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LETTERS TO THE EDITOR

Spin Glass Transition in Iron Antimonate: The Inducement by Cationic Ordering of Localized Magnetic Order in a Mixed Metal Oxide with a Superlattice

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Iron antimonate, which contains a superlattice composed of an ordered array of cations in the rutile-type structure, has been shown by magnetic measurements to undergo a spin glass transition at ca. 20 K which is induced by antisite cationic ordering. The ^{57}Fe and ^{121}Sb Mössbauer spectra recorded below the spin glass transition temperature show the existence of a supertransferred hyperfine magnetic field on the Fe^{3+} and Sb^{5+} species. © 1987 Academic Press, Inc.

Introduction

Spin glass behavior in solid mixed metal oxides is a relatively new phenomenon (*1*) and, although the experimental evidence which characterizes a spin glass transition is now well established (*2, 3*), the mechanism of spin glass behavior remains the subject of some uncertainty. We report here on evidence from magnetic susceptibility and hysteresis loop measurements for a spin glass transition at ca. 20 K in the iron antimonate of composition $FeSbO_4$ which has recently been shown (*4*) by electron diffraction to contain a superlattice composed of an ordered array of cations such that three rutile-type structures are stacked along the *c*-direction (Fig. 1). This is the first observation of the inducement by cationic antisite atomic ordering of spin glass magnetic ordering. We also report evidence from ^{57}Fe and ^{121}Sb Mössbauer spectroscopy for magnetic ordering between the Fe^{3+} species at temperatures below the spin glass transition temperature and of the presence of a supertransferred hyperfine magnetic field on the Fe^{3+} and Sb^{5+} species. This is the first determination of the supertransferred hyperfine magnetic field in a spin glass. These results constitute a unique set of ob-

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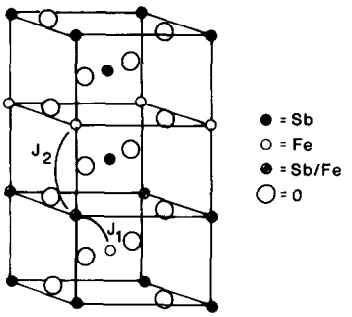

FIG. 1. Atomic ordering in iron antimonate. Nearest neighbor (J_1) and next nearest neighbor (J_2) exchange interactions are indicated.

servations for spin glass behavior in a mixed metal oxide which contains a superlattice.

Experimental

Iron antimonate was prepared by the calcination of a precipitate formed by the addition of aqueous ammonia to stirred mixtures of iron(III) nitrate nonahydrate and antimony(V) chloride at 1000°C (96 hr) in air. Magnetic susceptibility measurements in the range 4.2 to 900 K were performed with a Faraday balance and a vibrating sample magnetometer in an external magnetic field of 1 KOe. Both zero field cooled (ZFC) and field cooled (FC) measurements were recorded. Hysteresis loop measurements were performed at the termination of a field cooled process. The ^{57}Fe and ^{121}Sb Mössbauer spectra were recorded at various temperatures with a microprocessor controlled Mössbauer spectrometer using ^{57}Co/Rh and $Ca^{121m}SnO_3$ sources. All the spectra were computer fitted.

Results and Discussion

The temperature dependence of the inverse of the ZFC magnetic susceptibility of iron antimonate and the irreversible ZFC and FC susceptibilities at 1 KOe are shown in Fig. 2. The maximum in the ZFC susceptibility at ca. 20 K and the onset of magnetic irreversibility at a similar temperature are

