Spin-state transition and high-spin polarons in $LaCoO_3$

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The spin gap energy ($\approx$ 30 meV) associated with the low-spin ($S=0$) to high-spin ($S=2$) transition in $LaCoO_3$ was proved to be considerably smaller than the charge gap energy ($\approx$ 0.1 eV) which was estimated by optical spectroscopy. Hole doping in the low-spin ground state of $LaCoO_3$ leads to formation of localized magnetic polarons with unusually high spin number ($S=10$–16), which can be viewed as a precursor of the doping-induced ferromagnetic metallic state.

Dynamical correlation between doped holes and local spins in $3d$ transition-metal oxide compounds are of current interest since the discovery of the high-temperature superconductivity in the cuprate compounds. An example of the revived studies is on the spin-charge coupled phenomena in the double-exchange ferromagnets such as perovskite-type hole-doped manganese and cobalt oxides which have lately been found to show gigantic magnetotransport and magnetostructural phenomena.[1–8] Hole-doped $LaCoO_3$ with perovskite-type structure[9,10] is a member of ferromagnets with the double-exchange interaction,[11–13] in which the hole-type carriers in the hybridized $3d$-$2p$ bands strongly couple with the $3d$ spins. In this paper, we evaluate the respective magnitudes of the spin and charge gap in the parent insulator $LaCoO_3$ and argue the nature of doped holes in the spin-singlet (low-spin) ground state.

The electron configuration of Co^{3+} ions in $LaCoO_3$ is $3d^6$. The crystal-field splitting ($10Dq$) between the t_{2g} and e_g states and the Hund coupling energy is comparable, which seems to be a major origin of the temperature-dependent spin-state transition between the high-spin ($S=2; t_{2g}^4 e_g^2$) and low-spin ($S=0; t_{2g}^6$) states in this compound.[14–19] Furthermore, the charge gap, which should be assigned to the charge-transfer-type gap according to the Zaanen-Sawatzky-Allen scheme,[20] is fairly small (0.1−0.2 eV in the high-spin state[21]), which also places the compound on the verge of the Mott transition. Such a subtle energy balance seems to cause successive resistive as well as magnetic phase transformations which are observed in $LaCoO_3$ with change of temperature:[14,15,22–25] With decrease of temperature, the compound shows a phase change at around 500 K from a fairly conducting state with resistivity of about 1×10^{-3} Ω cm to a semiconducting state with the activation energy of about 0.11 eV (60–150 K). Then, the magnetic susceptibility steeply decreases below 100 K corresponding to the transition from the high-spin to low-spin states, while the compound remains semiconducting or insulating at temperatures below 500 K (See Fig. 1). In the present study, it was found that a doped hole in the spin-singlet ground state behaves as a high-spin ($S=10-16$) polaron which can be viewed as a precursor of the doping-induced high-spin state or ferromagnetic metallic state.

Crystals of $LaCoO_3$ and lightly hole-doped $La_{1-x}Sr_xCoO_3$ ($x\leqslant0.01$) were grown by the floating-zone method. Starting materials were La_2O_3, $SrCO_3$, and CoO. The raw materials were weighed to a prescribed ratio, mixed and ground in a ball mill. The mixture was heated in air at 1050 °C for 12 h. Then, the prereacted mixture was reground and pressed into a cylindrical form of feed rods (5 mm ϕ $\times$60 mm). The crystals were grown with use of a floating zone furnace equipped with two halogen incandescent lamps and a double hemielliptic focusing mirror. The feed and seed rods were rotated in opposite directions at a relative speed of 40 rpm and the melted zone was vertically scanned at a speed of 1.5 mm/h in 5 atm oxygen atmosphere. To keep the systematics valid, the growth condition was set as the same for all the crystals against such a slight variation of Sr con-

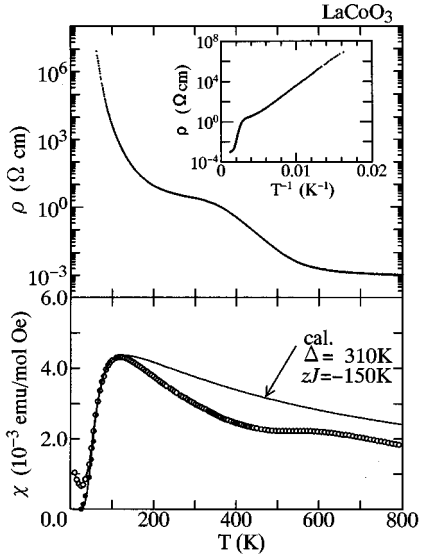

FIG. 1. Temperature dependence of electrical resistivity (upper panel) and magnetic susceptibility (lower panel) for a crystal of $LaCoO_3$. The inset in the upper panel shows the Arrhenius plot of the resistivity (ρ). Closed circles below 100 K for the susceptibility represent the result of the subtraction of the contribution from Curie-like impurities. A solid line in the lower panel shows the calculated curve based on the molecular field approximation with an energy level separation Δ between the $S=0$ (low-spin) and $S=2$ (high-spin) state of the Co ion and with the antiferromagnetic interaction (zJ) between the neighboring high-spin ($S=2$) Co ions (see text).

