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Reentrant Spin Glass Behavior in Polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-X}Fe_XO_3$

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The magnetic and transport properties of the compound $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($0.1 \leq x \leq 0.4$) have been studied by means of electrical resistivity, AC magnetic susceptibility, and DC magnetization. At low concentrations ($x \leq 0.1$), the system displays essentially para-to-ferromagnetic transitions as the temperature is decreased, although a decrease in the magnetic moment has been observed in previous studies at temperatures a little below T_C. This ferromagnetism is explained by double exchange theory in terms of the formation of Mn^{+3}/Mn^{+4} ions pairs in the system. At concentrations in the range $0.1 < x \leq 0.4$ the system is more complex. Increased Fe doping not only weakens the ferromagnetic (FM) order and augments the resistivity of the samples, but also induces the appearance of a reentrant spin glass phase at low temperatures ($T < 60$ K). Irreversibility of the magnetization measured with zero field cooling and with field cooling has been observed. In addition, the AC susceptibility peak position varies with frequency. All these effects are characteristic of spin glass behavior. The results have been interpreted based in an increase of frustration due to increasing competition between FM Mn^{+3}/Mn^{+4} interactions and antiferromagnetic interactions between ions at the boundaries of Fe clusters.

Keywords: *spin glass, manganite, rare earths*

1. Introduction

The discovery of important effects such as colossal magnetoresistance and rich phase diagrams in manganites of the type $LnAMnO_3$ (Ln = lanthanide: A = alkali metal) enhanced interest in these materials within the scientific community[1-3]. Partial substitution of the lanthanide (trivalent) by the alkali metal (divalent), which results in a double exchange (DE) interaction[4] between the mixed valence Mn^{+3} and Mn^{+4} ions, not only introduces a net concentration of charge carriers into the system, but also changes the Mn-O-Mn bond angle and length, which directly affect the structural, magnetic and transport properties of these systems[5]. Recent studies have concentrated mainly on two groups of these manganites: (1) compounds in which the Ln is partially substituted by another lanthanide; (2) compounds in which the Mn is partially substituted by another transition metal. The latter substitution directly affects the DE interation. The former results in strong lattice distortions that may influence ferromagnetic (FM) DE and antiferromagnetic (AFM) superexchange diferently. In both cases, interesting properties were observed. J. C. Nie *et al.*[6] studied a series of $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$ ($0 \leq x \leq 0.4$) oxides and observed a transition from FM to spin-glass (SG) order as $<r_A>$ decreases, and that, as $<r_A>$ decreases further, the ferromagnetism disappears and a direct transition from superparamagnetic to SG order occurs on cooling. R. Mathieu *et al.*[7] observed a formation of a magnetic disorder state as La is substituted by Nd in $La_{0.96-y}Nd_yK_{0.04}MnO_{3+d}$, reflecting the competition between FM DE and AFM superexchange interactions. Through time dependent zero field cooling (ZFC) magnetization measurements, they confirmed the presence of a reentrant spin glass (RSG) transition (after a transition from paramagnetic to a FM phase), with low field ageing properties in both RSG and FM phases, similar to those observed in archetypal spin glass materials.

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J-Wen Feng *et al.*[8] observed a nonlinearity of reciprocal magnetization (1/M(T)) in the paramagnetic state, indicating clustering of magnetic moments in $La_{1-x}Sr_xMn_{0.8}Ni_{0.2}O_3$ (x = 0.2, 0.3). Jun Takeuchi *et al*[9] studied the effect of Fe doping on the Mn site in $Nd_{0.67}Sr_{0.33}M_{1-x}Fe_xO_3$ ($x \leq 0.3$; M = Mn, Co) and argued that, for x = 0.1, this material shows a spin-glass-like behavior instead of a long-range ferromagnetic order. Results of recent works[10] suggest the formation of AFM clusters of Fe ions in the compound $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($x \leq 0.1$). This was checked by measuring the Weiss constant (θ) as a function of x, from a fit to reciprocal susceptibility in the paramagnetic phase. It was seen that θ decreased rapidly with increasing x, tending towards a negative value. In this work, we present results of measurements of DC electrical resistivity, AC magnetic susceptibility, and DC magnetization on samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ with $0.1 \leq x \leq 0.4$, through which we propose an explanation of how the increase of Fe concentration (and of AFM clusters) leads to an RSG behavior in the system.

