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Transport and magnetic properties in perovskite compound $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$

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Abstract. Magnetic and transport properties of the series $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ ($x = 0$, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1.0) have been investigated. It was found that with increasing Co content, the Curie temperature T_C decreases, while the spin glass transition temperature T_g decreases first then increases. As for the sample with $x = 0.3$, the relation of T_g and the merging point T_m (for the zero-field-cooled and field-cooled magnetization curves starting to merge) with the applied magnetic field H follows a relation $T_j/T_C = 1-\alpha H^{\beta}$ ($T_j = T_m$, T_g), where α and β are constants. The resistivity increases drastically with Co doping and a semiconductor-like behaviour is displayed in the sample $x = 0.3$. These facts strongly suggest that the double-exchange interaction in the perovskite materials is very fragile since a small Co content can change the magnetic and relevant transport properties of the system.

1. Introduction

Recently, the discovery of colossal magnetoresistivity (CMR) effects in materials $R_{1-x}X_xMnO_y$ (where R = La, Pr, Nd; X = Sr, Ca, Ba, Pb) [1–7] has induced renewed interest in these compounds. In these materials different substitutions can lead to different crystal structures, spin states and transport properties. Conventionally, the conductive and magnetic properties of manganese were explained within the framework of the double-exchange (DE) interaction [8], where the itinerant electrons coupled with core spin by a strong Hund rule can transfer between the two core Mn ions which are parallel aligned. The dominant DE interaction can lead to the occurrence of ferromagnetic, metal state and potential CMR effect. Recent experiments exhibit that the magnetoresistance effect of compound $La_{1-x}Sr_xCoO_3$ is due to the transfer of electrons between Co^{3+} and Co^{4+}, where the transfer probability of the electrons depends on the angle between the two Co ions on the adjacent sites [9] (the same as the double-exchange mechanism). An applied magnetic field can force the parallel alignment of the local core spins and reduce the electrons scattering. However, the investigation of $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_y$ revealed that the substitution of Mn by Co dilutes the double-exchange (DE) mechanism and changes the long range ferromagnetic order to a cluster-glass-type ferromagnetic phase [10]. Therefore the CMR effects of Mn-based and Co-based oxides may arise from distinct origins by taking account of their different spin structures and spin states. Some authors [11] found that double exchange alone cannot explain the MR

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effect in Mn perovskite systems, where a Jahn–Teller type electron–phonon coupling must be taken into account. But Co based materials fit in with the trend that relates CMR to charge carrier density [12]. Moreover, there are some materials showing the CMR effect which can be interpreted by other mechanisms [13].

Despite some previous studies on Co-substituted compounds, very little is known about the magnetic field induced effects on the thermodynamics in $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ systems. It is believed that the rearrangement of magnetic moments induced by magnetic field affects not only the physical properties but also the practical applications of the CMR materials. In order to study the magnetic characteristics of CMR compounds, the $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ system is a good candidate because Co has special spin states. In this paper, the effects of the substitution of Co for Mn on the magnetic and transport properties of perovskite compound $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ are reported.

2. Experimental details

$La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ ($x = 0$, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1) were prepared by a standard solid-state reaction method. Stoichiometric mixtures of La_2O_3, CoO, $SrCO_3$ and MnO_2 with nominal purity not less than 99.9% were heated in air at 1250 °C for 20 hours. After being ground they were heated again in air at 1300 °C for 10 hours, then pressed into bars and sintered in air at 1320 °C for 10 hours. The x-ray diffraction data were collected using a rotating-anode diffractometer (Rigaku, D/Max-γA) with Cu Kα radiation. The samples were found to be of high quality single phase.

The magnetizations were measured in both zero-field-cooled (ZFC) and field-cooled (FC) states with different measuring fields ranging from 10 to 10^4 G using a commercial superconducting quantum interference device magnetometer (SQUID). For the measurements of ZFC magnetization, the samples were initially cooled in zero magnetic field from above T_C to the measuring temperature, a magnetic field was then applied and the changes of magnetizations with temperature were collected. The sample size for the magnetic measurements is $2 \times 2 \times 2$ mm^3. The resistivity measurements were performed by a standard four-probe method.

