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Spin-state transition in layered perovskite cobalt oxides: $La_{2-x}Sr_xCoO_4$ $(0.4\leq x\leq 1.0)$

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Magnetic and transport properties are investigated for single crystals of layered perovskite cobalt oxides, $La_{2-x}Sr_xCoO_4$ $(0.4\leq x\leq 1.0)$. The effective magnetic moment $\mu_{\rm eff}$ is found to decrease with increasing x (or increasing the number of Co^{3+} ions) from $\approx 4.0\mu_B$ for $x=0.4$–0.5 to $\approx 2.6\mu_B$ for $x=0.8$–1.0, accompanied by a steep reduction of the resistivity ρ_{ab} and Wiess temperature Θ. These drastic changes of the magnetic and electronic properties suggest a spin-state transition of the Co^{3+} ions from the high-spin to the intermediate-spin state. [S0163-1829(97)51422-6]

Extensive studies on the normal-state properties in cuprate superconductors have aroused renewed interest in the correlated dynamics of spins and charges in perovskite transition-metal oxides with $3d$ electrons. Among a number of barely metallic $3d$-electron systems, the cobalt oxides are especially interesting because of their unusual magnetic behaviors originating from the subtle balance between the crystal-field-splitting Δ and the intersite interaction energy J (Hund's-rule coupling). The ground state of $LaCoO_3$ is a nonmagnetic insulator: Co^{3+} shows nominally the d^6 configuration and forms the low-spin (LS; configuration t_{2g}^6) state due to the crystal-field splitting barely dominating the exchange interaction ($\Delta > 3J$). $LaCoO_3$ undergoes a spin-state transition around 90 K from the nonmagnetic LS state to a magnetic state,[1,2] which was considered to be the high-spin (HS; $t_{2g}^4e_g^2$) state.[1,2] However, there is a controversy in the interpretations: for example, the valence-band x-ray photoemission spectroscopy (XPS) spectrum is quite different from that of a HS compound.[3] It has been recently pointed out that the oxides corresponding to the high formal oxidation state may be a negative charge-transfer system in the Zaanen-Sawatzky-Allen (ZSA) scheme,[4] resulting in an essential modification of the electronic structure, in particular possible stabilization of the intermediate-spin (IS) state.[5] Recently, Korotin *et al.*[6] calculated the electronic structure of $LaCoO_3$ in the local-density approximation LDA+U approach, and found two IS states ($t_{2g}^5e_g^1$) slightly above the LS ground state.

In this paper, we report on the magnetic and electronic properties of perovskite cobalt oxides $La_{2-x}Sr_xCoO_4$ $(0.4\leq x\leq 1.0)$ with a layered structure. The parent compound La_2CoO_4 ($x=0.0$; d^7) is an antiferromagnetic insulator with $S=3/2$ (HS state for Co^{2+}).[7] In the solid solution, we can control the averaged d-electron number per a Co site from 7 ($x=0$) to 6 ($x=1$) without changing the two-dimensional Co-O-Co network. In the ZSA scheme, La_2CoO_4 ($x=0$; d^7) and $LaSrCoO_4$ ($x=1$; d^6) are classified into the charge-transfer-type insulator with the optical gap of $E_{\rm gap}=5$–6 eV (Ref. 8) and 0.95 eV,[9] respectively. Matsuura *et al.*[10] have reported that the system remains insulating or semiconducting for $0.0\leq x\leq 1.5$. Nevertheless, the barely mobile e_g electrons may affect the spin state of the Co^{3+} ions in the intermediate concentration region. Another aspect of the layered-type perovskite oxides is that the two-dimensional confinement of the Co-O-Co network (CoO_2 sheet) significantly reduces the one-electron bandwidth of the e_g electrons as compared with the cubic perovskite compound with a three-dimensional Co-O-Co network. Then, it may be possible that repulsive Coulombic interaction between the less itinerant electrons induces a charge- and spin-ordered state. Such a charge-ordered state is frequently observed in the layered-type perovskite oxides, when the carrier concentration takes a commensurate value (e.g., $x=1/8$, 1/3, or 1/2).[11–13] We have grown single crystals of $La_{2-x}Sr_xCoO_4$ with finely controlling x and carefully investigated the change of the magnetic and electronic properties including their anisotropy. We have observed significant reduction of resistivity with increasing x beyond ~ 0.7, and concomitant reduction of the effective moment $\mu_{\rm eff}$ from $\approx 4.0\mu_B$ to $\approx 2.6\mu_B$. We have ascribed these changes to a transition of the spin state of the Co^{3+} ions from the HS ($x\leq 0.6$) to the IS state ($x\geq 0.8$), because the transfer of the e_g electron between the Co^{2+} (d^7) and Co^{3+} (d^6) sites is expected to stabilize the IS Co^{3+} state.

