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Neutron-scattering study of the spin-state transition and magnetic correlations in $La_{1-x}Sr_xCoO_3$ ($x=0$ and 0.08)

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$LaCoO_3$ exhibits two magnetic-electronic transitions, one near 90 K and a second near 500 K. A previous study of the paramagnetic scattering using polarized neutrons demonstrated that the low-temperature transition is associated with the thermal excitation of Co^{3+} ions from the low-spin to the high-spin state. In the present work, we extend the paramagnetic-scattering measurements up to a temperature of 700 K. We find that the magnetic-scattering intensity decreases monotonically for temperatures above 300 K, indicating that the high-temperature transition is not dominantly magnetic in origin. Furthermore, the anomalous thermal expansion associated with the low-temperature transition is measured and shown to be consistent with a simple theoretical model for the spin-state transition. For comparison, paramagnetic-scattering measurements for $La_{0.92}Sr_{0.08}CoO_3$ are also presented. In this material the ferromagnetic correlations are substantially stronger than in the undoped compound, and no transition to the low-spin state is observed. Instead, the paramagnetic scattering increases steadily with decreasing temperature until saturating below 24 K, the same temperature at which the magnetization of the zero-field-cooled specimen shows a sharp cusp. These results suggest that the magnetic moments in the doped compound freeze into a spin-glass state at low temperature.

I. INTRODUCTION

Lanthanum cobalt oxide ($LaCoO_3$) is a semiconductor with a rhombohedrally distorted perovskite structure. This oxide has been a subject of many investigations mainly because of its interesting and unusual magnetic properties[1-6] [see Fig. 1(a)]. The susceptibility increases with increasing temperature in a low-temperature region, and exhibits a broad peak at about 90 K. At higher temperatures, the susceptibility follows the Curie-Weiss law below 400 K ($\mu_{\rm eff}=3.1\mu_B$) (Ref. 1) and above 600 K ($\mu_{\rm eff}=4.0\mu_B$).[1] However, it is almost temperature independent in the region between the two temperatures. Remarkably, the electrical conductivity increases by more than two orders of magnitude on warming through this temperature region.[1,5,7,8] No magnetic long-range order is observed down to 4 K by neutron diffraction studies.[4,9]

The unusual temperature dependence of the susceptibility has been considered to arise from the spin-state transition of Co trivalent ions. However, two contradictory arguments have been presented concerning the temperature region where the spin-state transition takes place. According to one argument,[2,3,10] the increase of the susceptibility with increasing temperature below 90 K is interpreted as evidence for a temperature-induced paramagnetic moment due to the spin-state transition from a low-spin nonmagnetic ($S=0$) ground state to a high-spin magnetic ($S=2$) excited state. The estimated energy difference between the two states is 10 to 80 meV. On the other hand, Raccah and Goodenough[11] argued that the transition takes place predominantly in the 500 K region accompanying a growth of the rocksalt-type short-range order of the high-spin and the low-spin Co^{3+} ions. The argument is based on the crystal symmetry, $R\bar{3}c$ below 400 K and $R\bar{3}$ above 650 K, that they deduced from x-ray-diffraction measurements. However, the reduction in crystal symmetry in the high-temperature region is not supported by extensive neutron diffraction measurements.[7,12]

Most of the arguments in support of these contradictory interpretations of the transitions have been based on indirect measurements of the magnetic moment. The only direct measurement of the average spin state of the Co ions was provided by a polarized-neutron paramagnetic-scattering study, which established rather conclusively that the low-spin to high-spin transition takes place in the region about 100 K.[13] The paramagnetic scattering near the (100) reciprocal-lattice point increases drastically with increasing temperature around 100 K [see Fig. 1(b)]. The temperature dependence of the scattering intensity essentially agrees with that of the squared magnetic moment calculated from the susceptibility data.[5] An anomalous thermal expansion associated with the spin transition also has been observed below 100 K.[14] In spite of these works,[13,14] the authors of a recent high-resolution soft-x-ray absorption spectroscopy (XAS) and the x-ray photoelectron spectroscopy (XPS) study[15]

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chose to interpret the temperature dependence of their spectra on the basis of the picture in which the low-spin to high-spin transition occurs in the range 400–650 K. According to their interpretation, the spin transition does not occur at all between 80 and 300 K. In the latest theoretical work,[16] they argued that the results of band-structure and cluster-model calculations of $LaCoO_3$ of the low-spin phase are consistent with their interpretation of the spin transition.

