In-plane ferromagnetism in charge-ordering $Na_{0.55}CoO_2$

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The magnetic and transport properties are systematically studied on the single crystal $Na_{0.55}CoO_2$ with charge ordering and divergency in resistivity below 50 K. A long-range ferromagnetic ordering is observed in susceptibility below 20 K with the magnetic field parallel to Co-O plane, while a negligible behavior is observed with the field perpendicular to the Co-O plane. It definitely gives a direct evidence for the existence of in-plane ferromagnetism below 20 K. The observed magnetoresistance (MR) of 30% at the field of 6 T at low temperatures indicates an unexpectedly strong spin-charge coupling in triangle lattice systems.

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Discovery of superconductivity with $T_c \sim 5$ K in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ makes one consider that $Na_{2}CoO_2$ may be a good example like cuprates as a doped Mott insulator becomes superconducting. A characteristic of non-hydrate $Na_{2}CoO_2$ is the sensitivity of the electronic states to slight change in x. A charge ordering state with anomalous change in thermopower, Hall coefficient and thermal conductivity occurs in the sample $Na_{0.5}CoO_2$ with Co valence of +3.5.[1]

Takada et al. have reinvestigated the superconducting sodium cobalt oxide bilayer-hydrate and revised the stoichiometry of the superconductor to be $Na_{0.37}(H_2O)_{0.234}CoO_2 \cdot yH_2O$. It is found that the oxonium ions, $(H_2O)^+$, can occupy the same crystallographic sites as the Na ions when the sample of the $Na_{0.6}CoO_2$ is immersed in distilled water. The occupation of oxonium ions in the Na$^+$ layers in superconducting hydrate $Na_{2}CoO_2$ makes the Co valence to be +3.4, being much lower than +3.7 which is directly deduced from the Na content and is widely used to discuss the superconductivity, and to draw superconducting phase diagram and to make theoretical calculations.[2] Recently Barnes et al. mapped a dome-shaped superconducting phase diagram as a function of cobalt oxidation state. They found that the maximum $T_c$ in $Na_{2}CoO_2 \cdot yH_2O$ occurs when cobalt oxidation state is near +3.5.[2] The maximum $T_c$ occurs near the charge ordered insulating state that correlates with the average cobalt oxidation of +3.5. Sakurai et al. also gave a superconducting phase diagram with a cobalt valence of +3.48.[2] They found that the superconductivity was significantly affected by the isovalent exchange of $Na^+$ and $H_3O^+$, rather than by variation of Co valence. In addition, the superconducting phase has been revised by different groups.[2, 10, 11, 12] It is found that the superconductivity with the highest $T_c$ is observed in the vicinity of a magnetic phase, suggesting strongly that magnetic fluctuations play an important role in the occurrence of superconductivity.[11, 12] Based on the above results, the superconductivity occurs in the cobalt oxidation state near +3.5 instead of about +3.7. Therefore, one should take the $Na_{2}CoO_2$ with x ∼ 0.5 as the parent compound for the superconductor. It suggests that the superconducting state could compete with the charge ordering state. This assumption could be supported by the abrupt upturn at $T^* \sim 52$ K before superconducting transition in both the ab plane and the c direction resistivity.[13] Therefore, it is very significant to study the magnetic properties of $Na_{2}CoO_2$ with x around 0.5 for understanding the pairing mechanism.

We systematically study transport and magnetic properties for the $Na_{x}CoO_2$ crystals with x around 0.5. It is found that the single crystals show paramagnetic metallic behavior with x slightly less than 0.5 (cobalt oxidation of 3.5), while an insulating behavior below 50 K in resistivity and a complicated magnetic properties with x slightly larger than 0.5. In this letter, we present the transport and magnetic properties in $Na_{0.55}CoO_2$ with cobalt oxidation of 3.45. An in-plane ferromagnetism is observed below 20 K which depends on x. A large MR of 30% with field of 6 T at low temperatures are surprisingly sensitive to spin orientation, suggesting that charge transport is strongly coupled to spin. If superconductivity really occurs in the cobalt oxidation near 3.5, the strong spin-charge coupling should be considered for the superconducting mechanism.