Single crystals of $La_{2-x}Sr_xCoO_4$ $(0.4\leq x\leq 1.0)$ were grown by the floating-zone method at a feeding speed of 5 mm/h. A stoichiometric mixture of commercial La_2O_3, $SrCO_3$, and CoO powder was ground and calcined three times at 1050 °C for 24 h. Then, the resulting powder was pressed into a rod with a size of 5 mm$\phi\times$60 mm and sintered at 1300 °C for 48 h. The ingredient could be melted congruently in a flow of air ($0.4\leq x\leq 0.7$) or O_2 ($0.8\leq x\leq 1.0$). For the concentration range of $0.4\leq x\leq 0.7$, large single crystals, typically 4 mm in diameter and 30 mm in length, were obtained with two well-defined facets, which correspond to the crystallographic ab plane. For $x\geq 0.8$, however, the obtained crystal is rather small and is easily cleaved along the ab plane. Powder x-ray-diffraction measurements at room temperature and Reitveld analysis[14] indicate that the crystals were single phase without detectable impurity. The crystal symmetry is tetragonal ($I4/mmm$; $Z=2$) over the whole concentration range ($0.4\leq x\leq 1.0$). The obtained lattice constants are listed in Table I together with the conditions for the crystal growth. The lattice constant a monotonously decreases with increase of x, while c shows a local maximum at $x\sim 0.5$.

TABLE I. Lattice constants and growth conditions for $La_{2-x}Sr_xCoO_4$ single crystals

x	a (Å)	c (Å)	Atmosphere	Feed
0.4	3.8410(2)	12.5235(9)	air	5 mm/h
0.5	3.8404(1)	12.5379(3)	air	5 mm/h
0.6	3.8363(1)	12.5313(2)	air	5 mm/h
0.7	3.8303(2)	12.5089(7)	air	5 mm/h
0.8	3.8235(2)	12.4910(6)	air	5 mm/h
1.0	3.8097(4)	12.4788(6)	O_2	5 mm/h

First, we show in Fig. 1 the temperature dependence of in-plane component ρ_{ab} of resistivity measured up to ~500 K for $La_{2-x}Sr_xCoO_4$ with varying x. A broken curve represents resistivity for a $LaCoO_3$ crystal (cited from Ref. 15), which shows a crossover behavior around 500 K from a thermally activated semiconductive to a conducting state. For four-probe resistivity measurements, the crystal was cut into a rectangular shape, typically of 3×1×1 mm^3, and electrical contacts were made with a heat-treatment-type silver paint. We tried to measure the out-of-plane component ρ_c, but failed due to the large contact resistance. The ρ_{ab}-T curves for $0.4 \leqslant x \leqslant 0.7$ exhibit an insulating behavior with a thermal activation energy of ~500 meV, which is much larger than that for $LaSrMnO_4$ [~70 meV (Ref. 13)] with the same layered structure. With further hole doping, the absolute magnitude of ρ_{ab} steeply drops: resistivity at 300 K decreases from ~2000 Ω cm for $x=0.7$ to ~100 Ω cm for $x=0.8$. Especially, the ρ_{ab}-T curve for $x \geqslant 0.8$ does not obey the thermal-activation law and increases more weakly than $\sim\exp(-E_a/k_BT)$ with decreasing temperature. Note that the absolute magnitude of resistivity for $x=1.0$ is almost of the same order as that for $LaCoO_3$ (broken line).

