Preparation and transport properties of non-hydrated Na$_{0.5}$CoO$_2$ single crystals

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Abstract

Single crystals of Na$_{0.5}$CoO$_2$ were obtained through a flux method followed by de-intercalation of sodium. The Na$_{0.5}$CoO$_2$ samples were found to be vulnerable to water in the air and a hydration process in which H$_2$O molecules fill oxygen vacancies in CoO$_2$ layers is suggested to be responsible for the unusual vulnerability to water. The transport properties, including resistivity ($\rho$), thermopower ($S$) and Hall coefficient ($R_H$), were studied in a temperature range of 5-300 K. The compound shows a weak localization of carriers just below 200 K and Co$^{3+}$-Co$^{4+}$ charge ordering at about 30 K, a relatively lower temperature than previously reported. The results seem to be quite different from those previously reported for this system [Foo et al, Phys. Rev. Lett. 92 (2004) 247001]. Possible mechanism underlying this kind of inconsistency is discussed.

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A. Strongly correlated electrons; B. Metal-insulator transitions; C. Transport properties

Layered transition-metal oxide Na$_x$CoO$_2$ has attracted great interest for its unusual behaviors due to strongly correlated electrons in the past years. It has a crystal structure consisting of layers of edge shared CoO$_6$ octahedra, between which Na$^+$ ions are inserted. Early researches have found an unusually large thermoelectric power with Na content $x=2/3$ [1]. Spin entropy carried by holes (Co$^{4+}$) hoping in a Co$^{3+}$ background has been regarded as the likely source of enhanced thermopower [2]. Recently, superconductivity with a transition

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temperature $T_c$ of about 5 K has been found in water-intercalated compound Na$_{0.35}$CoO$_2$-1.3H$_2$O [3], which has been viewed as a breakthrough in search of exotic superconductors other than the copper oxides. Magnetic susceptibility studies [4,5] have showed that Na$_{0.35}$CoO$_2$-1.3H$_2$O is an extreme type II superconductor, just like high $T_c$ cuprates, and extensive Co NMR/NQR studies [6,7,8] have shown evidences for non-s-wave superconductivity. Besides the large thermopower and superconductivity, very recent research [9] found that as the sodium concentration $x$ increases from 0.30 to 0.75, non-hydrated Na$_x$CoO$_2$ goes from a paramagnetic metal to a charge ordered insulator (at $x=0.5$), and then to a Curie-Weiss metal. The sudden appearance of charge ordered state and unusual transport properties of Na$_{0.5}$CoO$_2$ have made it a focus of attention. The distinct properties of this compound have been determined to be related to the Na$^+$ ion-vacancy ordering and consequential Co$^{3+}$-Co$^{4+}$ charge ordering at low temperature.

In this paper, we prepared Na$_x$CoO$_2$ crystal samples with $x=0.5$ and studied the transport properties including resistivity, thermopower and Hall coefficient. The samples were found to be vulnerable to the water in the air and the reaction between crystals and water seemed to bring significant influence on transport properties of the samples. Furthermore, our results on the temperature dependence of thermopower, magnetic susceptibility and Hall coefficient were found quite different from those in Ref.[9], which may throw further complications on this compound.

The starting crystals of Na$_x$CoO$_2$ were grown by a flux method following the procedure reported in Ref. [10]. To remove Na content, the as-grown crystals were immersed in solutions obtained by dissolving different amounts I$_2$ in acetonitrile. After reacting for a month at ambient temperature, the samples were washed several times with acetonitrile and then dried. The crystal structure was characterized by X-Ray Diffraction (XRD). The measurements of in-plane electrical resistivity $\rho$, thermopower $S$, Hall coefficient $R_H$ and magnetic susceptibility $M$ were carried out using a Quantum-Design PPMS-9 system. Unless mentioned otherwise, the transport measurements were performed just after preparation procedure and different measurements of a sample were taken as soon as possible to ensure uniformity of the sample.

Fig. 1 shows the typical XRD patterns for the as-grown crystal (a) and for de-intercalated crystal (b). From these patterns, the crystals are considered to be of single phase. The Na content $x$ of starting crystals was determined to be 0.75 from the c-axis parameter, using the calibration of the relationship between c-axis parameter and Na content reported in Ref [9]. Na$_x$CoO$_2$ crystals with $x$ content near 0.5 can be easily obtained by de-intercalation using I$_2$-CH$_3$CN solution with excess I$_2$ concentrations for 30 days. The long reaction time assures the uniformity of Na content of de-intercalated crystals. It should be mentioned that so long as there is enough I$_2$ in the solution, the Na
Fig. 1. XRD patterns (Cu K radiation) for Na$_x$CoO$_2$ crystals. (a) As-grown crystals Na$_{0.75}$CoO$_2$, (b) de-intercalated crystal Na$_{0.5}$CoO$_2$.

content $x$ of de-intercalated crystals is always near 0.5 despite the different I$_2$ concentrations, which means that formation of the composition with $x$ near 0.5 is favored during the de-intercalation of Na.