High quality single crystals $Na_{0.7}CoO_2$ were grown using the flux method. The typical dimensional is about $2 \times 1.5 \times 0.01mm^3$ with the shortest dimension along the c axis. The $Na_{0.55}CoO_2$ sample is prepared by sodium de-intercalation from the $Na_{0.7}CoO_2$ singe crystals. The procedure is similar to the way to prepare the $Na_{0.5}CoO_2$ sample, the difference is that the lower $I_2$ concentration is used with the shorter reaction time compared to the preparation of $Na_{0.5}CoO_2$. About 5 mg $Na_{0.7}CoO_2$ single crystals were immersed in the sealed conical flask with
5ml 0.15 M solution of I₂ in acetonitrile at room temperature for about 30 hours. The actual Na concentration was determined by Atomscan Advantage inductively coupled plasma atomic emission spectrometer (ICP). Both the resistance and magnetic susceptibility were measured with the magnetic field parallel and perpendicular to the Co-O plane. The resistivity and magnetoresistance were performed in Quantum Design PPMS systems. The magnetic properties were measured with a Quantum Design SQUID magnetometer. It should be addressed that the magnetic properties were measured with a Quantum Design SQUID magnetometer. It should be addressed that the

The Co-O plane, respectively. As shown in Fig.1, the samples and all results discussed as follow are well reproducible.

Figure 1(a) and 1(b) show the zero-field cooled (ZFC) and field-cooled (FC) magnetic susceptibility χ as a function of temperature for single crystal Na₀.₅₅CoO₂ in different fields (H) with H ‖ Co-O plane and H ⊥ Co-O plane, respectively. As shown in Fig.1, the sample shows a Pauli paramagnetic behavior in the high temperature range, being similar to that of the sample Na₀.₅₅CoO₂.[²] However, the sample Na₀.₅₅CoO₂ exhibits only one anomaly at Tₕ ≈ 77 K in χ taken for the applied magnetic field parallel to the ab-plane, and no anomaly is observed in χ taken the applied magnetic field perpendicular to the ab-plane. This result is consistent with the antiferromagnetic ordering at Tₕ ≈ 87 K with spin direction within the ab-plane in Na₀.₅₅CoO₂.[³] No

low H, while the ZFC and FC data are the same with the H larger than 1 T. It suggests a weak ferromagnetic behavior. For the case of the applied magnetic field parallel to ab-plane, there exists a maximum in ZFC χ at a certain temperature Tₙ below the ferromagnetic transition temperature (Tₙ). As shown in the inset of Fig.1(a), the Tₙ decreases with increasing the applied field. This is because the applied field makes the spin frozen temperature to decrease. Compared to the case of H parallel to ab-plane, the χ slightly increases with decreasing the temperature and the FC χ for different fields is almost the same with the applied field perpendicular to ab-plane below the Tₙ. In addition, the χ for H ‖ Co-O plane is much larger (more than one order) than that for H ⊥ Co-O plane. It suggests that the spins align ferromagnetically with their direction with the ab-plane.

To confirm the in-plane ferromagnetic ordering, the magnetic hysteresis (M-H) is studied with the applied field parallel to and perpendicular to ab-plane. Figure 2(a) shows a M-H loop at 4 K with the magnetic field H ‖ Co-O plane. It suggests that there exists a ferromagnetic ordering in the low temperature. But the magnetic moment does not saturate and increases linearly with H in the high fields. The linear component could arise from the in-plane antiferromagnetic ordering at Tₕ ≈ 77 K.
bility with $H \perp$ Co-O plane shows a Curie-Weiss behavior below 50 K, while a weak ferromagnetic ordering occurs in $\chi$ with $H \parallel$ Co-O plane. This result is consistent with that observed in Fig.2(a).