3. Results and discussion

3.1. Magnetic properties

The x-ray powder diffraction patterns show that all samples are in clean single phase with rhombohedral distortion, see figure 1. The relevant structural parameters are summarized in table 1. The lattice parameter a decreases slightly with increasing Co content x which is in agreement with the smaller ionic radius of the Co ion than that of the Mn ion [10]. However, this substitution produces a minor change in the angle α. Figure 2(a) shows the temperature dependence of the dc magnetization M for samples ($0.03 \leqslant x \leqslant 0.5$) measured under a magnetic field of 10 G. The FC and ZFC magnetizations are denoted as M_{FC} and M_{ZFC}, respectively. In the FC curves M_{FC} decreases continuously with increasing temperature, while for the ZFC curves M_{ZFC} increases to its maximum value at temperature T_g (T_g is defined by $\mathrm{d}M_{ZFC}/\mathrm{d}T = 0$), then decreases with increasing temperature. The ZFC and FC curves for each sample split at a temperature T_m. The ZFC and FC magnetization behaviours imply a signature of a spin-glass (SG) state. A similar phenomenon also occurs in the Al-substituted Ca manganites [14]. The spin-glass behaviour often dominates in some semiconductors or alloys at low temperature arising from a locally random competition between ferromagnetic

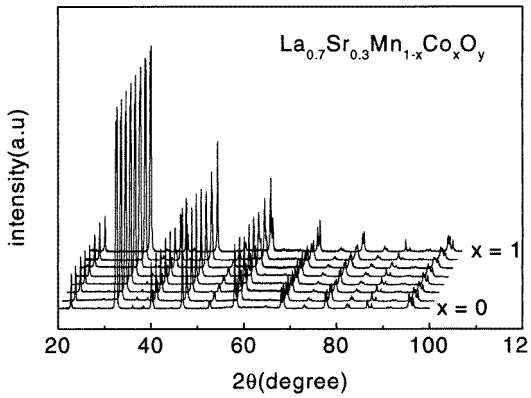

Figure 1. X-ray diffraction patterns of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ for $x = 0$, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1.0 corresponding to lines from bottom to top respectively.

Table 1. Lattice constant a (Å) and angle α versus Co content.

Co	a (Å)	α (°)
0.00	7.772	90.29
0.01	7.781	90.40
0.03	7.763	90.38
0.05	7.764	90.34
0.10	7.762	90.33
0.30	7.749	90.32
0.50	7.717	90.34
1.00	7.676	90.36

(FM) and antiferromagnetic (AFM) force [15, 16]. A gradual reduction in the peak value of M_{ZFC} with increasing Co implies that the long-range ferromagnetic order is suppressed owing to Co presence. It is known that $La_{0.7}Sr_{0.3}MnO_y$ has a proper ratio of Mn^{4+}/Mn^{3+} favouring the electron hopping within the circumstance of parallel aligned Mn ions. A slight Co-substitution at Mn sites may destroy the right ratio of Mn^{3+} to Mn^{4+}, which can modify the ferromagnetic circumstance of mobile carriers. For the M_{FC} curve, an applied magnetic field can induce a reorientation transition of the anti-parallel aligned spins to a parallel aligned spin state, even in a modest field (e.g. 10 G). Upon increasing Co content to near $x = 1$, the ferromagnetism is mainly displayed by Co ions [9, 17], the magnetization and conductivity are due to the transfer of electrons between Co^{3+} and Co^{4+}. For $x = 1$, the value of T_C is 237 K (T_C is obtained by fitting the Curie–Weiss expression in the paramagnetic state) which is approximately the same as the result of [17]. The larger spontaneous magnetization of the low doping sample reveals that the half-filling of Mn core spins has a stronger ferromagnetic coupling mediated by carriers than that of Co ions of the absence of half-filled orbits, so Co ions are magnetically less active. Figure 2(b) shows the cobalt composition dependence of T_C and T_g for all samples. The value of T_C reduces as x increases, showing a general weakening of the ferromagnetic DE interaction and an increasing contribution of AFM interactions arising from superexchange. The spin-glass transition temperature T_g decreases sharply and reaches the minimum at $x = 0.3$ then increases, indicating that with a small amount of Co the ferromagnetic order is suppressed and aligned spins give way to spin-glass behaviour similar to that of the pure cobaltates [17].

