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Unconventional magnetic transition and transport behavior in $Na_{0.75}CoO_2$

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Here we report an unconventional magnetic and transport phenomenon in a layered cobalt oxide Na_xCoO_2. Only for $x=0.75$, a magnetic transition of the second order was clearly detected at $T_m \sim 22$ K where an apparent specific-heat jump, an onset of extremely small spontaneous magnetization, and a kink in resistivity came in. Moreover large positive magnetoresistance effect was observed below T_m. These features of the transition strongly indicate the appearance of an unusual electronic state that may be attributed to the strongly correlated electrons in $Na_{0.75}CoO_2$.

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Since the discovery of the first high-T_c superconducting copper oxide, a tremendous amount of research has been conducted on $3d$ transition metal oxides to search for novel functions of the strongly correlated electron system. In such correlated-electron systems, spin-charge-orbital interactions are in a subtle balance such that various different electronic states could be stabilized depending on the thermodynamic conditions. As a consequence, unexpectedly large response could be induced against a slight change in, e.g., the carrier density and/or lattice distortions: as an example of the former serves the hole doping into insulating CuO_2 planes of layered copper oxides, which induces high-T_c superconductivity,[1] and as an example of the latter the isovalent rare-earth (R) substitution at the (R,Sr) site in $(R,Sr)MnO_3$, which controls the colossal magnetoresistance phenomenon.[2] It is thus probable that highly precise control on the chemical composition in a variety of correlated-electron-system materials yields unconventional electronic states accompanied by unexpected electronic/magnetic phase transitions.

Layered cobalt oxides of the Na_xCoO_2 system have been known as thermoelectric materials since Terasaki *et al.*[3] reported that some of them showed simultaneously large thermoelectric power (S) and low electrical resistivity (ρ). The large value reported for thermoelectric power of $Na_{0.5}CoO_2$, i.e., $S > 50 \mu V/K$ at 300 K, is hardly understood within the framework of the conventional one-electron picture. It has been suggested[4] that both the strong electron correlation and the cobalt spin state play a crucially important role in facilitating such a high value of thermoelectric power. The crystal structure of Na_xCoO_2 consists of a single atomic layer of Na ions sandwiched by two CoO_2 layers. The CoO_2-layer block is constructed with a two-dimensional triangular lattice of cobalt ions. For Na_xCoO_2, paramagnetic behavior was reported[5–7] in the whole temperature range studied (4.2–300 K) without any distinct magnetic orderings. Recently, we established a sample-preparation method named ‘‘rapid heat-up’’ technique that has enabled us to precisely control the Na content in Na_xCoO_2 samples.[8] For thus prepared samples of $Na_{0.75}CoO_2$, we detected a magnetic ordering below 22 K.

In this article, we report the magnetic transition observed only for samples with the solubility-limit Na content, i.e., $x=0.75$, in the layered-cobalt-oxide system Na_xCoO_2. A magnetic transition of the second order was clearly confirmed at $T_m = 22$ K, being accompanied by an apparent specific-heat jump, a small spontaneous magnetization, a kink in the ρ-T curve, and a drastic enhancement in the positive magnetoresistance. In Na_xCoO_2, any long-range ordering of spins is likely to be suppressed by the cobalt triangular lattice that tends to possess geometrical frustration amongst the competing interactions. The magnetism of unusual characteristics observed in the present work in our $Na_{0.75}CoO_2$ samples could be an example of the recently high-lighted phenomena coming out of the frustration systems[9] upon being triggered by a tiny stimulation only, i.e., in the present case by a precise control of the Na nonstoichiometry.