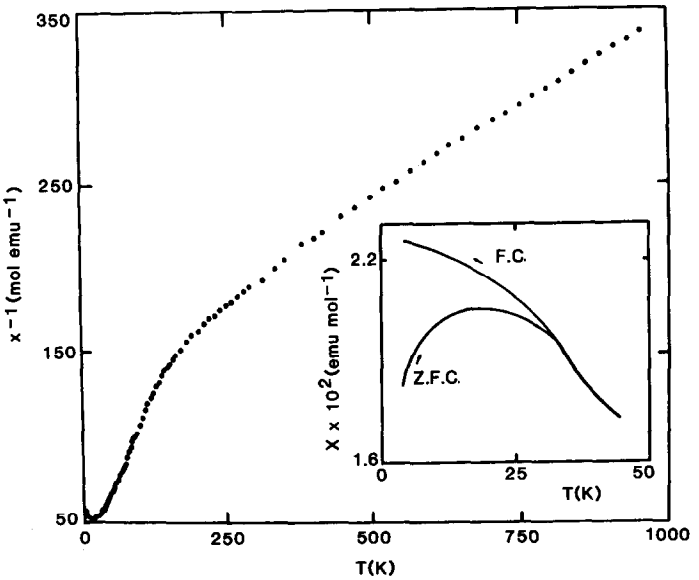

FIG. 2. Temperature dependence of the inverse of the ZFC magnetic susceptibility of iron antimonate. The inset shows the irreversible ZFC and FC susceptibilities at 1 KOe.

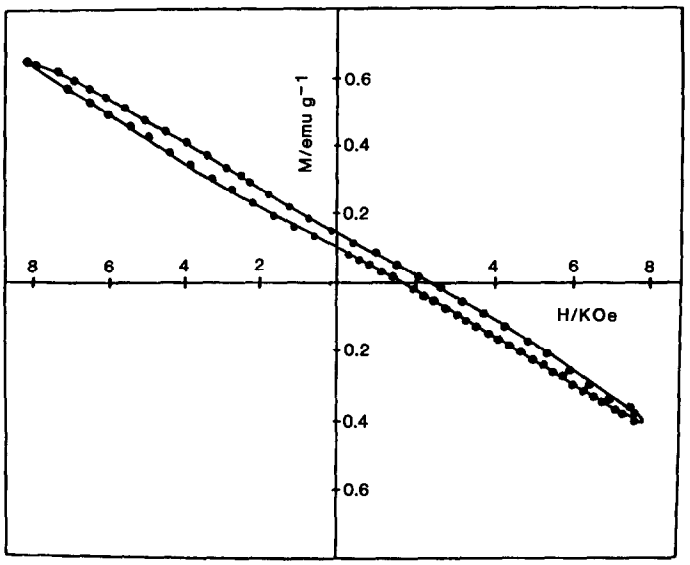

FIG. 3. Hysteresis loop recorded from iron antimonate at 4 K following FC treatment from 298 K at $H = 8$ KOe.

both characteristic of spin glass behavior at this temperature (*5*). The increase in the FC susceptibility as the temperature is decreased below the spin glass transition temperature, T_g, is typical of a system with short-range magnetic interactions (*6*). The displaced hysteresis loop (Fig. 3) is also characteristic of spin glass behavior (*5*).

Three different regions of magnetic susceptibility behavior may be distinguished in Fig. 2. In the region where the temperature exceeds ca. 600 K a Curie–Weiss Law ($\chi = C/T + \theta$) is obeyed with the effective magnetic moment of 6.0(1) BM/ion corresponding to high spin paramagnetic Fe^{3+} and the Curie temperature θ of +580 K being indicative of strong antiferromagnetic interactions. The first nearest neighbor antiferromagnetic exchange integral, J_1/k of −25, which was obtained from mean field analysis (*7*) when the calculation assumed a random distribution of cations over the lattice such that a given Fe^{3+} ion had a mean of four nearest neighbors, was significantly smaller than the value for J_1/k of −50, which was deduced for a situation in which the cations were perfectly ordered (4), i.e., a given Fe^{3+} species had a mean of two nearest neighbors. However, this latter value of J_1/k is large, especially when compared to typical exchange interactions of Fe^{3+} ions (*8*, *9*), and suggests that higher order neighbor exchange interactions are nonnegligible. In this way the magnetic frustration in iron antimonate which gives rise to spin glass behavior at low temperature may be associated with second nearest neighbor antiferromagnetic interactions, J_2, which compete with the first nearest neighbor antiferromagnetic interactions, J_1. It would seem that the antisite atomic ordering between iron and antimony, which increases the number of antimony nearest neighbors to a given Fe^{3+} species from that expected for a random distribution, results in the overall first and second Fe^{3+} nearest neighbor exchange interaction being of comparable magnitude. Hence we suggest the antisite atomic ordering which results from the ordered cationic array in iron antimonate is the origin of the spin glass behavior of iron antimonate.

