Thermodynamic and Transport Measurements on Superconducting $Na_xCoO_2 \cdot yH_2O$ Single Crystals Prepared by Electrochemical De-intercalation

F.C. Chou, J.H. Cho, P.A. Lee, P.A. Lee, E.T. Abel, K. Matan, Lee, and Y.S. Lee, and Y.S. Lee, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Dated: November 3, 2018)

Superconducting single crystal samples of $Na_xCoO_2 \cdot yH_2O$ have been produced using an electrochemical technique which dispenses with the usual bromine chemical de-intercalation step and permits much more precise control of the Na content. After careful hydration, nearly single-phase crystals have been obtained in which over 90% of the sample's volume corresponds to the superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ structure. 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. The estimated value of H_{c2} for $H \parallel c$ yields a coherence length of ~ 100 Å, consistent with an extremely narrow bandwidth.

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Sodium cobalt oxide, Na_xCoO_2 ($x \approx 0.65$ to 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 point 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 $(S = \frac{1}{2})$ Co⁴⁺ state, while the x fraction is in the $S = 0 \text{ Co}^{3+}$ 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 (RVB) idea,[5] and the new superconductor has been interpreted in this light. [6, 7, 8]

Until recently, the bulk properties of superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ has been studied mostly using powder samples.[9, 10, 11, 12, 13] Single crystal measurements [13] are much less plentiful, though such measurements are extremely important in order to understand this anisotropic layered compound. In this paper 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}CoO₂ polycrystalline material was prepared using Na₂CO₃ and Co₃O₄ with Na to Co ratio at 0.75 to 1. The thoroughly mixed and ground powder was calcined at 750C for 12 hours and then reacted at 850C for 24 hours with frequent grindings in between. Na loss was minimized with a fast-heating method. [14] A stoichiometric Na_{0.75}CoO₂ feed rod was melted and re-crystallized with an optical floating-zone furnace (4-Xe lamp design, CSI Japan) under oxygen atmosphere. Although Na vapor loss was observed from the white deposit on the walls of the quartz sample chamber, this loss was minimized by choosing a fast pulling rate. A stable molten zone can be maintained with various pulling rates from 1.5 to 10 mm/hr. Electron probe microscopy analysis (EPMA) indicates the FZ crystal has Na content between 0.71 and 0.74 for a crystal pulled with 2 mm/hrrate. We have grown large single crystals of Na_{0.75}CoO₂ (5mm diameter × 8 cm long) successfully with this FZ method. Powder neutron diffraction confirms that the Na level of the FZ crystal is essentially identical to that in the feed rod.[15]

A three-electrode electrochemical cell was set up using the $\mathrm{Na}_x\mathrm{CoO}_2$ sample as a working electrode, platinum foil as a counter electrode, Ag/AgCl as a reference electrode ($E_0=+0.222~\mathrm{V}$ vs. the standard hydrogen electrode), and 1M NaOH as an electrolyte. The proposed half reaction at the anodically polarized $\mathrm{Na}_x\mathrm{CoO}_2$ electrode responsible for Na extraction is

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

where the generated NaOH becomes dissolved in the electrolyte. Because Na_xCoO_2 is metallic, the work-

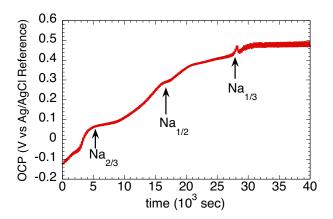


FIG. 1: The quasi-open circuit potential (OCP) as a function of time during charging of the EC cell. The arrows indicate regions of special stability and are labelled with possible Na concentrations associated with these regions.

ing electrode can be prepared directly using a compressed powder or a single crystal sample. 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 (of 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 vs. Ag/AgCl. Samples obtained directly from the cell are typically in a mixture of the partially hydrated [9] $(c \simeq 13.8 \text{ Å})$ and fully hydrated $(c \simeq 19.7 \text{ Å})$ 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 asprepared 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 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 seconds) and off (for 100 seconds). 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 vs. time where the charging current density is 0.01 A/g. The time axis is therefore 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 volts indicates a saturation of the Na concentration, at least on the surfaces of the grains of the crystal. Assuming that this saturation level corresponds to Na_{1/3} and knowing