As mentioned above, the spin transition in $LaCoO_3$ is a controversial subject. The only way to definitively resolve the issue is by polarized-neutron scattering. Unfortunately, the measurements in the previous study[13] only covered temperatures up to 300 K. The main purpose of the present study is to extend the measurements through the 500-K transition region. The results confirm the earlier work,[13] and show that the paramagnetic scattering decreases as the temperature is increased above 300 K. We also show that the anomalous thermal expansion associated with the low-temperature transition is in excellent agreement with the theoretical prediction[17] for the low-spin to high-spin transition. This work firmly establishes that the spin-state transition occurs at low temperature, and that the high-temperature transition is not dominantly magnetic in nature.

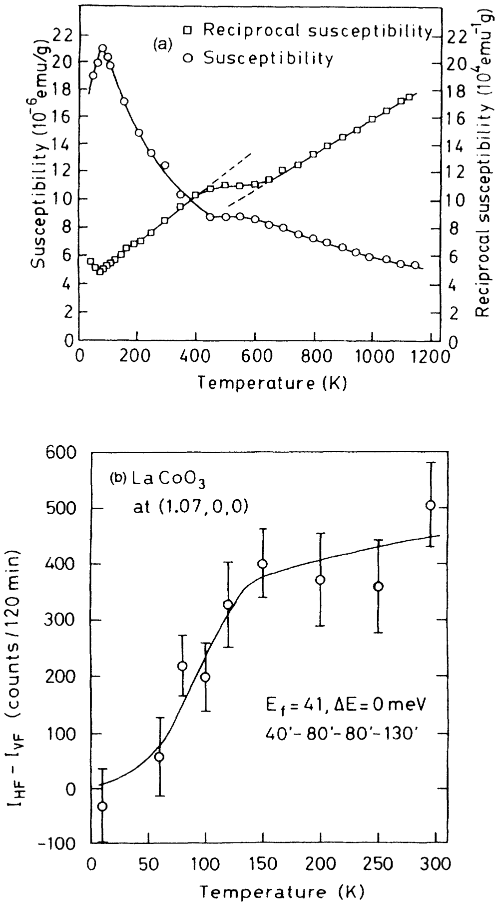

FIG. 1. (a) Temperature dependence of the magnetic susceptibility and its reciprocal for $LaCoO_3$ [after Bhide *et al.* (Ref. 5)]. (b) Temperature dependence of the paramagnetic scattering cross section at (1.07,0,0) with $E_f = 41$ and $\Delta E = 0$ meV for $LaCoO_3$ (Ref. 13). The solid line is a guide to the eye.

A complementary study of the magnetic correlations in $La_{0.92}Sr_{0.08}CoO_3$ is also presented. Strontium doping remarkably increases the magnetization and the system becomes metallic with Sr content larger than 0.2.[1,6,18–21] According to a recent study,[6] the magnetic phase at the lowest temperatures is a spin glass for $La_{1-x}Sr_xCoO_3$ with $0 < x \leq 0.18$. In that system, the lattice expansion due to the Sr substitution appears to stabilize the high-spin state of Co^{3+}; while the electronic doping induces some Co^{4+}. In the present study, ferromagnetically correlated clusters are observed up to 600 K, and a spin-glass state is observed near 24 K.

The rest of this paper is organized as follows. In Sec. II, we describe the experimental procedure. The results of polarized and unpolarized neutron experiments are presented in Secs. III and IV, respectively. The spin-state transition and the magnetic correlation of pure and Sr-doped $LaCoO_3$ are discussed in Sec. V.

II. EXPERIMENTAL PROCEDURE

The specimen of $LaCoO_3$ used in the present study is the same as the one used in the previous study.[13] The sample is an ingot 5 mm in diameter and 15 mm in length and it contains several large single crystals. A Sr-doped single crystal 5 mm in diameter and 25 mm in length was synthesized by melting polycrystalline $La_{0.9}Sr_{0.1}CoO_3$ using a lamp-image floating-zone furnace at Waseda University. A part of the single crystal was submitted to the magnetization measurement. The composition of the single crystal estimated from the magnetic transition temperature (24 K) is $La_{0.92}Sr_{0.08}CoO_3$ according to the magnetic phase diagram.[6] A preliminary electron microprobe analysis indicated an average composition consistent with this estimate for the majority phase, but also reveals the presence of a minority phase with the approximate composition $La_{4/3}Sr_{2/3}CoO_{4+\delta}$. Both pure and Sr-doped crystals have a slight rhombohedral distortion from cubic symmetry, and each single crystal consists of four twins due to the distortion. The lattice parameters at room temperature are $a = 3.825$ Å and $\alpha = 90.7°$ for $LaCoO_3$, and $a = 3.832$ Å and $\alpha = 90.6°$ for $La_{0.92}Sr_{0.08}CoO_3$.