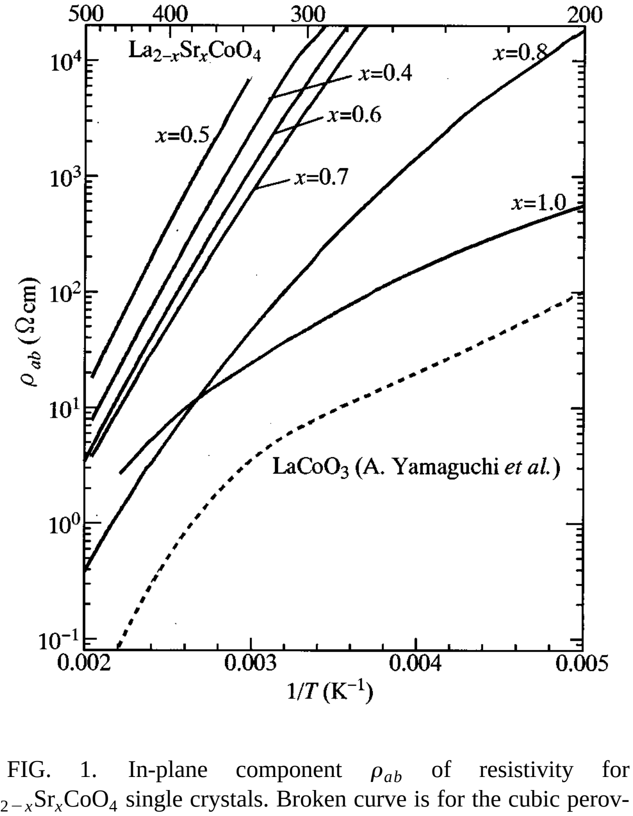

FIG. 1. In-plane component ρ_{ab} of resistivity for $La_{2-x}Sr_xCoO_4$ single crystals. Broken curve is for the cubic perovskite $LaCoO_3$(cited from Ref. 15).

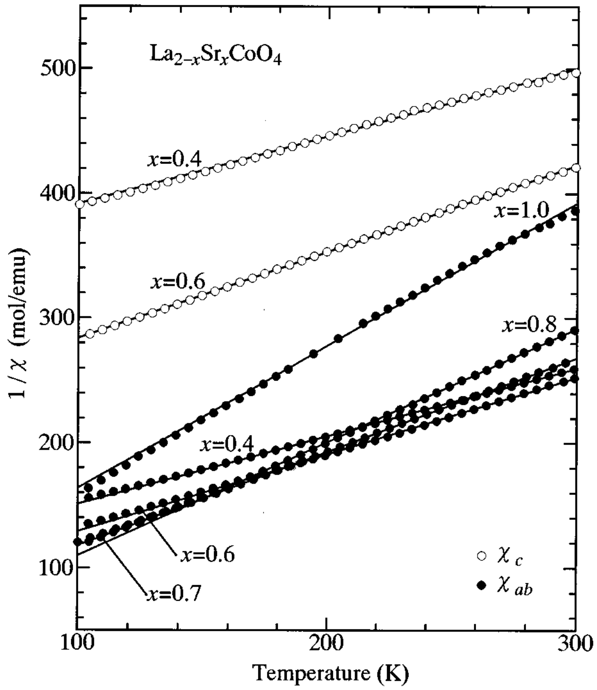

FIG. 2. In-plane (filled circles; $1/\chi_{ab}$) and out-of-plane (open circles; $1/\chi_c$) components of inverse susceptibility for $La_{2-x}Sr_xCoO_4$ single crystals. Susceptibilities were measured under a field of 0.5 T after cooling down to 5 K in the field (FC). The solid lines are the Curie-Weiss fittings.

