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Band structures, and magnetic and transport properties of La doped two dimensional Sr_2CoO_4

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In this work, we report on our studies on the band structure calculations, structures, transport, and magnetic properties in two dimensional layer structured perovskite compounds $Sr_{2-x}La_xCoO_4$. Structure refinement results reveal that these compounds crystallized in K_2NiF_4-type structures with space group $I4/mmm$. The temperature dependence of resistivity shows a semiconductorlike behavior over a wide range of temperatures, a metal-insulator transition at 240 K, and an upturn at 160 K for the $x=1$, 1.25, and 0.75 samples. A coercive field is about 1 T for the sample with $x=0.75$, while it is about 0.05 T for $x=0.75$ and 0.1 T for the $x=1.25$ samples. A negative field hysteresis magnetoresistance in close correlation with the coercive field has been observed and can be explained by the grain boundary tunneling effect. The first-principles band structure calculations were carried out for $Sr_{1.5}La_{0.5}CoO_4$ and the results indicate that the system is metallic with a high spin polarization which is responsible for the observed large magnetoresistance. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714196]

I. INTRODUCTION

The discovery of high temperature superconductivity and colossal magnetoresistance has aroused extended interest in the magnetic and electrical properties of perovskite transition metal oxides. The layered-type perovskite oxides A_2BO_4 with a K_2NiF_4-type structure are characterized by two dimensional confinement of the *B*-O-*B* network, which significantly reduces the one-electron band width of the e_g electrons, thus inducing strong electron correlation, and alters the degrees of freedom (charge, spin, orbital, and lattice) of the material. It has been reported that Sr_2CoO_4 single-crystalline thin films prepared by pulsed laser deposition and polycrystalline samples prepared by high temperature and high pressure (6 GPa) are metallic ferromagnets with the fairly high Curie temperature (T_C) of 255 K,[1,2] large magnetic anisotropy, and quasi-two-dimensional electrical transport properties. Y doping of Sr_2CoO_4 polycrystalline samples fabricated under high pressure was found to change the system from ferromagnetic metal to antiferromagnetic semiconductor.[2] Ferromagnetic semiconducting states have been observed in $La_{1-x}Sr_{1+x}CoO_4$ compounds made under ambient pressure in O_2.[3,4] With increasing Sr contents, the system changed from antiferromagnetic insulator to ferromagnetic semiconductor. The Curie temperature is about 200 K for $x=1.25$, as estimated from magnetization versus temperature dependence,[4] but the $LaSrCoO_4$ seemed to be a paramagnetic semiconductor. In this work, we report on our investigations into the structures, and the magnetic and magnetotransport properties of the La doped Sr_2CoO_4 using the conventional solid-state reaction and compare our results with what has been previously reported.

II. EXPERIMENT

Polycrystalline samples $Sr_{2-x}La_xCoO_4$ ($x=0.5, 0.75, 1, 1.25$) were synthesized by conventional solid-state reaction. Highly pure powders of La_2O_3, $SrCO_3$, and Co_3O_4 were mixed according to appropriate atomic ratios, pelletized, and then sintered in air at 1000 °C for 12 h with several intermediate grindings. The resultant phases and structures were studied using the powder x-ray diffraction (XRD). Structure refinements were carried out by the Rietveld method using the RIETICA program.[5] Magnetic and electrical transport properties were investigated using a commercial Quantum Design magnetic property measurement system (MPMS) and physical property measurement system (PPMS) system between 5 and 330 K in magnetic fields up to 8 T. A first-principles band structure calculation was performed using the CASTEP package.[6] We adopted the standard generalized gradient approximation (GGA), with the Perdew-Burke-Ernzerhof functional.

