Unconventional electronic transition in Na_xCoO_2 with a precisely controlled Na nonstoichiometry

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Abstract

An unconventional electronic transition was discovered in a layered cobalt oxide, Na_xCoO_2, with precisely controlled Na contents. Only for Na-rich samples with $x \simeq 0.75$, a weak-ferromagnetic transition of the second order was clearly detected at 22 K, being accompanied by a clear specific-heat jump, unexpectedly small spontaneous magnetization, kinks in both the resistivity vs temperature and the thermoelectric power vs temperature curves. Moreover, large positive magnetoresistance was observed at temperatures below ~ 22 K.

Key words: Na_xCoO_2; electronic transition; weak-ferromagnetic transition; positive magnetoresistance

Unconventional electromagnetic characteristics have been reported for various strongly-correlated transition-metal oxides. In many of such cases, spin-charge-orbital interactions are in a subtle balance such that very different electronic states may be stabilized depending on thermodynamic conditions. Consequently, a large response is often induced against a tiny stimulation such as charge carrier doping. Thus chances are that highly precise control on chemical composition in correlated-electron-system materials yields unknown electronic/magnetic phase transitions.

Here we report a novel electronic phase transition in layered cobalt oxide, Na_xCoO_2, with precisely controlled Na content. Only for samples with the solubility-limit Na content, i.e. $x = 0.75$, a weak-ferromagnetic transition of the second order was clearly detected at $T_C = 22$ K, being accompanied by a clear specific-heat jump, unexpectedly small spontaneous magnetization, kinks in both the resistivity (ρ) and thermoelectric-power (S) vs temperature curves. At the same time, large positive magnetoresistance was observed at temperatures exactly below T_C.

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Na_xCoO_2 samples were synthesized employing a “rapid heat-up” technique [1] to precisely control the Na content at $x = 0.75$. By x-ray powder diffraction, the pellet samples were confirmed to be single phase of hexagonal γ-Na_xCoO_2 [2]. The microstructure of the Na_xCoO_2 samples was examined using a TEM (Hitach H-9000NAR) with an acceleration voltage of 300 kV. Magnetization and magnetotransport measurements were performed using a SQUID magnetometer (Quantum Design; MPMS-XL) and a four-point-probe apparatus (Quantum Design; PPMS), respectively. Specific heat was measured using a home-made adiabatic calorimeter. Detailed descriptions of the experimental procedure are given elsewhere [3].

ED patterns were obtained from a large number of grains of an $Na_{0.75}CoO_2$ sample: for most grains (> 90%), a triangular diffraction pattern that is characteristic to the CoO_2 layer of Na_xCoO_2 was clearly observed (Fig. 1, inset). In some rare cases we could not observe clear diffraction patterns. The reason for this was considered to be a misalignment of the incident electron beam. This clearly indicates that the presently prepared sample is single phase without any traces of impurity phases. We successfully took atomic-

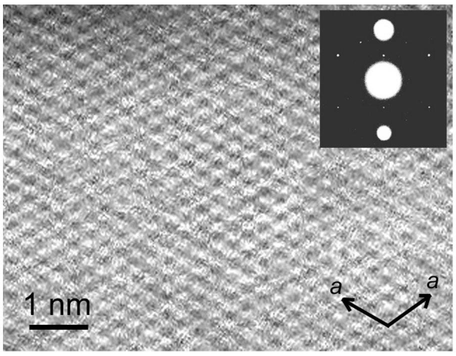

Fig. 1. High-resolution TEM image of $Na_{0.75}CoO_2$ sample. The observed triangular atomic arrangement is characteristic to the CoO_2 layer of Na_xCoO_2. The inset shows the ED pattern taken with an incident beam parallel to the c-axis.

resolution images where we can observe the triangular atomic arrangement (Fig. 1). From the TEM observations, the present samples were confirmed to be homogeneous, not containing any anomalous nano-scale clusterings.

Figure 2 shows the dependences on temperature of specific heat (C_p), magnetic susceptibility (χ), electrical resistivity (ρ), thermoelectric power (S), and MR effect ($\Delta\rho_H/\rho_0 \equiv (\rho_H - \rho_0)/\rho_0$) of the $Na_{0.75}CoO_2$ sample. A second-order transition was clearly detected at $T_C = 22$ K, being accompanied by a clear specific-heat jump. Below T_C, the magnetic susceptibility rapidly increases under an applied field of 1 to 100 Oe, exhibiting a weak ferromagnetism with a small but finite spontaneous magnetization ($1.2{\times}10^{-4}$ μ_B / Co site at 2 K) [3]. Both resistivity and thermoelectric power gradually decrease in the lower temperature region, yielding a kink at T_C in the $\rho - T$ and $S - T$ curves, respectively. Moreover, the degree of MR at 7 T abruptly increases with decreasing temperature and reaches up to ~ 0.3 at 2 K. As clearly shown in Fig. 2, all of the anomalies occur at the exactly same temperature, i.e. T_C.

It should be noted that the weak-ferromagnetic transition of $Na_{0.75}CoO_2$ involves with various anomalies as shown in Fig. 2, indicating a peculiar magnetic property as compared to, e.g. that of $ZrZn_2$ [4]. The large simultaneous responses in resistivity, thermoelectric power, and MR effect would suggest a significant modification in the Fermi-surface structure. The unconventional electronic transition at $T_C = 22$ K may be attributed to the strongly-correlated $3d$ electrons.

In summary, we have discovered an unconventional electronic phase transition at $T_C = 22$ K in Na_xCoO_2 with a precisely controlled Na content (x) of 0.75. The transition was of the second order, being accompanied with a clear specific-heat jump, a small spontaneous magnetization, a kink in both the $\rho - T$ and $S - T$ curves, and relatively large positive magnetoresistance

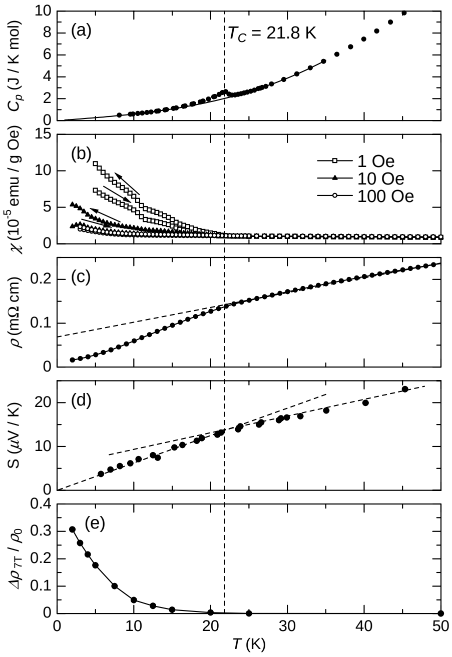

Fig. 2. (a) Specific heat, C_p, (b) magnetic susceptibility, χ, (c) electrical resistivity, ρ, (d) thermoelectric power, S, and (e) degree of MR at a field of 7 T, $\Delta\rho_H/\rho_0 \equiv (\rho_H - \rho_0)/\rho_0$, for the $Na_{0.75}CoO_2$ sample with respect to temperature.

effect. All these characteristics strongly indicate the occurance of an unusual electronic state stemmed from the strong correlation of electrons.

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