# Thermodynamic and Transport Measurements of Superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ Single Crystals Prepared by Electrochemical Deintercalation

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Superconducting single crystal samples of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ have been produced using an electrochemical technique which dispenses with the usual bromine chemical deintercalation method. In fully hydrated crystals, susceptibility and specific heat measurements confirm that bulk superconductivity has been achieved. The extracted normal state density of states indicates Fermi-liquid behavior with strong mass enhancement and a modest Wilson ratio. Measurements of $H_{c2}$ for $H \parallel c$ and $H \parallel ab$ reveal significant anisotropy, and the extracted value for the coherence length is about 100 Å, consistent with an extremely narrow bandwidth.

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Sodium cobalt oxide, $Na_xCoO_2$ ($x \approx 0.65$–$0.75$), has received considerable attention due to its unusual thermal electric properties [1]. Recent studies have revealed anomalous non-Fermi-liquid behavior in transport properties, which points to the importance of strong correlations [2,3]. The cobalt ions form a hexagonal layered structure, and the formally $1 - x$ fraction is in the low spin ($S = \frac{1}{2}$) $Co^{4+}$ state, while the $x$ fraction is in the $S = 0$ $Co^{3+}$ state. Interest in this material escalated with the discovery of superconductivity by Takada *et al.* [4] in $Na_xCoO_2 \cdot yH_2O$ when the sodium concentration is reduced to about 0.3 and water is intercalated between the layers. The ability to control the sodium content is an exciting development because, in principle, the limit of $x = 0$ corresponds to a Mott insulator on a triangular lattice with $S = \frac{1}{2}$. Then the hydrated compound can be viewed as electron doping of a Mott insulator with a doping concentration $x \approx 0.3$. As such, it is the second known example of superconductivity arising from doping a Mott insulator after the high- $T_c$ cuprates. The $S = \frac{1}{2}$ antiferromagnet on a triangular lattice was, in fact, the starting point of Anderson's resonating valence bond idea [5], and the new superconductor has been interpreted in this light [6–8].

Until recently, the bulk properties of superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ have been studied mostly using powder samples [9–14]. Single crystal measurements [13] are much less plentiful, though such measurements are extremely important in order to understand this anisotropic layered compound. In this Letter we report a new electrochemical method to extract Na from $Na_xCoO_2$. This is an alternative to the chemical deintercalation of Na using Br ions introduced by Takada *et al.* [4]. Our electrochemical method permits precise control of the Na content and avoids the environmental hazards associated with the use of high molar concentrations of Br. In addition, we have succeeded in growing large single crystals of $Na_xCoO_2$ by the floating-zone (FZ) method. By applying the electrochemical procedure to the FZ crystals, we have obtained superconducting single crystal samples with which we have carried out a variety of physical property measurements.

The initial $Na_{0.75}CoO_2$ polycrystalline material was prepared using $Na_2CO_3$ and $Co_3O_4$ with Na to Co ratio at 0.75 to 1. The thoroughly mixed and ground powder was calcined at 750 °C for 12 h and then reacted at 850 °C for 24 h with frequent grindings in between. Na loss was minimized with a fast-heating method [15]. A stoichiometric $Na_{0.75}CoO_2$ feed rod was melted and recrystallized with an optical floating-zone furnace (4-Xe lamp design, CSI Japan) under oxygen atmosphere. Although Na vapor loss was observed, this loss was minimized by choosing a fast pulling rate (up to 10 mm/h). Electron probe microscopy analysis indicates the FZ crystal has Na content between 0.71 and 0.74 for a crystal pulled with 2 mm/h rate. We have grown large single crystals of $Na_{0.75}CoO_2$ (5 mm diameter × 8 cm long) successfully with this FZ method.

A three-electrode electrochemical cell was set up using the $Na_xCoO_2$ sample as a working electrode, platinum foil as a counter electrode, Ag/AgCl as a reference electrode ($E_0 = +0.222$ V versus the standard hydrogen electrode), and 1 M NaOH as an electrolyte. The proposed half reaction at the anodically polarized $Na_xCoO_2$ electrode responsible for Na extraction is

$$Na_xCoO_2 + \delta(OH)^- \longrightarrow Na_{x-\delta}CoO_2 + \delta(NaOH) + \delta e^-.$$

Hydrated $Na_{0.3}CoO_2 \cdot yH_2O$ can be prepared by having the sample anodically polarized with a constant voltage (0.6–1.2 V) until the decaying anodic current reaches a constant value. Alternatively, a constant current (0.1–10 mA) can be used to achieve the same charge level by waiting until the final open circuit potential reaches ~0.5 V versus Ag/AgCl.

