Calorimetric study of $La_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leqslant x \leqslant 0.5$): Evidence for long-range ferromagnetic ordering for $x \geqslant 0.3$

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Heat capacities of $La_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leqslant x \leqslant 0.5$) were measured in a temperature range of 1.8–300 K and in magnetic fields of 0 and 9 T. In $x \geqslant 0.3$, a clear heat capacity anomaly was observed due to a paramagnetic-to-ferromagnetic phase transition. A ferromagnetic short-range ordering was observed in the $x = 0.1$ sample as a small heat capacity anomaly depending on a magnetic field. The electronic contribution to the heat capacity was observed in $x \geqslant 0.2$, which indicates that an insulator-to-metal phase transition occurs between $x = 0.1$ and 0.2. The nature of the magnetic ordering was discussed in the light of the earlier reports.

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I. INTRODUCTION

Perovskite-type cobalt oxide, $LaCoO_3$, has been investigated by many researchers for the elucidation of the peculiar electromagnetic properties which originate from the temperature-dependent spin-state change. $LaCoO_3$ has trivalent Co ions whose ground state is a low-spin configuration (t_{2g}^6). It is well-known that the spin-state change takes place successively around 100 and 500 K,[1,2] although it has not been clarified yet what spin state is achieved by the two spin-state changes. It has been reported that replacement of La^{3+} in $LaCoO_3$ by Sr^{2+} resulting in a metallicity and a ferromagnetism above $x \approx 0.2$.[3,4] However, there are many reports indicating the glass-like behavior with respect to the magnetic order even in the region $x \geqslant 0.2$. Itoh *et al.* have suggested from dc magnetization[5] and NMR measurements[6] that the x-T phase diagram is divided into two regions: a spin glass region in $x < 0.18$ and a cluster glass region in $x \geqslant 0.18$. Their NMR measurements at 4.2 K revealed the presence of a large distribution of the internal magnetic field at the Co site even for $x \geqslant 0.2$ samples, which indicates that $La_{1-x}Sr_xCoO_3$ is not a typical ferromagnet with a long-range order.[6] Nam *et al.* found aging effect in $La_{0.5}Sr_{0.5}CoO_3$, as often observed in a glassy system.[7] On the other hand, Ganguly *et al.* suggested, by ac susceptibility measurements, that the long-range ferromagnetic ordering takes place for $x \geqslant 0.3$.[3] Sathe *et al.* also reported the presence of long-range ferromagnetic order in $x \geqslant 0.2$ samples through the neutron diffraction measurements.[8] In addition, Anil Kumar *et al.* suggested that the cluster-glass-like behavior originates from its magnetocrystalline anisotropy because the splitting of dc magnetizations of zero-field and field cooled-sample are also observed in long-range ordered ferromagnetic systems, such as $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$.[9] As stated above, the temperature and the compositional dependences of magnetic order in $La_{1-x}Sr_xCoO_3$ have yet to be clarified.

In this study, we carried out heat capacity measurements of $La_{1-x}Sr_xCoO_{3-\delta}$ in order to examine the nature of magnetic ordering as a function of x and T. Evidence of long-range ferromagnetic ordering was obtained as a clear heat capacity anomaly in the range $x \geqslant 0.3$. We discuss the nature of the magnetic ordering based on the present results and on earlier reports.[3–9]

II. EXPERIMENT

Polycrystalline samples of $La_{1-x}Sr_xCoO_{3-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, and 0.5) were prepared by a conventional solid-state reaction method. The appropriate amounts of La_2O_3 [purity was determined by ethylenediaminetetraacetic acid (EDTA) titration], $CoC_2O_4 \cdot 2H_2O$, and $SrCO_3$ were ground with ethanol and calcined with flowing an O_2 gas at 1373 K for 12 h. The calcined powder was then ground again, and fired once more under the same condition. Finally, it was pressed into pellets, sintered at 1573 K for 24 h, and cooled down to room temperature at a rate of about 100 K/h. The samples were confirmed to be a single phase with a rhombohedrally distorted perovskite structure by powder x-ray diffraction measurements using Cu$K\alpha$ radiation (MAC Science MXP18-HF). The lattice constants of $x = 0.2$ and 0.5 samples were determined at 35 and 298 K using polycrystalline Si as an internal standard. The oxygen content of the sample, 3-δ, was determined by iodometric titrations within the experimental error of ± 0.01 as tabulated in Table I. All the samples indicated a deviation from the stoichiometric value, 3. The excess oxygen contents in $x \leqslant 0.4$ samples are different from the earlier reports indicating oxygen defecient.[4,10] It would be due to the difference of starting materials or preparation conditions. Heat capacities were measured by a relaxation method using a Quantum Design Physical Property Measurement System between 2 and 300 K and under the magnetic fields of 0 and 9 T. Dc magnetizations were measured using a superconducting quantum inteference device magnetometer (MPMS5S, Quantum Design) under a magnetic field of 10 Oe.