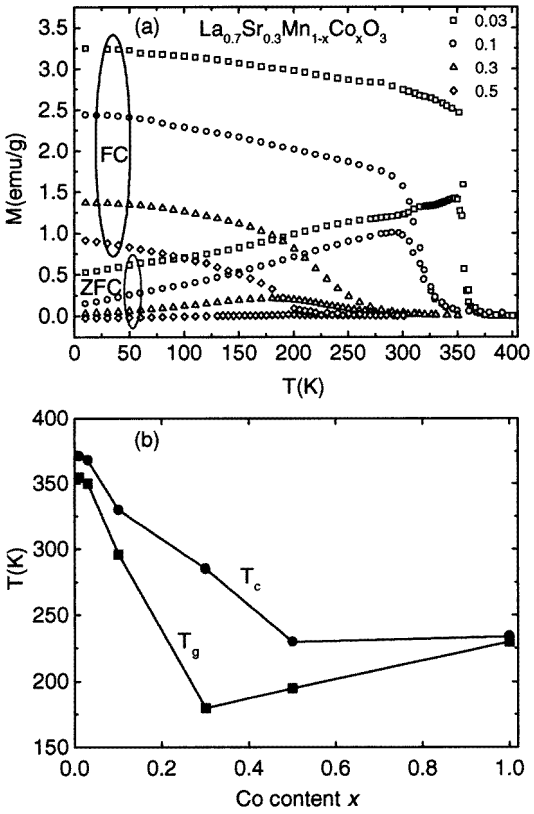

Figure 2. (a) Temperature dependencies of magnetizations for samples $x = 0.03$ (open squares), 0.1 (open circles), 0.3 (open triangles) and 0.5 (open diamonds), measured under a magnetic field of 10 G. (b) Paramagnetic to ferromagnetic transition temperature T_C and the spin-glass phase transition temperature T_g versus Co concentration.

In order to investigate the magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_y$ in more detail, we measured the temperature dependencies of susceptibilities, defined as $\chi = M/H$, for sample $x = 0.3$ under various magnetic fields as shown in figure 3(a). It gives strong evidence that high magnetic fields favour the spin alignment in such a system and suppresses the onset of the spin-glass state. According to the double-exchange scenario the effective transfer interaction is proportional to $\cos(\Delta\vartheta/2)$, where $\Delta\vartheta$ is the relative angle of the local spins. The external applied field forces the local t_{2g} spins ($\Delta\vartheta \to 0$) aligned and hence reduces the spin scattering. Thus a ferromagnetic state can be formed at a relatively low temperature under a magnetic field.

Figure 3(b) shows that both merging temperature T_m and spin-glass phase transition temperature T_g decrease rapidly with increasing field. The magnetic field dependence of T_m and T_g can be well fitted using the following experiential power law,

$$T_j/T_c = 1 - \alpha H^{\beta} \qquad (T_j = T_m, T_g) \tag{1}$$

where $\alpha = 4.91 \times 10^{-3}$, $\beta = 0.53$ for T_m, and $\alpha = 2.55 \times 10^{-1}$, $\beta = 0.15$ for T_g. However, it should be pointed out that the magnetic response to the applied field is not the same for each sample.

