Charge ordering in charge-compensated Na$_{0.41}$CoO$_2$ by oxonium ions

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Charge ordering behavior is observed in the crystal prepared through the immersion of the Na$_{0.41}$CoO$_2$ crystal in distilled water. Discovery of the charge ordering in the crystal with Na content less than 0.5 indicates that the immersion in water brings about the reduction of the Na$_{0.41}$CoO$_2$. The formal valence of Co changes from +3.59 estimated from the Na content to +3.50, the same as that in Na$_{0.5}$CoO$_2$. The charge compensation is confirmed to arise from the intercalation of the oxonium ions as occurred in the superconducting sodium cobalt oxide bilayer-hydrate. The charge ordering is the same as that observed in Na$_{0.5}$CoO$_2$. It suggests that the Co valence of +3.50 is necessary for the charge ordering.

I. INTRODUCTION

The layered sodium cobaltate Na$_x$CoO$_2$ has become one of the focus in research. Na doping leads to change spin 1/2 Co$^{4+}$ to spinless Co$^{3+}$. Discovery of superconductivity with $T_c \sim 5$ K in Na$_{0.35}$CoO$_2 \cdot 1.3\text{H}_2\text{O}$ makes one consider that Na$_x$CoO$_2$ may be a good example like cuprates as a doped Mott insulator becomes superconducting. Furthermore, the triangle lattice based cobaltates may also show the possibility to find some unique novel electronic phases, for example, the Anderson’s triangular lattice RVB phases and the strong topological frustration. Na$_2$CoO$_2$ system shows many novel properties. Large thermoelectric power (TEP) is magnetic field dependent and the TEP enhancement is believed to be due to spin entropy in Na$_{0.69}$CoO$_2$. The anomalous Hall signal shows no saturation up to 500 K. The unusual linear-T resistivity found in low temperatures belongs to non-Fermi liquid behavior. In addition, a so-called “incoherent-coherent” transition with decreasing temperature is observed in $\rho_c(T)$, a quasiparticle weight shows up well after a dimensional crossover in Na$_{0.75}$CoO$_2$.

A characteristic of non-hydrate Na$_x$CoO$_2$ is the sensitivity of the electronic states to slight change in x. An insulating state with anomalous change in thermopower, Hall coefficient and thermal conductivity occurs at x=0.5. The crystal structure involves an ordering of the Na ions into zigzag chains, which decorate charge ordered chains of Co ions. Charge ordering near the commensurate fillings x=1/4 and 1/3 is predicted by theory. However, such predicted charge ordering is not observed so far. Very recently, Takada et al. have reinvestigated the superconducting sodium cobalt oxide bilayer-hydrate. It is found that the oxonium ions, (H$_3$O)$^+$, can occupy the same crystallographic sites as the Na ions when the sample of the Na$_{0.4}$CoO$_2$ is immersed in distilled water and the Co valence is +3.4$. Due to the intercalation of (H$_3$O)$^+$, the optimal $T_c$ in the Co valence range of 3.24-3.35 is also reported. Furthermore, the oxygen nonstoichiometry is reported for x≤0.7. The occupation of oxonium ions in the Na$^+$ layers in superconducting hydrate Na$_x$CoO$_2$ and the existence of oxygen vacancies in Na$_x$CoO$_2$ make the Co valence to be much lower than the results that deduced from the Na content. While the Co oxidation state of about +3.7 is widely used to discuss physical properties, to draw phase diagram and to make theoretical calculations. Therefore, it is important to make out the effect of oxonium ions occupation on the formal valence of Co and the physical properties. In this paper, we report that the Na$_{0.41}$CoO$_2$ crystal with metallic behavior immersed in distilled water shows an insulating behavior, similar to that observed in Na$_{0.5}$CoO$_2$. The charge compensation by the intercalation of the oxonium ions leads to the change in Co valence from +3.59 to +3.50. It suggests that Co valence of +3.50 is necessary for the charge ordering, and the Co$^{3+}$ and Co$^{4+}$ ions arrange orderly.