III. RESULTS AND DISCUSSIONS

From XRD experiments, we found that samples with $x=0.75$, 1, and 1.25 are close to single Sr_2CoO_4 phase, while the $x=0.5$ sample contains the Sr_2CoO_4 as the main phase, but with $Sr_3Co_2O_7$ phases as a secondary phase. However, the single phase with $x=0.5$ can be successfully obtained by using different starting materials.[4,7] Figure 1 shows a typical powder XRD pattern of a $SrLaCoO_4$ sample. It can be seen

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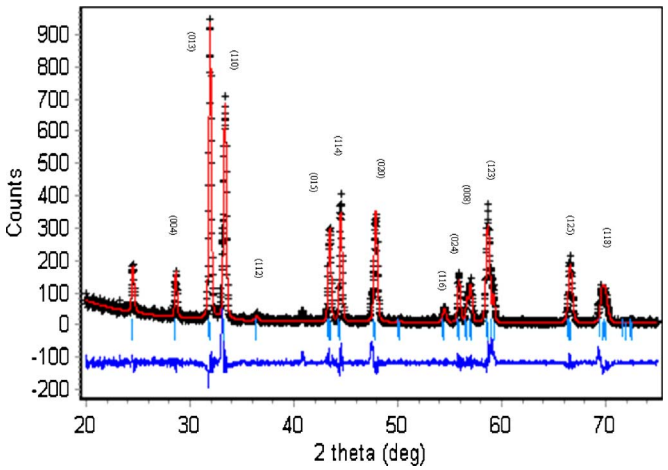

FIG. 1. The observed (crosses), calculated (solid line), and difference diffraction (bottom solid line) profiles at 300 K for $SrLaCoO_4$. All the indexed peaks belong to the Sr_2CoO_4 phase.

that the calculated pattern is in good agreement with the observed one. The lattice parameters and unit volumes increase with increasing La content, in agreement with the fact that the size of La^{3+} is greater than that of Sr^{2+}. Our refinement data are in accordance with what was determined from La doped Sr_2CoO_4 prepared using a solution method.[4,7]

The temperature dependence of the resistivity for the samples with $x=0.75$, 1, and 1.25 is shown in Fig. 2. The $x=1$ sample exhibits a semiconductorlike behavior over a wide range of temperatures below 350 K, in agreement with what has been reported in Ref. 4. A metal-insulator transition is seen around 255 K for the $x=1.25$ sample. However, the $x=0.75$ sample reveals an increase in resistivity at $T=150$ K. The room temperature resistivity of these samples increases with decreasing x. The resistivity for the $x=1$ and 1.25 samples has approximately the same value, which is about 10 Ω cm, while the resistivity of the $x=0.75$ sample is about one order of magnitude larger than the other two samples. In the lower temperature range (below 150 K), the rapid increase in resistivity with decreasing temperature for

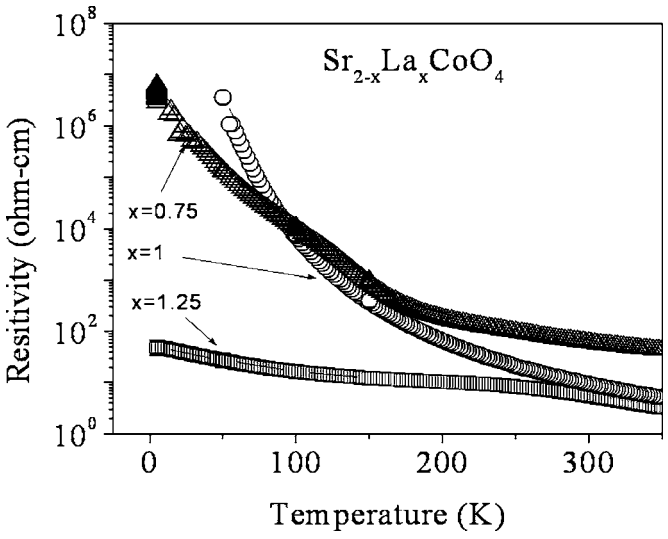

FIG. 2. The temperature dependence of the electrical resistivity.