Now, let us proceed to the magnetic properties for $La_{2-x}Sr_xCoO_4$. The temperature dependence of magnetization M was measured under various fields up to 5 T using a superconducting quantum interference device (SQUID) magnetometer.[16] The magnitude of M is proportional to the external field H apart from the low-temperature region (≤100 K), where a spin-glass behavior is observed (*vide infra*). Figure 2 shows temperature dependence of in-plane (filled circles; $1/\chi_{ab}=H/M_{ab}$) and out-of-plane (open circles; $1/\chi_c$) components of inverse susceptibility measured under a field of 0.5 T after cooling down to 5 K in the field (FC). The χ-T curves obey the Curie-Weiss law above ~100 K, as shown by least-square-fitted straight lines. The χ_{ab} (filled circles) is much larger than the χ_c (open circles), as exemplified by $x=0.4$ and 0.6. Nevertheless, the effective moments estimated from χ_{ab} and χ_c are almost the same (see the upper panel of Fig. 3). Judging from the magnitude of $\mu_{eff}(=3.5$–$4.2\mu_B)$ for $0.4 \leqslant x \leqslant 0.6$, the Co^{3+} and Co^{2+} ions are considered to take the HS state: the effective moment of the isolated HS Co^{3+} (Co^{2+}) ion is $4.90\mu_B$ ($3.87\mu_B$). With further increasing x, μ_{eff} considerably decreases and becomes $\approx 2.6\mu_B$. Such a small magnitude of μ_{eff} may be ascribed to the IS Co^{3+} state ($\mu_{eff}=2.85\mu_B$) or the LS Co^{3+} state ($\mu_{eff}=0$), rather than to the HS Co^{3+} state. Concomitantly, Θ estimated from χ_{ab} decreases with x from ~200 K for $x=0.4$ to ~0 K for $x=0.8$–1.0. A similar trend is also observed for the Θ value estimated from χ_c, even though the absolute value is different. Of course, we should

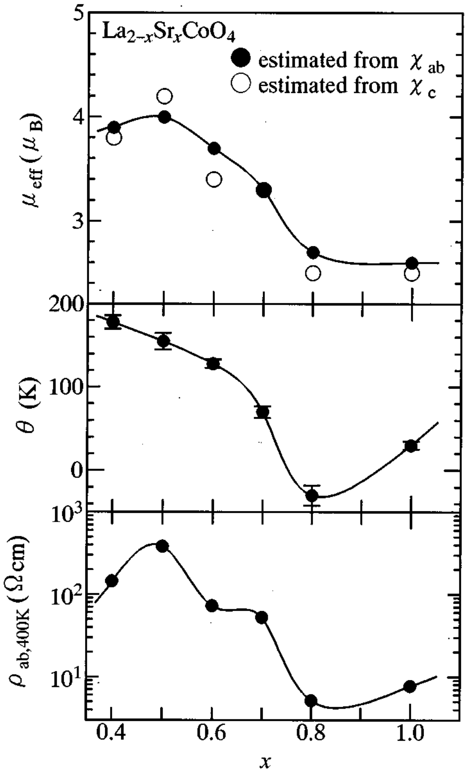

FIG. 3. Effective moment $\mu_{\rm eff}$ per Co site, Weiss temperature Θ, and in-plane component $\rho_{ab,400\ {\rm K}}$ of resistivity at 400 K for $La_{2-x}Sr_xCoO_4$ single crystals. Open and closed circles in the upper and middle panel mean that the values were estimated from the in-plane χ_{ab} and out-of-plane χ_c components of susceptibility, respectively.

be careful with the effect of hybridization of the d^6 state with the $d^7\underline{L}$ state in these materials due to the strong covalency, since the hybridazation may affect the $\mu_{\rm eff}$ and Θ values.