tent ($0 \leqslant x \leqslant 0.01$). Powder diffraction x-ray patterns showed that all the samples of $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.01$) were slightly distorted perovskites with rhombohedral structure ($R3c$) at room temperature in accord with the literature.[9,22] Analyses of composition were carried out using an electron probe microanalyzer (EPMA), indicating the nearly identical composition with the prescribed one.

Magnetization measurements were done up to a field of 5 T with a commercial superconducting quantum interference device (SQUID) magnetometer. At high temperatures above room temperature, the magnetic susceptibility was measured with a vibrating-sample magnetometer. Measurements of optical reflectivity spectra were done for the photon energy region between 0.01 and 35 eV on specularly polished surfaces of the samples using Fourier spectroscopy (0.01−0.8 eV) and grating spectroscopy (0.6−35 eV). The reflectivity data above 6 eV, which were necessary to execute the accurate Kramers-Kronig (KK) transformation, were obtained using a synchrotron radiation at INS-SOR, Institute for Solid State Physics, University of Tokyo, as a light source. The optical conductivity spectra were deduced by the KK analysis of the reflectivity data.

We show in Fig. 1 temperature dependence of electrical resistivity and magnetic susceptibility for the crystal of $LaCoO_3$. The susceptibility in pristine $LaCoO_3$ shows a noticeable increase around 50 K with increase of temperature reflecting the spin-state transition, and then exhibits a Curie-Weiss-like behavior at higher temperatures above 110 K. With further increase of temperature, the susceptibility shows a gradual change corresponding to the aforementioned resistive transition around 500 K. Increase in the susceptibility below 50 K corresponds to Curie paramagnetism caused perhaps by a small amount of impurities (*vide infra*). The result for nominally neat $LaCoO_3$ is in accord with those reported previously for the polycrystalline samples,[14,15] though the low-temperature Curie component is less conspicuous due to the improved quality of the present crystal. Since the contribution from the impurities is fairly small and well in compliance with the Curie law, we could subtract their contribution as shown with closed circles in Fig. 1. The thus obtained χ-T curve is clearly characteristic of the spin gap which arises perhaps from the level difference between the low-spin ($S=0$) and high-spin ($S=2$) state of the Co^{3+} ion.

In order to analyze the χ-T curve, we have adopted the following approximation: The Co^{3+} ion has two spin states; the nondegenerate low-spin (singlet) state with the configuration of t_{2g}^6 and the 15-fold degenerate high-spin ($S=2$) state with that of $t_{2g}^4 e_g^2$. The energy separation between the two states is Δ and the antiferromagnetic interaction J works between a nearest-neighbor pair of the high-spin ($S=2$) states. With use of a simple molecular field approximation, the thermal average of the Co spin moment (σ) along the magnetic field can be calculated by the following formula

$$\sigma = \frac{\eta \Sigma_{m=-S}^{S} m \exp[(2\sigma z J m + g\mu_B H m - \Delta)/k_B T]}{1 + \eta \Sigma_{m=-S}^{S} \exp[(2\sigma z J m + g\mu_B H m - \Delta)/k_B T]}. \quad (1)$$

Here, z is the coordination number ($z=6$), η the orbital degeneracy ($\eta = 3$), and g the g value for Co ions which is taken as 2.18.[26] The best-fit result is shown with a solid line in Fig. 1. The obtained parameters are $\Delta = 310$ K and $zJ = -150$ K. The calculated result well reproduces the spin-state transition around 100 K and the magnitude of the susceptibility in the thermally activated high-spin state above 120 K. Without the antiferromagnetic interaction between the high-spin Co ions, the calculated value would give a three times larger value than the observed one. The discrepancy above 120 K is perhaps due to the inappropriateness of the molecular field approximation of the Ising spin ($S=2$), since the system is rather adjacent to the magnetic insulator (Mott insulator)-metal phase boundary. Nevertheless, the magnetic behavior below 200 K seems to be well described by the low-high spin-state transition as modeled above.

