Magnetic and transport properties of $La_{1-x}Sr_xCoO_{3-\delta}$ ($0.15 \leqslant x \leqslant 0.5$) films prepared by laser ablation

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The magnetic and transport properties of $La_{1-x}Sr_xCoO_3$ films prepared by laser ablation have been investigated. It was found that a metal-insulator transition is observed at a Sr doping of $x \leqslant 0.25$. The analysis of experimental results shows that the transport of carriers in the metallic state is governed by the electron-electron scattering, taking into account the origin of a small energy gap in the spectrum of electron excitations. In the insulating state the transport of carriers is governed by the Mott-like variable-range hopping. Possible mechanisms for the negative magnetoresistance observed for the films are also discussed.

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I. INTRODUCTION

Interest in strontium-doped lantanium-cobalt oxides, $La_{1-x}Sr_xCoO_3$, has been motivated by the high electrical and the excellent ionic conductivity that make them a good candidate for electrode materials in fuel cells and for ferroelectric memory devices.[1] Recently a large negative magnetoresistance (MR) has observed in $La_{1-x}Sr_xCoO_3$ thin films with a doping of $0.15 < x \leqslant 0.40$, which stimulated reinvestigation of this perovskite system because of new applications to magnetic field sensors.[2–4]

$La_{1-x}Sr_xCoO_3$ belongs to a family of compounds with mixed valency. The parent compound $LaCoO_3$ is a charge-transfer-type insulator in which a charge gap is formed between the occupied O $2p$ band and the unoccupied Co $3d$ e_g band.[5] The crystal-field splitting ($10Dq$) between the t_{2g} and e_g states and the Hund coupling energy lead to a temperature-dependent spin-state transition between the high-spin ($t_{2g}^4 e_g^2$ with $S=2$) or, more likely, the intermediate-spin ($t_{2g}^5 e_g^1$ with $S=1$), and low-spin ($t_{2g}^6 e_g^0$) states around 100 K with an activation energy (i.e., spin gap) of 0.02–0.03 eV.[6] Substitution of Sr^{2+} for La^{3+} in $La_{1-x}Sr_xCoO_3$ induces alteration of the Co valency from Co^{3+} to Co^{4+} and introduction of mobile holes in the valence band.[4]

The complicated magnetic and electronic phase diagram invokes a baffling complexity in interpreting the transport properties. Even though the transport properties of $La_{1-x}Sr_xCoO_3$ have already been studied for a long time,[7–9] the mechanism of conductivity continues to be a matter of controversy.

II. EXPERIMENTAL RESULTS

$La_{1-x}Sr_xCoO_3$ films were prepared by pulsed laser deposition.[10] The substrate was a $SrTiO_3(100)$ single crystal. The substrate temperature during deposition was $\simeq 850\,^{\circ}C$. The oxygen pressure in the chamber was 450 mTorr during deposition and 750 Torr during cooling. At these conditions $La_{1-x}Sr_xCoO_3$ films were produced with a thickness of 200 nm. The specular θ–2θ x-ray diffraction (XRD) was performed using a Rigaku diffractometer with Cu K_α radiation. The resistance measurements were carried out by using the four-probe method in a temperature range of 4.2–300 K and a magnetic field up to 5 T. The magnetization in a field up to 100 Oe was obtained with a Quantum Design superconducting quantum interference device (SQUID) magnetometer in a temperature range of 4.2–300 K.

Figure 1 presents the θ–2θ XRD scans for four $La_{1-x}Sr_xCoO_3$ films with four kinds of compositions: $x = 0.15$, 0.25, 0.35, and 0.5 (from bottom to top in Fig. 1). The high intensity of $(00l)$ peaks shows that the deposition results in a highly c-oriented film. Therefore, in spite of the presence of (011), (022), and (112) peaks with much smaller intensities all the samples can be treated as chemically homogeneous epitaxial films. The analysis of XRD data reveals that all films have a pseudocubic crystal structure with the following parameters: $c \simeq 0.3835$ nm ($x=0.5$), 0.382 nm

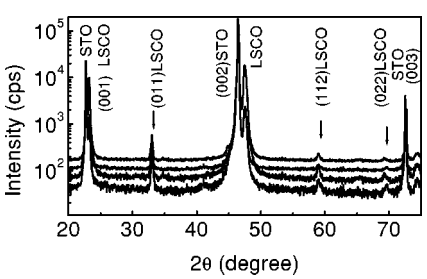

FIG. 1. θ–2θ XRD patterns for $La_{1-x}Sr_xCoO_{3-\delta}$ films: $x = 0.15$, 0.25, 0.35, and 0.5 (from the bottom).