The hysteresis curves for the samples with low doping ($x \leqslant 0.05$) are shown in figure 4(a): these curves have similar shape; both the residual magnetization and coercive force are very

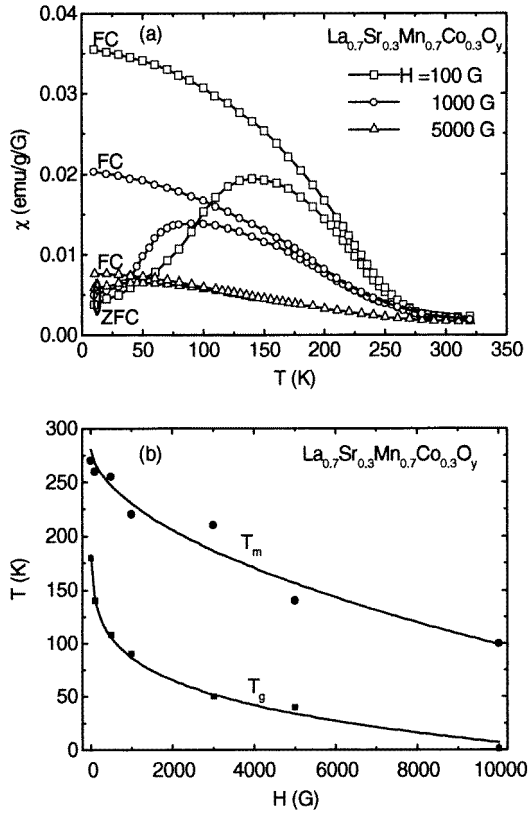

Figure 3. (a) ZFC and FC susceptibility as a function of temperature for $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_y$ compound, $H = 100$ G (open squares), 1000 G (open circles), 5000 G (open triangles). (b) Field dependence of merging point T_m and SG transition temperature T_g. The dots are the experimental data, and the solid lines are the fitting results using equation (1).

small for each sample. It seems to imply that the manganese with low Co doping is still a good soft ferromagnet easy to magnetize. With increasing Co content ($x \geqslant 0.1$), as shown in figure 4(b), there are big changes in the hysteresis curves: in particular for the $x = 0.5$ sample the residual magnetization and the magnetization value at 10^4 G become quite small. The Co composition dependencies of the magnetization M_1 at 10^4 G and the coercive force H_c are shown in figure 4(c). The coercive force increases with increasing Co content for samples ($x = 0.01, 0.03, 0.05, 0.3, 0.5$) then drops for $x = 1.0$, but the magnetization M_1 curve shows a different situation which displays the minimum around $x = 0.5$. It is inferred that the system has a transition in magnetized characteristics around $x = 0.5$. In order to study the influence of Co doped manganese on transport properties we will discuss the temperature dependencies of the resistivities below.

3.2. Resistivity

The temperature dependencies of the resistivities for samples with $x = 0.01, 0.03, 0.05, 0.1, 0.3$ are shown in figure 5. The resistivity values increase rapidly as the Co content increases. For the sample with $x = 0.1$, the resistivity slope changes its sign from positive to negative around 325 K (near $T_c = 330$ K). It can be regarded that the system experiences a metal-to-insulator