To further study the effect of the anisotropic susceptibility on the charge transport and the coupling between charge and spin, the charge transport is systematically studied. Figure 3 shows the in-plane resistivity and magnetoresistance with $H \perp$ Co-O plane and $H \parallel$ Co-O plane. As shown in the inset of Fig.3(a), the zero-field resistivity shows nearly the same behavior as that of the charge ordering $N_{0.5\text{CoO}_2}$. However, a transition of the slope $d\rho/dT$ from negative to positive is observed at about 17 K ($T_\rho$), which coincides with the ferromagnetic transition temperature shown in Fig.1. It suggests that such transition arises from the ferromagnetic ordering.

The in-plane resistivity $\rho_{ab}$ as a function of temperature at H=1, 3 and 6 T with $H \parallel$ Co-O plane and $H \perp$ Co-O plane is shown in Fig.3(a) and (b), respectively. It is found that the magnetic field has a remarkable effect on $\rho_{ab}$ below 25 K, while a negligible effect on $\rho_{ab}$ above 25 K. The effect of magnetic field on $\rho_{ab}$ with $H \parallel$ Co-O plane is much larger than that with $H \perp$ Co-O plane around the transition temperature ($T_\rho$). As shown in Fig.3(b), a large negative magnetoresistance (MR) is observed around $T_\rho$ with $H \parallel$ Co-O plane, and the $T_\rho$ increases with increasing H. For the case of $H \perp$ Co-O plane, the MR is much less than that with $H \parallel$ ab plane around $T_\rho$ and the $T_\rho$ is nearly independent on the field. These results can be well understood by the in-plane ferromagnetic ordering. This is because the in-plane ferromagnetic ordering is not affected by the H perpendicular to ab-plane. As shown in the inset of Fig.3(b), a maximum negative MR shows up around $T_\rho$ with $H \parallel$ Co-O plane, while a positive MR occurs at low temperatures. The isothermal MR with $H \perp$ Co-O plane and $H \parallel$ Co-O plane at 4, 10, 15, and 20 K is shown in Fig.3(c) and (d), respectively. For the case of $H \perp$ Co-O plane, the isothermal MR shows a complicated behavior. At 4 and 20 K, the MR is negative and increases monotonically with increasing H, while at 15 K the MR is negative and shows a maximum at $H \sim 3$ T; at 10 K a negative maximum in the MR is observed at $H \sim 2$ T, but with further increasing H the MR sign changes from negative to positive. It suggests that the isothermal MR at 10 and 15 K consists of two contributions: one negative and one positive component. For the case of $H \parallel$ Co-O plane, at 15 K and 20 K the isothermal MR is negative and increases monotonously with H, and the MR is as high as $\sim$30% at H=6 T and 15 K just below $T_\rho$. The large negative MR at 20 K arises from the enhancement of the ferromagnetic transition temperature induced by H. In contrast to the $H \perp$ Co-O plane, at 4 K the MR is positive and increases with increasing H. At 10 K, the MR shows a similar behavior to that with $H \parallel$ Co-O plane. These results definitely indicate that there exist two contributions (one negative and one positive component) to the MR. The large negative component should arise from the ferromagnetic ordering. In contrast to the case of $H \parallel$ Co-O plane, a negative MR is observed at low temperatures for $H \perp$ Co-O plane. Similar phenomena have been observed in $N_{0.5\text{CoO}_2}$. It suggests that the low temperature MR could be dominated by the antiferromagnetic ordering.