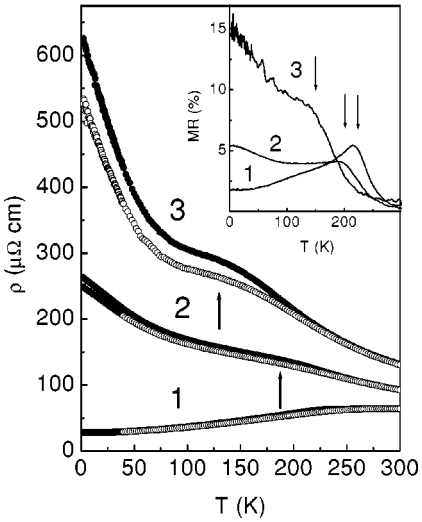

FIG. 2. Temperature-dependent resistivity for (1) $La_{0.65}Sr_{0.35}CoO_3$, (2) $La_{0.75}Sr_{0.25}CoO_3$, and (3) $La_{0.85}Sr_{0.15}CoO_3$ films measured in a magnetic field of zero (solid) and 5 T (open). The inset displays the magnetoresistance ratio for these films in a perpendicular magnetic field of 5 T.

($x=0.35$), 0.3809 nm ($x=0.25$), and 0.3798 nm ($x=0.15$), which are very close to the published results.[4,11]

Figure 2 shows the temperature dependence of resistivity, $\rho(T)$, without (solid circles) and with (open circles) an applied magnetic field of 5 T, for the films. (1) $La_{0.65}Sr_{0.35}CoO_3$, (2) $La_{0.75}Sr_{0.25}CoO_3$, and (3) $La_{0.85}Sr_{0.15}CoO_3$. The $\rho(T)$ curves do not differ from the data obtained for the bulk compounds,[6] except for two peculiarities. First, the absolute value of resistivity for our films is significantly smaller than that for the bulk materials. Second, the metal-insulator (MI) transition in our case is observed at a larger doping of Sr. The prepared film with $x=0.25$ already shows a semiconducting behavior of the conductivity (curve 2 in Fig. 2), while, according to the literature data,[6,9] in the bulk materials the MI transition was observed for $x \leqslant 0.2$. We are suggesting that two reasons can be given for the observed difference in the critical doping concentration between the film and bulk. First, the lattice strain that accumulates during deposition of the film can lead to a slight distortion of the crystal lattice (a change in the Co-O-Co angle, for example) and induce an altered Sr concentration for the MI transition.[12] On the other hand, the metal-semiconductor (or insulator) transition in the film could be induced by a reduction in the oxygen content.[10,13,14]

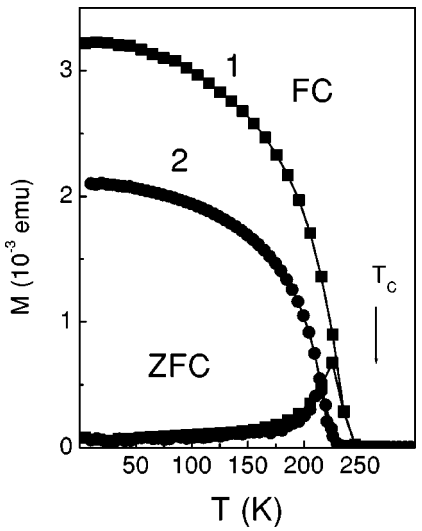

FIG. 3. Field-cooled and zero-field-cooled magnetization curves for (1) $La_{0.5}Sr_{0.5}CoO_3$ and (2) $La_{0.65}Sr_{0.35}CoO_3$ films measured at an in-plane magnetic field of 100 Oe. Solid lines are drawn to guide the eyes.

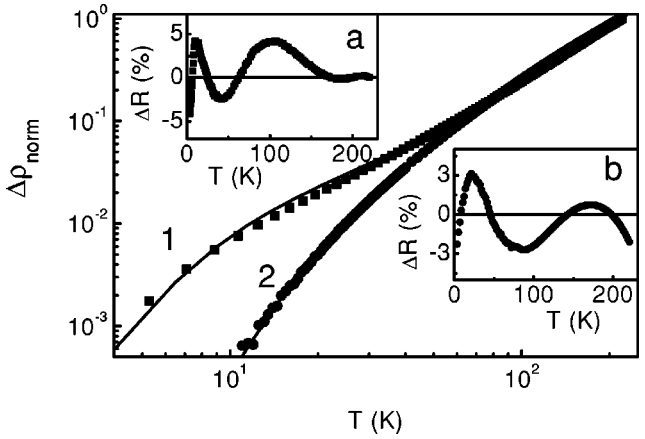

FIG. 4. Temperature-dependent normalized resistivity for (1) $La_{0.5}Sr_{0.5}CoO_3$ and (2) $La_{0.65}Sr_{0.35}CoO_3$ films. The solid lines are theoretical curves described in text. Inset (a) and (b) display the relative difference between experimental and theoretical data for both films, respectively.