III. RESULTS

Figure 1 shows the temperature dependence of heat capacities under zero magnetic field, C, for $x = 0$, 0.1, 0.2, 0.3,

TABLE I. Oxygen contents of $La_{1-x}Sr_xCoO_{3-\delta}$.

x	0	0.1	0.2	0.3	0.4	0.5
$3-\delta$	3.02	3.06	3.06	3.04	3.01	2.98

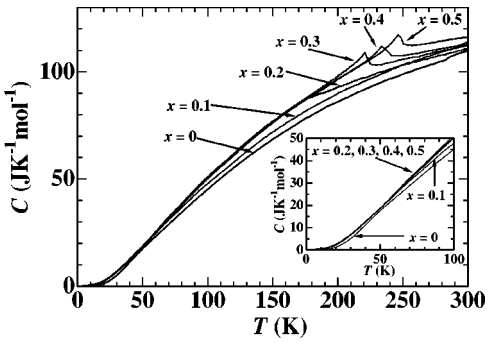

FIG. 1. Heat capacities of $La_{1-x}Sr_xCoO_{3-\delta}$ in the temperature range of 2–300 K and under zero magnetic field. The inset shows enlarged data in the range of 2–100 K.

0.4 and 0.5 samples. A clear heat capacity anomaly was observed in $x=0.3$, 0.4, and 0.5 samples due to a phase transition at around 220, 235, and 250 K, respectively. The heat capacity curve of $x=0.2$ sample showed a broad anomaly around 180 K. The heat capacities of $x=0.2$, 0.3, 0.4, and 0.5 samples are almost same below 180 K. On the other hand, the heat capacities of $x=0$ and 0.1 samples were smaller than those of $x=0.2$–0.5 samples at least below 250 K. As shown in the inset of Fig. 1, it was found that the heat capacity of $x=0$ sample becomes close to those of $x\geqslant 0.1$ samples around 50 K, while it departs from those below and above the temperature. The behavior is due to a Schottky anomaly in $LaCoO_3$ originating from the thermal excitation from the low-spin ground state to the excited state.[11,12]

Figure 2 shows the difference between the heat capacities measured under 9 and 0 T, $\Delta C_H(=C_{9\,\mathrm{T}}-C_{0\,\mathrm{T}})$. As indicated by open circles in the inset, ΔC_H of $x=0$ sample is positive up to 50 K, and changes to negative above the temperature due to the spin-state excitation.[13] On the other hand, $x=0.1$, 0.2, 0.3, 0.4, and 0.5 samples showed the opposite tendency, namely, ΔC_H changes its sign from negative to positive with an increase in temperature. This character concludes that the phase transitions observed in $x=0.3$, 0.4, and 0.5 samples are a paramagnetic-to-ferromagnetic phase transition, because the ferromagnetic critical fluctuation is suppressed by applying the magnetic field.[14] In addition, the

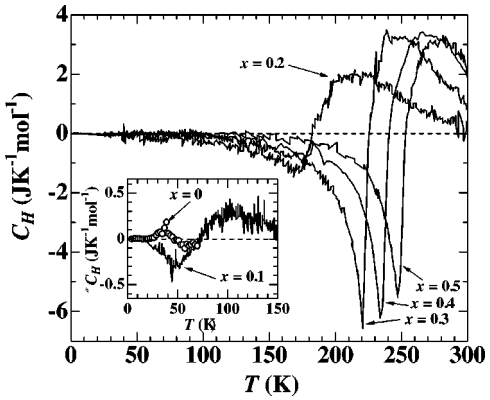

FIG. 2. ΔC_H vs T plots of $x=0.2$, 0.3, 0.4, and 0.5 samples, where $\Delta C_H=C_{9\,\mathrm{T}}-C_{0\,\mathrm{T}}$. The inset shows those of $x=0$ and 0.1 samples on an enlarged scale.

