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Effect of cobalt on the magnetoresistance characteristics of rare-earth doped manganites*

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The effect of cobalt-doping on the magnetic, transport and magnetoresistance characteristics of $La_{1-x}Sr_xMnO_3$ was investigated. The results show that the magnetoelectric property of rare-earth doped manganites is greatly affected by substitution of Co for Mn sites. The Curie temperature as well as the magnetic moment decreases with the increase of doping concentration, and the samples exhibit obvious characteristics of the spin glass state. Moreover, the magnetoresistance is evidently modulated by doping concentration, and the relevant temperature dependence is also suppressed. In addition, low-temperature magnetoresistance is significantly promoted as doping concentration increases, which renders a value of approximately 50% in the temperature range of 5–200 K and varies within 12.5%. It can be attributed to the effect of spin scattering, induced by cobalt doping, on the itinerant electrons of Mn ions, thus introducing a spin-disorder region into the ferromagnetic region of double-exchange interaction between neighbouring Mn^{3+} and Mn^{4+} ions.

Keywords: cobalt-doped $La_{1-x}Sr_xMnO_3$, spin scattering, magnetoresistance enhancement
PACC: 7550D, 7210, 7530V

1. Introduction

A mixed-valence perovskite-manganite $RE_{1-x}A_xMnO_3$ (RE denotes a trivalent rare-earth ion and A a divalent dopant) can undergo the metal–insulator transition (MIT), accompanied by ferromagnetic–paramagnetic (FM–PM) transition, from a high-temperature insulating phase to a low-temperature metallic phase. The magnetoresistance (MR) of manganite achieves 60%–80% near Curie temperature and even exceeds 80%, exhibiting colossal magnetoresistance (CMR) effect.[1−6] Therefore, it is promising for manganite to be used as magnetic recorder, magnetic detector and magnetic random-access memory (MRAM). However, it is difficult to develop the magnetoelectronic devices based on manganite in the view of application, since the CMR effect appears only under very high magnetic field and the MR shows high temperature and structure dependence.[1] Accordingly, current research works concentrate on improving the CMR effect of manganite and reducing its temperature dependence, so as to obtain materials with high MR and low temperature dependence.

As for the reduction of magnetic field and improvement of CMR effect, great progress has been achieved. Under magnetic field of $8\times10^6/4\pi$ A/m, the MR of bulk $La_{1-x}Ba_xMnO_3$ (LBMO) is only 20%, while that of thin film is nearly 60%. However, the MR of the single crystal manganite and the single crystal thin film shows strong temperature dependence, since the observable MR effect only appears near the Curie temperature (T_C) and almost disappears at temperatures deviating from T_C. It is demonstrated that the CMR effect near T_C originates from magnetic phase separation.[4,5,7,8]

With respect to the reduction of temperature dependence, it is significant to find the low-field magnetoresistance (LFMR) effect in polycrystalline manganite,[9−16] based on spin scattering of conduction electrons induced by grain boundary. The MR of this kind of materials keeps relatively high at $T \ll T_C$, although the peak value appears near T_C; nevertheless, it decreases as temperature rises, thereby rendering strong temperature dependence. In addition, high MR also can be achieved in superlattice thin films

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with $La_{1-x}Sr_xMnO_3$(LSMO) and $SrTiO_3$(STO) alternating architecture and in LSMO/STO/LSMO tunnel junction due to the spin scattering effect. In view of these, the MR of doped manganite can be significantly enhanced by spin scattering.

The spin scattering effect discussed above is based mainly on the doping on La sites in the manganite system. Recently, it has been discovered that the LFMR can also occur by doping on Mn sites. For example, the MR of $La_{2/3}Ca_{1/3}Mn_{0.955}Cu_{0.045}O_3$, obtained by Cu-doping on Mn sites, can reach 90% at $3\times10^6/4\pi$ A/m, while that of $La_{2/3}Ca_{1/3}MnO_3$ is only about 25%.[17] Thus in this paper, $La_{0.8}Sr_{0.2}MnO_3$ was selected and investigated, as a typical double-exchange system. The effect of spin scattering, induced by Co substitution for Mn, on itinerant electrons of Mn ions, as well as on the magnetoresistance characteristics is studied.

2. Experiment

High purity (> 99.9%) chemicals of $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_3{\cdot}6H_2O$ and $Mn(NO_3)_3{\cdot}6H_2O$ were employed as the raw materials to synthesize the desired compounds. The nominal compounds $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ (y = 0, 0.05, 0.1, 0.2, 0.25 and 0.3) and $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ were prepared using the sol–gel method, and the sample preparation process was divided into two steps: powder synthesis and sintering.