Na$_x$CoO$_2$ samples with low Na content ($x < 0.35$) are easy to absorb water in the atmosphere and form hydrated Na$_x$CoO$_2$-yH$_2$O with H$_2$O molecules being inserted between CoO$_2$ layers. However, when $x$ comes as high as 0.45, the inserting of inter-layer H$_2$O is not favored [11]. Meanwhile, our results show that Na$_{0.5}$CoO$_2$ samples are vulnerable to the small content of water in air. We have studied the time dependence of resistivity of Na$_{0.5}$CoO$_2$ samples preserved in dry air as well as humid air, as shown in Fig. 2. The original samples (Sample A) were newly obtained by de-intercalation process mentioned above, with c-axis lattice constant of 11.131 Å, for which Na content $x$ was estimated to be near 0.50. After each measurement, the samples were preserved in dry air (cabinet with humidity 35%, Sample B, C, D) and humid air (Sample E). As can be seen from Fig. 2 (a), the fresh samples (Sample A) show a transition below 50 K and the resistivity increases quickly after this transition (The detailed behaviors of fresh samples will be discussed below). The transition broaden and becomes less evident and finally unobservable after the samples were kept in air for a long period of time, which is shown in Fig. 2 (a) for Sample B, Sample C and Sample D. The same variation of resistivity occurs much
more rapidly when the samples were put in humid air (Fig. 2 (b), Sample E). Sample F and G were obtained by annealing Sample E at 100 °C and 250 °C respectively for an hour, and their resistivity curves were shown in Fig. 2(b). It is very interesting that Sample F (annealed at 100 °C) shows little difference in resistivity with Sample E while Sample G has almost the same behaviors in resistivity as Sample A, which means sintering at 250 °C has restore Sample E to its original state (Sample A). It should be mentioned that, according to our XRD studies, no observable structural changes corresponding to this resistivity variation can be found and all the samples remain single phase.

To give further insight into this process, we combined thermogravimetric (TG) and differential-thermal-analysis (DTA) studies with resistivity measurements. Fig. 3 shows TG and DTA curves for Samples E. From Fig. 3, two weight losses can be observed, one below 100 °C and one at about 245 °C, and the later is accompanied by a negative peak in DTA curve. The first weight loss below 100 °C may come from the release of water absorbed on the surface of samples and it makes no contribution to the variation in resistivity. We believe that the weight loss at 245 °C is responsible for all resistivity variations. According to some previous reports on superconducting Na$_x$CoO$_2$-yH$_2$O, intercalation of water between CoO$_2$ layers will increasingly separate neighboring layers and thus affect resistivity [12]. This part of water will lose quickly when samples were put in dry even at room temperature and resistivity is restored [12]. However, it’s quite different in our case. First, the small portion of water accounting for resistivity variations in our samples will not be released from the sample until 245 °C, a much higher temperature than the usual temperature for releasing inter-layered water. Second, only a very small proportion of water (about 0.015 H$_2$O per formula unit estimated from the weight loss at 245 °C) can be absorbed into crystals even when they are put in humid atmosphere for a long time. Third, no structural changes were observed from XRD studies in spite of dramatic changes in resistivity. All these differences make the hydration process seem complicated. One of the probable mechanisms is that H$_2$O molecules are scattered in CoO$_2$ layers instead of being inserted between them [13]. In such model, the O$^{2-}$ ions of H$_2$O fill the oxygen vacancies in CoO$_2$ while leaving H$^+$ suspended. If this is the truth, only a small portion of water depending on the density of O$^{2-}$ vacancies can be absorbed and definitely it will modify the periodic potential, have influence on the Na$^+$ ion-Na vacancy ordering and consequently contribute to transport properties of the system. The density of O$^{2-}$ vacancies in CoO$_2$ layers can be created during de-intercalation of Na content [14], depending on the preparation process. The special vulnerability of Na$_{0.5}$CoO$_2$ samples to water makes consistent studies on this system difficult, for instance, special care is required to preserve samples and all measurements should be taken as soon as possible to assure the uniformity of test samples.

The transport measurements of Na$_{0.5}$CoO$_2$, including resistivity $\rho$, Hall co-
Fig. 2. Temperature dependence of resistivity for Na$_{0.5}$CoO$_2$ crystals with different water content. Sample A: newly prepared samples (no water content), Sample B: expose Sample A to dry air for 40 days, Sample C: expose Sample A to dry air for 80 days, Sample D: expose Sample A to dry air for 300 days, Sample E: expose Sample A to humid air for 5 hours, Sample F: anneal Sample E at 100 °C for an hour, Sample G: anneal Sample E at 250 °C for an hour. All the samples are of single phase, and no structural differences between samples can be observed from XRD studies.

