Magnetic field induced spin-flop transition in Na$_x$CoO$_2$ (0.5<x<0.55)

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The isothermal magnetoresistance (MR) with magnetic field (H) parallel and perpendicular to ab plane is systematically studied on the single crystal Na$_{0.52}$CoO$_2$ with charge ordering at $\sim$ 50 K and an in-plane ferromagnetism below 25 K. The isothermal MR behavior with H || ab plane and H \perp ab plane is quite different. When H || ab plane, the MR is always negative and the in-plane ferromagnetic behavior is enhanced. While the MR with H \perp ab plane changes from negative to positive with decreasing temperature or increasing H, and the in-plane ferromagnetic behavior is suppressed. A striking feature is that the MR with H \perp ab plane shows a hysteresis behavior below 25 K, which is absent for the case of H || ab plane. These results provide strong evidence for a spin-flop transition of small moments of Co$_{3.5-\delta}$ sites induced by H \perp ab plane, leading to a metamagnetic transition for small moments of Co$_{3.5-\delta}$ sites. These complex magnetism suggests an unconventional superconductivity in Na$_x$CoO$_2$ system because the Na$_x$CoO$_2$ around x=0.5 is considered to be the parent compound of superconductivity.

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The frustrated spin system Na$_x$CoO$_2$ has become a focus in research due to the discovery of superconductivity with T$_c \approx$ 5 K in Na$_{0.35}$CoO$_2$·1.3H$_2$O 

It is believed that strong electronic correlations and the possible novel magnetic ground-states due to geometrical frustration play an important role in the physics, and a rich phase diagram has been reported as a function of the Na concentration.

A charge-ordering state is found at x=0.5 and novel magnetism is reported for charge-ordering Na$_{0.5}$CoO$_2$.

Recently, the charge-ordering Na$_{0.5}$CoO$_2$ is considered to be the parent compound of superconductivity in this system because the valence of Na$_2$CoO$_2$·1.3H$_2$O is found close to +3.5

The superconductivity with the highest $T_c$ was observed in the vicinity of a magnetic phase by many groups.

The understanding of the novel magnetism is believed to shed light on the mechanism of superconductivity.

NMR and neutron diffraction studies have given spin structure for the charge ordering Na$_{0.5}$CoO$_2$.

They reported that there exist two kinds of Co sites with large and small magnetic moments in Na$_{0.5}$CoO$_2$.

The large moments of Co$_{3.5+\delta}$ sites align antiferromagnetically at $T_{c1}$ \approx 87 K with spin direction within ab plane, while the small magnetic moments Co$_{3.5-\delta}$ sites align along the direction parallel to the c-axis. It cannot be distinguished if the in-plane spin correlation of the small moment sites is ferromagnetic or antiferromagnetic. Recently, our group et al. found a six-fold symmetry in angular dependent in-plane magnetoresistance below a certain temperature ($T_{c2}$) for charge-ordering Na$_{0.34}$(H$_2$O)$_{0.15}$CoO$_2$ sample. It gives a definite evidence that the small moments of Co$_{3.5-\delta}$ sites align antiferromagnetically with spin direction along c axis. The magnetic structure for Na$_{0.5}$CoO$_2$ is shown in Fig.1(a). Subsequently, Wang et al. have found in-plane ferromagnetism below 17 K in Na$_{0.55}$CoO$_2$ which enriches the magnetic phase diagram around x=0.55. We found that the small moments of Co$_{3.5-\delta}$ sites align ferromagnetically in ab plane, and the large moments of Co$_{3.5+\delta}$ sites still align antiferromagnetically in ab plane. The magnetic structure proposed by Wang et al. is shown in Fig. 1(b). This result suggests that a spin-flop transition of the small moments of Co$_{3.5-\delta}$ sites takes place with slight change of Na content around x=0.5, and the magnetic coupling of small moments of Co$_{3.5-\delta}$ sites changes from antiferromagnetic for x=0.5 to ferromagnetic for x=0.55. Further investigation

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of the evolution of magnetism in this region is needed to understand these intriguing magnetic properties, which is helpful to understand the mechanism of superconductivity and novel magnetic ground states in this frustrated spin system.

