Metamagnetic Transition in Na$_{0.85}$CoO$_2$ Single Crystal

J. L. Luo, N. L. Wang, G. T. Liu, D. Wu, X. N. Jing$^1$ and F. Hu, T. Xiang$^2$

$^1$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China
$^2$Institute of Theoretical Physics and Interdisciplinary Center of Theoretical Studies, Chinese Academy of Sciences, P. O. Box 2735, Beijing 100080, China

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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 14T. In high temperatures, the system is in a paramagnetic phase. It undergoes a magnetic phase transition below ~20K. For field $H \parallel c$, the measurement data of magnetization, specific heat and magnetoresistance reveal a metamagnetic transition from an antiferromagnetic state to a quasi-ferromagnetic state at about 8T in low temperatures. However, no transition is observed in the magnetization measurements up to 14T 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 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$_2$RuO$_4$. The Na$_x$CoO$_2$ crystal consists of two-dimensional CoO$_2$ layers separated by Na layers, similar to that of high $T_c$ cuprates and Sr$_2$RuO$_4$ except that in each layer Co atoms form a triangular lattice rather than a square one. Superconductivity is observed when $x \sim 0.3$, and sufficient water is intercalated between the CoO$_2$ layers. A number of experiments and theoretical works suggested that superconductivity in Na$_x$CoO$_2$-H$_2$O is unconventional, probably with spin triplet pairing.

With change of Na content $x$, Na$_x$CoO$_2$ exhibits a rich phase diagram. Foo et al. studied transport and magnetic properties of a series of Na$_x$CoO$_2$ samples with $x$ varying from 0.3 to 0.75. They found that the ground state is a paramagnetic metal at $x$=0.3, becomes a charge-ordered insulator at $x$=0.5, and then to a ‘Curie-Weiss metal’ at $x$ $\sim$ 0.70. The ground state of Na$_x$CoO$_2$ for $x$ > 0.75 is still not clear. Sugiyama and co-workers carried out the muon-spin-rotation experiments ($\mu$SR) on 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 incommensurate spin density wave state (IC-SDW). They claimed that the IC-SDW occurs within the CoO$_2$ plane, and the oscillating moments pointed along the c-axis. However, Bayrakci et al. found that Na$_{0.82}$CoO$_2$ exhibits a bulk antiferromagnetic (AF) long range order with a Neel temperature about 20K, which is consistent with 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. showed that there exists strong in-plane ferromagnetic (FM) correlations with an energy scale much higher than 20K, 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.

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 14T. For $H \parallel c$, we find that there is a metamagnetic transition from an AF to a quasi-FM state at $\sim$8T below 20K. However, for $H \perp c$, no transition is observed in magnetization measurements up to 14T. 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$_3$O$_4$ 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 10cm in length and 8mm in diameter for feed. The growth rate is 2mm 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±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 10.62Å. The $c$ dependence of $x$ is consistent with the data published by other groups. Detailed preparation procedure will be published elsewhere.

The magnetization, specific heat and resistivity measurements were performed in Quantum Design PPMS systems. The field dependence of thermometer and ad-
denda was carefully calibrated before specific heat measurement. The in-plane resistivity was measured using a 4-probe low frequency ac method.

Fig. 1 shows the magnetic susceptibility $\chi = M/H$ as a function of temperature $T$ in a field of 1T applied both along and perpendicular to the c-axis. $\chi$ exhibits a Curie-Weiss-like behavior in high temperatures. A broad peak appears around 27K. Below 18.5K, $\chi$ drops down sharply for $H \parallel c$ but goes up rapidly for $H \perp c$. Similar temperature dependence of $\chi$ was observed by Bayrakci et al. [14] for a Na$_{0.85}$CoO$_2$ single crystal. The broad peak around 30K can be attributed to quasi-two-dimensional AF fluctuations. The sharp drop of $\chi$ at about 20K reveals a phase transition from a paramagnetic to an AF state with staggered magnetization along the c-axis. Above 50K, $\chi$ 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.[25] 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 2K to 40K in different applied fields. The Curie tail in low temperatures at 1T might be due to paramagnetic impurities. It is suppressed at 5T. However, at 12T, $\chi$ 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 5T and 12T.