The neutron scattering experiments were performed on triple-axis spectrometers at the High Flux Beam Reactor in Brookhaven National Laboratory. The crystals were oriented so as to make their $[01\bar{1}]$ directions vertical. In the case of $LaCoO_3$, the orientation is referred to the largest single crystal, but the whole specimen contributes to the scattering. Both polarized and unpolarized neutrons were used to measure the magnetic scattering. In the polarized-neutron experiment, the magnetic scattering was measured by taking the difference in intensity between the spin-flipped neutrons scattered in the horizontal-field (HF) and vertical-field (VF) modes. In the HF and VF modes, incoming neutrons are polarized

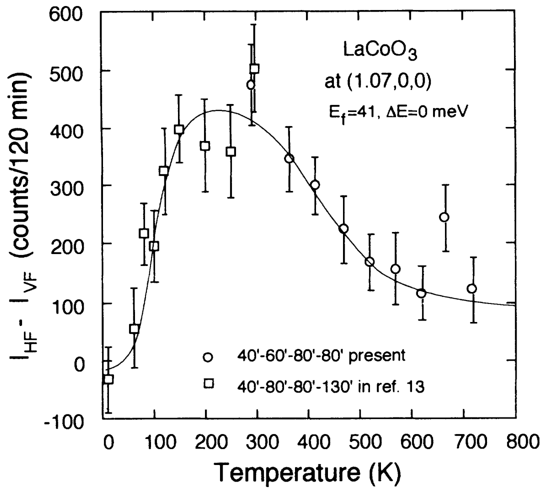

FIG. 2. Temperature dependence of the paramagnetic scattering cross section at (1.07,0,0) with $E_f=41$ and $\Delta E=0$ meV for $LaCoO_3$. The solid line is a guide to the eye.

parallel to and perpendicular to the horizontal scattering vector, respectively. The difference between the cross sections for these two modes is free from nuclear contributions and is related to the paramagnetic cross section, σ_{mag}, according to[22]

$$\left[\frac{d^2\sigma(+-)}{d\omega\, d\Omega}\right]_{HF}-\left[\frac{d^2\sigma(+-)}{d\omega\, d\Omega}\right]_{VF}=\frac{1}{2}\left[\frac{d^2\sigma_{mag}}{d\omega\, d\Omega}\right], \tag{1}$$

where $\sigma(+-)$ denotes the cross section of the spin-flipped scattering. The data were taken with a fixed final neutron energy of 41 meV and with a horizontal collimation of 40′-60′-80′-80′. The flipping ratio of the flipper was about 18. Unpolarized-neutron scattering was measured with an energy of 13.7 meV and the horizontal collimation of 20′-20′-20′-40′ unless otherwise stated.

III. POLARIZED-NEUTRON MEASUREMENT

A. $LaCoO_3$

The temperature dependence of the magnetic scattering from $LaCoO_3$ taken at (1.07,0,0) with the energy transfer $\Delta E=0$ meV is shown in Fig. 2. The vertical axis represents the intensity difference between the spin-flipped neutrons scattered in the HF and VF modes (denoted I_{HF} and I_{VF}, respectively) per measuring time of 120 min. The data taken in the previous study[13] are also shown in the figure. Since the energy width of the scattering is almost resolution limited as described in the previous study,[13] the quantity is in proportion to the squared magnetic moment M^2 (1.07,0,0). The squared moment decreases monotonically with increasing temperature above 300 K, and there is no indication of a magnetic transition at high temperatures. Figure 3 shows the Q dependence of the magnetic scattering at 295 K with $\Delta E=0$; along $(h,0,0)$ in Fig. 3(a) and along $(1.07,k,k)$ in Fig. 3(b). Although the statistical accuracy is not ideal, these data are consistent with a broad peak around (1,0,0) indicating a weak ferromagnetic correlation in the oxide.

B. $La_{0.92}Sr_{0.08}CoO_3$

The Q dependence of the magnetic scattering along $(h,0,0)$ from $La_{0.92}Sr_{0.08}CoO_3$ is shown in Fig. 4. A peak of the magnetic scattering is observed around (1,0,0) at all measuring temperatures. The peak intensity per unit measuring time at 8 K is one order of magnitude stronger than the strongest magnetic scattering from $LaCoO_3$. The width of the peak is far larger than the instrumental resolution ($=0.025$ Å^{-1}), which was measured at (1,0,0) Bragg peak with nonflipped neutrons. The Q dependence of the magnetic scattering can be fitted with the Lorentzian line shape,

$$I(q)=I(0)\frac{\kappa^2}{\kappa^2+q^2}, \tag{2}$$

where q is the distance from (1,0,0) in the Q space. The fitted values of the width, κ, are 0.13 ± 0.01, 0.19 ± 0.05, and 0.14 ± 0.08 Å^{-1} at 8, 100, and 618 K, respectively. The fitted curves are shown in Fig. 4.

