# Metamagnetic Transition in $Na_{0.85}CoO_2$ Single Crystals

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We report the magnetization, specific heat, and transport measurements of a high quality $Na_{0.85}CoO_2$ single crystal in applied magnetic fields up to 14 T. At high temperatures, the system is in a paramagnetic phase. It undergoes a magnetic phase transition below ~20 K. For the field $H \parallel c$, the measurement data of magnetization, specific heat, and magnetoresistance reveal a metamagnetic transition from an antiferromagnetic state to a quasiferromagnetic state at about 8 T at low temperatures. However, no transition is observed in the magnetization measurements up to 14 T for $H \perp c$. The low temperature magnetic phase diagram of $Na_{0.85}CoO_2$ is determined.

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The recent discovery of superconductivity in the hydrated cobalt oxides [1–3] has attracted extensive attention, since it is the only known layered transition metal oxide which exhibits superconductivity other than high $T_c$ cuprates and $Sr_2RuO_4$ [4]. The $Na_xCoO_2$ crystal consists of two-dimensional $CoO_2$ layers separated by Na layers, similar to that of high $T_c$ cuprates and $Sr_2RuO_4$ except that in each layer Co atoms form a triangular lattice rather than a square one [5,6]. Superconductivity is observed when $x \sim 0.3$ and sufficient water is intercalated between the $CoO_2$ layers. A number of experiments [7–9] and theoretical works [10,11] suggested that superconductivity in $Na_xCoO_2 \cdot H_2O$ is unconventional, probably with spin triplet pairing.

With a change of Na content $x$, $Na_xCoO_2$ exhibits a rich phase diagram. Foo *et al.* [12] studied transport and magnetic properties of a series of $Na_xCoO_2$ samples with $x$ varying from 0.3 to 0.75. They found that the ground state is a paramagnetic metal at $x \sim 0.3$, becomes a charge-ordered insulator at $x = 0.5$, and then a "Curie-Weiss metal" at $x \sim 0.70$. The ground state of $Na_xCoO_2$ for $x > 0.75$ is still not clear. Sugiyama and co-workers [13] carried out the muon-spin-rotation experiments ($\mu$SR) on a $Na_{0.9}CoO_2$ single crystal prepared by a flux method. They found that the $\mu$SR signal was fitted best by a zeroth-order Bessel function, and concluded that $Na_{0.9}CoO_2$ undergoes a transition from a paramagnetic to an incommensurate spin density wave (IC-SDW) state. They claimed that the IC-SDW occurs within the $CoO_2$ plane and that the oscillating moments pointed along the $c$ axis. However, Bayrakci *et al.* [14] found that $Na_{0.82}CoO_2$ exhibits a bulk antiferromagnetic (AF) long range order with a Néel temperature of about 20 K by the susceptibility, specific heat, and $\mu$SR measurements for $Na_{0.82}CoO_2$ single crystals prepared by floating-zone method. They found that the magnetic order encompasses nearly 100% of the crystal volume. The inelastic neutron scattering experiment on $Na_{0.75}CoO_2$ single crystals by Boothroyd *et al.* [15] showed that there exists strong in-plane ferromagnetic (FM) correlations with an energy scale much higher than 20 K, consistent with an AF correlation modulation perpendicular to the $CoO_2$ planes. The existence of strong in-plane FM correlations is also consistent with the band structure calculations [16].

In this Letter, we report the magnetization, specific heat, and magnetoresistance measurements on a high quality single $Na_{0.85}CoO_2$ crystal in magnetic fields up to 14 T. For $H \parallel c$, we find that there is a metamagnetic transition from an AF to a quasi-FM state at ~8 T below 20 K. However, for $H \perp c$, no transition is observed in magnetization measurements up to 14 T. Our results suggest that the competition between the AF and FM correlations controls the physics of low-lying excitations in this material.

A single crystal of $Na_{0.85}CoO_2$ was prepared in flowing $O_2$ in a floating-zone optical image furnace. The starting feed and seed materials were prepared using $NaCO_3$ and $Co_3O_4$ powders with Na:Co ratio of 0.85:1. The well-mixed powders were heated at 750 °C overnight, and then the powders were reground and heated at 850 °C for a day. The mixture was then pressed to form a cylinder of about 10 cm in length and 8 mm in diameter for feed. The growth rate is 2 mm per hour. The end part of this crystal, which is the most homogeneous part of the crystal, was cut into several pieces and used in our measurements. The Na:Co ratio of the crystal, determined by the induction-coupled plasma measurements, is $0.85 \pm 0.02$. From the x-ray diffraction measurements, no impure phase is detected within experimental error of 2% and the $c$-axis lattice constant $c$ is determined to be 10.62 Å. The $c$ dependence of $x$ is consistent with the data published by other groups [12,14,17]. A detailed preparation procedure will be published elsewhere [18]. The magnetization, specific heat, and resistivity measurements were performed in quantum design physical properties measurement systems. The field dependence of the thermome-

  

ter and addenda was carefully calibrated before specific heat measurements. The in-plane resistivity was measured using a four-probe low frequency ac method.