Fig. 2(a) shows the field dependence of magnetization $M$ at 5K, 10K, 15K and 20K for $H \parallel c$, and at 2K, 10K, and 20K for $H \perp c$. For $H \parallel c$, a rapid superlinear rise in $M(H)$ is observed at $\sim 8.0$T for $T=5$K. With increasing temperatures, this superlinear rise feature is weakened and disappears above 20K. 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 $\sim 8.0$T at $T=5$K to $\sim 9.0$T at $T=15$K. For $H \perp c$, the magnetization shows a typical paramagnetic behavior, and $M$ increases linearly with $H$ up to 14T. 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 8T in low temperatures. Metamagnetism refers to two different kinds of magnetic phenomena. It describes a transition or crossover from a paramagnetic state to a more polarized state, or from a less polarized state to a more polarized state. This transition has been observed in LaCuO$_4$ [15] and La$_{2-x}$Sr$_x$CuO$_4$ with $x=0.01$ [19], and layered manganite La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ [22], spin flop transitions from an AF state to a ferromagnetically polarized state [20]. 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$_4$ [15] and La$_{2-x}$Sr$_x$CuO$_4$ with $x=0.01$ [19], and layered manganite La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ [22], spin flop transitions from an AF state to a ferromagnetically polarized state were observed by magnetization measurements. The metamagnetic transition in metallic systems were also observed in the bilayer perovskite ruthenate Sr$_3$RuO$_7$ [20,21], and heavy fermion systems URu$_2$Si$_2$ [23] and UPt$_3$ [24] with possible quantum critical phenomena.

The metamagnetic transition has also been observed in the ruthenate Sr$_3$RuO$_7$ [20,21].
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 18.5K at zero field. It corresponds to the magnetic ordering transition as observed in the susceptibility measurements. Figs. 3(a) and 3(b) show the specific heat $C$ from 16K to 20K in eight different fields applied along the c-axis. The magnetic ordering transition temperature $T_m$ decreases with increasing $H$ below 10T [Fig. 3(a)], but increases with $H$ above 10T [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 22K, 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 $\sim 24 \text{mJ/mol.K}^2$. This value of $\gamma$ is close to the value (27 mJ/mol.K$^2$) estimated by Sales et al. and by Motohashi et al. for Na$_{0.75}$CoO$_2$ crystals. The Debye temperature $\theta_D$ deduced from $\beta$ is about 598K, slightly higher than the corresponding value 550K for Na$_{0.75}$CoO$_2$ [25, 26]. The values of $\gamma$ and $\theta_D$ obtained by Bayrakci et al. for Na$_{0.82}$CoO$_2$ [14] differ from ours since their values were deduced from the data below $T_m$, and the magnetic contribution was not considered.

Fig. 3(d) shows the field dependence of $C$ at 5K for $H \parallel c$. In low fields, $C$ increases with increasing field, but drops down above 8T. 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 18K. Below 18K, $\rho_{ab}$ increases with decreasing temperature. Fig. 4 shows the in-plane MR from 2K to 20K up to 14T. 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 8T, a 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 FM phase boundary were observed in Layered Ruthenates [24] and CMR 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 [12], this suggests that the inter-layer spins are AF coupled but become ferromagnetic correlated after the spin flop transition in.

FIG. 3: The specific heat $C$ of Na$_{0.85}$CoO$_2$ crystal for $H \parallel c$ up to 14T. (a) $C$ versus $T$ in the transition temperature regime at 0T, 2T, 4T, 6T, 8T and 10T (from the top to the bottom), respectively. (b) Same as for (a), but at 10T, 12T and 14T (from the bottom to the top), respectively. (c) $C/T$ versus $T^2$ in zero field. (d) $C$ versus $H$ at 5K.

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.
Netoresistance were measured for a NaCoO$_2$ crystal in applied magnetic fields up to 14T. It is found that there is a metamagnetic phase transition around 8T. The magnetic phase diagram of NaCoO$_2$ with x=0.85 is determined from the susceptibility, specific heat and magnetoresistance data. In high temperatures, the system is in a Curie-Weiss-like paramagnetic phase. However, in low temperatures, the system can be either in an AF ordered phase in low fields, or in a partially FM phase in high fields. The AF phase is connected with the ferromagnetically polarized phase in high fields. The AF phase via a spin flop transition. For a x=0.8 phase is connected with the ferromagnetically polarized phase in high fields. The AF phase in low fields, or in a partially FM phase in high fields.

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±0.02 single crystal, we have observed a similar metamagnetic transition. In this case, the zero field AF transition temperature is 20.2K and the metamagnetic transition occurs at about 9.5T in low temperatures. Since our measurements data of $\chi$, $C$, and $\rho_{ab}$ behave similarly as for other Na$_x$CoO$_2$ with x > 0.75, we believe that this magnetic phase diagram is applicable to all Na$_x$CoO$_2$ 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 14T. It is found that there is a metamagnetic phase transition around 8T for $H \parallel c$ below 20K. No transition is observed in magnetization measurements up to 14T for $H \perp c$. The magnetic phase diagram of Na$_x$CoO$_2$ with x≈0.85 is determined from the susceptibility, specific heat and magnetoresistance data. In high temperatures, the system is in a Curie-Weiss-like paramagnetic phase. However, in 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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