The temperature dependence of the magnetic scattering at (1.05,0,0) is shown in Fig. 5. The intensity of the scattering increases with decreasing temperature and

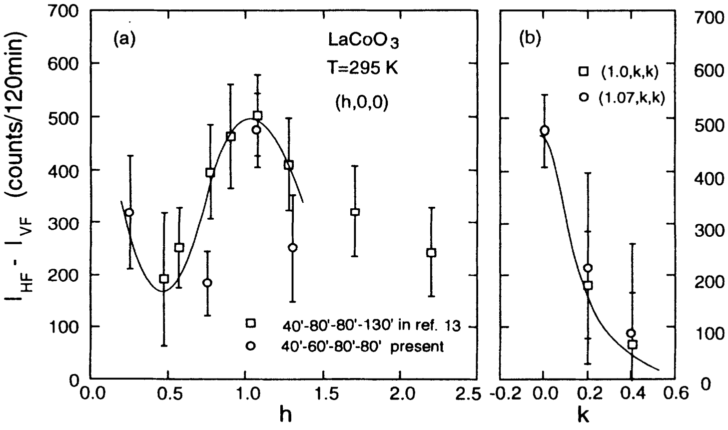

FIG. 3. Q dependence of the paramagnetic cross section at 295 K with $E_f=41$ and $\Delta E=0$ meV for $LaCoO_3$; (a) along $(h,0,0)$ and (b) along $(1.07,k,k)$ and $(1.0,k,k)$. The solid lines are guides to the eye.

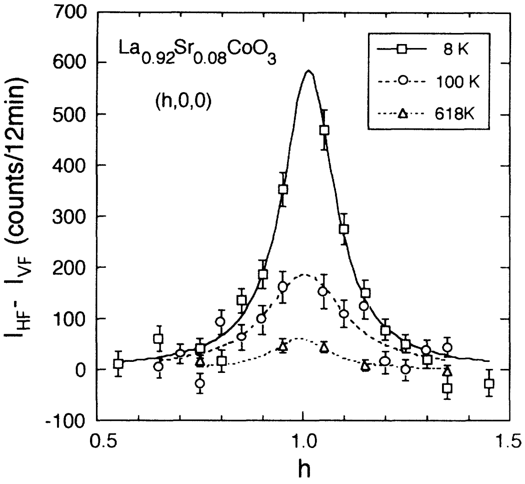

FIG. 4. Q dependence of the magnetic cross section along $(h,0,0)$ with $E_f=41$ and $\Delta E=0$ meV for $La_{0.92}Sr_{0.08}CoO_3$. The lines are the fitted ones with the Lorentzian shape.

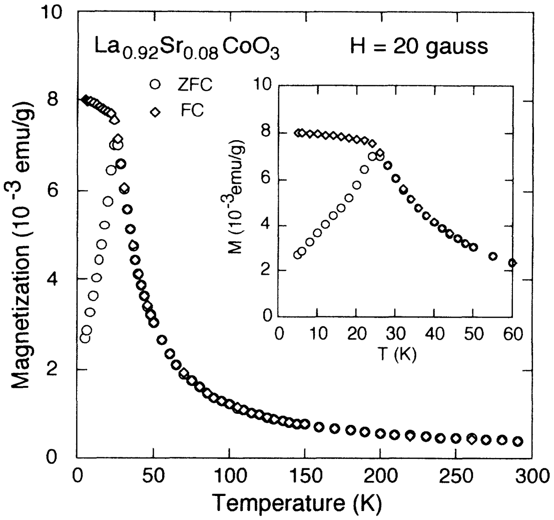

FIG. 6. Temperature dependence of the magnetization of $La_{0.92}Sr_{0.08}CoO_3$ in a magnetic field of 20 Oe for zero-field cooled (ZFC) and field cooled (FC) specimens.

tends to level off below about 25 K. Once again, no anomaly is observed around 500 K. The temperature dependence of the magnetization of the sample in a magnetic field of 20 Oe is shown in Fig. 6. The magnetization was measured on warming after the specimen was cooled with or without the field, denoted FC (field cooling) and ZFC (zero-field cooling), respectively. A sharp cusp can be seen in the temperature dependence of the magnetization after ZFC at 24 K, below which a large difference is observed between the magnetizations after FC and ZFC. This temperature dependence of the magnetization is a characteristic one of the spin glass. The temperature of the cusp coincides with the temperature below which the intensity of the neutron magnetic scattering tends to level off.