2. Experimental Method

Polycrystalline samples were prepared using the sol-gel technique[11] and examined by x-ray diffraction. The results show a single phase perovskite structure.

All the samples were pressed in pellets with 5× 2× 1 mm³ to the measurements. Resistivity was measured by the usual four point method. AC magnetic susceptibility and DC magnetization were measured using a superconducting quantum interference device (SQUID).

3. Results and Discussion

Figure 1 shows curves of magnetization as a function of temperature for x = 0.1, 0.15 and 0.2. AC magnetic susceptiblity measurements yield similar curves. For x = 0.1, the magnetization curve shows essentially FM behavior, as previously seen for lower Fe concentrations[10]. For x = 0.15 and 0.2, the magnetization curves display, at temperatures of about 160 K and 120 K respectively, a behavior similar to that of the paramagnetic/FM transition observed in the x = 0.1 sample at about 270 K. However, at lower temperatures (T < 60 K) the magnetization falls rapidly. The sharp drop in the magnetic moment indicates that the FM phase disappears at these temperatures. The magnetization curves for the x = 0.3 and x = 0.4 (inset Fig. 1) are very similar to each other and display the same behavior as those with x = 0.15 and 0.2 at low temperature (T < 60 K), suggesting that the magnetic phase in this temperature region is similar for these four samples.

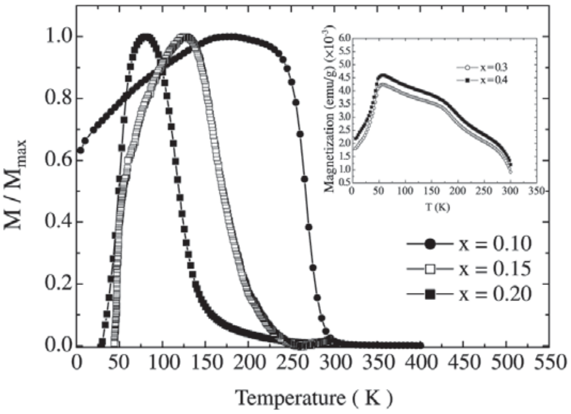

Figure 1. Temperature dependence of the magnetization (normalized to the maximum value) of the system $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ for x = 0.1, 0.15 and 0.2. Inset: Temperature dependence of the magnetization of the system $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ for x = 0.3 and 0.4, using a 50 Oe field.

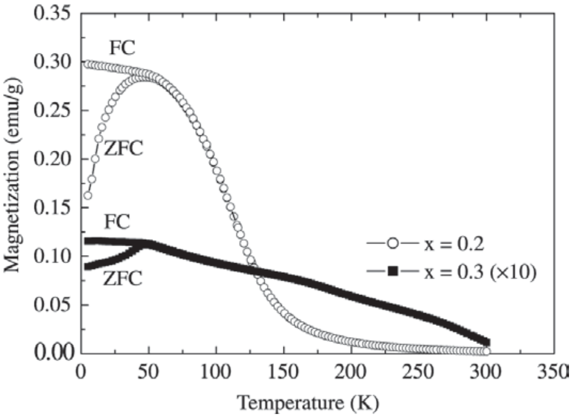

Figure 2. Temperature dependence of the magnetization of the system $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ for x = 0.2 and 0.3 measured for ZFC and FC in a field of 1000 Oe.