Figure 1 shows the magnetic susceptibility $\chi = M/H$ as a function of temperature $T$ in a field of 1 T applied both along and perpendicular to the $c$ axis. $\chi$ exhibits a Curie-Weiss–like behavior at high temperatures. A broad peak appears around 27 K. Below 18.5 K, $\chi$ drops down sharply for $H \parallel c$ but goes up rapidly for $H \perp c$. A similar temperature dependence of $\chi$ was observed by Bayrakci *et al.* [14] for a $Na_{0.82}CoO_2$ single crystal. The broad peak around 30 K can be attributed to quasi-two-dimensional AF fluctuations. The sharp drop of $\chi$ at about 20 K reveals a phase transition from a paramagnetic to an AF state with staggered magnetization along the $c$ axis. Above 50 K, $\chi$ can be well fitted by the formula $\chi(T) = \chi_0 + C/(T + \theta)$. From the fitting parameters, the effective moments are determined to be $0.66\mu_B$/Co for $H \parallel c$ and $0.92\mu_B$/Co for $H \parallel ab$. They are consistent with the data published by Sales *et al.* [17] if we assume that the effective moments are proportional to the content of $Co^{+4}$ ions in this material.

The inset of Fig. 1 shows $\chi$ as a function of temperature from 2 to 40 K in different applied fields. The Curie tail at low temperatures at 1 T might be due to paramagnetic impurities. It is suppressed at 5 T. However, at 12 T, $\chi$ rises up below $T_m \sim 17.4$ K and tends to saturate at low temperatures. This indicates that a phase transition from an AF (or SDW) to a partially FM state occurs at a field between 5 and 12 T.

Figure 2(a) shows the field dependence of magnetization $M$ at 5, 10, 15, and 20 K for $H \parallel c$, and at 2, 10, and 20 K for $H \perp c$. For $H \parallel c$, a rapid superlinear rise in $M(H)$ is observed at ~8.0 T for $T = 5$ K. With increasing temperatures, this superlinear rise feature is weakened and disappears above 20 K. This can be more clearly seen from the $dM/dH$ plot [Fig. 2(b)]. The appearance of the sharp peaks in $dM/dH$ is an indication of a phase transition. The peak position of $dM/dH$ increases from ~8.0 T at $T = 5K$ to ~9.0 T at $T = 15$ K. For $H \perp c$, the magnetization shows typical paramagnetic behavior, and $M$ increases linearly with $H$ up to 14 T. This anisotropic magnetic response of the system suggests that the magnetic moments of Co ions are along the $c$ axis, consistent with other experiments [13,14].

The above results suggest that there is a metamagnetic transition around 8 T at low temperatures. Metamagnetism refers to two different kinds of magnetic phenomena. It describes a transition or crossover from a paramagnetic state in low fields to a more polarized state in high fields, or the spin-flop transition from an AF state to a spin ferromagnetically polarized state [19]. The spin-flop jump here is small compared with that in a conventional AF state. The $\mu$SR experiments indicate that there are three kinds of local spins pointing in different directions in these materials [14]. Probably only one kind of these local spins is involved in the metamagnetic transition. In cuprates $LaCuO_4$ [20] and $La_{2-x}Sr_xCuO_4$ with $x = 0.01$ [21], and layered manganite $La_{1.4}Sr_{1.6}Mn_2O_7$ [22], spin-flop transitions from an AF state to a ferromagnetically polarized state were observed by magneti-