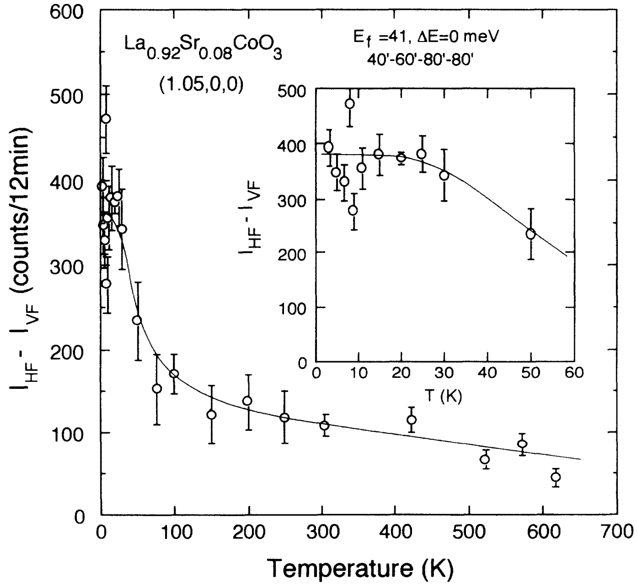

FIG. 5. Temperature dependence of the magnetic scattering cross section at (1.05,0,0) with $E_f=41$ and $\Delta E=0$ meV for $La_{0.92}Sr_{0.08}CoO_3$. The solid line is a guide to the eye.

IV. UNPOLARIZED-NEUTRON MEASUREMENT

A. Magnetic scattering of $La_{0.92}Sr_{0.08}CoO_3$

The main features of magnetic scattering in this crystal are clarified by the use of polarized neutrons. However, once the magnetic signal has been identified, data can be collected more rapidly using the unpolarized beam. The Q dependence of the scattering of unpolarized neutrons from $La_{0.92}Sr_{0.08}CoO_3$ is shown in Fig. 7. In the h scan, [Figs. 7(a) and 7(b)] some subsidiary peaks can be seen besides the huge (1,0,0) Bragg peak. These peaks are rather sharp and the intensities of some peaks are remarkably temperature dependent. The peak intensity of the largest one near (1,0,0) [at (1.04,0,0)] is about 4% of the intensity of the Bragg peak at 3.3 K. We suspect that these peaks come from an impurity phase, as will be discussed later. In contrast, a broad tail can be seen with no significant peaks in the k-scan around (1,0,0) [see Fig. 7(c)]. The intensity of the scattering in the tail part is remarkably temperature dependent as can be seen in this figure. The temperature dependence of the intensity at $(1,-0.06,-0.06)$ is shown in Fig. 8 after the vertical axis is properly scaled. The temperature dependence of the magnetic scattering measured with polarized neutrons is also shown in the figure. Both temperature dependences are suitably scaled; we conclude that the tail part around (1,0,0) in the k scan is the magnetic scattering. In unpolarized-neutron experiments, we can attain a better resolution in Q space and better statistics as can be seen in Figs. 7 and 8, respectively, when they are free from contamination.

We measured the temperature dependence of the subsi-

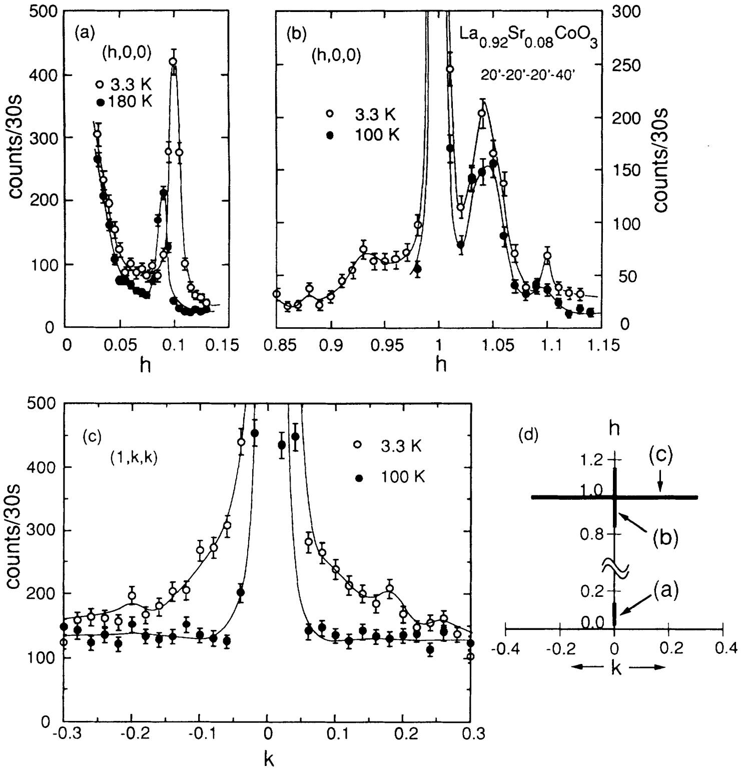

FIG. 7. Q dependence of the unpolarized-neutron scattering intensity with $E_f = 13.7$ and $\Delta E = 0$ meV for $La_{0.92}Sr_{0.08}CoO_3$; (a) and (b) along $(h,0,0)$, and (c) along $(1,k,k)$. The scan trajectories are shown in (d), and the solid lines in (a)–(c) are guides to the eye.