The out-of-plane resistivity $\rho_c$ under H and the isothermal MR are also studied. Figure 4 shows the c-axis magnetotransport and the isothermal MR with $H \parallel$ Co-O plane and $H \perp$ Co-O plane, respectively. The effect of

![FIG. 3: Temperature dependence of in-plane resistivity under different fields with (a):$H \perp$ Co-O plane and (b): $H \parallel$ Co-O plane; Isothermal magnetoresistance with (c): $H \perp$ Co-O plane and (d): $H \parallel$ Co-O plane.](image)

![FIG. 4: Temperature dependence of out-of-plane resistivity under different fields with (a):$H \perp$ Co-O plane and (b): $H \parallel$ Co-O plane; Isothermal magnetoresistance with (c): $H \perp$ Co-O plane and (d): $H \parallel$ Co-O plane.](image)
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 in-plane behavior, the \( T_c \) is not affected by \( H \) applied along c-axis, and is enhanced by \( H \) parallel to the ab plane. These results further support that ferromagnetic ordering occurs with spin direction within Co-O plane. In addition, the MR with \( H \) ab plane is negative at low temperatures, while the MR with \( \perp \) ab plane.

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 \( Na_{0.5}CoO_2 \). As shown in Fig.5, the large magnetic moments align antiferromagnetically at \( T_{c1} \sim 87 \) K with their direction within the ab plane, while the small magnetic moments 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. The splitting of the zero-field NMR signals from the Co sites with small moment has been observed at \( T_{c2} \sim 53 \) K. It suggests that the transition at \( T_{c2} \sim 53 \) K arises from the spin correlation of the small magnetic moment. As shown in Fig.1, the anomaly at \( T_{c2} \sim 53 \) K is not observed, while the antiferromagnetic transition at \( T_{c1} \) still occurs in \( Na_{0.55}CoO_2 \). It implies that the in-plane ferromagnetic ordering with the spin direction within Co-O plane should originate from the Co sites with small magnetic ordering. Therefore, the Co sites with large magnetic moment align antiferromagnetically at \( T_{c1} \sim 77 \) K with the spin direction within the plane, similar to that in \( Na_{0.5}CoO_2 \), while the Co sites with small magnetic moment couple ferromagnetically at \( T_c \sim 17 \) K with the spin alignment in Co-O plane. A spin structure shown in Fig.5(c) is proposed for \( Na_{0.55}CoO_2 \). The neutron scattering studies on \( Na_{0.82}CoO_2 \) and \( Na_{0.75}CoO_2 \) indicate that the in-plane and interplane spin correlation is ferromagnetic and antiferromagnetic, respectively, and the spins align along the c-axis. A spin-flop takes place with decreasing Na, that is: the spin direction changes from along c-axis to within Co-O plane. For the \( Na_{0.5}CoO_2 \), the small magnetic moment of the Co sites still is along c-axis, while the large magnetic moments of the Co sites align in ab-plane. Compared to the \( Na_{0.5}CoO_2 \), the spin-flop occurs and the spin direction of the Co sites with small magnetic moment changes from along c-axis to in Co-O plane in \( Na_{0.55}CoO_2 \). It indicates that the spin structure is sensitive to Na content. From the point of effective carrier concentration, the Co oxidation state is +3.45 in \( Na_{0.55}CoO_2 \), being close to +3.48 in the superconductor \( Na_{0.337}(H_3O)_{0.234}CoO_2 \cdot yH_2O \). Therefore, we give a direct evidence that there exists a ferromagnetic state in the vicinity of the superconducting state. It further confirms the results reported by Sakurai and co-workers. The ferromagnetic ordering with spin direction within Co-plane indicates that it is possible for spin-triplet superconductivity. Indeed, a theoretical calculation has predicted spin-triplet superconductivity with \( T_c \) negligibly reduced by the magnetic field.

In conclusion, the magnetic properties and magnetotransport are systematically studied in \( Na_{0.55}CoO_2 \). The results of susceptibility and magnetotransport definitely indicate an in-plane ferromagnetic ordering below 20 K. In Co-O plane, there exist an antiferromagnetic ordering from the Co-sites with large magnetic moment and a ferromagnetic ordering from the Co-sites with small magnetic moment, and their spin direction is within Co-O plane. The Co oxidation state of +3.45 in \( Na_{0.55}CoO_2 \) is close to +3.48 in the superconductor \( Na_{0.337}(H_3O)_{0.234}CoO_2 \cdot yH_2O \), suggesting that it is possible for spin-triplet superconductivity in Co-triangle lattice system.

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