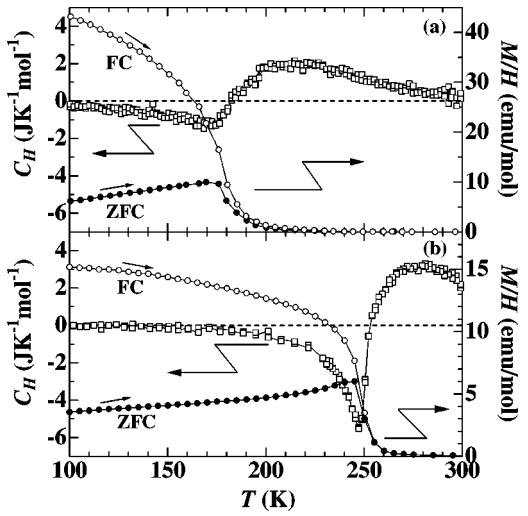

FIG. 3. ΔC_H and M/H vs T plots of $x=0.2$ (a) and $x=0.5$ sample (b). Solid and open circles represent the results obtained on heating after zero field cooling (ZFC) and field cooling (FC), respectively. Open squares indicate ΔC_H.

results imply that the (short- or long-range) ferromagnetic ordering occurs even in $x=0.1$ and 0.2 samples. Here, the temperature showing the minimum of ΔC_H is defined as the ferromagnetic ordering temperature, T_C. Itoh *et al.*[5] defined the spin glass or cluster glass transition temperature as a temperature, T_S, below which dc magnetizations measured after zero-field and field cooling depart from each other. We confirmed that T_S is coincident with T_C at least above $x=0.2$ as found from Fig. 3 (only the results of $x=0.2$ and 0.5 samples were shown there). Therefore, the splitting of the dc magnetizations of zero-field cooled and field cooled samples below $T_S(=T_C)$ would not be due to the freezing-in of clusters but to the coercive force problem as suggested by Anil Kumar *et al.*[9]

Figure 4 shows C/T vs T^2 plots in the temperature range 2–10 K when $H=0$ T. The heat capacity of a metallic ferromagnet at low temperature generally consists of contributions from the excitations of conduction electrons, spin waves, and phonons. The heat capacities at the low temperatures are almost same even by applying a 9-T magnetic field which should enhance the energy gap of spin wave excita-

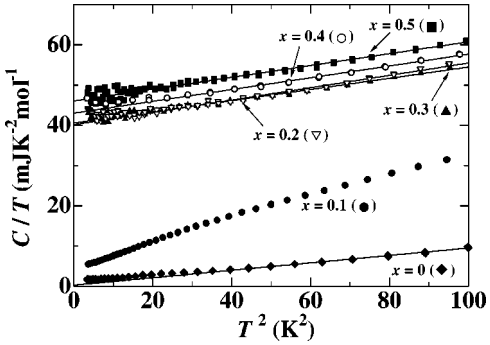

FIG. 4. C/T vs T^2 plots of $x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5 samples under a zero magnetic field. Solid lines show the results of least-square fitting with Eq. (1).

TABLE II. The best fit β and γ of $La_{1-x}Sr_xCoO_{3-\delta}$ obtained by the least-square fitting of the data in the range of 2–10 K with Eq. (1). Those of $x=0.1$ sample were not estimated.

x	β (mJ K^{-4} mol^{-1})	γ (mJ K^{-2} mol^{-1})
0	0.09	0
0.1	*	*
0.2	0.15	40
0.3	0.14	41
0.4	0.15	43
0.5	0.15	46

tion. This result indicates that the spin wave contribution is small as compared to the other contributions even if it is present, possibly because of the large exchange interaction or the large energy gap. Therefore, the data in Fig. 4 were fitted by the following equation:

$$C = \gamma T + \beta T^3 \tag{1}$$

The best fit β and γ of each sample are tabulated in Table II. The β's are almost same above $x=0.2$, but β of $x=0$ sample is small as compared to the other samples. The γ's of $x=0.2$, 0.3, 0.4, and 0.5 samples are in the same order. The magnitude of γ is so large as compared to other metallic perovskite-type oxides (~ 3 mJ K^{-2} mol^{-1} for $La_{1-x}Sr_xMnO_3$,[15] ~ 14 mJ K^{-2} mol^{-1} for $LaNiO_3$,[16] and ~ 8 mJ K^{-2} mol^{-1} for $SrVO_3$.[17]) Though the reason is unclear yet, the γ may be enhanced by electron-electron and/or electron-phonon interaction. The large γ may be a character of the perovskite-type cobalt oxides, because γ is also large in $La_{1-x}Ca_xCoO_3$ (Ref. 18) and $Pr_{1-x}Ca_xCoO_3$.[19] The results of $x=0.1$ sample are not shown there because the C/T vs T^2 curve could not be fitted even by including the contribution from spin waves into Eq. (1). The reason is unclear at present, but such a behavior has been reported also in $La_{1-x}Sr_xVO_3$ around the boundary between insulating and metallic phases.[20] However, it is clear that γ's of $x=0$ and 0.1 samples vanish or could be much smaller (even if it is present) than those of $x \geqslant 0.2$ samples.

