Magnetoresistance and magnetocaloric properties of La$_{0.7}$Sr$_{0.3}$Co$_{0.95}$Mn$_{0.05}$O$_3$ compound

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Abstract. The magnetoresistance and magnetocaloric effects were studied via magnetic and electric properties measurements. The ferromagnetic transition temperature and critical exponents, which are determined by analyzing the Arott plots, to be $T_C = 190.665$K, $\beta = 0.456$, $\gamma = 1.0623$ and $\delta = 3.2845$, respectively. Although ferro-paramagnetic transition was observed clearly with $T_C$ of 190 K but the insulating behaviour is remained in a whole in a temperature region of 5 K up to 300 K. Moreover the negative magnetoresistance shows a shoulder at $\sim T_C$, broadens toward lower temperature and reach maximum of 11.5% at 174 K in applied field of 5 T. This result is explained as due to the competing between ferromagnetic and non-ferromagnetic phases in the sample. The magnetization measurements were performed in a narrow temperature range, close to $T_C$ and external magnetic fields up to 4.5T. The adiabatic magnetic entropy changes, $\Delta S$, determined from magnetization data, shows a maximum at $T_C$.

Keywords: Magnetoresistance, magnetocaloric, cobaltite, perovskite.

1. Introduction

Much attention has been devoted to the hole-doped manganite $Ln_{1-x}A_xMnO_3$ and cobaltite $Ln_{1-x}A_xCoO_3$ ($Ln$: lanthanides, $A$: alkali elements) systems that are strongly attractive to research and technology due to their rich physics. Colossal magnetoresistance phenomena were observed in the perovskite-type hole-doped manganites and explained by DE mechanism, phase separation and spin-polarized tunneling effect [1-3]. The chemical randomness or the impurity doping may cause major modifications in the electronic phase diagram as well as in the magnetoelectronic. Besides, magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [4, 5]. Refrigeration in the temperature range 250-300 K is of particular interest due to the potential impact on energy savings and environmental concerns perovskite-type hole-doped manganites in which the double-exchange ferromagnetic metal phase and the charge–orbital ordered antiferromagnetic phase compete with each other. Cobaltites and magnanites are double-exchange ferromagnetic compounds.

Doping on the Mn- or Co-site has been widely used as a method to directly probe the character of the interaction between the magnetic ions. Magnetic and transport properties of Co-doped La$_{0.7}$Sr$_{0.3}$MnO$_3$ were previously reported by several other authors [6, 7]. Although both La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$CoO$_3$ are double-exchange (DE) ferromagnets, the interaction between Mn and Co ions in fact is super-exchange antiferromagnetic (AF), as observed in La$_{0.7}$Sr$_{0.3}$Co$_{1-x}$Mn$_x$O$_3$[8, 9].
The observation of the magnetoresistance in cobaltites is more difficult than in maganites. Moreover the magnetocaloric in maganites is larger than in cobaltites. In this paper we analyze the magneto-caloric and magneto-resistance properties in the mixed perovskite: \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.95}\text{Mn}_{0.05}\text{O}_3\).

2. Experiment

Polycrystalline \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.95}\text{Mn}_{0.05}\text{O}_3\) sample was prepared by the conventional solid-state reaction method. X-ray powder diffraction measurements confirmed the single-phase property of the sample. Temperature dependences of resistivity were measured using a Closed Cycle Helium Refrigerator. Temperature dependent field-cooled, \(M_{\text{FC}}(T)\), zero-field-cooled, \(M_{\text{ZFC}}(T)\), and field dependent magnetization \(M(H)\) measurements were carried out by a SQUID Quantum Design MPMS5 Magnetometer. Resistance measurements are carried out by a 4-probe method, in an OXFORD 2000 system at the Ångström laboratory, Sweden. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field \(H_0\) using the thermodynamic relation:

\[
\Delta S_m(T,\Delta H) = \int_0^{\Delta H} \left( \frac{\partial M(T,H)}{\partial T} \right)_H dH.
\]