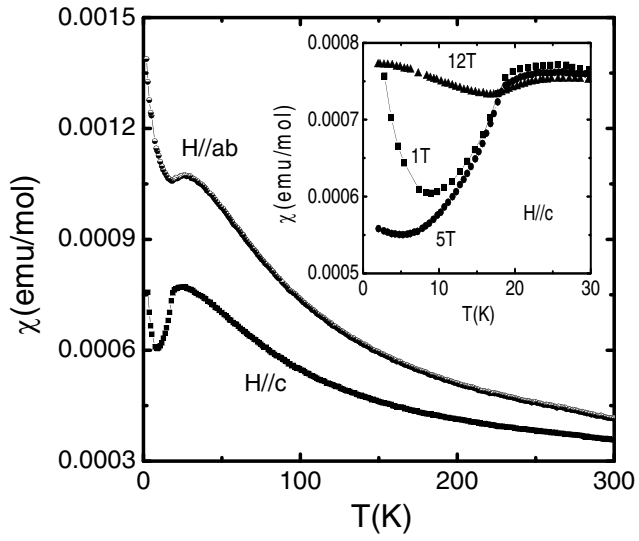


FIG. 1. The magnetic susceptibility $\chi = M/H$ versus temperature $T$ of $Na_{0.85}CoO_2$ in a magnetic field of 1 T applied along and perpendicular to the $c$ axis. Inset: Low temperature susceptibility $\chi$ versus temperature $T$ in applied fields of 1, 5, and 12 T along the $c$ axis.

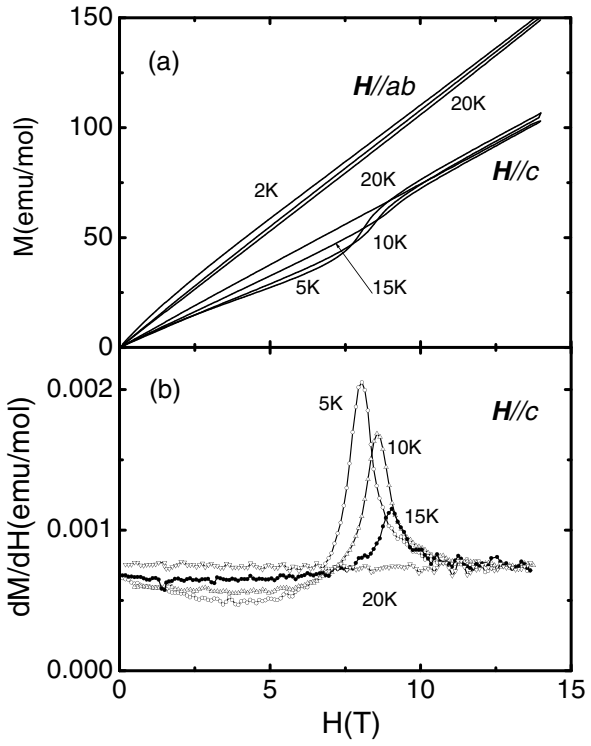


FIG. 2. (a) The magnetization $M$ versus field $H$ of $Na_{0.85}CoO_2$ at 5, 10, 15, and 20 K for $H \parallel c$, and at 2, 10, and 20 K for $H \perp c$, respectively. (b) $dM/dH$ versus $H$ at 5, 10, 15, and 20 K for $H \parallel c$.

zation measurements. The metamagnetic transition in metallic systems were also observed in the bilayer perovskite ruthenate $Sr_3RuO_7$ [19,23] and heavy fermion systems $URu_2Si_2$ [24] and $UPt_3$ [25] with possible quantum critical phenomena.

The metamagnetic transition has also been observed in the field dependent specific heat and in-plane magnetoresistance (MR) measurements. The specific heat of $Na_{0.85}CoO_2$ shows a sharp peak at about 18.5 K at zero field. It corresponds to the magnetic ordering transition as observed in the susceptibility measurements. Figures 3(a) and 3(b) show the specific heat $C$ from 16 to 20 K in eight different fields applied along the $c$ axis. The magnetic ordering transition temperature $T_m$ decreases with increasing $H$ below 10 T [Fig. 3(a)], but increases with $H$ above 10 T [Fig. 3(b)]. For a magnetic transition from a paramagnetic state to an AF state, the applied magnetic fields suppress the AF correlations as well as the transition temperature. However, for a transition from a paramagnetic state to a FM state, the transition temperature increases with increasing fields since the FM correlations are enhanced in an applied field. Our specific heat results indicate that the magnetic ordering is AF-like in low fields but FM-like in high fields, consistent with the magnetization measurement given above.