The quasi-open-circuit potential (OCP) was measured as a function of time during a repeated sequence of having a current density of 0.01 A/g turned on (for 100 s) and off (for 100 s). Here, the quasi-OCP is the potential recorded during the time the current is off. We can interpret the OCP measured in this manner as the chemical potential of the surface layer of the sample. In Fig. 1 we plot the quasi-OCP versus time (where the time axis is proportional to the total charge supplied to the sample surface). A plateau in the OCP corresponds to two-phase coexistence. We can identify three prominent plateaus in Fig. 1. The last plateau at 0.48 V indicates a saturation of the Na concentration. Assuming that this saturation level corresponds to $Na_{1/3}$ and knowing that the starting material is $Na_{0.75}$, we have drawn arrows in Fig. 1 to indicate the expected Na content with the assumption that the Na extraction is proportional to the charging. The close match of these arrows with the plateaus suggests that stable intermediate phases exist for $Na_{2/3}$ and $Na_{1/2}$. We speculate that the special fractions of $x \simeq 1/3$, $1/2$, and $2/3$ may be indicative of at least partial Na ordering relative to the hexagonal Co structure. The role of Na ordering on the physics of these materials is an important subject for future studies.

Samples obtained directly from the cell are typically in a mixture of the partially hydrated [9] ($c \simeq 13.8$ Å) and fully hydrated ($c \simeq 19.7$ Å) structures and show only trace amounts of superconductivity. Fully hydrated superconducting crystals can be achieved by sealing the sample in a water vapor saturated container at room temperature. We find that the rate of hydration depends on grain size and several months are required to fully hydrate mm-sized single crystals. The sodium content in each sample was checked by electron probe microanalysis. After electrochemical treatment, our as-prepared floating-zone single crystals with $x = 0.75$ typically break apart into smaller crystals ($\sim 5 \times 5 \times 2$ mm), with $x \simeq 0.28$–$0.32$. The largest crystals that we measured in this study had been hydrated for three months after electrochemical deintercalation. X-ray diffraction on a pulverized piece indicates that ~94(5)% of the sample consists of the fully hydrated structure. Furthermore, neutron diffraction on a superconducting crystal revealed that the sample is characterized by a single phase (>90% of the sample, within the errors) with a $c$-axis lattice constant of 19.65 Å at room temperature.

Magnetic susceptibility, specific heat, and resistivity have been measured on our superconducting single crystal samples. As shown in Fig. 2, the susceptibility shows a large anisotropy, similar to that reported for $Na_{0.68}CoO_2$ [2]. However, the Curie-Weiss susceptibility that is so prominent there is now absent. The small cusp at 42 K is likely due to a $Co_3O_4$ impurity phase, which is known to have an antiferromagnetic transition near this temperature [16]. The size of the magnetization cusp suggests that the $Co_3O_4$ impurity fraction of our sample is small (at the 1% level); we cannot detect the existence of $Co_3O_4$ within our x-ray diffraction sensitivity. Apart from this anomaly and the low-temperature Curie tail (which arises from only 0.5% of the Co moments), the susceptibility is nearly temperature independent. Note the large magnitude and strong anisotropy. For comparison, the magnitude is about 5 times that of lanthanum strontium cuprate ($La_{2-x}Sr_xCuO_4$) and 30 times that of a simple metal like Na. The anisotropy is probably due to a combination of anisotropy in the $g$ factor and the van Vleck term. DC susceptibility measurements were taken in a field of 10 G under both field-cooled (FC) and zero-field-cooled (ZFC) conditions, as shown in the inset of Fig. 2. The diamagnetic signal is indicative of a superconducting phase with an onset temperature of about 4.2 K. The value of the ZFC susceptibility at 2 K corresponds to a shielding fraction equal to ~70% of the sample, without applying a geometric correction. The FC susceptibility corresponds to a much smaller Meissner fraction, presumably due to flux pinning effects.