3. Results and discussion

Figure 1 presents the temperature dependence of the magnetization of in both two modes: field-cooled, \(M_{\text{FC}}(T)\), and zero-field-cooled, \(M_{\text{ZFC}}(T)\). As seen, there is a cusp in the \(M_{\text{FC}}(T)\) curves and a large separation between \(M_{\text{FC}}(T)\) and \(M_{\text{ZFC}}(T)\) curves with decreasing temperature below \(T_C\). A quite similar behaviour has been observed in \(\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3\), \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\) compound was classified as “cluster glass” (CG) compounds [10]. The ferromagnetic-paramagnetic transition observed for \(x=0\) is at \(T_C=220\) K and the ferromagnetic property of this sample is explained by DE mechanism [1].

![Figure 1. The dependence temperature of \(M_{\text{FC}}\) and \(M_{\text{ZFC}}\) of \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.95}\text{Mn}_{0.05}\text{O}_3\).](image)

The doping 5% Mn for Co ions drastically decreases magnetization value and \(T_C\) decreases down to \(~190\) K. Those results, probably due to the replacement of Mn for Co, cause a dilution of the magnetic network formed by Co-O-Co DE interaction and create a new Mn-O-Co super-exchange interaction competing with the remained DE interaction [8]. The substitution of Mn for Co in low concentration region results in an increase of degree of frustration and disorder.

To understand the essence of phase transition in this sample, we have used Arrott plots derived from magnetization isotherm curves (not shown here) to determine the Curie temperature and critical exponent parameters in the vicinity of phase transition temperature. The critical exponents to be determined are \(\beta\), \(\gamma\), and \(\delta\), among which \(\beta\) describes the temperature dependence of the spontaneous magnetization, \(\gamma\) describe the temperature dependence of the zero-field susceptibility, and \(\delta\) describes
the field dependence of the magnetization at the Curie temperature, $T_C$. The values of $T_C$ obtained in the present investigation match very well those reported in the literature.

In the vicinity of a second-order phase transition with a Curie temperature $T_C$, the scaling laws for the spontaneous magnetization $M_S$ and susceptibility $\chi$ are given by [11-13]

$$M_S(T) = M_0 \left( \frac{T - T_c}{T_C} \right)^\beta, \quad (T < T_C) \tag{1}$$

$$\chi^{-1}_0 = \frac{h_0}{M_0} \left( \frac{T - T_c}{T_C} \right)^\gamma, \quad (T > T_C) \tag{2}$$

These relations define the critical exponents $\beta$ and $\gamma$, where the spontaneous magnetization is determined by $M_S(T) = \lim_{H \to 0} H$ below $T_C$, and the inverse initial susceptibility is determined by $\chi^{-1}_0 = \lim_{M \to 0} \frac{H}{M}$. At the transition temperature, the dependence of the magnetization on the applied field is of the form

$$M = D H^{\frac{1}{\delta}}, \quad (T = T_C)$$

with the critical exponent $\delta = 1 + \gamma/\beta$. The exponent $\delta$ can be obtained from the slope of the log($M$) versus log($H$) plot at $T_C$. The critical exponent as well as the critical amplitudes $M_0$, $h_0/M_0$ and $D$, exhibits the universal behavior near the phase transition point.

![Figure 2](image_url). The $M_S(T)$ and $\chi^{-1}(T)$ derived by extrapolation the Arott plots $M^2$ vs. $H^2$ to $H=0$ and $M=0$ respectively. The solid lines are best fits to equation (1) and (2) in the text.

By extrapolating the Arott plots $M^2$ vs. $H^2$ curves to $H^2=0$ for $T<T_C$ and $M^2=0$ for $T>T_C$, the spontaneous magnetisation $M_S(T)$ and the inverse initial susceptibility values have been recovered. Those results are displayed in the figure 2. By fitting those data to equation (1) and (2) we obtain $T_c = 190.67$ K, $\beta = 0.465$, $\gamma = 1.0623$ and, therefore, $\delta = 1 + \gamma/\beta = 3.2845$. Those values of critical exponents are close to the mean field values ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3$). Hence, we believe that the experimental data agree with the mean-field model.