Efficient $R_H$, thermopower $S$ and magnetic susceptibility $M/H$ were carried out in newly prepared sample (Sample A) in a temperature range of 5-300 K. Fig. 4 shows the in-plane resistivity $\rho$ and Hall coefficient $R_H$, and Fig. 5 shows thermopower $S$ and magnetic susceptibility $M/H$ (H||c = 1 T) as a function of temperature. $\rho$ and $R_H$ show quite similar temperature dependence. They both decrease gradually while temperature drops from room temperature. However, below 200 K, they start to increase slowly (see the enlargement of
Fig. 3. TG and DTA curves for water-incorporated Na$_{0.5}$CoO$_2$ sample (Sample E). The arrows show the water loss at about 245 °C.

$\rho$-$T$ curve in the inset of Fig.4). Correspondingly, $S$ starts to decrease below 200K, as shown in Fig.5. A sharp transition in transport properties can be observed at about 30 K. Below 30 K, the increasing trend of $\rho$ and $R_H$ become much rapid, associated with a quick increase in $M$ which is similar to the result reported in Ref. [16]. $S$ drop linearly to zero below 30 K (Fig.5). There is a tiny cusp below 50 K in magnetic susceptibility and no anomaly can be seen around 88 K.

According to previous study [9,15], superlattice of ordered Na$^+$ ion-Na vacancy has been observed by electron diffraction in Na$_{0.5}$CoO$_2$ even at room temperature and the long-range ordering of Na$^+$ ion-vacancy at low temperature are suggested for this compound by thermal conductivity measurement. We presume that the changes starting around 200 K in $\rho$, $R_H$ and $S$ result from the ordering of Na$^+$ ion-vacancy. The ordering of Na$^+$ ion-vacancy introduces potential fluctuation which modulates electronic state and consequently leads to Co$^{3+}$-Co$^{4+}$ charge ordering in CoO$_2$ conduction layers. In our case, the Hall density at 100 K for Na$_{0.5}$CoO$_2$ is 40 times smaller than that for Na$_{0.75}$CoO$_2$(not shown in the paper). Below 30 K, $\rho$, $R_H$ and $M$ start to grow quickly, these may come from Co$^{3+}$-Co$^{4+}$ charge ordering transition.

However, there are many apparent differences between our results and those reported in Ref. [9]. First, no evident transition in $R_H$ or $S$ at 87 K is observed from our results. Second, the sharp transition in $\rho$ in our case is around 30 K,
Fig. 4. Temperature dependences of in-plane resistivity $\rho$ and Hall coefficient $R_H$ for Na$_{0.5}$CoO$_2$. The arrow shows the transition at about 30 K. Inset is the enlarged plot for $T \geq 50$ K.

Fig. 5. Temperature dependences of thermopower $S$ and magnetic susceptibility $M$ ($H \parallel c$) for Na$_{0.5}$CoO$_2$. The arrow shows the transition at 30 K.
while a sharp transition in $\rho$ at 53 K is observed in Ref. [9]. And third, the system in Ref [9] shows evidence for electron-hole symmetry (Both $S$ and $R_H$ fall toward zero as $T \to 0$), while in our case the system remains hole-like in the whole temperature investigated and Hall density ($1/eR_H$) instead of $R_H$ goes to zero as $T \to 0$. It should be noted that the behaviors of resistivity, thermopower and Hall coefficient of our parent crystals ($x=0.75$) are very similar to the those reported in Ref. [9] (not shown here). Therefore the above differences for the samples with $x=0.5$ seem to be surprising. Recalled that the Na$_{0.5}$CoO$_2$ crystals are vulnerable to water, we suggested that the oxygen vacancies in the CoO$_2$ layers could account for these differences. For the ideal composition of Na$_x$CoO$_2$ with $x=0.5$, the ratio of $\text{Co}^{3+}/\text{Co}^{4+}$ (electron/hole) is 1. If a certain amount of oxygen vacancies are introduced into the CoO$_2$ layers during preparing process (this is quite likely to happen in Na$_{0.5}$CoO$_2$), it will destroy not only the electron-hole symmetry, but also translation symmetry of the periodic potential. Thus, we can expect that even a small number O$^{2-}$ vacancies will have great influence on the transport properties of the system. This is supported by the result that only 0.015 H$_2$O per formula unit filling into O$^{2-}$ vacancies will substantially change the resistivity of the system.

In summary, the single crystals of Na$_{0.5}$CoO$_2$ were prepared and the transport properties were investigated. The unusual vulnerability of the sample to water in the air was found and may result from filling oxygen vacancies in CoO$_2$ layers with H$_2$O molecules. The temperature dependence of resistivity, Hall coefficient, and thermopower shows a weak localization of carriers just below 200 K and Co$^{3+}$-Co$^{4+}$ charge ordering at about 30 K, a relatively lower temperature than previously reported. The differences in transport properties between our results and those reported in Ref. [9] may be caused by the oxygen vacancies in CoO$_2$ layers. More studies are needed to discover the underlying mechanism for the novel transport properties of this system.

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