The $Na_{0.75}CoO_2$ samples were synthesized employing the ‘‘rapid heat-up’’ (RH) technique.[8] By x-ray powder diffraction, the pellet samples were confirmed to be single phase of the hexagonal γ-Na_xCoO_2 (Refs. 10,11) without any traces of impurity phases. Careful high-resolution TEM and ED investigations revealed that the samples were homogeneous and contained no anomalous nanoscale clusterings.[12] Magnetization was measured by a SQUID magnetometer (Quantum Design; MPMS-XL). Magnetotransport measurements were performed using a four-point-probe apparatus (Quantum Design; PPMS) in a transverse-field condition, i.e., under a magnetic field normal to the applied current. For every kind of characterization, multiple number of specimens were measured to confirm reproducibility. Heat capacity was measured using a homemade adiabatic calorimeter. Measurements were carried out between 8 and 330 K for a powder sample of ~6 g prepared at 900 °C by the rapid heat-up technique. More detailed descriptions of the present method for heat capacity measurements are given elsewhere.[13]

Figure 1 shows the dependences of specific heat (C_p), magnetic susceptibility (M/H), and electrical resistivity (ρ) of $Na_{0.75}CoO_2$ on temperature (T). A sharp jump at 21.8 K in the C_p-T curve [Fig. 1(a)] represents the magnetic transition temperature (T_m). The jump exhibits a shape typical for the second-order phase transition. Below T_m, magnetic susceptibility rapidly increases under an applied magnetic field of 1 to 100 Oe, exhibiting a distinct hysteresis between the zero-field-cooled (ZFC) and field-cooled (FC) curves [Fig. 1(b)]. Moreover, the resistivity gradually decreases in the

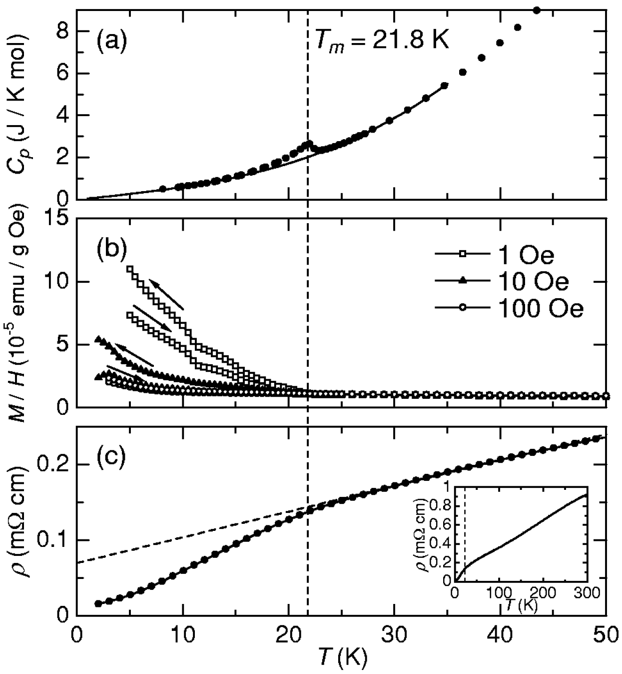

FIG. 1. (a) Specific heat C_p, (b) magnetic susceptibility M/H, and (c) electrical resistivity ρ for the $Na_{0.75}CoO_2$ sample with respect to temperature. The inset in (c) shows the ρ-T relation for a wider temperature range.

lower temperature region, yielding a kink around T_m in the ρ-T curve [Fig. 1(c)]. Note that the ρ-T curve has a steeper slope below T_m and decreases toward a very low residual resistivity (ρ_r) of $\sim 15 \mu\Omega$ cm. As clearly shown in Fig. 1, all of these anomalies occur at the same temperature, i.e., at T_m.

In order to estimate the baseline about the specific-heat jump in Fig. 1(a), the C_p-T curve was fitted using the following formula:

$$C_p(T) = f_D(T/\Theta_D) + \gamma T,$$

where Θ_D, γ, and f_D denote, respectively, the Debye temperature, the electronic specific-heat coefficient, and Debye's formula for which the degree of freedom was assumed to be three per atom. Based on least-square calculations, the values of Θ_D and γ were determined to be 553 K and 25.9 mJ / K^2 mol, respectively. The present value of Θ_D is larger than those reported for $(Na,Ca)Co_2O_4$ samples by Ando *et al.*, i.e., 350–390 K,[14] but the γ value is in good agreement with those for the same samples, i.e., 52–56 mJ / K^2 mol [$(Na,Ca)Co_2O_4$]. After subtracting the baseline [shown by the solid line in Fig. 1(a)], the enthalpy and entropy changes were calculated at $\Delta H = 0.975$ J / mol and $\Delta S = 0.0481$ J / K mol, respectively.