Initially the sol was transformed into transparent gel at 130 °C, and then the remnant of organic substance was removed by increasing the temperature up to 300 °C, to form powders. The powders obtained were heat-treated at 900 °C for 12 h in air, and after that characterized by x-ray diffraction (XRD) to confirm single phase. Single phase powders were pressed to produce high density pellets with a diameter of 1 mm, which were sintered at 900 °C for 24 h in air. Subsequently a pressure up to 10^5 kg/cm^2 was slowly applied to these high density pellets to make samples, and slowly unloaded after the pressure was kept a few minutes. These samples were resintered in a high-temperature furnace at 1400 °C for 24 h, at a heating rate of 60 °C/h from room temperature to 1400 °C and a cooling rate of 60 °C/h from 1400 °C to 900 °C. Below 900 °C, the samples were cooled down to room temperature in the furnace. This process was carried out to cause the pellets to be in a partially molten state, so as to form high density samples.

The magnetic and transport properties of the samples were measured by using a superconducting quantum interference device (SQUID) and a physical property measurement system (Quantum Design PPMS-9) in the temperature range of 5–350 K. The resistances of samples with dimensions of $5\times1\times0.5$ mm^3 were measured by the standard four-probe method with magnetic field applied perpendicular to the direction of current.

3. Results and discussion

Figure 1 is the magnetization as a function of temperature for $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ (y = 0.00, 0.05, 0.10, 0.20 and 0.25) measured at $10^5/4\pi$ A/m under zero-field cooling (ZFC) and field cooling (FC) conditions. We can see that the Curie temperature significantly decreases as the cobalt doping concentration increases. On the basis of the Curie–Weiss law $1/\chi = C/(T-\Theta)$, the values of T_C for the sample of y = 0.00, 0.05, 0.10, 0.20 and 0.25 are 336, 280, 260, 240 and 220 K, respectively, suggesting a linear relation between T_C and cobalt doping concentration. In addition, the magnetic moment gradually reduces with the increase of doping concentration, and the discrepancy between ZFC and FC curves becomes more and more obvious. According to the results for $La_{1-x}Sr_xCoO_3$ ($0\leq x \leq 0.18$) and $La_{0.46}Sr_{0.54}Mn_{1-y}Cr_yO_3$ ($0\leq y \leq 0.08$),[18,19]

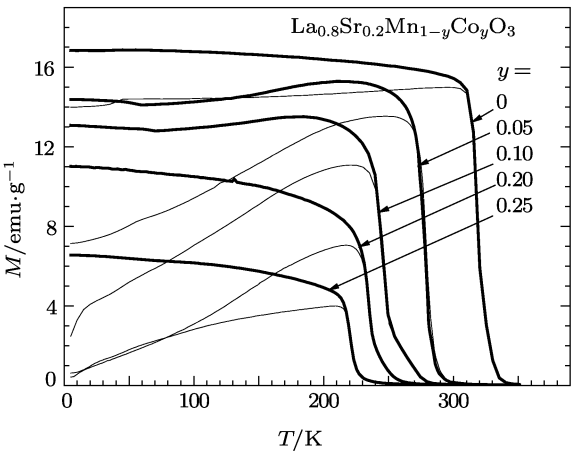


Fig.1. Magnetization as a function of temperature for $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ (y = 0, 0.05, 0.10, 0.20 and 0.25) measured at $10^5/4\pi$ A/m under zero-field cooling (thin lines) and field cooling (thick lines) conditions.

the samples exhibit the characteristics of the spin glass state. Since the spin glass state originates from the

competition between ferromagnetic and antiferromagnetic interactions, it manifests the existence of competition between ferromagnetic coupling induced by double-exchange interactions of e_g electrons of Mn ions, and antiferromagnetic coupling between Co ions and itinerant electrons of Mn ions. According to the Kondo theory, this kind of antiferromagnetic coupling can cause a spin scattering effect on itinerant electrons, therefore it is reasonable to study the effect of spin scattering, induced by Mn-site doping, on magnetoresistance properties by using these samples.

The results indicate that the long-range ferromagnetic order, induced by double-exchange interaction between neighbouring Mn^{3+} and Mn^{4+} ions, is destroyed by Co substitution for Mn sites,[20,21] and these ferromagnetic regions will contract with the increase of doping concentration. Therefore, the samples can be used to study the effect of spin scattering due to Mn-site doping on the magnetoresistance characteristics.