IV. DISCUSSION

Figure 5 shows a possible schematic x-T phase diagram of $La_{1-x}Sr_xCoO_3$ deduced from the present results and the earlier reports. T_C was indicated by solid circles. The present study clarified that the electronic specific heat coefficient, γ, appears abruptly between $x=0.1$ and 0.2. The abrupt appearance of γ suggests that the phase diagram is divided into the insulating and metallic regions below and above $x=x_{IM}$ locating between 0.1 and 0.2. This is consistent with the transport studies.[3,4,21] It has been reported that the resistivity shows insulating and metallic natures in $x \leqslant 0.1$ and $\geqslant 0.3$, respectively. On the other hand, $x=0.2$ sample has been reported to be semiconducting by Senaris-Rodriguez *et al.*,[4] but on the other hand, metallic by Yamaguchi *et al.*[21] Taking account of the same γ of $x=0.2$ sample as $x \geqslant 0.3$ samples, the semiconducting behavior would be due to the grain boundary in their polycrystalline sample.[4]

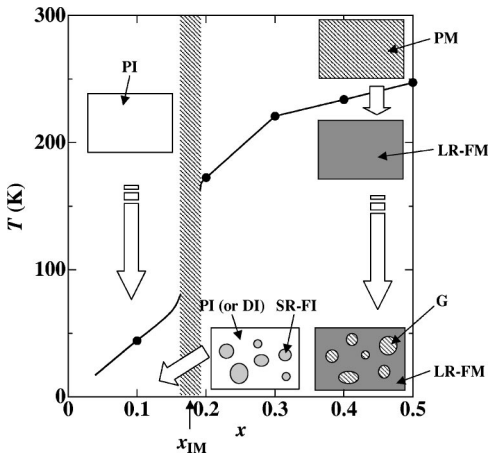

FIG. 5. Schematic phase diagram of $La_{1-x}Sr_xCoO_{3-\delta}$. Solid circles indicate T_C which is estimated by heat capacity measurements in this study. See the text for the definition. A thick solid line is a visual guide. Squares show schematic figures in each phase. PI, DI, SR-FI, PM, LR-FM, and G represent paramagnetic insulator, diamagnetic insulator, short-range ferromagnetic insulator, paramagnetic metal, long-range ferromagnetic metal, and glass-like regions (orders), respectively.

In the insulating region, a ferromagnetic-like anomaly was observed in ΔC_H of the $x=0.1$ sample. The magnitude much smaller than those of $x \geqslant 0.3$ samples, and a spin-glass-like anomaly observed by the magnetization measurements[5] concluded that the ferromagnetic-like ordering is a short-range type. Therefore, it is suggested that ferromagnetic and insulating clusters are created below T_C in $x < x_{IM}$. In the metallic region above $x=x_{IM}$, the present study clarified that a long-range ferromagnetic ordering occurs at T_C (at least in $x \geqslant 0.3$), because a clear heat capacity anomaly was observed at the temperature. However, NMR and ac magnetic susceptibility studies[6,7,22] suggested that the phase below T_C has a certain glasslike nature. On the other hand, a neutron diffraction study[8] suggested a presence of long-range order even at 10 K. Because the earlier experiments were carried out far-away below T_C, the results force us to conclude that the long-range ferromagnetic order and the glasslike order coexist at least at low temperatures. Such a coexistence was reported in many materials, so-called reentrant spin glass systems, e.g., $Au_{0.81}Fe_{0.19}$,[23,24] $Al_{0.3}Fe_{0.7}$,[24] $Eu_{0.6}Sr_{0.4}S$,[25,26] $Fe_{0.55}Mg_{0.45}Cl_2$,[27] and so on. However, the heat capacity anomaly around the magnetic ordering temperature in these materials is broad[23,26,27] as compared to the anomaly of $La_{1-x}Sr_xCoO_3$ observed in $x \geqslant 0.3$. Judging from the facts that long-range antiferromagnetic and spin glass orders coexist in $Fe_{0.55}Mg_{0.45}Cl_2$ even just below T_N and that the corresponding heat capacity anomaly is broad,[27] it is supposed that the broadness originates from such a coexistence present even at the magnetic ordering temperature. Therefore, it is natural to conclude that there is no such a coexistence in $La_{1-x}Sr_xCoO_3$ ($x \geqslant 0.3$), at least just below T_C, even if such two kinds of orders coexist at low temperatures. However, the heat capacity anomaly of $x=0.2$ sample is broad, which is similar to the heat capacity anomaly of $Fe_{0.55}Mg_{0.45}Cl_2$

(Ref. 27) at T_N. Therefore, the long-range ferromagnetic and glasslike orders might coexist in $x=0.2$ sample even around T_C.