Figure 2 shows the inverse susceptibility (χ^{-1}) vs temperature plot at $H = 10$ Oe. The plot follows the Curie-Weiss law above T_m: $\chi = C/(T - \Theta)$, where C and Θ denote the Curie constant and the Weiss temperature, respectively. The values for C and Θ were determined to be 0.234 emu K / mol Oe and -166.4 K, respectively. The negative value of Θ suggests an antiferromagnetic interaction (some negative values were also reported for Θ's of Na_xCoO_2 in previous works[6,7]). This value for C yields an effective moment (μ_{eff}) of (1) $1.37 \mu_B$/Co site if all the cobalt atoms are assumed equivalent, and (2) $2.74 \mu_B / Co^{4+}$ if only Co^{4+} spins contribute (and all other Co^{3+} are in the low spin state, i.e., $S = 0$). At least the latter case is unlikely since the theoretical "spin-only" value of Co^{4+} in the low spin state is $1.73 \mu_B$ which is much less than $2.74 \mu_B$. Nonetheless there are no other evidences to possitively support $\mu_{\text{eff}} = 1.37 \mu_B$ for the former model.

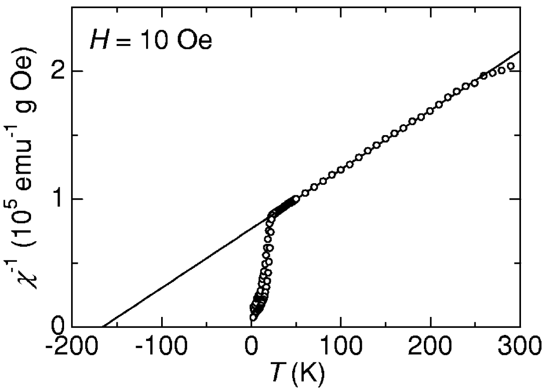

FIG. 2. Inverse susceptibility (χ^{-1}) vs temperature relation at $H = 10$ Oe for $Na_{0.75}CoO_2$. The solid line represents the best fit to the Curie-Weiss law above $T_m = 22$ K.

Figure 3 shows the magnetization (M) as a function of the applied field (H) at various temperatures: 2, 5, 10, 20, and 50 K. In the M-H loop at 2 K, nonlinear increase in magnetization and a narrow hysteresis are observed in the low field region. A nonlinear M-H relation is also seen at 5 and 10 K, though the distinct hysteresis is hardly seen. On the other hand, at 20 K (just below T_m) and 50 K (above T_m), the magnetization is linearly proportional to the applied field, indicating the absence of long-range order at these temperatures. Spontaneous magnetization M_s was estimated at $H = 0$ through linearly extrapolating the M-H curve and plotted in Fig. 4 as a function of temperature. The magnitude of

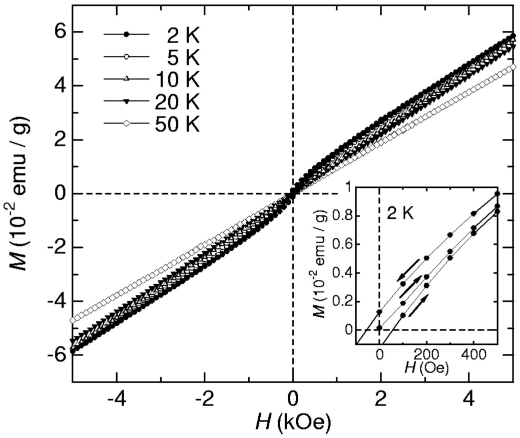

FIG. 3. M-H loops for the $Na_{0.75}CoO_2$ sample at 2, 10, 20, and 50 K. The inset shows a magnified M-H loop at 2 K in the weak-field region.