diary peak at (0.1,0,0) up to 250 K. The temperature dependence reveals that the peak originates from a magnetic impurity phase with a magnetic transition temperature of about 300 K. The temperature dependence of the peak at (1.1,0,0) is similar to that at (0.1,0,0). We found a similar small-angle peak also in Sr-free $LaCoO_3$ at (0.125,0,0) which comes from another magnetic impurity phase with a transition temperature of about 250 K.

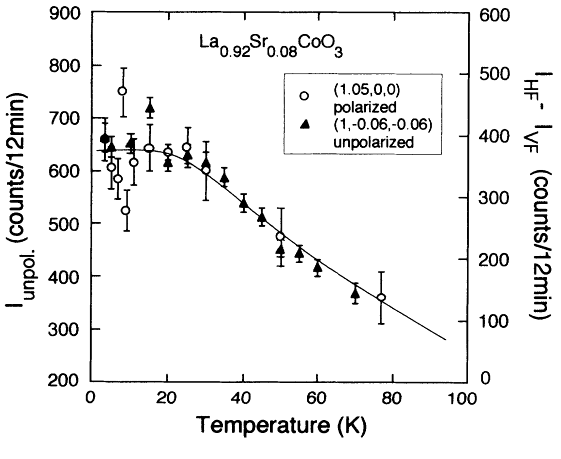

FIG. 8. Temperature dependence of the magnetic scattering cross section around (1,0,0) measured with unpolarized ($E_f = 13.7$ and $\Delta E = 0$ meV) and polarized ($E_f = 41$ and $\Delta E = 0$ meV) neutrons for $La_{0.92}Sr_{0.08}CoO_3$. The solid line is a guide to the eye.

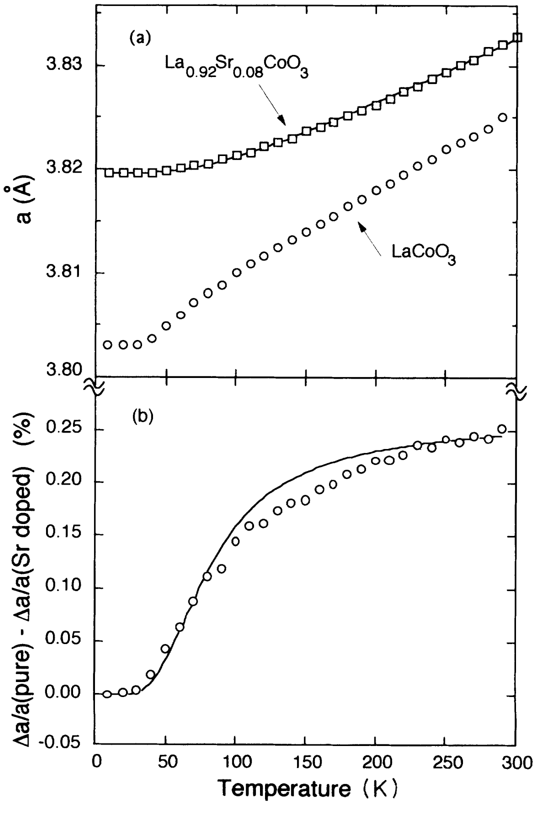

FIG. 9. (a) Temperature dependence of the lattice constants of $LaCoO_3$ and $La_{0.92}Sr_{0.08}CoO_3$. (b) The difference of the relative thermal expansions between $LaCoO_3$ and $La_{0.92}Sr_{0.08}CoO_3$.

Menyuk, Dwight, and Raccah[4] found unidentified magnetic peaks in the neutron powder diffraction of $LaCoO_3$ at 4 K although no evidence of impurity phases can be detected at higher temperatures. It seems that some magnetic impurity phase, which is crystallographically coherent with $LaCoO_3$, is easily incorporated into $LaCoO_3$ and related compounds.