Magnetoresistance (MR) provides insight into the coupling between charge and background magnetism. This is particularly valuable because, as shown in previous work\cite{40}, small magnetic moments order in the background of magnetic ordering with large magnetic moments, and such ordering is difficult to detect by magnetization measurement. In this paper, we systematically study MR for the Na$_x$CoO$_2$ crystals with $x$ between 0.5 and 0.55. The MR is defined by $\text{MR} = (\rho(H) - \rho(0)) / \rho(0)$. An in-plane ferromagnetism is observed below 25 K. Isothermal MR shows quite different behaviors between $H \perp ab$ plane and $H \parallel ab$ plane. A magnetic field induced spin-flop transition of small moments of Co\textsuperscript{3+,5-,7} sites is proposed to explain these complex phenomena.

High quality single crystals Na$_{0.7}$CoO$_2$ were grown using the flux method. The typical dimension is about $2 \times 1.5 \times 0.01$ mm$^3$ with the shortest dimension along the c axis. The Na$_{0.52}$CoO$_2$ sample is prepared by sodium deintercalation of the Na$_{0.7}$CoO$_2$ single crystals. The procedure is similar to the way to prepare the Na$_{0.55}$CoO$_2$ sample; the difference is that a longer reaction time is needed for the same concentration compared to the preparation of Na$_{0.55}$CoO$_2$. About 5 mg of Na$_{0.7}$CoO$_2$ single crystals were immersed in the sealed conical flask with 5 ml 0.15 M solution of I$_2$ in acetonitrile at room temperature for about 40 hours. The $x$ values of the samples were estimated by the lattice parameter $c$ determined by X-ray diffraction. The resistance was measured by an AC resistance bridge (LR-700, Linear Research). A superconducting magnet system (Oxford Instruments) was used to achieve magnetic field up to 14 T. Temperature measurement used a magnetic field insensitive temperature sensor (CERNOX, Lakeshore Cryotronics). It
should be addressed that all results discussed as follow are well reproducible.

Fig. 2 shows the in-plane resistivity and magnetoresistance for H || ab plane and H ⊥ ab plane, respectively. As shown in Fig. 2(a), the zero-field resistivity shows charge ordering behavior at ~ 50 K and a kink at 25 K, being similar as that of the in-plane ferromagnetic Na$_{0.55}$CoO$_2$. The transition of the slope $d\rho/dT$ from negative to positive around 25 K ($T_\rho$) is believed to arise from the in-plane ferromagnetic ordering for the small moments of Co$^{3.5-\delta}$ sites. A rapid upturn around 50 K should be due to the charge ordering as that in Na$_{0.5}$CoO$_2$. In addition, another anomaly in slope $d\rho/dT$ is observed at 83 K which corresponds to the antiferromagnetic ordering temperature ($T_{c1}$) as the case of Na$_{0.5}$CoO$_2$. The temperature in Na$_{0.55}$CoO$_2$ and Na$_{0.56}$CoO$_2$ is 77 K and 87 K, respectively. It further indicates that the Na content of the current sample is between x=0.5 and x=0.55, consistent with single crystalline XRD result. In Fig. 2(a) and (b), resistivity under 14 T shows different behavior below $T_\rho$ with different field direction. When H ⊥ ab plane, $T_\rho$ is independent on H and the in-plane ferromagnetic behavior is suppressed below $T_\rho$. Descending of resistivity due to in-plane ferromagnetism is killed and an upturn in resistivity below $T_\rho$ is induced by magnetic field H ⊥ ab plane, so that the resistivity shows similar behavior to that of Na$_{0.5}$CoO$_2$. When H || ab plane, $T_\rho$ increases with H and the charge-ordering behavior is suppressed. Similar behavior is also observed in Na$_{0.5}$CoO$_2$ with high magnetic field as high as 45 T by Balicas et al. They found that the field H || ab plane enhances the charge-ordering state and the field H ⊥ ab plane strongly suppresses the charge-ordering state.

