Spin-glass behavior in mixed metal oxides with a rutile-type structure

A. Labarta, X. Obradors, and J. Tejada

Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

F. J. Berry and M. Sarson

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

We report here on the magnetic properties of compounds of composition $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ and $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$. The introduction of paramagnetic Cr^{3+} and diamagnetic Ga^{3+} into the rutile-related iron antimonate lattice does not destroy the antisite atomic ordering which exists in iron antimonate of composition FeSbO_4 . The initial slope of the Curie temperature dependence on x is similar in both series, indicating that $\text{Fe}^{3+}\text{-Cr}^{3+}$ interactions are very small. The magnetic susceptibility measurements recorded from the compounds of composition $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$, $x < 0.4$, and $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{SbO}_4$ show them to behave as spin glasses at low temperatures. The inhibition of compounds of the type $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$, $x > 0.4$, and $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$, $x > 0.1$ to undergo a spin-glass transition above 4.2 K is associated with a dilution effect.

INTRODUCTION

We have recently reported¹ on the observation of spin-glass behavior in the rutile-related iron antimonate of composition FeSbO_4 , which contains a superlattice,² and have associated the spin-glass transition with antisite atomic ordering.¹ We are currently accumulating experimental data to increase the general understanding of the mechanisms involved in spin-glass behavior, in this paper we describe the changes in the magnetic properties of this rutile-related material which result from the substitution of the Fe^{3+} species by paramagnetic Cr^{3+} and diamagnetic Ga^{3+} .

EXPERIMENT

The compounds of composition $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ ($x = 1, 0.7, 0.6, 0.4, 0.1$) and $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$ ($x = 0.7, 0.5, 0.3, 0.1$) were prepared by coprecipitation techniques.

^{57}Fe and ^{121}Sb Mössbauer spectra were recorded at various temperatures between 77 and 298 K with a microprocessor controlled Mössbauer spectrometer using $^{57}\text{Co/Rh}$ and $\text{Ca}^{121}\text{SnO}_3$ sources. All the spectra were computer fitted. The magnetic susceptibility measurements were performed in the temperature range between 1.7 and 80 K with a SHE SQUID magnetometer with applied fields up to 100 Oe, and with a Faraday balance in the temperature range between 80 and 1000 K with applied fields up to 5000 Oe.

RESULTS AND DISCUSSION

The magnetic susceptibility data recorded between 1.7 and 1000 K for the compounds of composition $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{SbO}_4$ and $\text{Fe}_{0.6}\text{Cr}_{0.4}\text{SbO}_4$ are shown in Figs. 1 and 2, respectively. The maximum in the zero-field-cooled (ZFC) magnetic susceptibility recorded from

FIG. 1. Temperature dependence of the inverse of the magnetic susceptibility of the compound $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{SbO}_4$.

FIG. 2. Temperature dependence of the inverse of the magnetic susceptibility of the compound $\text{Fe}_{0.6}\text{Cr}_{0.4}\text{SbO}_4$. The inset shows the irreversible zero-field-cooled and field-cooled susceptibilities.

$\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ ($x = 0.1, 0.4$) and $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{SbO}_4$ at low temperatures, together with the irreversible ZFC and FC magnetic susceptibilities at 1000 Oe, suggest that these three compounds behave as spin glasses. Compounds in which the Cr^{3+} concentration exceeds 0.4, or those in which the concentration of Ga^{3+} is larger than 0.1 show no minimum in the low-temperature susceptibility data which suggests the disappearance of the spin-glass behavior or a decrease of the spin-freezing temperature below 4.2 K (Fig. 3).

The ^{57}Fe Mössbauer spectra recorded at 298 and 77 K from the compounds in the series $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$ and $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ were all similar (Fig. 4) and show the presence of high-spin Fe^{3+} cations. The similarities between the chemical isomer shift and quadrupole splitting data recorded from the two series of mixed oxides are consistent with the

antisite atomic ordering which exists in iron antimonate being conserved when Cr^{3+} and Ga^{3+} enter the lattice. The ^{121}Sb Mössbauer spectra recorded at 298 K from all the samples were characteristics of Sb^{5+} . The observation of broadened lines in the spectra recorded at 77 K is indicative of the presence of a supertransferred magnetic hyperfine field at the ^{121}Sb nuclei.²

The magnetic susceptibility data recorded from all the compounds in the high-temperature regime, i.e., $T > 300$ K, obey Curie-Weiss laws which allow an evaluation of both the Curie temperature θ and the effective dipolar magnetic moment μ_{eff} . The results are collected in Table I. The θ value increase with decreasing values of x , and the effective dipolar magnetic moment varies within each series according to the concentration of paramagnetic Fe^{3+} and Cr^{3+} ions or dia-

FIG. 3. Temperature dependence of the inverse of the magnetic susceptibility of the compound $\text{Fe}_{0.7}\text{Ga}_{0.3}\text{SbO}_4$.