The inset of Fig. 2 displays the temperature dependence of the negative MR for the $La_{1-x}Sr_xCoO_3$ films with the following compositions: (1) $x=0.35$, (2) $x=0.25$, and (3) $x=0.15$. The MR value (in percent) was estimated by the formula $100\% \times [R(0)-R(H)]/R(0)$, where $R(0)$ and $R(H)$ are the film resistance without and with a magnetic field of 5 T, respectively. The figure shows that the MR value sharply increases in the low-temperature range with decreasing the Sr doping and achieves a maximum for the films with the semiconducting type of conductivity.

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves $M(T)$ for (1) $La_{0.5}Sr_{0.5}CoO_3$ and (2) $La_{0.65}Sr_{0.35}CoO_3$ films are shown in Fig. 3. First, the ferromagnetic transition takes place at $T_C \simeq 250$ K and 230 K for curves 1 and 2, respectively, which are coincident with the published data.[14,15] Second, the reduction in Sr doping leads to the a decrease of the FC $M(T)$ magnitude, and hence to frustration of the long-range spin ordering in this film. Third, a very large difference between ZFC and FC states is distinct, providing evidence for the existence of magnetically ordered small regions separated by a matrix of disordered spins, which is usually treated as ''cluster'' glass state.[15,16]

III. DISCUSSION

Figure 4 displays the temperature-dependent normalized resistivity, $\Delta\rho_{\rm norm}(T)=[\rho(T)-\rho_0]/(\rho_{250}-\rho_0)$, for both

$La_{0.5}Sr_{0.5}CoO_3$ (curve 1) and $La_{0.65}Sr_{0.35}CoO_3$ (curve 2) films, which reveals metal-like behavior of resistivity in the whole temperature range. ρ_0 is the residual resistivity and ρ_{250} is the resistivity at the temperature of magnetic transition ($T_C \approx 250$ K). It is seen that at high temperatures ($T \geqslant 150$ K) both experimental curves are practically coincident, while at low temperatures the behavior is significantly different. The analysis shows that the temperature-dependent normalized resistivity for both films in the whole temperature range can be described by (solid lines) $\Delta\rho_{\text{norm}}(T) = \alpha T^2 \exp(-T_{SG}/T) + \beta \exp(-T_{SG}/T)$ with the following fitting parameters: $\alpha = 2\times10^{-5}$, $\beta = 0.05$, and $T_{SG} = 20$ K (for $La_{0.5}Sr_{0.5}CoO_3$), and $\alpha = 3\times10^{-5}$, $\beta = 0.001$, and $T_{SG} = 25$ K (for $La_{0.65}Sr_{0.35}CoO_3$). Insets (a) and (b) in Fig. 4 show that the relative difference between the experimental data and the fitting curves does not exceed $\pm 5\%$.

Existence of the exponential term in the temperature-dependent resistivity has already predicted the reason for the $\rho(T)$ behavior for the magnetic rare-earth metals and alloys.[17,18] The authors assumed that it was connected with the appearance of the spin gap in the spectrum of spin-wave excitations due to the magnetic anisotropy[17] or to double degeneracy of the ion levels under the action of internal crystal field.[18] The latter idea seems to be more reasonable for such compounds that contain different types of Co^{3+} ions (low-spin and high-spin states) separated by a small energy gap.[6] Recently it was shown that the spin gap value can be obtained for the semiconductorlike $\rho(T)$ behavior of the slightly doped $La_{1-x}Sr_xCoO_3$ compounds ($x \leqslant 0.15$) at low temperatures.[9] However, in our case the magnitude of the spin-gap temperature (T_{SG}) is smaller than that predicted for the corresponding composition and can originate from another physical property, for example, the twofold orbital degeneracy.

The best agreement between experimental and theoretical curves of $\rho(T)$ for $La_{0.85}Sr_{0.15}CoO_3$ and $La_{0.75}Sr_{02.5}CoO_3$ films in the paramagnetic state was achieved with the fitting parameters $\rho_\infty = 1.21\ \mu\Omega$ cm, $T_0 = 1.4\times10^5$ K and $\rho_\infty = 2.53\ \mu\Omega$ cm, $T_0 = 0.51\times10^5$ K, respectively, for the variable-range hopping (VRH) Mott model.[19] The value of T_0 in the VRH model depends on the electron localization length, l_0, and the density of states at the Fermi level, $N(E_F)$: $k_B T_0 = 18/[l_0^3 N(E_F)]$. Using the e_g-band width of $E_F \approx 0.3$ eV (Ref. 6) and the estimated carrier concentration n, which corresponds to the concentration of divalent Sr, one can obtain the value of electron localization length for both films, $l_0 \approx 0.49$ nm ($x = 0.15$) and 0.68 nm ($x = 0.25$), which are quite reasonable.