In Fig. 3 are summarized the thus obtained x dependence of $\mu_{\rm eff}$, (upper panel), Θ (middle panel), and in-plane component $\rho_{ab,400\ {\rm K}}$ of resistivity at 400 K (lower panel) for $La_{2-x}Sr_xCoO_4$. Filled and open circles in the upper and middle panel represent the values estimated from χ_{ab} and $\chi_{\rm c}$, respectively. Θ and $\rho_{ab,400\ K}$ are the crude measures for the strength of the intersite exchange interaction and the itineracy of the doped carriers, respectively. With increasing x, $\mu_{\rm eff}$ steeply decreases at $x=0.7$–0.8 and becomes a small value ($\mu_{\rm eff}\approx 2.6\mu_{\rm B}$). Concomitantly, Θ and $\rho_{ab,400\ K}$ drop to small values, implying that the itinerant e_g electrons induce some ferromagnetic interaction, which competes with the original superexchange antiferromagnetic interaction. These observed changes of the magnetic and transport properties in the higher-x ($\geqslant 0.8$) region are well explained if we consider the IS state for Co^{3+} (d^6). In an ionic picture, the Co^{3+} ions are considered to take either the LS or HS state, depending on the ratio between Δ and J: if the energy of the LS state $E_{\rm LS}$ is taken to be zero, then $E_{\rm IS}=\Delta-J$ and $E_{\rm HS}=2\Delta-6J$, and hence the IS state would always lie higher. Now, let us consider the transfer of e_g electron of the neighboring d^7 state to the d^6 states with various spin configurations. Figure 4 shows the schematic representations of the d^6 state with (a) LS, (b) IS, and (c) HS spin configurations. The system gains the maximal kinetic energy with the IS spin configuration [Fig. 4(b)], because the d^7 state produced by the electron transfer would have the lowest energy. It should be noted that the itinerant e_g electrons can mediate a ferromagnetic interaction between the neighboring Co spins, analogous to the case of the double-exchange mechanism.[17] This can be the origin of the reduction of Θ in the high-x region.

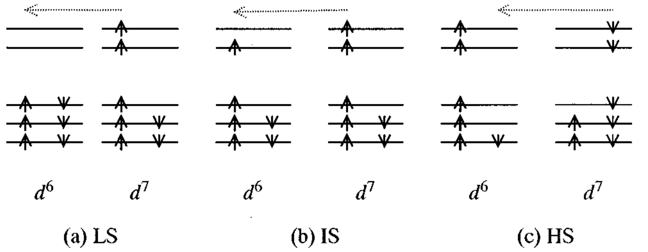

FIG. 4. Schematic representations of transfer of an e_g electron of the d^7 state to the d^6 states with various spin configurations: (a) low-, (b) intermediate-, and (c) high-spin states.

The above idea, i.e., filling-induced spin-state transition from the HS state to the IS state, is supported also by the optical conductivity $\sigma(\omega)$ spectrum for $L_{2-x}Sr_xCoO_4$.[8,9] In the case of $La_{1.5}Sr_{0.5}CoO_4$ ($x=0.5$), a single broad band is observed at ~ 3 eV, making a contrast with the spectrum of $LaSrCoO_4$ ($x=1.0$), in which two broad bands are observed at ~ 2 eV and ~ 3.5 eV. Such a change of the electronic structure suggests variation of the spin state of the Co^{3+} ions. Especially, the overall $\sigma(\omega)$ spectrum for $LaSrCoO_4$ ($x=1.0$) bears a close resemblance to that for $LaCoO_3$,[18]