The MR for H || ab plane and H ⊥ ab plane in Fig. 2(c) and (d) shows different MR behavior. When H || ab plane, the isothermal MR is negative and monotonously increases with H. The magnitude of MR below $T_\rho$ is al-

FIG. 3: (color online). Temperature dependence of out-of-plane resistivity under different fields with (a) H ⊥ Co-O plane and (b) H || Co-O plane; isothermal magnetoresistance with (c) H ⊥ Co-O plane and (d) H || Co-O plane. The inset in (a) and (c) shows $d\rho_c/dT$ with H=0 and the isothermal MR hysteresis, respectively.
most temperature independent with varying H, and as high as 22% under H=13.5 T at 20 K just below T$\rho$. MR at 6 K is positive below 1 T and changes to negative with increasing H as shown in the inset of Fig. 2(d). The positive part at low field is considered to come from antiferromagnetic background of large moments of Co$^{3.5-\delta}$ sites, and the negative part from contribution of in-plane ferromagnetic of small moments of Co$^{3.5-\delta}$ sites overwhelms the positive part at high field. When H $\perp$ ab plane, a crossover from negative to positive with increasing H is observed in the isothermal MR. At 6 K, the MR is always positive and as high as 12.5% under 13.5 T. Compared to resistivity under magnetic field and MR of Na$_{0.5}$CoO$_{2.5}$ and Na$_{0.55}$CoO$_{2}$, the results of resistivity under H and MR indicate that the magnetic coupling of small moments of Co$^{3.5-\delta}$ sites can be changed by magnetic field perpendicular to ab plane from ferromagnetic to antiferromagnetic. An intriguing MR hysteresis phenomenon is found below T$\rho$, with increasing H to 14 T and then decreasing to zero. The inset in Fig. 2(c) shows the irreversible behavior. Below T$\rho$, the MR hysteresis is induced by H $\perp$ ab plane. The critical field (H$C$) is temperature dependent. Above T$\rho$, the hysteresis phenomenon is not observed with H as high as 14 T, indicating that the hysteresis is related to in-plane ferromagnetism. In addition, the direction of hysteresis varies with decreasing T. At 22 K and 25 K, the direction is clockwise. But the direction is anti-clockwise at 18 K. Such hysteresis is absent for H $\parallel$ ab plane. These phenomena can be explained with a spin-flop transition of small moments of Co$^{3.5-\delta}$ induced by the magnetic field perpendicular to ab plane. The spin-flop transition makes the magnetic state from in-plane ferromagnetic to antiferromagnetic state. The hysteresis is caused by the different spin-flop energy of FM$\rightarrow$AF (E$_{FM\rightarrow AF}$) and AF$\rightarrow$FM (E$_{AF\rightarrow FM}$). The difference of hysteresis direction between 18 K and 22 K suggests that the relation of E$_{FM\rightarrow AF}$ and E$_{AF\rightarrow FM}$ is changed with decreasing T.

The out-of-plane resistivity $\rho_c$ under H and the isothermal out-of-plane MR are also studied. Fig. 3 shows the out-of-plane magnetotransport and the isothermal out-of-plane MR with H $\parallel$ ab plane and H $\perp$ ab plane, respectively. The values of T$\rho$ and T$C$ are the same as that of in-plane. The effect of magnetic field on $\rho_c$ is quite similar to that on $\rho_{ab}$ although the out-of-plane MR is less than the in-plane MR. Similar to the in-plane behavior, T$\rho$ is not affected by H applied along c axis, while T$\rho$ is enhanced by H parallel to the ab plane. The charge-ordering behavior is suppressed by H $\parallel$ ab plane and enhanced by H $\perp$ ab plane. The behavior of isothermal out-of-plane MR is also similar to that of the in-plane MR, and the MR hysteresis is also observed only when H $\perp$ ab plane. These results further confirm the spin-flop transition in this system.