From the above discussion, the temperature dependence of magnetic order in the metallic region is quite different from the reentrant spin glass system. As a reason for the peculiar magnetic ordering, we propose a temperature-induced spin-state transition, namely the population of σ^* band depends on the temperature. In order to obtain evidence to support this proposition, the lattice constants of $x=0.2$ and 0.5 samples were measured at 35 and 298 K. The volume changes between the temperatures were $\sim 1.0\%$ and $\sim 0.7\%$ for $x=0.2$ and 0.5 samples, respectively. The volume changes of $x=0$ and 0.08 samples are $\sim 2.0\%$ and $\sim 1.0\%$, respectively, according to the literature.[2,28] These volume changes are relatively large as compared to other perovskite-type oxides, e.g., $\sim 0.5\%$ for $PrCoO_3$,[19] $\sim 0.3\%$ for $LaMnO_3$,[29] $\sim 0.5\%$ for $LaNiO_3$,[30] and $\sim 0.4\%$ for $LaAlO_3$.[31,32] This suggests that the spin state gradually changes in $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.5$) with decreasing temperature. Therefore, the long-range ferromagnetic order formed at T_C might run into the coexistence of the long-range and glasslike orders as decreasing temperature, because of the difference in the spin state (and thus the exchange interaction) between around T_C and at low temperatures.

In addition, the present study suggests that the spin state gradually changes as increasing x from 0 to x_{IM} from the following reasons. β and the heat capacity below 180 K are nearly same in the range $x \geqslant 0.2$. On the other hand, the heat capacity decreases as decreasing x from 0.2 to 0 (not abruptly). It would be impossible to attribute the increased heat capacity from 0 to 0.2 only to the difference in the mean valence of Co ions and the Sr content, because the increased heat capacity from 0 to 0.2 is much larger than that from 0.2 to 0.5. Therefore, it is natural to consider that the increased heat capacity from 0 to 0.2 originates from a certain spin state change, namely a composition-dependent spin-state change, because the magnetic excitation should increase due to the nonzero spin quantum number of trivalent Co and the expanded volume due to the spin state change would reduce the atomic force constant and thus enhances the excitation of phonon as demonstrated by the β of $x \geqslant 0.2$ samples 1.7 times larger than that of $x=0$ sample. The magnitude of the large β change is consistent with the occurrence of composition-dependent spin-state change as described below. It has been reported that the elastic modulus of $LaCoO_3$ around 100 K is 0.7 times as large as that around 5 K because of the spin-state change.[33] This change corresponds to $\sim 70\%$ increase in β, because $\beta \propto \theta_D^{-3} \propto v^{-3} \propto C_e^{-3/2}$, where θ_D, v, and C_e represent the Debye temperature, sound velocity, and elastic modulus. Therefore, β of $La_{1-x}Sr_xCoO_3$ would also increase by $\sim 70\%$ if such a spin-state change occurs at $x=x_{IM}$. The insulator-to-metal transition at $x=x_{IM}$ might occur when the average occupation of e_g orbitals reaches a critical value.

V. CONCLUSIONS

We have measured heat capacities of polycrystalline $La_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leqslant x \leqslant 0.5$) samples. As reported by Itoh *et al.*,[5] the x-T phase diagram was divided at around $x=0.18$ into two regions which are clearly distinguished by the absence or presence of electronic specific heat. In the insulating small x region, a short-range ferromagnetic ordering occurs around 50 K. In the metallic large x region, a long-range ferromagnetic ordering occurs around 250 K. According to the earlier reports indicating both long-range ferromagnetic and cluster glass behaviors, it was suggested that the long-range ferromagnetic order formed at T_C runs into the coexistence of the long-range and glasslike orders as decreasing the temperature, possibly due to the temperature-dependent spin state change. The character of low temperature heat capacity (large electronic specific heat coefficient, small spin wave contribution, and anomalous behavior in $x=0.1$ sample) should be clarified in connection with the coexistence or the presence of ferromagnetic clusters in a paramagnetic or diamagnetic matrix.

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