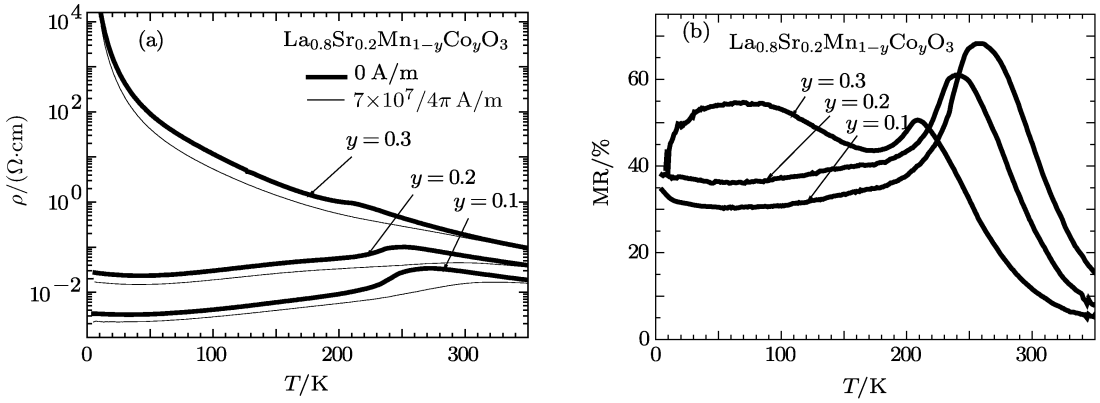


Fig.2. (a) Electrical resistivity as a function of temperature for $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ ($y = 0.10$, 0.20 and 0.30) under zero field cooling at 0 A/m (thick lines) and $7\times10^7/4\pi$ A/m (thin lines); (b) Relevant temperature dependence of magnetoresistance at $7\times10^7/4\pi$ A/m.

MR is defined as follows:

$$\mathrm{MR}(\%) = \frac{\rho(T, H=0) - \rho(T, H)}{\rho(T, H=0)} \times 100\% \quad (1)$$

where $\rho(T, 0)$ and $\rho(T, H)$ are the resistivities at zero magnetic field and at a magnetic field of H, respectively.

Figure 2(a) illustrates the temperature dependence of resistivity for $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ ($y =$ 0.10, 0.20 and 0.30) under zero field cooling at 0 A/m and at $7\times10^7/4\pi$ A/m, and the corresponding value of MR calculated by Eq.(1). The MR as a function of temperature is displayed in Fig.2(b).

Figure 2(a) illustrates the resistivity of samples, increasesing remarkably with doping concentration, which is in agreement with the variation of magnetic moment shown in Fig.1. The transport characteristics of each sample were obtained on the basis of the following two relations: the temperature dependence of metal resistivity $\rho(T) \propto T^2$, where T^2 is the scattering relation between electrons, and the temperature dependence of insulator resistivity $\rho(T) \propto \exp(E_a/k_B T)$, where k_B is Boltzmann's constant and E_a is activation energy. Metal–insulator transition occurs near 260 K and 240 K for the samples of $y = 0.1$ and 0.2 under $H = 0$ A/m, respectively, the temperature of which obviously corresponds to that of ferromagnetic–paramagnetic transition displayed Fig.1. It is apparent that the resistivity of the sample is reduced due to magnetic field, while the transition temperature is increased, which can be interpreted by the double-exchange model and the Anderson–Hasegawa relationship.[22,23] Furthermore, the low-temperature transport property shows typical insulator characteristics when the doping concentration is increased to $y = 0.3$, demonstrating that the critical Co-doping concentration is around 0.2.

Figure 2(b) exhibits that there is an evident peak value of MR for each $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ ($y =$

0.10, 0.20 and 0.30) sample, though the MR increases, and the peak value decreases with increasing doping concentration. The relevant peak values are 70%, 62% and 50% for doping concentration of 0.1, 0.2 and 0.3, respectively, and the pertinent temperatures are 255, 240 and 210 K, adjacent to their respective T_C. Moreover, the low-temperature MR is greatly affected by doping concentration, which increases with increasing cobalt content. The maximum MR's in the temperature range of 5–200 K are 30%, 38% and 55% for $y = 0.1$, 0.2 and 0.3 respectively. It indicates that the MR of LSMO can be modulated by cobalt doping.