II. EXPERIMENTAL

High quality single crystals Na$_{0.7}$CoO$_2$ were grown using the flux method. The typical dimensional is about 2 × 1.5 × 0.1 mm$^3$ with the shortest dimension along the c axis. The Na$_{0.41}$CoO$_2$ samples were achieved by Na deintercalation of 5 mg Na$_{0.7}$CoO$_2$ crystal in 5 ml of 6 M Br$_2$ in acetonitrile at ambient temperature for one week. The actual Na concentration was determined by Atomscan Advantage inductively coupled plasma atomic emission spectrometer (ICP). The content of OH$^-$ was determined by titration with a standard HCl solution. The oxidation states of Co in the samples were determined by redox titration. The Na$_{0.41}$CoO$_2$ crystal (20 mg) is immersed in distilled water (120 ml) for 48 hours to yield the hydrated Na$_x$CoO$_2$. To study the effect of the water immersion on the physical properties, the in-plane and out-plane resistivities for the Na$_{0.41}$CoO$_2$ crys-
tals were measured by standard four probe method before their immersion in distilled water. The four electrodes on the crystal $N_{0.41}CoO_2$ were made by silver deposition. Then these crystals with the electrodes were immersed in distilled water. All crystals were characterized by Rigaku D/max-A X-Ray diffractometer (XRD) with graphite monochromatized CuK$_\alpha$ radiation ($\lambda=1.5406$ Å) in the $\theta$ range of 10-70° with the step of 0.02 degree at room temperature. The crystals were characterized by transmission electron microscopy (TEM). The TEM investigations were performed on an H-9000NA TEM operating at 300 kV, and a TECNAI 20 operating at a voltage 200 kV. Thin single crystalline samples for TEM observations were obtained by peeling them from large single crystals with a tape, and then mounting them on standard electron microscopy grids. It is noted that the $N_{0.x}CoO_2$ materials intercalated by water are easily damaged under electron beam due to the high mobility of Na atoms as well as the weak bonding of $H_2O$ molecules inside the crystals. We therefore performed all TEM observations at the low temperature of around 100K. It is found that radiation damage can be almost eliminated during our measurements. It should be addressed that all results discussed as follow are well reproducible.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of resistivity for the $N_{0.41}CoO_2$ crystal and $N_{0.41}CoO_2$ crystal immersed in water. The resistivity behavior of $N_{0.41}CoO_2$ is similar to the previous report. It is found that the $T^2$ behavior is observed in in-plane resistivity ($\rho_{ab}(T)$) below about 30 K. A $T^{3/2}$ temperature dependence is observed from 30 to about 100 K, then a $T$-linear behavior between about 100 and 220 K. Above 220 K, $\rho_{ab}(T)$ can be described by $T^n$ with $n\approx 1$ as the case of $N_{0.5}CoO_2$. $N_{0.41}CoO_2$ shows a metallic behavior in the whole temperature range. A striking feature is that the $N_{0.41}CoO_2$ crystal immersed in water shows a divergent behavior in resistivity below about 50 K as shown in curve b. This behavior is quite similar to that observed in $N_{0.5}CoO_2$, in which the resistivity divergency in the low temperatures is ascribed to the charge ordering. It suggests that the charge ordering occurs in the $N_{0.41}CoO_2$ crystal immersed in water. In order to confirm that the charge ordering behavior is intrinsic, the out-of-plane resistivity $\rho_{c}(T)$ is also measured and the result is shown in curve c. The out-of-plane resistivity shows a similar divergent behavior to that of in-plane resistivity, and the temperature corresponding to the divergence is the same as that observed in $\rho_{ab}(T)$. These results indicate that the charge ordering is bulk behavior in $N_{0.41}CoO_2$ crystal immersed in water. Therefore, the natural question is why the charge ordering occurs in the $N_{0.41}CoO_2$ crystal immersed in water and what happens when the $N_{0.41}CoO_2$ is immersed in the distilled water. However, the charge ordering behavior can be only observed at $x=0.5$ in the phase diagram of $N_{0.x}CoO_2$ system.