FIG. 4. ^{57}Fe Mössbauer spectra recorded from $\text{Fe}_{0.6}\text{Cr}_{0.4}\text{SbO}_4$ at (a) 298 K and (b) 77 K.

magnetic Ga^{3+} ions. The initial slopes of the $\theta(x)$ curves are similar for the two series showing that the magnetic interactions between Cr^{3+} and Fe^{3+} and between Cr^{3+} and Cr^{3+} are very small. Although the results obtained in this high-temperature regime are characteristic of pure paramagnetic behavior, the large values of θ indicate that strong antiferromagnetic interactions exist between the spins. The paramagnetic behavior in both series is conserved until a temperature of 80 K is attained for compounds in which the iron concentration is less than 0.6, i.e., $x > 0.4$. The magnetic susceptibility data for compounds in which $x < 0.4$ begins to deviate from the Curie-Weiss behavior at temperatures below 200 K. The decrease of the effective paramagnetic moment in this regime is indicative of onset of clustering between the individual Fe^{3+} species at these temperatures. However, after a regime in which the data follow a Curie-type dependence on temperature a new straight line relationship with smaller magnetic moments is observed which corresponds to the formation of clusters with antiferromagnetic correlations. The positive θ values of this new Curie-Weiss behav-

TABLE I. Effective magnetic moments per formula unit and Curie temperatures for compounds of composition $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ and $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$ deduced from the high-temperature regime ($T > 300$ K).

x	μ_{eff} (Bohr magnetons)	θ (K)
$\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$		
1	4.01	108
0.7	4.62	189
0.6	4.86	250
0.4	5.29	356
0.1	5.73	446
$\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$		
0.7	3.05	99
0.5	4.09	210
0.3	4.96	347
0.1	5.62	447

ior may be related with ferromagnetic interactions between clusters. In the final temperature regime, i.e., $T < 20$ K, a minimum is observed in the ZFC susceptibility which corresponds to the freezing of the spins. The freezing temperature decreases when x increases, and no minimum in the ZFC susceptibility is observed above 4.2 K in compounds in which $x > 0.4$.

Despite evidence of the cluster formation below 200 K, the Mössbauer data above 77 K do not show any slow relaxation phenomena. The results indicate that the relaxation times of the short-range magnetically ordered clusters are significantly faster than the Mössbauer time scale τ_M .³ Further Mössbauer spectroscopic experiments below 77 K are currently in progress to examine the variation of the relaxation times with temperature. In this respect it is pertinent to note that the broad-lined unresolved ^{57}Fe Mössbauer spectrum recorded¹ at 77 K from iron antimonate, FeSbO_4 , shows that at this lower temperature some of the short-range magnetically ordered clusters have a relaxation time τ comparable to the Mössbauer time scale. It therefore appears that although the introduction of Cr^{3+} and Ga^{3+} into the rutile-type structure does not affect the occurrence of cluster formation, the relaxation times at given temperatures of the clusters in the $\text{Fe}_{1-x}\text{Cr}_x\text{SbO}_4$ and $\text{Fe}_{1-x}\text{Ga}_x\text{SbO}_4$ systems are faster than both τ and τ_M as a consequence of the decrease in the cluster-cluster magnetic correlation.

¹F. J. Berry, M. Sarson, A. Labarta, X. Obradors, R. Rodriguez, and J. Tejada, *J. Solid State Chem.* (to be published).

²F. J. Berry, J. G. Holden, and M. H. Loretto, *J. Chem. Soc. Faraday Trans. 1* **83**, 615 (1987).

³J. A. Mydosh, in *Heidelberg Colloquium in Spin Glasses*, edited by J. L. Van Hemmen and I. Morgenstern (Springer, Berlin, 1983), p. 79, and references therein.