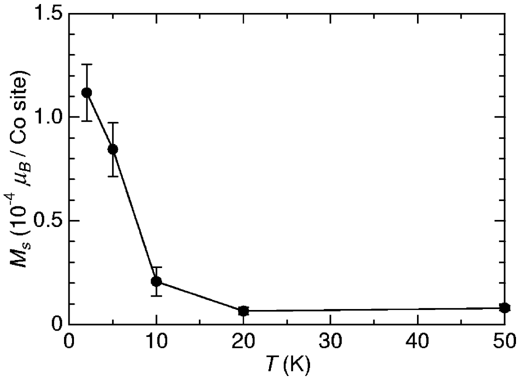

FIG. 4. Spontaneous magnetization M_s of the $Na_{0.75}CoO_2$ sample as a function of temperature. The M_s value was obtained at $H=0$ by linearly extrapolating the M-H curve.

M_s increases rapidly as temperature is lowered. However, it is as small as $10^{-4}\mu_B$/Co site even at 2 K: this value is extraordinarily small in comparison with those of conventional ferromagnetic compounds.

One of the most characteristic features of the present compound is large positive magnetoresistance (MR) effect seen in the magnetically ordered state. Figure 5 shows the dependence on temperature of the degree of MR effect, as defined by $\Delta\rho_H/\rho_0 \equiv (\rho_H-\rho_0)/\rho_0$, where ρ_H is the resistivity in an applied field of *H*. The magnitude of MR effect was below the detection limit ($\sim$0.1%) at temperatures higher than 25 K. With decreasing temperature, on the other hand, the $\Delta\rho_H/\rho_0$ value at 7 T abruptly increases and reaches up to $\sim$0.3 at 2 K. The onset temperature of the MR effect is in good agreement with $T_m=22$ K, which clearly indicates that the positive MR effect is triggered by the magnetic transition. As shown in the inset of Fig. 5, the degree of MR effect also depends on the applied magnetic field such that $\Delta\rho_H/\rho_0 \propto H^2$.

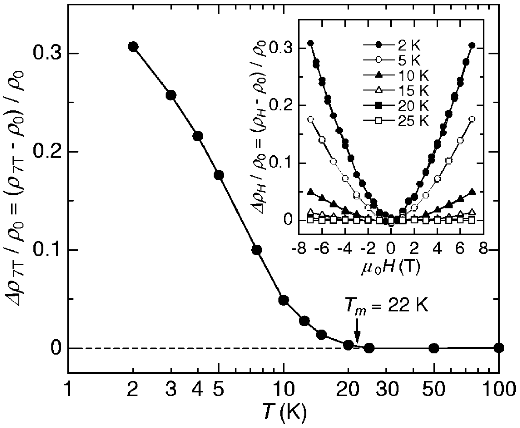

FIG. 5. Dependence of the degree of MR effect on temperature at a field of 7 T for the $Na_{0.75}CoO_2$ sample. The MR degree is defined as $\Delta\rho_H/\rho_0 \equiv (\rho_H-\rho_0)/\rho_0$ where ρ_H is the electrical resistivity under an applied magnetic field (*H*) while ρ_0 is that at zero field. The inset shows the $(\Delta\rho_H/\rho_0)-H$ relation at various temperatures. Note that the $\Delta\rho_H/\rho_0$ values (below T_m) are all positive.

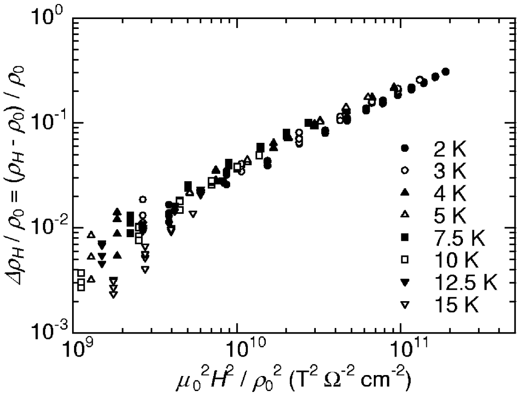

FIG. 6. Kohler's plot for the $Na_{0.75}CoO_2$ sample at various temperatures below $T_m=22$ K. Note that a temperature-independent relationship is established between $\Delta\rho_H/\rho_0$ and $(H/\rho_0)^2$, which indicates that the positive MR effect of $Na_{0.75}CoO_2$ is most likely originated from the conventional orbital motion of carriers.