In order to compare the charge ordering observed in the $N_{0.41}CoO_2$ crystal immersed in water with that appeared in $N_{0.5}CoO_2$, the derivative of in-plane resistivity for the $N_{0.41}CoO_2$ crystal immersed in water as a function of the temperature is shown in Fig.2. A dip is observed at about 85 K, the derivative rapidly decreases at 51 K and 32 K, respectively. These behaviors are almost the same as that observed in $N_{0.5}CoO_2$, in which the features coincide with the cusps occurred in susceptibility. It suggests that the $N_{0.41}CoO_2$ crystal immersed in water shows the same charge behavior as in $N_{0.5}CoO_2$. To make clear the effect of the immersion on the transport properties, the $N_{0.41}CoO_2$ crystal immersed in water was baked at 100 °C for 2 days. The temperature dependence of in-plane resistivity for the baked crystal is shown in Fig.2. It shows a metallic behavior above about 130 K, then slight insulating behavior. A peak shows up around 80 K, and a weak diverging behavior is observed at 53 K. A intriguing fea-
ture is that an insulator-metal transition occurs at about 31 K. This is in contrast to the behavior observed in the $Na_{0.41}CoO_2$ crystal immersed in water or $Na_{0.5}CoO_2$, in which another rapid divergent behavior is observed at about 30 K as the behavior of $d\rho/dT$ shown in Fig.2. It suggests that some change has taken place for the baking. In one word, a charge ordering behavior is found in $Na_{x}CoO_2$ with $x < 0.5$, and is the same as that observed in $Na_{0.5}CoO_2$.

To understand what happened in the $Na_{0.41}CoO_2$ crystal immersed in the distilled water, all crystals discussed above are characterized by X-ray diffraction measurement. The x-ray diffraction patterns for the crystals are shown in Fig.3. Figure 3 shows that only (001) diffraction peaks are observed. No impurity peak is observed and the structure remains unchanged except for the slight change in the c-axis lattice parameter for the crystal immersed in distilled water. It suggests that the superconducting hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ is not formed.

The $Na_{0.41}CoO_2$ crystals immersed in distilled water and baked at 100 °C for 48 hours are denoted as immersed and baked crystals in table 1, respectively.

In $Na_{0.5}CoO_2$ with charge ordering, the crystal structure involves an ordering of the Na ions into zigzag chains, and the chains are believed to decorate charge-ordered chains of the Co ions, giving a basis for the highly unusual properties observed. In order to confirm it, the $Na_{0.41}CoO_2$ crystal and the $Na_{0.41}CoO_2$ crystal immersed in the distilled water with charge ordering are characterized by electron diffraction. The results are shown in Fig.4. Figure 4(a) shows [001] diffraction pattern for the $Na_{0.41}CoO_2$ crystal. The compound shows a superstructure. The superstructure reflections can be described by an incommensurate vector $q$, oriented along [110]. Which is the same as that reported by Zandbergen et al. in $Na_{0.35}CoO_2$. The $Na_{0.41}CoO_2$ crystal immersed in the distilled water shows different superstructure, and the typical [001] diffraction pattern is shown in Fig.4(b). It should be pointed out that the patterns shown in Fig.4 are taken with only a relatively low exposure to the electron beam. The superstructure is the same as that observed in $Na_{0.5}CoO_2$ and the superstructure reflections can be described by a commensurate vector $q$, oriented [110] and having a length of 0.25 [110]. It further indicates that the charge ordering in the $Na_{0.41}CoO_2$ crystal immersed in the distilled water is the same as that in $Na_{0.5}CoO_2$. So far, it has been found that only charge ordering occurs in $Na_{0.5}CoO_2$, in which the insulating state is believed to arise from the interaction between the charge carriers and the Na ions, and at Na content of 0.5 the density of states of the carriers is sharply peaked. Therefore, the valence of Co ions with $+3.50$ is necessary to observe the charge ordering.