For ferromagnetic manganites, the conductivity is metallic below $T_C$ but insulating above $T_C$ showing a metallic-insulating (MI) transition and the magnetoresistance is observed at $T_C$, in the consistence with the DE mechanism. However the $\rho(T)$ curve of La$_{0.7}$Sr$_{0.3}$CoO$_3$ merely changes its slope at $T_C$ and still exhibits metallic behaviour in the PM state [8]. This feature is not expected for a typical DE system but can be understood considering the fact that the electronic configuration of the Co ions does not strictly obey Hund’s rule, an ingredient of the DE mechanism. That makes the $e_g$ electron of the Co ions quite mobile in the sense that it can hop between Co sites without strict requirement of a parallel localized-$t_{2g}$-spin configuration or a high applied field. By the way, this is
one of the reasons for the magneto-resistance in cobaltites to be usually small compared to that of the manganites.

As shown in the figure 3, by doping 5% Mn for Co ions, the metallic-insulating transition is observed at $T_C$. In the previous article [8] we suggested that an appreciable amount of the Co atoms is converted to a higher-spin state when an amount of Co ions are replaced by Mn ions in La$_{0.7}$Sr$_{0.3}$CoO$_3$. Moreover, the substitution Mn for Co can decreases the concentration of charge carriers [14]. In the results, the spin configurations of Co ions became more stable. The conductivity then becomes consistent with the DE mechanism. In figure 3, the negative magnetoresistance shows a shoulder at $\sim T_C$ (can be explained by DE mechanism) and broadens toward lower temperature and reaches maximum of 11.5% at 174 K in applied filed of 5T. This result can be a consequence of the competition between metallic-ferromagnetic and insulator-ferromagnetic phases in the sample. It is interesting that the magnetoresistance at low temperatures far from $T_C$ increases as decreasing temperature. This can be explained by spin-polarized tunnelling effect, similar to manganites [3] and the competition of phases in the sample.

In Ref. [15] the maximum value of entropy change is found to be 1.37 J/kgK. This value is smaller than those evidenced in manganites [16, 17]. This can be explained by the existence of various spin states of Co ions and by the broadening magnetic transition in cobaltites. Substitution of 5% Mn for Co can favour the entropy change.
The temperature dependence of magnetic entropy on external applied fields for La$_{0.7}$Sr$_{0.3}$Co$_{0.95}$Mn$_{0.05}$O$_3$ compound is plotted in figure 4. The maximum values of entropy change occur almost around the transition temperature. In our case the maximum value is around 1.41 J/(kg K) in a 4.5T magnetic field. The magnetic entropy changes about 0.43 J/kgK in field of 1T. Despite of small value the entropy change is high enough for technical interest and especially in broad temperature range which is beneficial for active magnetic refrigeration.

4. Conclusions
A metallic-insulator transition is observed in the La$_{0.7}$Sr$_{0.3}$Co$_{0.95}$Mn$_{0.05}$O$_3$. The $T_C$ is fixed at 190.66K and the critical exponents values suggest that the experimental data agree with the mean-field model. The magnetoresistance is observed at $T_C$ and reaches maximum at $T$~174 K, below $T_C$, especially increases in low temperatures far from $T_C$ as decreasing temperature. The magnetoresistance property can be explained by DE mechanism, the competition between magnetic phase and the spin-polarized tunnelling in the sample. The magnetocaloric effect is investigated in this compound. The entropy changes in a broad temperature range are beneficial for active magnetic refrigeration.

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Acknowledgments
This work has been sponsored by the Institute of Materials Science (VAST, Vietnam) and Hong Duc University (Vietnam). L V Bau would like to thank Prof. Per. Nordblad for support and performing the experimental measurements.