The spin-flop transition for small moments of Co$^{3.5-\delta}$ leads to the metamagnetism. Such metamagnetism is difficult to detect by susceptibility measurements because small magnetic moments order in the background of magnetic ordering with large magnetic moments. To further understand the spin-flop transition, a formula consisting of negative and positive contributions to MR, $-A^2_s \ln(1+A^2_s H^2)+B^2_s H^2$, is used to qualitatively describe MR. The first term in the formula is derived from the third-perturbation expansion of s-d exchange Hamiltonian in the local magnetic moment model of Toyozawa. The formula has been used to explain the isothermal MR behavior for Na$_{0.55}$CoO$_{2.5}$ and another triangle lattice cobalt oxide (Bi,Pb)$_2$Sr$_2$CoO$_{4.5}$. Here, the negative part is due to the contribution of in-plane magnetism ordered by small moments of Co$^{3.5-\delta}$ sites. When the magnetic coupling of small moments of Co$^{3.5-\delta}$ sites is changed from ferromagnetic to antiferromagnetic due to spin-flop transition induced by H $\perp$ ab plane, the contribution of negative part to MR is enhanced. A 2D project picture of $\frac{dMR}{dT}$ is plotted in Fig. 4. The in-plane $\frac{dMR}{dT}$ with H $\parallel$ ab plane and H $\perp$ ab plane is shown in Fig. 4(a) and (b), respectively. The black region and white region stand for negative and positive slope $\frac{dMR}{dT}$, respectively. It is found that the negative maximum of the slope changes continuously for H $\parallel$ Co-O plane and discontinuously for H $\perp$ ab plane with decreasing temperature around the T$\rho$. We believe that these differences are due to metamagnetism induced by magnetic field perpendicular ab plane. The derivation of the negative part is $2A^2_s A^2_y 1/A_s H^2$. When H=1, the $\frac{dMR}{dT}$ reach to the maximum. Khosla et al. gave the expression of $A_2$: $\lambda=F(J)$. The parameter J is s-d exchange integral. It suggests that the maximum of $\frac{dMR}{dT}$ can be changed by variety of exchange integral. Therefore, the discontinuity in $\frac{dMR}{dT}$ may come from the change of magnetic coupling under s-d exchange model. It suggests
that the field $H \perp ab$ plane can induce antiferromagnetic coupling of small moments of Co$^{3.5-\delta}$ sites below $T_p$, which is corresponding to distinct change of the exchange integral. The white region covers large area with $H \perp ab$ plane and the transition point $H_c \left( \frac{dMR}{dH}, H_c = 0 \right)$ is dependent on temperature. No apparent transition from negative slope to positive slope is observed with $H \parallel ab$ plane. These results confirm that the field $H \perp ab$ plane can induce antiferromagnetic coupling and the field $H \parallel ab$ plane enhances the in-plane ferromagnetism. The out-of-plane $\frac{dMR}{dH}$ is shown in Fig. 4(c) and (d), respectively. Similar behavior to the in-plane case is observed for out-of-plane $\frac{dMR}{dH}$.

Based on the results that a spin-flop for small moments of Co$^{3.5-\delta}$ sites is induced by $H \perp ab$ plane and the in-plane ferromagnetism is suppressed, a H-T phase diagram with $H \perp ab$ plane is derived as shown in Fig. 5. Three different magnetic regions of small moments of Co$^{3.5-\delta}$ sites are defined in H-T phase diagram: a) I: In-plane ferromagnetic region; b) II: spin-flop region; c) III: paramagnetic region. The boundary of I and II region is determined by $\frac{dMR}{dH} = 0$. The maximum of $H_c$ is 8.8 T for in-plane resistivity and 6.3 T for out-of-plane resistivity, respectively. This phase diagram indicates the instability of in-plane ferromagnetism with magnetic field $H \perp ab$ plane. This instability suggests the existence of novel magnetic ground state in this spin frustrated system around $x=0.5$.

The characteristics of spin-flop in Na$_x$CoO$_2$ have been also reported for high Na content. The neutron scattering studies on Na$_{0.82}$CoO$_2$ and Na$_{0.75}$CoO$_2$ indicate that the in-plane and inter-plane spin correlations are ferromagnetic and antiferromagnetic, respectively, and all the spins align along the $c$ axis. These results indicate that a spin-flop transition takes place with decreasing Na content; that is, the spin direction changes from along $c$ axis to within $ab$ plane. In Na$_{0.85}$CoO$_2$, a magnetic field induced spin-flop has been reported by Luo et al. Analogously, magnetic field induced spin-flop transition of the small moments of Co$^{3.5-\delta}$ sites occurs in our samples below $T_p$. When $H \perp ab$ plane, the small moments of Co$^{3.5-\delta}$ sites flop to $c$ axis and the magnetic coupling changes from ferromagnetic to antiferromagnetic. When $H \parallel ab$ plane, the in-plane ferromagnetism is enhanced. As shown in Fig. 5, the spin-flop transition occurs with decreasing temperature or increasing magnetic field.