The question is how to compensate the charge to make the valence of Co ions from $+3.59$ to $+3.50$ when the $Na_{0.41}CoO_2$ crystal is immersed in distilled water. Very recently, Takada et al. reported that the oxonium ions occupy the same crystallographic sites as the $Na^+$ ions and the composition of the superconducting phase was determined to be $Na_{0.343}(H_2O)_{0.237}CoO_2 \cdot 1.19H_2O$. When the $Na_{x}CoO_2$ crystal is immersed in the distilled water, the two reactions could take place as reported by Takada et

![Image](326x385 to 553x477)

**FIG. 3:** The X-ray diffraction patterns for (a): the $Na_{0.41}CoO_2$ crystal; (b): the $Na_{0.41}CoO_2$ crystal immersed in water; (c): the baked crystal (b); (d): the crystal (c) re-immersed in distilled water. Inset: enlarge the 2θ range of 65 to 69 degree to clearly show the change in c-axis lattice parameter.

This could be because the time for the immersion of the crystal in distilled water is not enough for the intercalation of the water to form the superconducting phase. It is confirmed by the observation of superconductivity for the immersion of the crystal in distilled water for more than two months. For the $Na_{0.41}CoO_2$ crystal, the c-axis lattice parameter is 11.218 Å. The lattice parameter of the $Na_{0.41}CoO_2$ crystal immersed in the distilled water (11.203 Å) is slightly less than that of $Na_{0.41}CoO_2$ crystal. While a remarkable change in the lattice parameter (about 0.1 Å) is observed by baking at 100 °C for 48 hours. It is considered that some crystal water is gone for the baking, this assumption is confirmed by the re-immersion of the baked crystal in distilled water for 48 hours as shown in the curve (d) of Fig.3. The c-axis lattice parameter for the crystals is listed in the table 1.
The decease content of Na ions is determined by ICP, that is:

$$N_{0.41}CoO_2 + 0.14H_2O \rightarrow N_{0.34}(H_3O)_{0.07}CoO_2 + 0.07Na^+ + 0.07OH^-$$

$$N_{0.34}(H_3O)_{0.07}CoO_2 + 0.12H_2O \rightarrow N_{0.34}(H_3O)_{0.15}CoO_2 + 0.02O_2$$

In reaction (1), the decrease in the Na content could be explained by partial ion-exchange of Na ions in the cobalt oxide with protons or the oxonium ions. The decrease content of Na ion is determined by ICP, that is: the decease content of Na ions is determined by detecting Na ions in the aqueous filtrate in which the $N_{0.41}CoO_2$ crystal has been immersed. In addition, the Na content for the $N_{0.41}CoO_2$ crystal immersed in distilled water for 120 hours was determined by ICP. It is found that the ratio of Na to Co is 0.343(3):1, consistent with the Na loss by determining Na ions in the aqueous filtrate. It indicates that the Na content of the crystal with charge ordering is 0.34 per formula. It should be pointed out that the content of Na ion for ion-exchange is the same as that reported by Takada et al. It suggests that the content of Na ions for ion-exchange is limited. There exists a discrepancy for the $N_{0.41}CoO_2$ crystal immersed in water between the oxidation state of Co calculated from the $Na^+$ and $H_3O^+$ content (+3.59) and that (+3.50) expected for the appearance of charge ordering. This suggests that the immersion in water brought about the reduction of the host. As discussed by Takada et al., the reduction of the host occurs by accompanying with the intercalation of $H_3O^+$ ions instead of $Na^+$ ions. This is because the intercalation of $Na^+$ will consume the $Na^+$ ions in the solution and decrease its pH, while the lower the pH, the higher the potential of oxygen evolution, which suppresses the reduction of $N_{0.3}CoO_2$. As pointed out by Takada et al., it is not clear that the reaction (1) and (2) occurred sequentially or simultaneously. Reaction (1) leads to the substitution of the $H_3O^+$ ions for $Na^+$, while Reaction (2) involves reductive incorporation of the additional $H_3O^+$ ions.