B. Lattice parameters

Recently, an anomalous thermal expansion associated with the spin transition was reported on $LaCoO_3$ in the temperature region between 30 and 100 K.[14] The expansion was measured for an ingot with a dilatometer using a differential transformer. In the present work, we measured the temperature dependences of the lattice constants of $LaCoO_3$ and $La_{0.92}Sr_{0.08}CoO_3$ by the neutron diffraction of (1,0,0), (0,1,1), and $(0,1,\bar{1})$ Bragg peaks. The measurement was performed with a neutron energy of 3.5 meV and effective horizontal collimations of 30′-40′-20′-20′. The results are shown in Fig. 9(a). The temperature dependence for $La_{0.92}Sr_{0.08}CoO_3$ is typical for a solid, and can be reproduced by the Grüneisen formula applied for the Einstein model.

$$a(T)=a(0)\left\{1+\alpha\left[\coth\left[\frac{T_E}{2T}\right]-1\right]\right\}, \tag{3}$$

where $a(T)$ is the lattice constant at temperature T, T_E the Einstein temperature, and α the thermal expansion coefficient for $T \gg T_E$. The solid line drawn for $La_{0.92}Sr_{0.08}CoO_3$ in Fig. 9(a) corresponds to a fit with Eq. (3) using the parameters $a(0)=3.820$ Å, $T_E=246$ K, and $\alpha=1.75\times10^{-5}$. In contrast, an anomalous behavior can be seen in the temperature dependence of the lattice constant of $LaCoO_3$, consistent with the previous study.[14] The lattice constant of $LaCoO_3$ exhibits a steep increase with increasing temperature above around 50 K in addition to the normal thermal expansion. The anomalous part of the thermal expansion is extracted by subtracting the relative thermal expansion, $\Delta a/a(0)$, of $La_{0.92}Sr_{0.08}CoO_3$ from that of $LaCoO_3$. Here $\Delta a=a(T)-a(0)$. The anomalous expansion thus deduced is shown in Fig. 9(b); it starts around 50 K and almost saturates at 300 K. We notice a resemblance between the temperature dependences of the anomalous lattice expansion and the paramagnetic scattering intensity shown in Fig. 2. The solid line in Fig. 9(b) is the result of a fit to the formula[17]

$$\left[\frac{\Delta a}{a(0)}\right]_{\text{pure}}-\left[\frac{\Delta a}{a(0)}\right]_{\text{Sr doped}}=\frac{\nu\exp(-\Delta/T)}{1+\nu\exp(-\Delta/T)} \tag{4}$$

with the values of $\nu=15$, $\Delta=250$ K. The meaning of the formula will be discussed later. The angles, α, of the rhombohedral lattices of both specimens show only a small, smooth change with temperature. The typical values of α are $\alpha=90.87°$ at 9 K and $\alpha=90.70°$ at 290 K for $LaCoO_3$, and $\alpha=90.73°$ at 9 K and $\alpha=90.60°$ at 290 K for $La_{0.92}Sr_{0.08}CoO_3$.

V. DISCUSSION

A. Spin-state transition of $LaCoO_3$

We proposed in the previous study that the spin transition from the low- to the high-spin state takes place around 100 K in the oxide based on the temperature dependence of the paramagnetic scattering shown in Fig. 1(b). In the present study, we have observed the anomalous thermal expansion of the oxide around 100 K, and we regard this as further evidence for the spin transition in this temperature region. According to Chestnut's theory[23] of the spin transition as described in Ref. 17, the population, x, of the high-spin Co ion per site and a measure of the distance, Q, from the ion to the nearby ions are given by the equations

$$x=\frac{\nu}{\nu+\exp[(\Delta-VQ)/k_BT]} \tag{5a}$$

and

$$Q=\frac{V}{2\xi}x \tag{5b}$$

where T is the temperature, ν the multiplicity of the high-spin state, $\Delta-VQ$ the difference in energy between the high- and low-spin Co ions, and ξ the relevant elastic constant. In this model, the lattice expansion induced by the population of the high-spin state is expressed by Q and is proportional to the population x. The latter fact is in accordance with the resemblance between the temperature dependences of the paramagnetic scattering in Fig. 2 and the anomalous lattice expansion in Fig. 9(b). As can be seen in the latter figure, the anomalous part of the temperature dependence of the lattice constant can be reproduced fairly well with Eq. (4) which represents the case when the term VQ in Eq. (5a) is negligible compared to Δ. This result means that the spin transition of each Co ion takes place almost independently in the oxide. In the fitting the value of 15 for the multiplicity ν is assumed, i.e., the possible splitting of the 3d orbitals due to the trigonal crystalline field and/or the ls coupling are not taken into account. Although further refinements are possible,[24] the simple model[17] gives a quite adequate description of the measurements.