In order to investigate the effect of cobalt doping on the temperature characteristics of MR, δMR is defined as follows:

$$\delta\mathrm{MR} = \frac{\mathrm{MR}^{\max} - \mathrm{MR}^{\min}}{\mathrm{MR}^{\max}} \times 100\% \qquad (2)$$

where $\mathrm{MR}^{\max}$ and $\mathrm{MR}^{\min}$ are the maximum and minimum values of MR at $T \leq T_{\mathrm{MI}}$, respectively. Accordingly, the δMR of $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ is calculated to be respectively 56%, 40% and 31% for $y = 0.1$, 0.2 and 0.3, suggesting that the temperature dependence of MR is suppressed by cobalt doping.

The above results indicate that cobalt doping can improve the MR value in low temperature range and reduce the MR value near T_C. Consequently, it can be expected that relatively low temperature dependence of MR is achievable in the whole temperature range of $T \leq T_C$ by cobalt doping. Based on the above results, a sample with cobalt concentration of 0.25, was chosen and studied, which could render metal transport characteristics at low temperatures by varying Sr doping content, in order to further investigate the effect of spin scattering on itinerant electrons on MR property.

Figures 3(a) and (b) are the plot of resistivity and MR of $La_{1-x}Sr_xMn_{0.75}Co_{0.25}O_3$ ($x = 0.2$ and 0.3) as functions of temperature, where the MR is calculated by using Eq.(1). It demonstrates that the transport property of $La_{0.8}Sr_{0.2}Mn_{0.75}Co_{0.25}O_3$ is similar to that of $La_{0.8}Sr_{0.2}Mn_{0.7}Co_{0.3}O_3$, and can be converted from insulator to metal at 200 K when Sr doping concentration increases to 0.3. This indicates that the critical doping concentration of $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ is $y = 0.2$, while that of $La_{1-x}Sr_xMn_{0.75}Co_{0.25}O_3$ is $x = 0.3$.

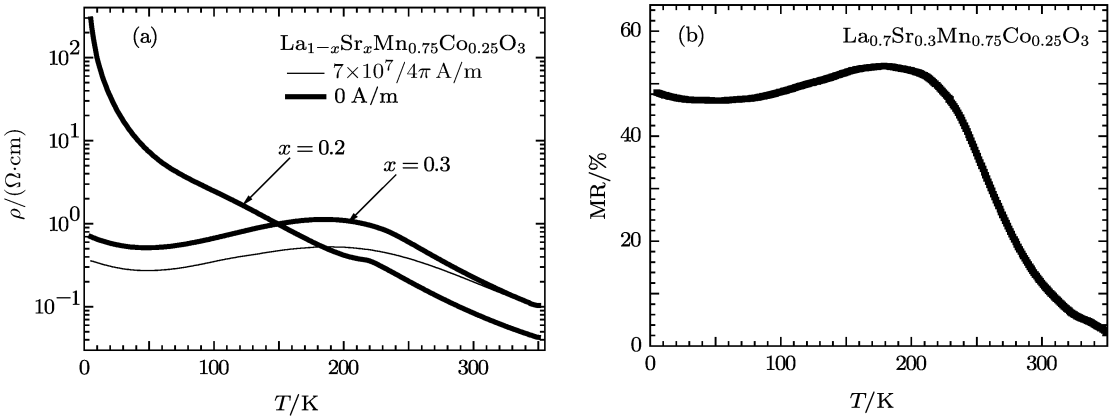


Fig.3. (a) Resistivity as a function of temperature for $La_{1-x}Sr_xMn_{0.75}Co_{0.25}O_3$ ($x = 0.20$ and 0.30) under zero filed cooling at 0 A/m (thick lines) and $7\times10^7/4\pi$ A/m (thin line); (b) Relevant temperature dependence of magnetoresistance at $7\times10^7/4\pi$ A/m.

In addition, the MR peak value of $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ is 55%, which is obviously lower than that of $La_{0.8}Sr_{0.2}Mn_{1-y}Co_yO_3$ ($y = 0.1$ and 0.2). However, the corresponding MR value in the temperature range of 5–200 K is remarkably higher by 48% and 38% than that of the samples of $La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_3$. Moreover, the variation of MR is only 12.5%, calculated using Eq.(2). The results show that the effect of spin scattering on itinerant electrons is enhanced as cobalt doping concentration increases, thus increasing the low-temperature MR value.