Below ca. 600 K a progressive deviation of the high temperature Curie–Weiss behavior is observed which indicates the development of short-range magnetic order or spin clusters among the Fe^{3+} species. Finally, at temperatures between 130 K and T_g, i.e., ca. 20 K, a new Curie–Weiss Law is obeyed in which μ_{eff} is ca. 3.2 BM/ion and which shows that the short-range correlations between the Fe^{3+} ions within the clusters are antiferromagnetic in nature. Hence, at temperatures just above that of the spin glass state, the iron antimonate may be envisaged in terms of clusters of Fe^{3+} magnetic moments which each give a fixed overall magnetic moment and which behave as superparamagnetic particles. This low temperature paramagnetic-like behavior has been observed in other spin glasses (*10–13*). The extrapolated Curie temperature θ' of +31 K which is observed in this temperature range is indicative of antiferromagnetic residual exchange interactions between the rigid clusters.

The ^{57}Fe Mössbauer spectra recorded from iron antimonate at 298, 77, and 4 K are shown in Fig. 4. The spectrum recorded at 298 K is characteristic of paramagnetic high spin Fe^{3+} species despite the evidence from the magnetic susceptibility measurements (Fig. 2) that some short-range magnetic order exists at this temperature. The result indicates that the relaxation time of the short-range magnetically ordered clusters is significantly faster than the Mössbauer time scale of ca. 10^{-8} sec and nearer to that of the true paramagnetic, i.e., noninteracting spins, regime of ca. 10^{-13} sec. It would be expected that at lower temperatures the development of spin interactions within the clusters would result in some clusters having relaxation times near to ca. 10^{-8} sec. The broad lined unresolved ^{57}Fe Mössbauer spectrum recorded at 77 K confirms this and shows that at this lower temperature some of the short-range magnetically ordered clusters have a relaxation time comparable to that of the Mössbauer time scale while the remainder retain a faster relaxation time. The spectrum at 4 K is composed of six peaks, indicative of a slow relaxation time regime, and is similar to that reported for other iron-containing oxides below the spin glass transition temperature (*14–16*). The broader linewidths of the outer peaks demonstrate the existence of a hyperfine magnetic field distribution at Fe^{3+} in iron antimonate with a mean value of 487 KOe. This mean value is a little larger than the contact field of 475 KOe evaluated for Fe^{3+} in octahedral sites in garnets (*17*) and suggests that the hyperfine magnetic field in iron antimonate contains a supertransferred contribution from the nearest neighbor Fe^{3+} ions.

The ^{121}Sb Mössbauer spectra recorded from iron antimonate at 298, 77 and 4 K are shown in Fig. 5 and are characteristic of the

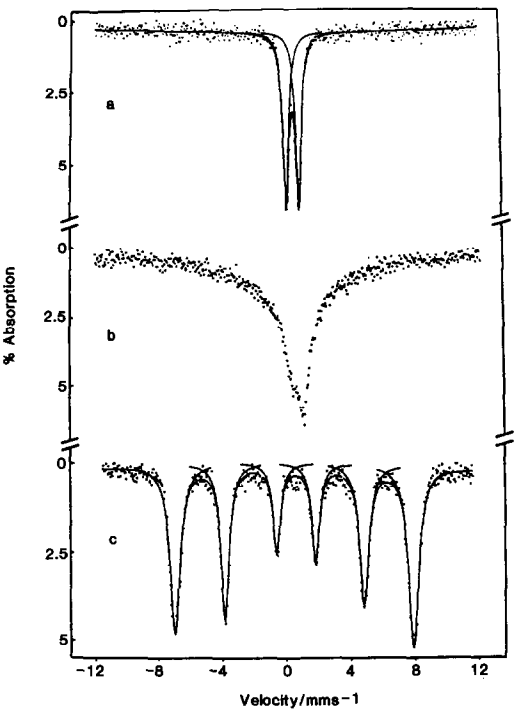

FIG. 4. Iron-57 Mössbauer spectra recorded at (a) 298, (b) 77, and (c) 4 K from iron antimonate.