FIG. 5: Phase diagram for the spin of Co$^{3.5-\delta}$ in Na$_{0.52}$CoO$_2$ with magnetic field perpendicular to ab plane and temperature. (a): derived from in-plane data; (b): derived from out-of-plane data. I region: in-plane ferromagnetic region; II region: spin-flop region; III region: paramagnetic region. Open square is determined by the kink of $\frac{dMR}{dH}$ and filled square is determined by $\frac{dMR}{dH} = 0$

FIG. 6: The renewed magnetic phase diagram of Na$_x$CoO$_2$. The $\mu_1$-AF, AF, FM, MM, SC and SDW stand Antiferromagnetism of Co$^{3.5+\delta}$, Antiferromagnetism of Co$^{3.5-\delta}$, Ferromagnetism of Co$^{3.5-\delta}$, Metamagnetism of Co$^{3.5-\delta}$, Superconductivity and Spin density wave respectively. The open and filled circles stand for the ferromagnetic transition point for Na$_{0.52}$CoO$_2$ and Na$_{0.55}$CoO$_2$, respectively. The right corner magnetic structure is proposed for $x=0.55$ with field $H \perp ab$ plane.

Based on the results for $x=0.5$ and 0.55 reported by us, we renew the phase diagram around $x=0.5$ as shown in Fig. 6. At $x=0.5$, the magnetic coupling of the small moments of Co$^{3.5-\delta}$ sites are antiferromagnetic and the direction of magnetic moments is along $c$ axis. With increasing Na content, the small moments of Co$^{3.5-\delta}$ sites flop to $ab$ plane and the magnetic coupling changes to ferromagnetic. For the samples with $x$ between $x=0.5$ and 0.55, magnetic field can induce spin-flop transition. Because the spin-flop transition is accompanied with the change of magnetic coupling, this region can be defined as Metamagnetic region (MM). The magnetic structure for this region with field $H \perp ab$ plane is shown in Fig. 6. Many different groups have revised the superconducting phase. It is found that the superconductivity with the highest $T_C$ is observed in the vicinity of a magnetic phase,
strongly suggesting that magnetic fluctuations play an important role in the occurrence of superconductivity.\textsuperscript{9,10} The valence of our sample is closed to +3.48 in the superconductor Na$_{0.337}$(H$_3$O)$_{0.234}$CoO$_2$ · yH$_2$O. Therefore, our result suggests that there exists strong correlation between the superconductivity and novel magnetism around x=0.5. Recently, a nesting scenario for charge-ordering Na$_{0.5}$CoO$_2$ has been proposed by NMR and ARPES result.\textsuperscript{22,23} The nesting leads to either spin density wave (SDW) or charge density wave at low temperature which opens a gap on the nested parts of the fermi surface. When the in-plane ferromagnetic is replaced by antiferromagnetic coupling with field H $\perp$ ab plane, the charge-ordering behavior is enhanced in Na$_{0.52}$CoO$_2$ as shown in Fig. 1 and Fig. 2. Therefore, our result provides indirect evidence to this nesting scenario. In addition, this instability of fermi surface is considered to lead to unconventional superconductivity.

In conclusion, the isothermal MR for the Na$_x$CoO$_2$ crystals with x between 0.5 and 0.55 is systematically studied. An in-plane ferromagnetism is observed below 25 K. When H $\perp$ ab plane, the in-plane ferromagnetism is suppressed and the antiferromagnetism of small moments of Co$^{3.5-\delta}$ sites is enhanced, so that the resistivity shows similar behavior to that observed in Na$_{0.5}$CoO$_2$. A striking feature is observed that a MR hysteresis below the Curie temperature occurs with H $\perp$ ab plane. A magnetic field induced spin-flop transition of small moments of Co$^{3.5-\delta}$ sites can explain these complex phenomena well. Although the sample Na$_{0.52}$CoO$_2$ shows the same in-plane ferromagnetism as that of Na$_{0.55}$CoO$_2$, their resistivity under H and MR show quite different behavior. It further indicates that the complicated magnetic structure around x=0.5 is very sensitive to the Na content. Under the nesting scenario, the instability in magnetism is related to the instability of fermi surface, which is considered to lead to unconventional superconductivity.

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