While our results unambiguously demonstrate that there is a single spin-state transition that occurs at low temperature, the nature of the broad transition that occurs near 500 K remains unresolved. The temperature dependence of the electronic structure has been probed in a number of photoemission and x-ray absorption studies.[15,25–29] A clear change in spectral features is observed on heating from 300 to 600 K, associated with the conductivity change. The core-level photoemission[29,30] and x-ray absorption spectra,[15] as well as valence-band photoemission spectra,[15,25–28,30] have generally been interpreted in terms of the different excitation multiplets expected for low-spin and high-spin Co^{3+} ground states. Based on simulations of the spectra, a number of studies have concluded that the spectral changes are associated with low-spin to high-spin transition. However, none of the simulations (including the recent x-ray absorption work) seem to give a convincing description of the measurements, and the proposed interpretation is contradicted by our neutron scattering results. There is definitely a dramatic change in electronic properties near 500 K, but it is not magnetic in origin. Thornton *et al.* have emphasized the crossover from localized to itinerant behavior,[7,8,25] and we believe that this is the change that is reflected in the spectroscopic data. The high-temperature transition remains quite interesting, and deserves further consideration.

The present experimental results, both temperature dependences of the paramagnetic scattering and the lattice constant, reveal that the spin transition does not take place in $La_{0.92}Sr_{0.08}CoO_3$. This result can be understood as a result of the lattice expansion induced by Sr doping. The ionic radius, 1.44 Å of Sr^{2+} is appreciably larger than that, 1.36 Å, of La^{3+}.[31] Therefore, Sr doping expands the distance between cobalt and oxygen ions and favors the high-spin state Co^{3+} with a larger ionic radius, 0.61 Å, than the low-spin state with the radius of 0.55 Å.

B. Spin glass state of $La_{0.92}Sr_{0.08}CoO_3$

The temperature dependence of the magnetization of $La_{0.92}Sr_{0.08}CoO_3$ is characteristic of a spin-glass system, and the Q dependence of the magnetic scattering shows a predominant ferromagnetic correlation with a correlation length of about 8 Å. In general, the spin-glass state is brought about as a result of competition of ferromagnetic and antiferromagnetic exchange interactions.[32] From the analysis of the paramagnetic Curie temperature of $La_{1-x}Sr_xCoO_3$, a relatively strong and negative superexchange interaction (-200 K) has been proposed between high-spin Co^{3+} ions in the system,[33] and this interaction is considered to play a role in the formation of the spin-glass state.[6] However, the present experiment of pure $LaCoO_3$ shows that the magnetic correlation between high-spin Co^{3+} ions is not antiferromagnetic but ferromagnetic as shown in Fig. 3, although it is very weak. Therefore, the appearance of spin-glass state in $La_{0.92}Sr_{0.08}CoO_3$ means that the introduction of Sr^{2+}, or nominal Co^{4+} ions, brings about not only ferromagnetic interactions but also antiferromagnetic interactions in the system.

The ferromagnetic short-range correlation persists up to the highest temperature of the observation. The temperature (~ 600 K) is far beyond the spin-glass transition temperature ($T_S = 24$ K). This fact suggests that there are two types of exchange interactions in $La_{1-x}Sr_xCoO_3$. One type is relatively strong but short-range interactions which are responsible for the formation of the ferromagnetic correlation. The other type is relatively weak interactions which are effective in freezing the ferromagnetically correlated magnetic moments into the spin-glass state. We consider the double exchange interactions between neighboring Co^{3+} and Co^{4+} ions as the former type, and long-range Ruderman-Kittel-Kasuya-Yosida (RKKY)-type interactions between Co^{4+} as the latter. The magnitude and the sign of the long-range interactions depend on the distance between the Co^{4+} ions and consequently introduce frustration into the system. The fact that the ferromagnetic correlation length does not show appreciable change on passing through T_s is consistent with the model.

It has been pointed out that $LaCoO_3$ is a highly covalent oxide.[7,8,15,16,25,30] Hitherto, we have used the term "high-spin Co^{3+} ion" for the magnetic Co ions in $LaCoO_3$. However the magnetic property of "high-spin Co^{3+} ions" in $LaCoO_3$ is much different from that in a more ionic oxide $SrCoO_{2.5}$.[34,35] This oxide is a *G*-type antiferromagnet with the Néel temperature of 570 K.[34] The magnitude of the magnetic moment measured by neutron diffraction is $3.3 \pm 0.5 \mu_B$ at 77 K, which is near the spin-only value for high-spin Co^{3+} ion, and the superexchange interaction between the ions is negative and strong as predicted by Anderson.[36] This fact makes a sharp contrast with the weakly ferromagnetic correlation of high-spin Co^{3+} ions in $LaCoO_3$. This difference of the magnetic character suggests that the electronic states of high-spin state Co^{3+} in $LaCoO_3$ is appreciably different from that in ionic oxides. Further studies to elucidate the electronic states and the microscopic origin of the magnetic correlation in the oxide are desired.

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