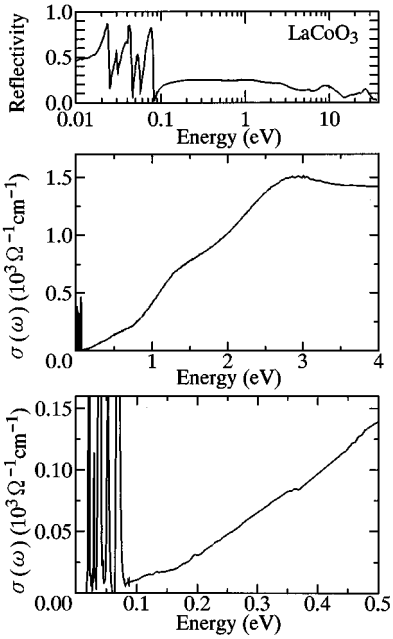

FIG. 2. Optical conductivity spectrum (middle panel) and its magnified low-energy part (bottom panel) for $LaCoO_3$ at 9 K which were derived by the analysis of the reflectivity data (top panel). The reflectivity data above 3 eV are those at 300 K, which are essentially independent of temperature and were connected to the low temperature (9 K) data below 3 eV.

The obtained spin-gap value Δ seems to be fairly small as compared with the charge gap value. We show in the middle panel of Fig. 2 the optical conductivity spectrum of $LaCoO_3$ at 9 K (in the low-spin state) which was obtained by Kramers-Kronig analysis of the reflectivity data (shown in the upper panel) in the photon energy range of 0.01−35 eV. The lower-lying optical excitations can be ascribed to the interband transitions between the O $2p$ states and Co $3d$ (mainly of the e_g orbital character) states. There is seen in a plot with a magnified energy scale (the bottom panel of Fig. 2) a gradual onset of the optical conductivity around 0.1 eV. Considering the uncertainty of the Kramers-Kronig analysis especially for the low optical-conductivity values, it is rather difficult to pinpoint accurately the gap position. However, the whole features of the optical phonon modes in the reflectivity spectrum (up to 0.08 eV) are least dumped as shown in the top panel of Fig. 2, indicating essentially no overlapping interband absorption in the corresponding energy region be-

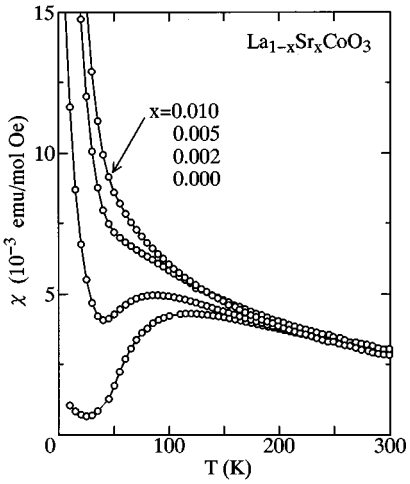

FIG. 3. Temperature dependence of the magnetic susceptibility for lightly doped crystals of $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.010$). Solid lines are guides to the eye.

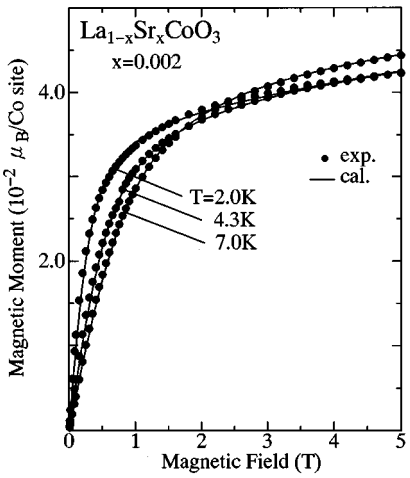

FIG. 4. Field dependence of the magnetization (M) at various temperatures in the low-spin ($S=0$) state for a lightly doped crystal, $La_{1-x}Sr_xCoO_3$ ($x=0.002$). Solid lines are fitted results with use of the Brillouin function plus the field-linear term of the magnetization (see text). The adopted parameters are listed in Table I together with the results for the other crystals.

low 0.08 eV. Thus, the charge gap is likely to be about 0.1 eV or slightly larger than 0.1 eV. Furthermore, the activation energy of the resistivity at 60–100 K is about 0.11 eV (see the upper panel of Fig. 1), which is at least not in contradiction with the present optical data. A fairly large difference between the gaps for the spin excitation (0.03 eV) and the charge excitation ($\geqslant 0.1$ eV) indicates that $LaCoO_3$ is not a simple band insulator in analogy to the case of the Kondo insulator.