Figure 2 shows that the $\rho(T)$ behavior for both $La_{0.75}Sr_{0.25}CoO_3$ and $La_{0.85}Sr_{0.15}CoO_3$ films at temperatures below the magnetic transition (indicated by arrows) undergoes the following transformation with decreasing temperature. There is a noticeable change in the slope near T_C, which is more emphasized at lower temperatures. This can be interpreted as an onset of the formation of ferromagnetic (FM) clusters (containing Co^{4+} ions) in the insulating matrix (IM) that contains only the trivalent Co ions. Recently it was shown that the temperature dependence of the resistivity for manganites is excellently fitted by the two-parallel-resistor model, where one resistor corresponds to the FM-cluster network and the other to the IM.[20] At high temperatures the IM resistance is smaller than the FM one, and most of the conduction in this regime occurs through the insulator. On the other hand, the IM resistance is so large at low temperatures that the current flows only through the FM network. Appearance of the spin gap below $T \simeq 100$ K leads to a considerable rise of resistance in the FM-cluster channel as temperature is decreased. The transition of Co^{3+} ions to the low-spin state can be treated as a decrease in the number of e_g electrons participating in the double-exchange (DE) mechanism of conductivity.[21]

The analysis of temperature-dependent MR shows principally two different behaviors for $La_{1-x}Sr_xCoO_3$ films in the metallic and the insulating states. For the films in the metallic state ($x > 0.25$) the MR(T) dependence shows a small peak near the T_C (see curve 1 of inset in Fig. 2) that coincides with the literature results obtained for the bulk single-crystalline and polycrystalline samples.[7,9] The transition of the films into the insulating state ($x < 0.25$) is accompanied by an essential growth of the MR value and results in a significant increase of $MR(T)$ with decreasing temperature (see inset in Fig. 2). Therefore, one can suggest that the observed negative MR in the metallic and the insulating states of the $La_{1-x}Sr_xCoO_3$ compound has distinct physical properties. In the ferromagnetic metal, appearance of the negative MR, on one hand, can be connected with a decrease in the s-d electron-electron scattering contribution to the resistance due to shifts of the d subbands with different spin orientations with respect to the Fermi level under the action of an internal magnetic field. On the other hand, the internal magnetic field can lead to suppression of the electron scattering with the disordered localized spins (t_{2g}) and to a reduction of the resistance below the Curie temperature.[7] In both cases the slope of the $\rho(T)$ dependence is changed at T_C and the small peak in MR(T) should occur under the action of the external magnetic field owing to a shift of the Curie point.

In the insulating state the negative MR effect for such a type of compound is explained, as a rule, on the base of the DE model.[21] The effective transfer t_{ij} of the e_g electrons (or holes) between the nearest-neighbor pairs (i, j) of Co sites in the framework of the DE model depends on the relative angle $\Delta\theta_{ij}$ between neighboring t_{2g} spins at sites i and j, $t_{ij} = t_0 \cos(\Delta\theta_{ij}/2)$. Thus the ferromagnetic state reduces the spin disordering (of the localized t_{2g} spins) and the mobility of carriers will increase in an applied magnetic field ($\Delta\theta_{ij} \rightarrow 0$), which results in a drop in resistance.

Therefore, in the metallic state ($x > 0.25$) the e_g electrons form a conductivity band and the DE mechanism plays a minor role in the transport of carriers. In this case the MR effect is provided by a change in the electron scattering rate induced by the magnetic field and becomes apparent as a small peak at the Curie temperature. In the insulating state ($x \leqslant 0.25$) the phase separation into the FM clusters and the IM is formed and an applied magnetic field leads to a growth of the FM phase over the DE mechanism.

IV. CONCLUSIONS

The magnetic and transport properties of $La_{1-x}Sr_xCoO_3$ films prepared by laser ablation were studied. The MI transition was observed with decreasing Sr^{2+} doping ($x \leqslant 0.25$). The analysis of experimental results testifies that the transport of carriers in the metallic state is governed by the electron-electron scattering taking into account the origin of a small energy gap in the spectrum of electron excitations. The transport of carriers at high temperatures (above the temperature for magnetic transition) in the insulating state ($x \leqslant 0.25$) is governed by the Mott-like VRH. In the low-temperature range (below the temperature for magnetic transition) the $\rho(T)$ dependence is similar to the temperature behavior of two parallel resistances, where one resistance corresponds to the FM-cluster network and the other to the IM.

It was shown that two mechanisms of MR work for the investigated films. In the metallic state ($x > 0.25$) the MR is provided by a change in the electron scattering rate affected by the magnetic field and revealed as a small peak at the Curie temperature. In the insulating state ($x \leqslant 0.25$) the phase separation into the FM clusters and the insulating matrix occurs and an applied magnetic field leads to the growth of the FM phase over the DE mechanism.

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