The specific heat of an array of coaligned single crystals (combined mass of 4.7 mg) was measured using a

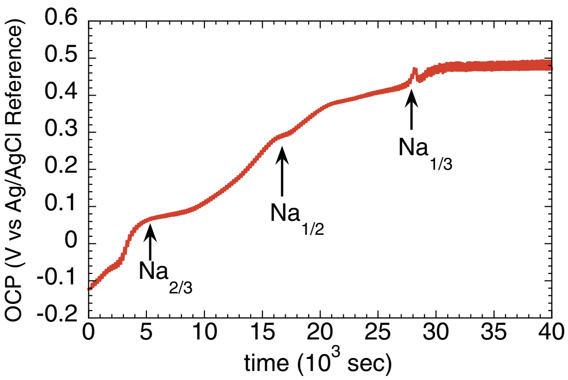

FIG. 1 (color online). The quasi-open-circuit potential as a function of time during charging of the EC cell. The arrows indicate regions of special stability and are labelled with possible Na concentrations associated with these regions.

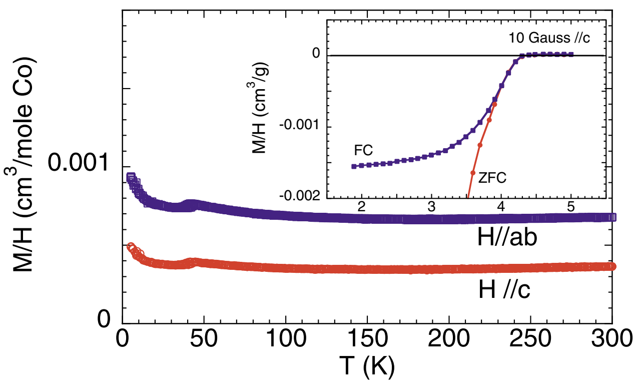

FIG. 2 (color online). The magnetic susceptibility measured using a SQUID magnetometer with an applied field of 1 T with $H \parallel ab$ and $H \parallel c$. Inset: The DC susceptibility measured under FC and ZFC conditions in an applied field of 10 G with $H \parallel c$.

physical property measurement system (Quantum Design) in applied magnetic fields ranging from 0 to 14 T and temperatures ranging from 0.37 to 10 K as shown in Fig. 3. In zero field, a pronounced peak is observed at 4.2 K, indicating the transition to bulk superconductivity. A second broad peak exists at lower temperature around 1.5 K. In a field of 1 T, the superconducting anomaly at 4.2 K is strongly suppressed; in contrast, the peak at 1.5 K is slightly enhanced. This suggests that the peak around 1.5 K is not related to a second superconducting phase with a lower $T_c$. Such a peak may be compatible with a model of weakly interacting localized Co moments, analogous to the effects seen in impurity-doped semiconductors [17]. In fields larger than 5 T, both peaks disappear and are replaced by a broad enhancement of $C/T$ over a wide range of temperatures. With increasing field, the enhancement of $C/T$ shifts to higher temperatures. At the lowest measured temperatures, the data exhibit an upturn which increases with increasing field. This is most likely due to a Schottky contribution from the nuclear spins.

In the inset of Fig. 3, the top panel compares the suppression of the superconducting anomaly for $H \parallel c$ and $H \parallel ab$. In order to achieve a comparable suppression, an in-plane field with a magnitude 5 times that of the out-of-plane field is required. This reflects the anisotropy of $H_{c2}$ in the different field orientations and is consistent with our resistivity measurements of $H_{c2}$ (discussed below). We note that $\Delta C/T_c$ in zero field for our single crystal sample is comparable to that reported by other groups in powder samples [11–14]. This suggests that a comparable level of bulk superconductivity is achieved in our electrochemically deintercalated crystals. The bottom panel of the inset shows $C/T$ data at high-fields in which a nuclear Schottky contribution ($6.7 \times 10^{-6}\ B^2/T^2$) has been subtracted. These data demonstrate that in fields greater than ~10 T superconductivity is almost completely suppressed in our sample.