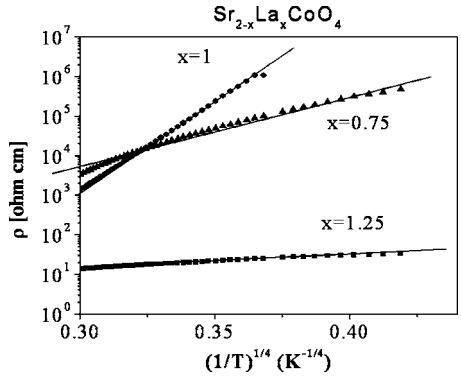

FIG. 3. ρ vs $\exp(1/T)^{1/4}$. Straight lines are linear fitting to the 3D VRH model.

the $x=1$ sample indicates more electron localization than with the $x=0.75$ and 1.25 samples. This means that the $x=1$ sample looks more insulating at low temperature than the $x=0.75$ and $x=1.25$ samples. This is a possibility that because the valence of Co is 3+ in $SrLaCoO_4$ ($x=1$), however, it is $<3+$ or $>3+$ in the $x=1.25$ and $x=0.75$ samples. The introduction of La^{3+} can bring more electrons (for $x=1.25$) or holes ($x=0.75$) and lead to better conductivity than the $x=1$ sample.

The ρ below 120 K for all the three samples can be well fitted by the equation $\rho=\rho_0 \exp(T_0/T)^{1/4}$, as shown in Fig. 3. This suggests that the three dimensional (3D) variable-range hopping (VRH) mechanism that has been proposed by Mott and the validity of which has been confirmed in manganite compounds[8] can be used to account for the conducting mechanism at the low temperatures for the La doped Sr_2CoO_4 compounds.

Figure 4 shows the temperature dependence of the magnetization measured in a magnetic field of 0.2 T. All samples exhibit a paramagnetic to ferromagnetic transition at temperatures of about 250, 230, and 220 K (estimated by extrapolating the moment in the middle of the transition to the temperature axis) for the $x=1.25$, 1, and 0.75 samples, respectively. The kink at about 160 K for the $x=0.75$ sample may be related to the upturn at 160 K in the resistivity versus temperature dependence.

The magnetic hysteresis (MH) loops for these three samples are shown in Fig. 5. The $x=0.75$ sample shows a large coercive field of 1 T. This implies a large crystal an-

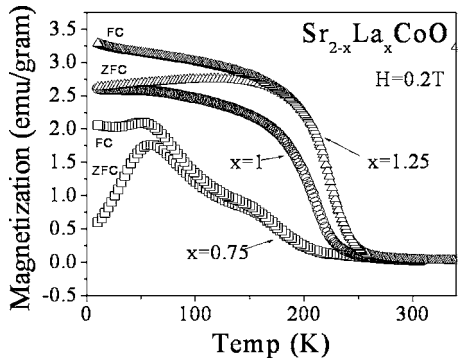

FIG. 4. The temperature dependence of the field cooled and the zero field cooled magnetization measured in 0.2 T.

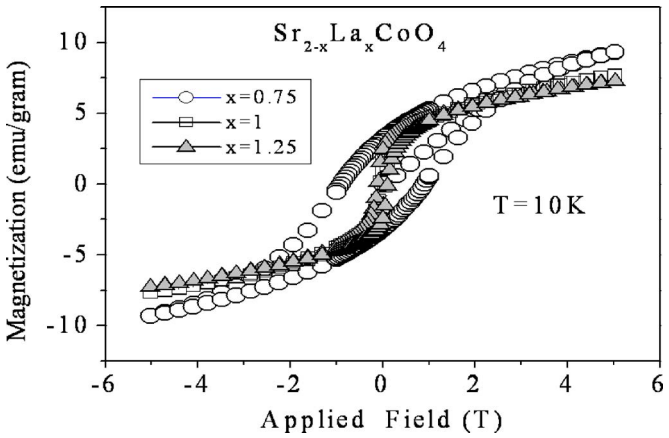

FIG. 5. Magnetization vs field at 10 K.

isotropic energy. For the other two samples, their coercive fields are 0.05 T for $x=1$ and 0.1 T for $x=1.25$, respectively.

The magnetoresistance (MR) effect is observed for all three samples. The MR values (defined as $[\rho(H)-\rho(H=0)]/\rho(H=0)$ are 1%, 2%, and 3% at 150 K for the $x=1$, 0.75, and 1.25 samples, respectively, as shown in Fig. 6(a). The MR is enhanced to 7% at 5 K for the $x=1.25$ sample [Fig. 6(b)]. The MR values below 10 K were not measurable for the other two samples as their resistance rapidly increased beyond the range of measurement. A hysteresis corresponding to the magnetization curve is also observed for the $x=1.25$ sample. The MR shows a maximum at a field which is close to the coercive field of around 0.1 T. This behavior can be explained by the granular-type MR effect in which the grain boundaries play a dominant role in the spin-dependent scattering of charge carriers.[9,10] Our observation is in agreement with what was seen in Ref. 4.