Above 22 K, the specific heat is well described by a sum of the phonon and electronic contributions $C \sim \gamma T + \beta T^3$ [Fig. 3(c)]. From the fitting, $\gamma$ is found to be $\sim 24\ \mathrm{mJ/mol\,K^2}$. This value of $\gamma$ is close to the value ($27\ \mathrm{mJ/mol\,K^2}$) estimated by Sales *et al.* [17] and by Motohashi *et al.* [26] for $Na_{0.75}CoO_2$ crystals. The Debye temperature $\theta_D$ deduced from $\beta$ is about 598 K, slightly higher than the corresponding value 550 K for $Na_{0.75}CoO_2$ [17,26]. The values of $\gamma$ and $\theta_D$ obtained by Bayrakci *et al.* [14] for $Na_{0.82}CoO_2$ differ from ours since their values were deduced from the data below $T_m$ and the magnetic contribution was not considered.

Figure 3(d) shows the field dependence of $C$ at 5 K for $H \parallel c$. In low fields, $C$ increases with increasing field, but drops down above 8 T. The critical field $H_m$ obtained from the specific heat is consistent with that obtained from magnetization measurements. The increase of the specific heat in low fields can be explained by the field induced enhancement of spin density of states. The electronic specific heat is proportional to the total density of low-lying excitations. The applied field suppresses the AF coupling between the $CoO_2$ layers and enhances the density of spin excitations. Above $H_m$, a transition to a ferromagnetically polarized state occurs and the specific heat decreases with further increasing field. When the field is large enough to polarize all the spins, the spin excitations will be completely suppressed and will have no contribution to the specific heat.

The inset of Fig. 4 shows the temperature dependence of the in-plane resistivity. The in-plane resistivity exhibits a metallic behavior above 18 K. Below 18 K, $\rho_{ab}$ increases with decreasing temperature. Figure 4 shows the in-plane MR from 2 to 20 K up to 14 T. In low fields, a positive MR is observed. This is due to the suppression of the AF order and the enhancement of spin scattering of conducting electrons by the applied field. However, around 8 T, a

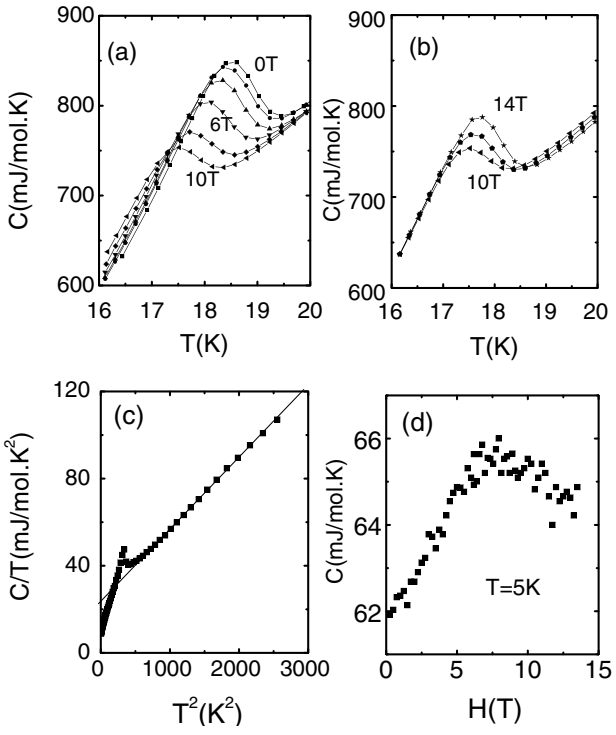


FIG. 3. The specific heat $C$ of $Na_{0.85}CoO_2$ crystal for $H \parallel c$ up to 14 T. (a) $C$ versus $T$ in the transition temperature regime at 0, 2, 4, 6, 8, and 10 T (from the top to the bottom), respectively. (b) Same as for (a) but at 10, 12, and 14 T (from the bottom to the top), respectively. (c) $C/T$ versus $T^2$ in zero field. (d) $C$ versus $H$ at 5 K.

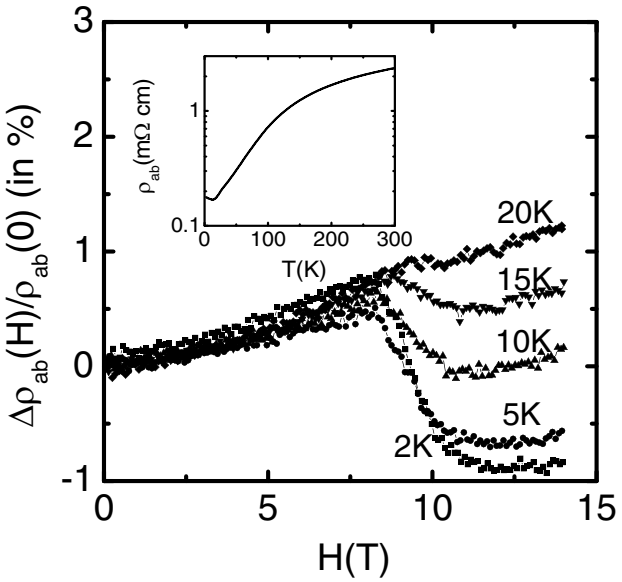


FIG. 4. The in-plane magnetoresistance of $Na_{0.85}CoO_2$ at five different temperatures for $H \parallel c$. Inset: The temperature dependence of the in-plane resistivity at zero field.