Figure 2 shows ZFC and field cooled (FC) measurements for the x = 0.2 and 0.3 samples. Both exhibit a pronounced irreversibility characteristic of SG behavior. In addition, the AC magnetic susceptibility peak position was found change with frequency, it means the peak is shifting towards high temperature as frequency is increased such is expected for an archetypal spin glass system, as shown in Fig. 3. These results lead us to believe that, below 60 K, the samples with x < 0.4 can be characterized by an RSG phase, with a mixture of phases for 0.1 < x < 0.3.

The x = 0.15 sample displays metallic behavior in a the narrow temperature at about 80 K, as shown in the resistivity curve in Fig. 4. This behavior is associated with the magnetism of the material. It is seen that, for this value of x, the compound shows ferromagnetism in a temperature band between 60 K and 160 K. As the metal-insulating transition occurs well below of the para-ferromagnetic transition (as

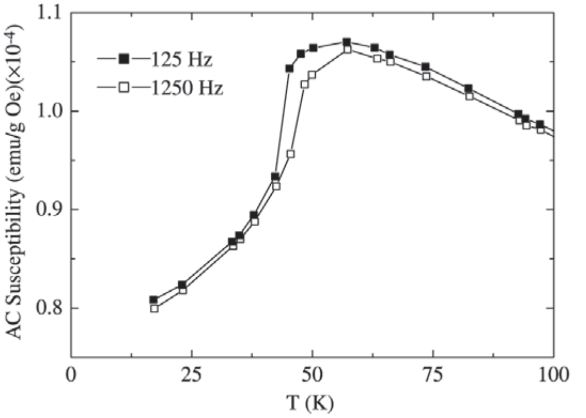

Figure 3. Dependence of the AC susceptibility peak position on frequency for polycrystalline $La_{0.7}Sr_{0.3}Mn_{0.7}Fe_{0.3}O_3$ measured in a 50 Oe field.

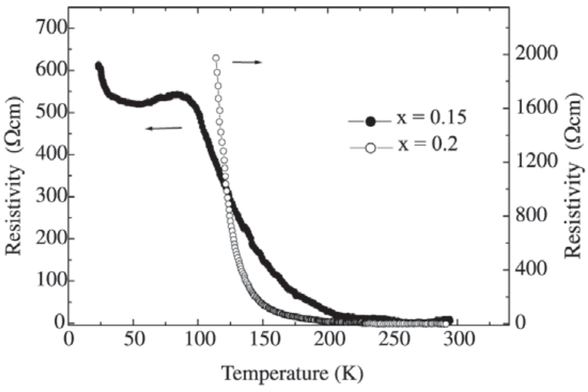

Figure 4. Temperature dependence of the resistivity of the system $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ for x = 0.15 (open circles) and 0.2 (closed circles).

T is decreased), there remains a narrow temperature range in which system can be metallic in character, because DE ferromagnetism is forbidden below 60 K. The x = 0.2 sample, in contrast, is insulating at all temperatures. In this case, FM order occurs in a much narrower temperature band (60 K - 120 K) than that for x = 0.15. For x = 0.3 and 0.4, the samples are insulating at all temperatures. We suggest that this is due to SG ordering, which is inconsistent with DE interactions.

The SG behavior in this system can be attributed to increased frustration as the Fe content is increased. It is known that Fe couples antiferromagnetically[12,13] with its Mn neighbors in these systems, and therefore it does not participate in DE. An increase in the Fe concentration increases the competition between AF superexchange interactions involving Fe ions and the FM double exchange interactions between Mn ions. This leads to a large number of frustrated couplings, so that at a certain x value FM ordering is completely destroyed, and SG behavior occurs. The appearance of an SG transition at a temperature below that of FM ordering characterizes the reentrant spin glass phase.

Sumary

In summary, we have studied the effect of Fe doping on the magnetic and transport properties of the system $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$. An increase of the Fe concentration up to 40% destroys the FM order and induces an RSG behavior at low temperatures. These results have been explained as due to an increase in the number of frustrated interactions, with the addition of Fe due to the competition between the FM coupling between Mn^{+3}/Mn^{+4} ions pairs and the AF coupling between Fe ions.

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