In order to confirm the occurrence of the host reduction (or Reaction (2)), the oxidation states of Co ions in the $N_{0.41}CoO_2$ crystal immersed in water were determined by redox titration as described in Ref. 1. To get precise oxidation state and avoid the moisture to affect the precision, the mass of the crystal (18.126 mg) was weighed by high precise (1 $\mu$g) balance in glove box, in which the $H_2O$ content is less than 1 ppm, after the crystal was vacuumed for 12 hours to remove the moisture from the crystal. It should be mentioned that the resistivity behavior is the same before the vacuum and after. It suggests that the water in the structure is stable under vacuum at room temperature. The result obtained by redox titration indicates that the oxidation state of Co is +3.49(1). It indicates that the Reaction (2) takes place when the $N_{0.41}CoO_2$ crystal was immersed in water and the host was reduced. The chemical composition data and the oxidation state of Co are listed in the table 1, too. It is found that the Na content, x, decreases from 0.412(2) to 0.343(3) after the immersion. The oxidation state of Co ion should be (4.0-x) according to chemical formula $N_{a_x}CO_2$. The $N_{0.41}CoO_2$ crystal follows this relation as shown in table 1. While the oxidation state determined by redox titration for the $N_{0.41}CoO_2$ crystal immersed in water for 120 hours is 3.49. It should be pointed out that the results listed in table 1 is well reproducible. It supports that the the oxidation state of Co with +3.50 is necessary to observe the charge ordering. The $H_3O^+$ ions is monovalent, the same as the $Na^+$ ion. Therefore, it can be reasonably expected that the $H_3O^+$ ions are accommodated in the $Na^+$ sites. The same superstructure in the $N_{0.41}CoO_2$ crystal immersed in water as in $N_{0.5}CoO_2$ crystal has given a definite evidence for the accommodation of $H_3O^+$ ions in the $Na^+$ sites. In addition, the c-axis lattice parameter of $N_{0.34}(H_3O)_{0.15}CoO_2$ crystal is 11.203 Å, which is larger than that (11.125 Å) of $N_{0.3}CoO_2$. This discrepancy should arise from the substitution of large $H_3O^+$ ions for small $Na^+$ ions. After $N_{0.34}(H_3O)_{0.15}CoO_2$ was baked at 100 °C for 48 hours, its lattice parameter changes to 11.114 Å, slightly less than that (11.125 Å) of $N_{0.3}CoO_2$. We assume that the baking results in the decomposition of $H_3O^+$ ions into $H^+$ and $H_2O$. This assumption is confirmed by the mass loss after the $N_{0.34}(H_3O)_{0.15}CoO_2$ was baked. The mass loss is evaluated by weighing their mass with high precise (1 $\mu$g) balance before and after the baking. After the $N_{0.41}CoO_2$ crystal immersed in water was vacuumed for 12 hours to remove the moisture in glove box, the mass was weighed to be 2.221 mg. After baking at 100 °C for 48 hours in glove box, the mass of the crystal decreases to 2.162 mg. The mass loss corresponds to the mass of 0.15 $H_2O$ per the molecular formula $N_{0.34}(H_3O)_{0.15}CoO_2$. This result coincides with the intercalation of 0.15 $H_2O^-$ per formula determined by redox titration. It should be pointed out that the resistivity behavior does not change after

| crystal          | c-axis lattice parameter (Å) | Na (wt%) | Co (wt %) | x   | oxidation state of Co |
|------------------|------------------------------|----------|-----------|-----|-----------------------|
| $N_{0.41}CoO_2$  | 11.218(3)                    | 9.30(3)  | 57.8(1)   | 0.412(2) | 3.60(2)               |
| immersed crystal | 11.203(3)                    | 7.21(3)  | 53.85(1)  | 0.343(3) | 3.49(1)               |
| baked crystal    | 11.114(3)                    |          |           |      |                       |