It should be pointed out that the occurrence of magnetic ordering was theoretically predicted for Na_xCoO_2 at $x=0.5$ by Singh.[15] He predicted that this compound possesses a large density of state at E_F and therefore an inherent electronic instability yielding an itinerant ferromagnetism. However, the magnetic behavior of the present $Na_{0.75}CoO_2$ sample is difficult to be ascribed to conventional itinerant ferromagnetism. Reasons for this are as follows. (1) It was found that Arrott plots [M^2 vs H/M relation][16] do not to form a straight line nor passes the origin at T_m. (2) The Weiss temperature (Θ) is negative, being in contrast to positive Θ values for conventional ferromagnets. (3) The M_s value does not rapidly increase starting at T_m as temperature is lowered. Taking into account these facts as well as the distinct thermomagnetic irreversibility below T_m [see Fig. 1(b)], it is considered that in the present compound a ferromagnetic interaction starts to develop at T_m, and eventually forms a long-range order among the magnetic moments at lower temperatures.[17]

Tsukada *et al.*[18] found a ferromagnetic ordering below 3.2 K with small M_s and large negative MR in single-crystal samples of a Pb-doped Bi-Sr-Co-O misfit-layer compound. However, the magnetism in $Na_{0.75}CoO_2$ should be different from that of the (Bi,Pb)-Sr-Co-O compound, because signs of MR are opposite between the two compounds. Therefore, the key to understand the electronic state of $Na_{0.75}CoO_2$ must be lying in the nature of the positive MR effect. Recently, a similar positive MR effect was reported in a weak-ferromagnetic Co-doped FeSi alloy, and it was attributed to some quantum interference effects.[19] For $Na_{0.75}CoO_2$, however, the MR characteristics were much different from those of the (Fe,Co)Si alloy in terms of the dependences on temperature and field. We also drew a scaling plot as that given in Ref. 19 and confirmed that our plot for $Na_{0.75}CoO_2$ does not form a single universal relation, implying totally different mechanisms for the two cases. In conventional metals the MR effect arises from the "bending" of electron trajectory by the Lorentz force such that Kohler's plot, i.e., $\Delta\rho_H/\rho_0$ vs $(H/\rho_0)^2$, forms a single universal relation that is independent of temperature.[20] In Fig. 6, shown are the MR data collected for the present $Na_{0.75}CoO_2$ sample at various temperatures below T_m. Obviously, all the data points in the temperature range of 2–15 K follow more or less a universal relation, i.e., the present MR data obey Kohler's rule. Therefore, we conclude that the positive MR effect of $Na_{0.75}CoO_2$ is most likely originated from the conventional orbital motion of carriers. Since it is known that in such a situation the degree of MR effect is proportional to the square of carrier mobility, the large magnitude of MR effect is considered to be caused by a drastic enhancement in carrier mobility in the magnetically ordered state.

It is noteworthy that the observed entropy change at T_m, i.e., $\Delta S = 0.0481$ J / K mol, is exceedingly small, corresponding to only $\sim 1\%$ of the theoretical value, i.e., $R \ln 2 = 5.76$ J / K mol for the state in which F (degree of freedom) = 1 and S (spin quantum number) = 1/2, and spins are all perfectly ordered. On the other hand, as seen in Fig. 1(c), the resistivity slope, i.e., $d\rho/dT$, is enhanced by a factor of 2 below 22 K, implying that the Drude weight n/m^* (where n is the carrier concentration and m^* the carrier effective mass), has been significantly reduced. Such a reduction in Drude weight is considered to be caused by a (pseudo) gap opening. As a possible ordered state accompanied by the tiny entropy change and an open pseudogap, either a charge-density-wave (CDW) or a spin-density-wave (SDW) state is inferred. Upon assuming a state with an open pseudogap at temperatures below T_m, both the resistivity drop towards an extremely low residual resistivity and the large positive MR effect can be consistently explained. The strong dependence of resistivity on temperature [Fig. 1(c)] implies that the electrical conduction is mainly influenced by the electron-electron scattering. In such a situation, the total carrier-mobility is expected to be enhanced if one of the Fermi surfaces that yields the lower-mobility carriers disappears, as resistivity is inversely proportional to the *total* scattering time averaged over the whole Fermi surfaces. It is considered that below T_m the Fermi surface for the lower-mobility carriers vanishes upon a CDW or SDW formation, whereas the other for the higher-mobility carriers still survives.[21]. Note that this view is consistent with the calculated band picture by Singh[15] who predicted that in $Na_{0.5}CoO_2$ there exist two Fermi surfaces of different natures: one is a cylindrical/hexagonal hole-surface originated from the localized a_{1g} band, and the other a holelike section with the itinerant $a_{1g} + e_g$ character. It is plausible that the localized a_{1g} and itinerant $a_{1g} + e_g$ bands correspond respectively to the low-mobility and to the high-mobility carriers in our present model.