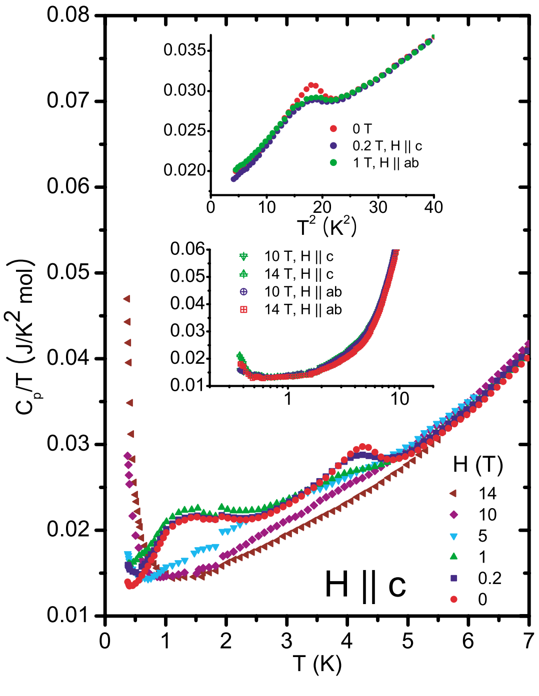

FIG. 3 (color online). The specific heat measured on a single crystal plotted as $c_p/T$ versus $T$ in various applied magnetic fields. In the top panel of the inset, we plot $c_p/T$ versus $T^2$, showing the suppression of the superconducting anomaly for $H \parallel c$ and $H \parallel ab$. In the bottom panel of the inset, we plot $c_p/T$ for fields of 10 and 14 T.

From our specific heat data, we extract a normal state $\gamma$ value of 16.6 mJ/K$^2$ Co mole. This corresponds to a free electron density of states (DOS), including both spins of 7.09 states/eV. At first sight, this seems to compare well with the local density approximation (LDA) band structure result [18] of 4.4 states/eV. However, this apparent agreement is misleading because the LDA band consists of three overlapping $t_{2g}$ bands, whereas the true quasiparticle is expected to form a single band out of the $A_{1g}$ orbital (symmetric combination of $t_{2g}$), split off from the rest by correlation. A better way is to extract a bandwidth which we estimate to be 1.4 eV. Even though the LDA calculation was done for $x = 0.5$ and without hydration, the bandwidth should be insensitive to these differences. On the other hand, we can fit the observed DOS to that of the free electron tight binding band on a triangular lattice with hopping matrix element $t_{\text{eff}}$. With $t_{\text{eff}} < 0$ and $x = 0.35$, the tight binding DOS for both spins is $0.16/|t_{\text{eff}}|$ [7]. The measured DOS then implies that $|t_{\text{eff}}| \approx 23$ meV, or a full bandwidth of $9|t_{\text{eff}}| \approx 0.2$ eV, which is a factor of 7 smaller than the LDA bandwidth. We therefore conclude that there is a mass enhancement of ~7 compared with band theory.

By assuming $g = 2$, we find that the measured $\chi_c$ of $3.5 \times 10^{-4}$ cm$^3$/Co mole corresponds to a free electron DOS of 10.86 states/eV. This gives a Wilson ratio $[4\pi^2 k^2/3(g\mu_B)^2]\chi/\gamma$ of 1.53. In case a significant portion of $\chi$ comes from the van Vleck term, the Wilson ratio will be even smaller. The combination of

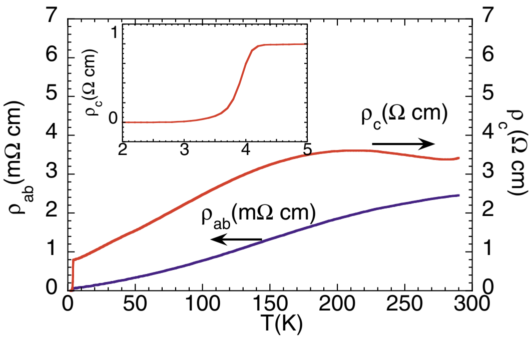

FIG. 4 (color online). Resistivity in the $ab$ plane and along the $c$ axis. Low temperature results for $\rho_c$ are shown in an expanded scale in the inset.