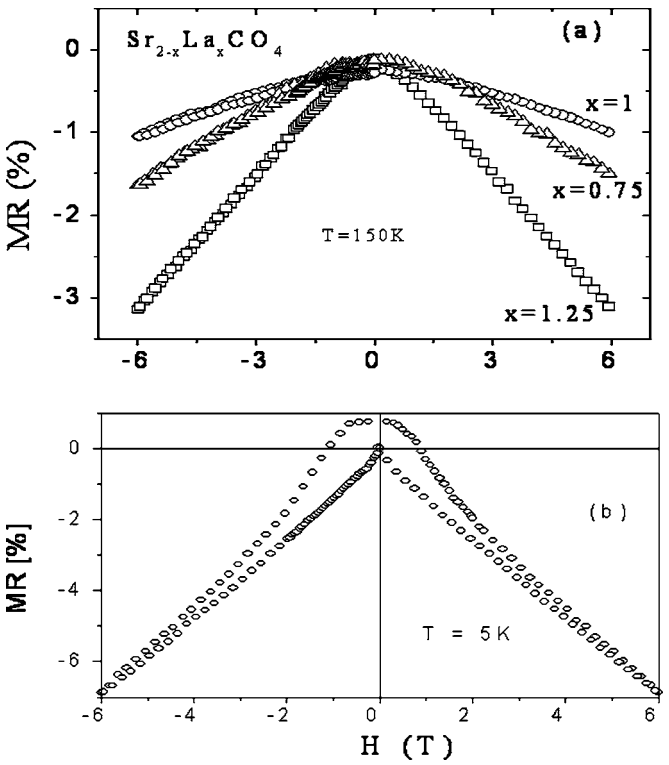

FIG. 6. Field hysteretic magnetoresistance for $Sr_{1.25}La_{0.75}CoO_4$ at 150 K (a) and 5 K (b).

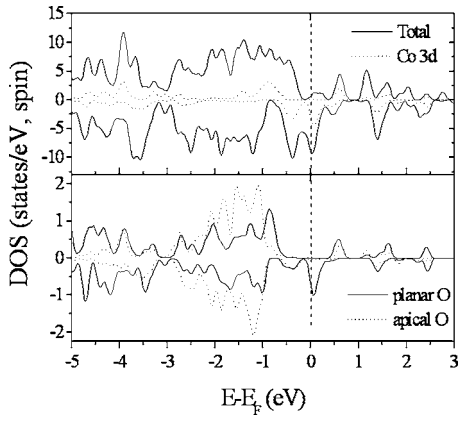

FIG. 7. Total density of states (upper panel) and partial density of states for oxygen (lower panel) of $Sr_{1.5}La_{0.5}CoO_4$, with the Fermi energy set at zero.

We performed band structure calculations for $Sr_{1.5}La_{0.5}CoO_4$ compound and the results of the total and partial density of states (DOS) for Co and for in-plane and epical oxygen are shown in Fig. 7. It can be seen that the compound shows a metallic nature in accordance with what was calculated for pure Sr_2CoO_4.[1] A significant density of states for the spin down band is formed at the Fermi energy E_F, indicating that this compound exhibits a high spin polarization. The partial DOS reveals that the Co 3*d* electrons and planar oxygen are responsible for the high spin polarization in this compound. The band structure results indicate that the metallicity with the highly spin polarization is responsible for the observed spin polarized magnetoresistance. It should be noted that although the results of the DOS we presented in this work are only for the $x=0.5$ sample, it can explain the magnetism and metalliclike properties in the $x=0.5$ samples reported in Refs. 3 and 4, and the similar results of the DOS are expected for the $x=0.75$ sample. A further study on the band structure calculations is needed for the Sr_2CoO_4 with other La doping levels.

ACKNOWLEDGMENTS

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