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Table I: c-axis lattice parameters, chemical compositions and oxidation state of Co for the different crystals
the vacuum. However, the charge ordering behavior is destroyed by the baking at 100 °C. It suggests that the baking results in the removal of the water in structure, while the vacuum has no effect on the water in structure. Therefore, it is easily understood that the c-axis lattice parameter (11.14 Å) of the baked Na$_{0.34}$(H$_3$O)$_{0.15}$CoO$_2$ is less than 11.125 Å of the Na$_{0.5}$CoO$_2$ because the baked Na$_{0.34}$(H$_3$O)$_{0.15}$CoO$_2$ should be Na$_{0.34}$H$_{0.15}$CoO$_2$, that is: the large Na$^+$ ions was partially substituted by the small H$^+$ relative to the Na$_{0.5}$CoO$_2$. Another evidence for it is that the c-axis lattice parameter returns to 11.203 Å after the baked crystal is re-immersed in distilled water for 48 hours as shown in Fig.3. So far, it is well understood that the Na$_x$CoO$_2$ crystal with x<0.5 shows the insulating behavior in the low temperature after the Na$_{0.41}$CoO$_2$ crystal is immersed in water.

In order to confirm the existence of the H$_3$O$^+$ ion, Raman measurement was carried out with a LABRAM-HR Confocal Laser MicroRaman Spectrometer using 514.5 nm line from an argon-ion laser. Figure 5 shows the Raman spectra for the Na$_{0.41}$CoO$_2$ and Na$_{0.34}$(H$_3$O)$_{0.15}$CoO$_2$ in the wave number range from 1500 cm$^{-1}$ to 4000 cm$^{-1}$. The solid lines is the fitting results.

![Raman spectra](image)

**FIG. 5:** Raman spectra for Na$_{0.41}$CoO$_2$ and Na$_{0.34}$(H$_3$O)$_{0.15}$CoO$_2$ in the wave number range from 1500 cm$^{-1}$ to 4000 cm$^{-1}$. The solid lines is the fitting results.

The broad peaks in the wave number range from 2300 cm$^{-1}$ to 4000 cm$^{-1}$ were decomposed into three modes. The most distinct peak at 2995 cm$^{-1}$ can be assigned to the stretching mode of the H$_3$O$^+$ ion. These results indicate that the crystal immersed in water for 120 hours definitely contains a considerable amount of the the H$_3$O$^+$ ion.

**IV. CONCLUSIONS**

We report that a charge ordering occurs in Na$_{0.41}$CoO$_2$ compound with x less than 0.5 for first time. The charge ordering is the same as that observed in Na$_{0.5}$CoO$_2$. The charge is compensated by the oxonium (H$_3$O$^+$) ions, which can be intercalated into Na$_x$CoO$_2$ crystal by simple immersion of the Na$_x$CoO$_2$ crystal in distilled water and occupy the Na$^+$ crystallographic sites. The oxidation state of Co is +3.50, the same as that in Na$_{0.5}$CoO$_2$. It suggests that the valence of Co ions with +3.50 is critical to observe the charge ordering. In addition, it provides another way to dope the charge carrier in conducting CoO$_2$ layers. It further supports the intercalation of the oxonium ions into the superconducting phase: the hydrated Na$_{0.35}$CoO$_2$. Which will lead to different carrier density of the CoO$_2$ layers in superconducting phase from 3.7 estimated from the Na content. It will challenge the phase diagram for superconducting phase and its theory.

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