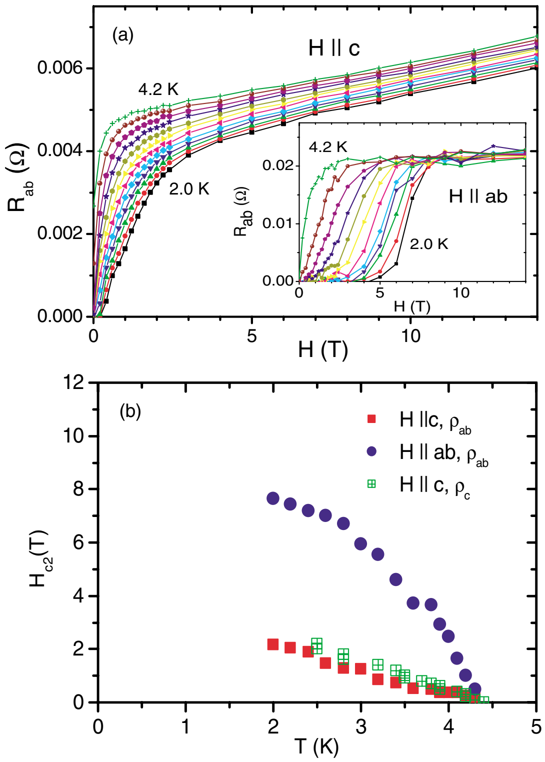

FIG. 5 (color online). (a) The in-plane resistance curves $R_{ab}(H)$ measured for temperatures ranging from 2.0 to 4.2 K. Field orientations with $H \parallel c$ and $H \parallel ab$ (inset) are measured. (b) $H_{c2}$ versus $T$ for both field orientations.

susceptibility and specific heat measurements indicate that $Na_{0.3}CoO_2 \cdot yH_2O$ may be viewed as a Fermi liquid with strong mass enhancement due to correlations. The occurrence of superconductivity in such a narrow band material suggests an electronic rather than phononic mechanism.

Four terminal resistivity measurements on a single crystal are shown in Fig. 4. The zero resistance state is achieved in $\rho_c$ and $\rho_{ab}$ at low temperatures below $T_c \simeq 4.2$ K (the inset shows an expanded view of $\rho_c(T)$ near the transition). The large room- to low-temperature resistance ratio ( $\sim 40$) indicates that the sample is a good metal with large anisotropy between $\rho_c$ and $\rho_{ab}$ (growing to $10^4$ at low temperatures). The conductance per square at low $T$ of each layer is $50\,(e^2/h)$, indicative of a long mean free path. The current and voltage leads were attached with silver paste which was allowed to dry in atmosphere for 12 h. Even though partial dehydration may have occurred during this process, it appears that the superconductivity of our single crystal sample is more robust than in powder samples where superconductivity is found to degrade in a matter of minutes [9]. The large peak below 52 K reported by Jin *et al.* [13] is absent.

In order to make an estimate of $H_{c2}$, we have measured the in-plane resistance $R_{ab}$ versus $H$ at various temperatures as shown in Fig. 5(a). There are two regimes (at low fields and high fields) where the resistance is roughly proportional to $H$. We define $H_{c2}$ as the field at the crossing point of the extrapolation of these regimes. In Fig. 5(b) we plot $H_{c2}$ versus $T$ for both field orientations. There is about a factor of 5 difference in the slopes near $T_c$, consistent with the heat capacity data. From the $H_{c2}$ versus $T$ curve for $H \parallel c$, we determine a coherence length of $\xi \approx 100$ Å. This relatively short coherence length is surprising for a superconductor with such a low $T_c$, but is entirely consistent with the narrow bandwidth. Assuming a parabolic band, the BCS formula for $\xi_0$ can be expressed in terms of the DOS $\rho(\epsilon_F)$ in the following way: $\xi_0 = v_F/\pi\Delta_0 = \sqrt{3}k_F a^2/2\pi^2\rho(\epsilon_F)\Delta_0$. Using $\rho(\epsilon_F) = 7.09\ \mathrm{eV}^{-1}$ extracted from specific heat and assuming $2\Delta_0 = 3.52\,kT_c$, we obtain $\xi_0 \approx 27a \approx 76$ Å, in reasonable agreement with the measured value.

In conclusion, by combining a novel electrochemical method and floating-zone crystal growth, we have succeeded in producing high quality single crystals of the hydrated $Na_xCoO_2 \cdot yH_2O$ system which show bulk superconductivity. Our measurements indicate that the low-temperature properties are consistent with those of a Fermi liquid with strong mass enhancement. The availability of high quality single crystals opens the door to other microscopic probes, which should further improve our understanding of this strongly correlated material.

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