temperature is depicted. The results indicate that a progressive increase in the spin correlation length with decreasing temperature occurs at temperatures above ca. 70 K while at lower temperatures, where irreversibility is observed in the magnetic susceptibility data, the correlation length within the (001) plane saturates to ca. 30 Å and does not change with decreasing temperature.

The complex magnetic behavior of iron antimonate at low temperatures is not easily explained in terms of current theories. It is possible to associate the low field magnetic susceptibility data and the neutron diffraction data with inhibited antiferromagnetism such that the peak at ca. 70 K in the ZFC magnetic susceptibility data may be associated with two-dimensional antiferromagnetic correlations within the (001) plane. This behavior would be analogous to that observed in anisotropic spin glasses. Given the observation of magnetic scattering only 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.

The result can also be related to 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 (*1*). The earlier results (*1*) showed that a Curie–Weiss law was obeyed at temperatures between ca. 130 and 70 K which was associated with the formation of imperfectly ordered clusters of Fe^{3+} ions such that each cluster carried a magnetic moment. Hence the first peak at ca. 70 K in the magnetic susceptibility data recorded in low magnetic fields may be related to the formation of clusters of imperfectly antiferromagnetically ordered Fe^{3+} ions. We envisage that the antiferromagnetic interactions within the clusters extend over a maximum distance of ca. 30 Å. The second peak at ca. 25 K may be associated with the onset of magnetic interactions between clusters such as the freezing of the magnetic moments on the imperfectly antiferromagnetically ordered clusters in an ordered fashion.

It is important to record that the plot of the nonlinear terms of the magnetization against field does not show any divergence. Hence we contend that the magnetization data recorded in the temperature range 4.2 to 130 K are not indicative of a phase transition.

Acknowledgments

We thank the SERC, The British Council, and Ministerio de Education Y Ciencia for support.

References

1. F. J. Berry, M. I. Sarson, A. Labarta, X. Obradors, R. Rodriguez, and J. Tejada, *J. Solid State Chem.* **71**, 582 (1987).

2. J. Rodriguez, M. Anne, and J. Pannetier, I. L. L. Internal Report 87R014T (1987).

3. A. F. J. Morgownik, J. A. Mydosh, and L. E. Wenger, *J. Appl. Phys.* **53**, 2211 (1982).