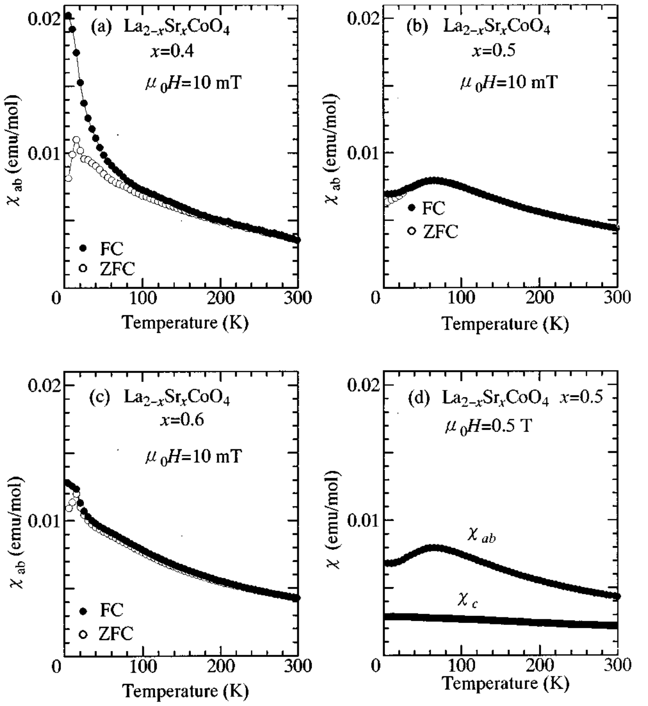

FIG. 5. (a)–(c) Temperature dependence of in-plane component χ_{ab} of susceptibility for $La_{2-x}Sr_xCoO_4$ single crystals. Open and filled circles represent that the data were obtained after cooling down to 5 K in zero field (ZFC) and in the field of $\mu_0H=10$ mT (FC), respectively. (d) Anisotropy of susceptibility for $x=0.5$.

implying that the spin state of the Co^{3+} ions for $LaSrCoO_4$ is similar to that for $LaCoO_3$, i.e., the IS state.

Finally, let us discuss the magnetic transitions at lower temperature for $La_{2-x}Sr_xCoO_4$. We show in Figs. 5(a), 5(b), and 5(c) the in-plane component χ_{ab} of magnetic susceptibility measured under a field of 10 mT; open and filled circles indicate that the data was measured after cooling down to 5 K in zero field (ZFC) and in the field (FC), respectively. For $x=0.4$ [Fig. 5(a)] and 0.6 [Fig. 5(c)], a cusp structure is observed at $T_g \sim 20$ K in the ZFC data, suggesting a spin-glass (SG) transition. Similar SG transitions are observed for the $La_{1-x}Sr_{1+x}MnO_4$ system[13] at $T_g=20$–25 K as well as $La_{0.92}Sr_{0.08}CoO_3$ (Ref. 2) at $T_g=24$ K. However, the spin-glass behavior seems to disappear for $x=0.5$ [see Fig. 5(b)], and χ_{ab} shows a broad maximum at ~ 60 K. As seen in Fig. 5(d), χ_c is nearly temperature independent. These behaviors suggest a long-range spin ordering below ~ 60 K.[19] Such a peculiarity for $x=0.5$ might be originating in the commensurability of x with the lattice periodicity and resultant real- space ordering of the doped carriers. Detailed neutron-scattering measurements using the single crystal are now in progress.

In summary, we have measured magnetic and transport properties for single crystals of layered perovskite-type cobalt oxide, $La_{2-x}Sr_xCoO_4$ ($0.4 \leqslant x \leqslant 1.0$). Effective magnetic moment μ_{eff}, Weiss temperature Θ, and in-plane component $\rho_{ab,400\ \mathrm{K}}$ of resistivity were found to decrease significantly with increasing x beyond ~ 0.7. These abrupt changes in the magnetic and electronic properties suggest a spin-state transition of the Co^{3+} ions from the HS state to the IS state.

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