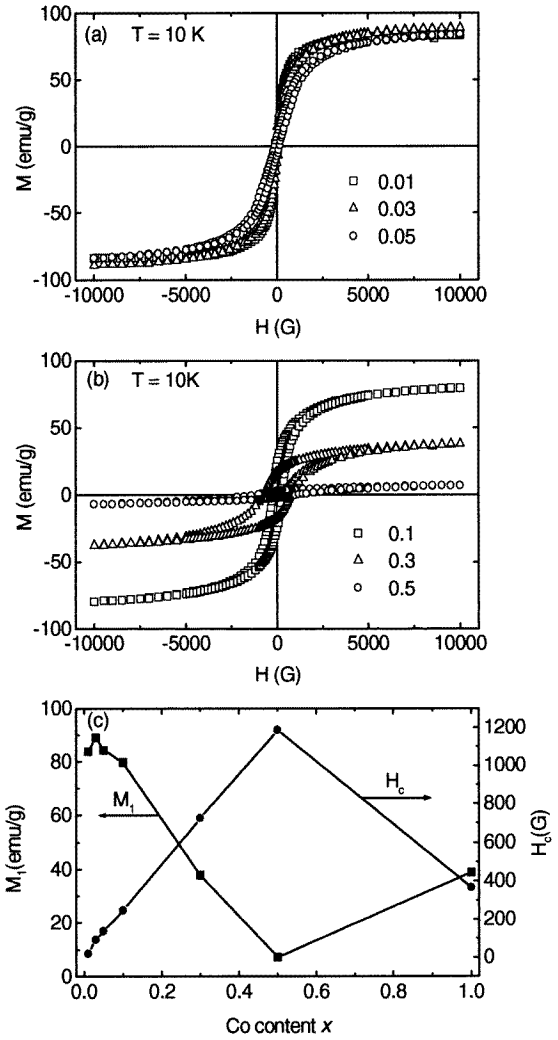

Figure 4. (a) Hysteresis curves for $x = 0.01$ (open squares), 0.03 (open triangles), 0.05 (open circles). (b) The hysteresis curves for $x = 0.1$ (open squares), 0.3 (open triangles), 0.5 (open circles). (c) Co composition dependencies of the magnetization M_1 at 10^4 G and coercive force H_c. The solid lines are guides for the eyes.

transition around that temperature. In addition, as for $x \leqslant 0.1$, each curve displays an anomaly at the temperature range (from 150 to 280 K) lower than T_C, which is similar to that obtained by Hwang *et al* [18]. The anomaly is probably owing to the grain boundary effect [19], but for $x = 0.3$, the situation is quite different, this curve shows a semiconductor-like behaviour, and the magnitude of resistivity is much larger (about one to two orders) than that of slightly doped samples ($x \leqslant 0.1$). At high temperature, the resistivity for $x = 0.3$ can be fitted by the following equation concerning to the hopping of small polarons [20–22]

$$\rho = \rho_0 \frac{T}{T_p} \exp(E_p/T) \tag{2}$$

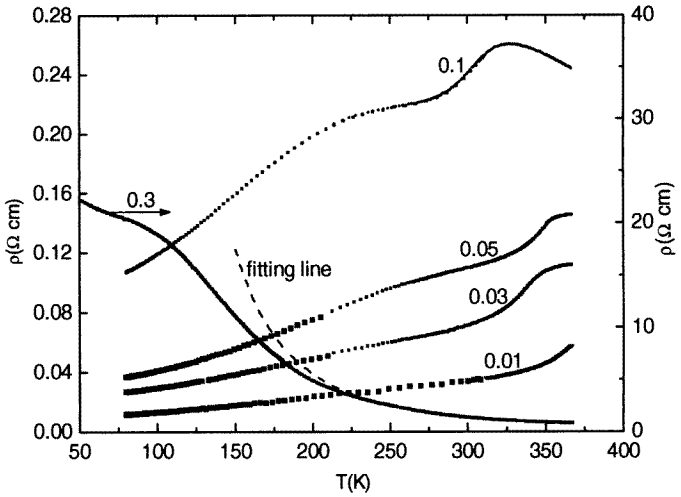

Figure 5. Temperature dependencies of resistivities for samples $x = 0.01$, 0.03, 0.05, 0.1, 0.3. The dashed line is the fitting curve for $x = 0.3$ by equation (2).

with the activation energy $E_p \approx 100$ meV, which is of the same order as the magnitude obtained by Jaime *et al* [21]. As can be seen in figure 5, the fitted line deviates from the experimental data around 250 K, that is lower than T_C (285 K) of the sample. It seems that the small-polaron mechanism is valid in the vicinity of T_C for this system. As the temperature decreases far T_C the variation of resistivity cannot be described alone by the effect of small polarons arising from the strong lattice–electron interaction owing to the Jahn–Teller distortion. With Co doping, the competition between the ferromagnetism and antiferromagnetism plays an important role in the magnetization and transport properties of this compound.

4. Conclusion

In summary, the Co substitution on the Mn site weakens the double-exchange interaction, and the long-range ferromagnetism is thus frustrated and the spin-glass phase appears at temperature lower than T_C. But a small external magnetic field can force the glassy spin parallel alignment at low temperature. The material becomes a semiconductor for $x = 0.3$ and the resistivity magnitude is nearly one to two orders larger than that of the slightly doped systems ($x \leqslant 0.1$).

Acknowledgments

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