The simultaneous onsets of thermomagnetic irreversibility, finite entropy jump, resistivity drop, and large positive MR effect imply that the magnetism of $Na_{0.75}CoO_2$ is unusual in comparison with any cases of classical magnetic states. In fact, the simultaneous enhancement in magnetization is difficult to understand by assuming a CDW/SDW state below T_m: this is the most mysterious feature of the present "unconventional" magnetic transition in $Na_{0.75}CoO_2$. To solve this difficulty, two distinct ordered states may be required to coexist below T_m: one is a CDW or SDW state, and the other is a magnetically ordered state which alone is mainly responsible for the magnetization anomaly. In such a case, cobalt species in the two different states are required to coexist. A previous NMR study[6] suggested two inequivalent cobalt sites in a Na_xCoO_2 sample with $x = 0.5$. On the other hand, judging from the magnitude of spontaneous magnetization of $Na_{0.75}CoO_2$, the magnetically ordered state should arise from a very small number of cobalt species, which may be difficult to be confirmed by any existing site-specific spectroscopy techniques. A similar behavior was reported for a Cu-substituted Na_xCoO_2 in which an SDW-like transition was induced by the Cu-for-Co substitution.[22] The similarity of the two cases suggests that spatial inhomogeneity in the cobalt state does not drastically modify the pristine electronic structure: the existence of inequivalent cobalt species itself is not an intrinsic feature of the present magnetic transition.

Finally, we comment on our successful observation of this unconventional magnetism in $Na_{0.75}CoO_2$. The key technique to have an Na_xCoO_2 sample exhibit the magnetic transition is to precisely control the Na nonstoichiometry. It is known that Na-rich Na_xCoO_2 samples are difficult to be synthesized with a conventional solid-state reaction method, as a large deficiency results in the Na content inevitably.[23] Using various Na_xCoO_2 samples with $x = 0.65–0.75$ prepared with both our RH technique and a conventional method, *only the* $x = 0.75$ RH *sample* showed the low-temperature second order transition. Very recently, Takeuchi *et al.*[24] studied the magnetic properties of their Na_xCoO_2 samples with a nominal composition of $x = 0.75$ and found an irreversible magnetic behavior below 13 K, suggesting a short-range ferromagnetic coupling. However, the samples showed no indication of spontaneous magnetization down to 2 K, though a spinglass-like anomaly was seen at 3 K. This result implies that the magnetic property of Na_xCoO_2 is highly sensitive to the Na nonstoichiometry. The reasons why no magnetic transitions were detected for various Na_xCoO_2 samples of previous works were (1) samples with high enough Na contents had not been synthesized, that is, in previous works even the starting compositions were rather Na-poor, e.g., $x = 0.50–0.55$ for Refs. 5,6,14, respectively and (2) conventional powder methods that most likely resulted in Na losses were employed.

In summary, we have confirmed the existence of an unconventional magnetic and transport phenomenon in Na_xCoO_2 with a precisely controlled Na content, $x = 0.75$. The magnetic transition with $T_m = 22$ K was of the second order, being accompanied with a specific-heat jump. At the same temperature T_m, weak spontaneous magnetization ($M_s = 1.2 \times 10^{-4} \mu_B$/Co site at 2 K), rapid resistivity drop towards an extremely low residual resistivity ($\rho_r \sim 15 \mu\Omega$ cm), and large positive magnetoresistance effect ($\Delta\rho_{7T}/\rho_0 \sim 0.3$ at 2 K) were found to occur simultaneously. All these strongly indicate the appearance of an unconventional electronic state stemmed from the strong correlation of electrons.

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