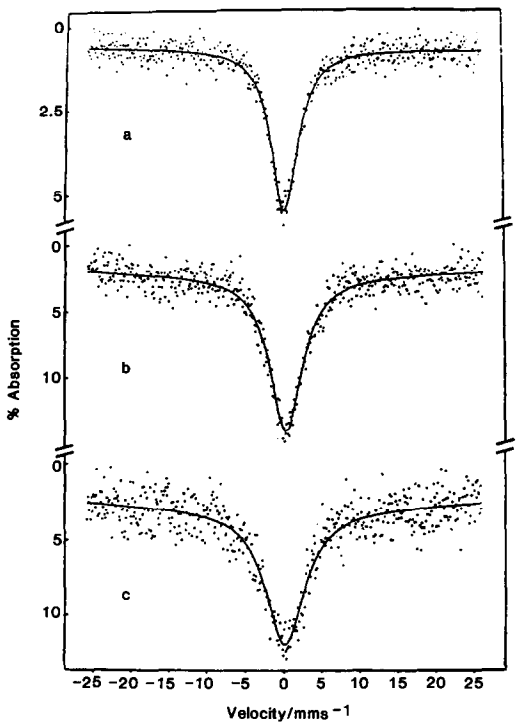

FIG. 5. Antimony-121 Mössbauer spectra recorded at (a) 298, (b) 77, and (c) 4 K from iron antimonate.

presence of Sb^{5+}. It is interesting to note the increase in the linewidth of the single peak at increasingly lower temperatures; indeed the spectrum recorded at 4 K can be fitted to 18 lines. The results are consistent with the presence of a supertransferred hyperfine magnetic field at the Sb^{5+} species of ca. 16 kG. The result is consistent with the detection of the supertransferred hyperfine magnetic field at Fe^{3+} which was observed in the ^{57}Fe Mössbauer spectrum at 4 K.

Acknowledgments

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References

1. D. FIORANI, S. VITICOLI, J. L. DORMANN, J. L. THOLENCE, AND A. P. MURANI, *Phys. Rev. B* **30,** 2776 (1984).
2. K. H. FISCHER, *Phys. Stat. Sol. (B)* **116,** 357 (1983).
3. G. TOLOUSE, *Commun. Phys.* **2,** 115 (1977).
4. F. J. BERRY, J. G. HOLDEN, AND M. H. LORETTO, *J. Chem. Soc. Faraday Trans. 1* **83,** 615 (1987).
5. K. H. FISCHER, *Phys. Stat. Sol. (B)* **130,** 13 (1985).
6. Y. YESHURUN AND H. SOMPOLINSKY, *Phys. Rev. B* **31,** 3191 (1985).
7. J. S. SMART "Effective Field Theories of Magnetism," Saunders, Philadelphia (1966).
8. R. PANTHENET, *Ann. Phys.* **3,** 429 (1958).
9. A. ISALGUE, A. LABARTA, J. TEJADA, AND X. OBRADORS, *Appl. Phys. A* **39,** 221 (1986).
10. R. RODRIGUEZ, A. FERNANDEZ, A. ISALGUE, J. RODRIGUEZ, A. LABARTA, J. TEJADA, AND X. OBRADORS, *J. Phys. C: Solid State Phys.* **18,** L401 (1985).
11. D. BERTRAND, F. BENSANKA, A. R. FERT, I. GELARD, J. P. REDOULES, AND J. LEGRAND, *J. Phys. C: Solid State Phys.* **17,** 1725 (1984).
12. M. ALBA, J. HAMMAN, AND M. NOGUES, *J. Phys. C: Solid State Phys.* **15,** 5441 (1982).
13. E. AGOSTINELLI, P. FILACI, D. FIORANI, AND E. PAPERAZZO, *Solid State Commun.* **56,** 541 (1985).
14. U. ATZMONY, E. GUREWITZ, M. MELAMUD, H. PINTO, H. SHAKED, G. GORODETSKY, H. HERMON, R. M. HORNREICH, S. SHTRIKMAN, AND B. WANKLYN, *Phys. Rev. Lett.* **43,** 782 (1979).
15. J. L. DORMANN, A. SAIFI, AND D. FIORANI, *Hyperfine Interactions* **28,** 561 (1986).
16. H. LASS, J. PEBLER, M. PEKALA, AND A. POLOCZEK, *Phys. Stat. Sol. (A)* **93,** 233 (1986).
17. M. E. LINES AND M. EIBSCHUTZ, *Phys. Rev. B* **30,** 1416 (1984).