Besides the effect of spin scattering on itinerant electrons induced by cobalt ions, there may exist the competition of various interactions between Coulomb effect, exchange effect and Jahn–Teller effect; furthermore, the variation of bond length and angle of Mn–O–Mn bonds reduces the energy gap of e_g electrons, thus resulting

in the instability or interactions of other electrons that compete with double-exchange interactions, for example charge-orbital ordered states, super-exchange interactions etc., especially the effect of phase separation on CMR that has been gradually clarified recently.[7,8] Although the temperature range of steady MR and the high applied magnetic field cannot meet the requirement of applications, the strong temperature dependence of MR in single crystal and polycrystalline manganite is reduced after all, and the spin-disorder region is introduced into the microstructure of the materials without complicated experimental techniques. These may be helpful for future research on this sort of material.

4. Conclusion

The effect of cobalt doping on the magnetic, transport and magnetoresistance characteristics of $La_{1-x}Sr_xMnO_3$ has been studied in the present work. The results of magnetic property measurement indicate that ferromagnetic order, induced by double-exchange interactions between neighbouring Mn^{3+} and Mn^{4+} ions, is destroyed, as a consequence of the competition between antiferromagnetic coupling of Co ions and e_g itinerant electrons and ferromagnetic coupling of Mn^{3+} and Mn^{4+} ions, hence exhibiting obvious characteristics of the spin glass state in the doped system. The results of transport and MR measurement demonstrate that metal–insulator transition occurs in low-temperature region with the increase of cobalt doping concentration, due to the spin scattering effect of cobalt ions on the itinerant electrons of Mn ions, and cobalt doping within the critical doping concentration significantly enhances the low-temperature MR and effectively suppresses the temperature dependence of MR.

References

[1] Urushibara A, Moritimo Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 *Phys. Rev.* B **51** 14103

[2] Tokura Y, Urushibara A, Moritimo Y, Arima T, Asamitsu A, Kido G and Furukawa N 1994 *J. Phys. Soc. Jpn* **63** 3931

[3] Kanki T, Tanaka H and Kawai T 2003 *J. Appl. Phys* **93** 4718

[4] Jain M, Li Y, Hundley M F, Hawley M, Maiorov B, Campbell I H, Civale L and Jia Q X 2006 *Appl. Phys. Lett.* **88** 232510

[5] Jain M, Shukla P, Li Y, Hundley M F, Wang H, Foltyn S R, Burrell A K, Mccleskey T M and Jia Q X 2006 *Adv. Mater* **18** 2695

[6] Fäth M, Feisem S, Menovsky A A, Tomioka Y, Aarts J and Mydosh J A 1999 *Science* **285** 1540

[7] Zhang L W, Lsrael C, Biswas A, Greene R L and de Lozanne Alex 2002 *Science* **298** 805

[8] Li X W, Gupta A, Xiao G and Gong G Q 1997 *Appl. Phys. Lett.* **71** 1124

[9] Hwang H Y, Cheong S W, Ong N P and Batlogg B 1996 *Phys. Rev. Lett.* **77** 2041

[10] Schiffer P, Ramirez A P, Bao W and Cheong S W 1995 *Phys. Rev. Lett.* **75** 3336

[11] Zhang N, Ding W, Zhong W, Xing D Y and Du Y W 1997 *Phys. Rev.* B **56** 8138

[12] Wang X L, Dou S X, Liu H K, Lonescu M and Zeimtz B 1998 *Appl. Phys. Lett.* **73** 396

[13] Peng H B, Zhao B R, Xie Z, Lin Y, Zhu B Y, Zhao Z, Ni Y M, Tao J H, Dong X L and Xu B 1999 *Appl. Phys. Lett.* **74** 1606

[14] Bibes M, Hrabovsky D, Martinez B, Fert A R, Trlik V, Varela M and Fontuberla J 2001 *J. Appl. Phys.* **89** 6958

[15] Zies M, Martinez B, Fontuberla J, Trlik V, Benitez F, Sarchiz F and Varola M 1999 *Appl. Phys. Lett.* **74** 1481

[16] Bibes M, Martinez B, Fontuberla J, Trlik V, Benitez F, Sarchiz F and Varola M 1999 *Appl. Phys. Lett.* **75** 2120

[17] Yuan S L, Yang Y P, Xia Z C, Liu L, Zhang G H, Feng W, Tang J, Zhang J L and Liu S 2002 *Phys. Rev.* B **66** 172402

[18] Dho Joonghoe, Kim W S and Hur N H 2002 *Phys. Rev. Lett.* **89** 027202

[19] Wu J and Leighton C 2003 *Phys. Rev.* B **67** 174408

[20] Edwards S F and Anderson P W 1975 *J. Phys.* F **5** 965

[21] Kondo J 1969 *Solid State Physics* **23** 183

[22] Zener C 1951 *Phys. Rev.* **82** 403

[23] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675