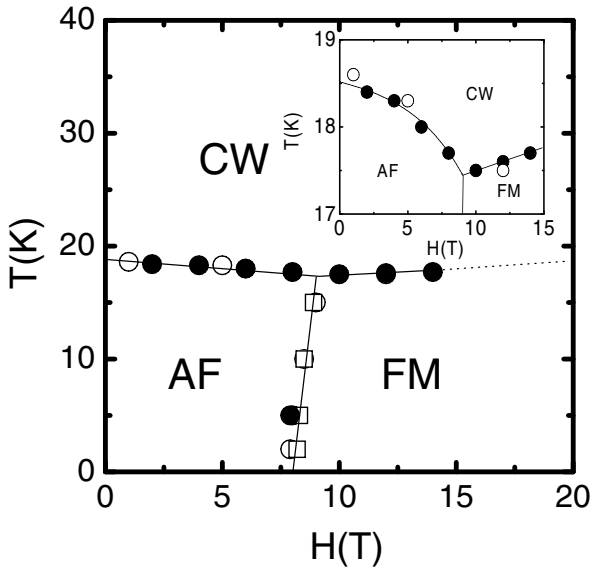


FIG. 5. The magnetic phase diagram of $Na_{0.85}CoO_2$. The inset shows the data around the tricritical point in an enlarged scale. CW, AF, and FM represent a Curie-Weiss, an antiferromagnetically ordered, a spin ferromagnetically polarized state, respectively. The phase boundary points are obtained from the susceptibility (open circle), specific heat (solid circle), and magnetoresistance (open square) measurements.

sharp drop in MR occurs at low temperatures. This is because the presence of the FM order tends to suppress the spin scattering. Similar MR behaviors across the AF and the FM phase boundary were observed in layered ruthenates [27] and colossal magnetoresistance materials.

The above discussion shows unambiguously that the ground state of $Na_{0.85}CoO_2$ is AF ordered in low fields and FM ordered in high fields. Since the in-plane spin correlations revealed by the neutron scattering measurements are predominately FM [15], this suggests that the interlayer spins are AF coupled but become ferromagnetic correlated after the spin-flop transition in $Na_{0.85}CoO_2$. Thus the metamagnetic transition here corresponds to a spin-flop transition from an AF to a FM state along the $c$ axis. From the transition field, the characteristic energy of the interlayer antiferromagntic coupling is estimated to be $\sim$1 meV.

From the above measurements, we can draw a low temperature magnetic phase diagram for $Na_{0.85}CoO_2$. As shown in Fig. 5, in higher temperatures, $Na_{0.85}CoO_2$ is in a Curie-Weiss–like phase. But by lowering temperature, it falls into either an AF phase in low fields or into a ferromagnetically polarized phase in high fields. The AF phase is connected with the ferromagnetically polarized phase via a spin-flop transition. For a $x = 0.8 \pm 0.02$ single crystal, we have observed a similar metamagnetic transition. In this case, the zero field AF transition temperature is 20.2 K and the metamagnetic transition occurs at about 9.5 T at low temperatures. Since our measurement data of $\chi$, $C$, and $\rho_{ab}$ behave similarly as for other $Na_xCoO_2$ with $x > 0.75$, we believe that this magnetic phase diagram is applicable to all $Na_xCoO_2$ with $x > 0.75$.

In summary, the magnetization, specific heat, and magnetoresistance were measured for a $Na_{0.85}CoO_2$ single crystal in applied magnetic fields up to 14 T. It is found that there is a metamagnetic phase transition around 8 T for $H \parallel c$ below 20 K. No transition is observed in magnetization measurements up to 14 T for $H \perp c$. The magnetic phase diagram of $Na_xCoO_2$ with $x \sim 0.85$ is determined from the susceptibility, specific heat, and magnetoresistance data. At high temperatures, the system is in a Curie-Weiss–like paramagnetic phase. However, at low temperatures, the system can be either in an AF ordered phase in low fields or in a partially FM phase in high fields.

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