We show in Fig. 3 the temperature dependence of susceptibility for lightly hole-doped crystals, $La_{1-x}Sr_xCoO_3$ ($x=0$, 0.002, 0.005, and 0.010). At a glance, one may notice that the susceptibility drop due to the high-to-low spin-state transition is suppressed and instead a Curie-like contribution is remarkably increased with such a light doping. To interpret the behavior, it is worth noting that a doped hole with a character of O $2p$ state in $LaCoO_3$ may behave as a polaron heavily dressed by spin and/or lattice excitations. Such a rapid collapse of the spin-gap behavior as observed for the minimal doping implies that a doped hole can have a high-spin number in the singlet ground state of $LaCoO_3$. In fact, it is anticipated that there should be a strong exchange interaction between a $2p$ hole and $3d$ spins (in the high-spin state) because of a small charge-transfer gap nature and hence an extended wave function of a $2p$ hole is expected to form a spin polaron with a high-spin quantum number. In other words, a doped hole can cause locally the low-to-high spin-state transitions of Co sites around itself via the double-exchange mechanism.[11–13] In this context, the ferromagnetic metallic state realized for $x>0.2$ can be viewed as composed of such mobile high-spin polarons. A concentration of doped holes in $La_{1-x}Sr_xCoO_3$ would be nominally x in the ideal stoichiometry, but in the real systems it deviates from the nominal value mainly due to the presence of slight offstoichiometry (e.g., of oxygen). A real concentration as well as spin quantum number of doped holes (spin polarons) was estimated by the following procedure.

We have measured the magnetization (M) versus magnetic field (H) curves at relatively low temperatures where the Curie-like contribution is dominating. The results for the $x=0.002$ sample are exemplified in Fig. 4. To reproduce the observed M-H curves, we have assumed the following functional form, that is, a combination of the conventional Brillouin function $B_J(z)$ and a H-linear term which is necessary for fitting of the behavior in the higher-field region:

$$M(H) = NgS\mu_B B_J(z) + \chi_0 H \quad \left(z = \frac{\mu_0 g S \mu_B H}{k_B T} \right). \quad (2)$$

Here, N is a number of holes with spin quantum number S per unit volume. The best-fit results are shown in Fig. 4 by solid lines. Adjusted parameters for each crystal at each temperature are summarized in Table I. Apart from the χ_0 values, the parameters are little temperature dependent, indicating that the picture of the spin-polaron adopted here holds good in the present regions of hole concentration and temperature. Provided that all the doped holes are spin-carrying

TABLE I. Magnetic parameters of the doped hole in the low-spin state, which are obtained by the best-fit procedure for the M-H curves of $La_{1-x}Sr_xCoO_3$ samples; S: spin quantum number, N: spin-polaron density, χ_0: coefficient of the H-linear term [see Eq. (2) in the text].

x	Temperature (K)	S	N (10^{-3}/Co site)	χ_0 (10^{-3} emu/mol Oe)
	2.0	10	1.66	0.7
0.002	4.3	11	1.60	0.6
	7.0	12	1.63	0.4
	2.0	14	2.26	3.2
0.005	4.3	15	2.33	1.6
	7.0	14	2.16	1.8
	2.0	15	2.33	3.2
0.010	4.3	15	2.50	2.4
	7.0	16	2.40	2.1

polarons, the estimated concentration of holes (N) per Co site is 0.0016, 0.0023, and 0.0024 for $x=0.002$, 0.005, and 0.010, respectively, and a discrepancy between N and x is likely due to the oxygen nonstoichiometry (perhaps ≈ 0.1 % of the total oxygen content). As seen in Table I, a doped hole in the singlet ground state of $LaCoO_3$ bears a remarkably high spin value with $S=10-16$. The $2p$ hole is likely to cause the low-to-high spin-state transition ($S=0$ to 2) on the relevant Co sites and hence the wave function of the hole (spin polaron) should be extended over the neighboring 5−8 Co sites.

The average spin quantum number S as well as the χ_0 value appears to steeply increase with N. This indicates that the extent of the polaron wave function is expanding with the concentration. At the same time, the increase in the H-linear term χ_0 implies that the spin polarons are no longer isolated from each other and that the antiferromagnetic interaction perhaps begins to act in the overlapping region of the individual spin polarons. It is worth noting here that the higher-doped crystals, $La_{1-x}Sr_xCoO_3$ with $x=0.03-0.15$, show the spin-glass-like phase[17] which is viewed as composed of interacting localized spin polarons. Thus, the high-spin polarons preserve the features precursory of the magnetic phases (the spin glass and ferromagnetic phases) of $La_{1-x}Sr_xCoO_3$ at higher doping levels.

In summary, the spin-state transition in $LaCoO_3$ is argued in terms of spin gap ($\approx$30 meV), which was proved to be considerably smaller than the charge gap ($\approx$0.1 eV). A doped hole in the spin-singlet ground state of $LaCoO_3$ behaves as a localized magnetic impurity with a very high spin value ($S=10-16$). Such a nature of high-spin polaron is likely to arise from the strong exchange interaction between the $2p$ hole and the Co high-spin ($S=2$) state.

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