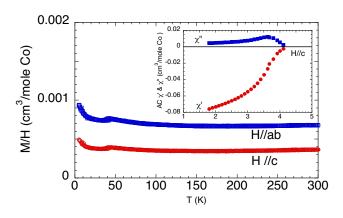


FIG. 2: The magnetic susceptibility measured using a SQUID magnetometer with an applied field of 1 Tesla with H||ab and H||c. Inset: The AC susceptibilities (in-phase χ' and out-of-phase χ'') at low temperatures.

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 $x \simeq \frac{1}{3}, \frac{1}{2}$, and $\frac{2}{3}$ 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.

Magnetic susceptibility, specific heat and resistivity have been measured on our superconducting single crys-As shown in Fig. 2, the susceptibility tal samples. shows a large anisotropy, similar to that reported for Na_{0.68}CoO₂.[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 Co₃O₄ impurity phase, which is known to have an antiferromagnetic transition in the 33 to 46 K range. [16] By comparing the size the magnetization cusp with that for bulk Co_3O_4 , we estimate that the Co₃O₄ impurity fraction of our sample is small, at the 1% level. However, we cannot detect the existence of Co₃O₄ 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. AC susceptibility measurements were taken in a field of 3 Gauss/100 Hz 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, and the screening fraction is estimated to be about 120% (without geometric correction).

The specific heat of an array of co-aligned single crys-

tals (combined mass of 4.7 mg) was measured using a Physical Property Measurement System (Quantum Design) in applied magnetic fields ranging from 0 T to 14 T and temperatures ranging from 0.37 K to 10 K as shown in Fig. 3. The sample had been hydrated for three months after electrochemical de-intercalation, and x-ray diffraction indicates that 94% of the sample consists of the fully hydrated superconducting structure. 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.

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 magnitude 5 times that of the 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, 12] The data plotted in the main part of Fig. 3 exhibit an upturn at the lowest measured temperatures which increases with increasing field. This is most likely due to a Schottky contribution from the nuclear spins. 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 $\sim 10 \text{ T}$ superconductivity is completely suppressed. Hence, 10 T may be taken as an upper limit for H_{c2} with $H \parallel ab$.

On different single crystal sample which had a smaller hydrated phase fraction, we had observed an anomaly in the specific heat at T=6 K. This feature is also noticeable in the powder data of Jin $et\ al.,[13]$. We found that this anomaly was insensitive to magnetic fields as large as 14 T. The origin of this anomaly is not clear, and it may be related to another order parameter in the vicinity of the superconducting phase on the phase diagram.

From our specific heat data, we extract a normal state γ value of 16.6 mJ/K² 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 LDA band structure result[18] of 4.4 states/eV. However, this apparent agreement is misleading because the LDA band consists of 3 overlapping t_{2g}

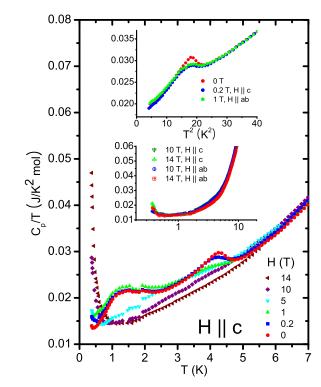


FIG. 3: The specific heat measured on a single crystal plotted as c_p/T versus T in various applied magnetic fields. In the top panel of the inset, we plot c_p/T versus T^2 showing the suppression of the superconducting anomaly for H||c and H||ab. In the bottom panel of the inset, we plot c_p/T for fields of 10 T and 14 T (a nuclear Schottky contribution has been subtracted).

bands whereas the true quasiparticle is expected to form a single band out of the A_{1q} 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_{eff} . With $t_{eff} < 0$ and x = 0.35, the tight binding DOS for both spins is $0.16/|t_{eff}|$.[7] The measured DOS then implies that $|t_{eff}| \approx 23$ meV, or a full bandwidth of $9|t_{eff}| \approx 0.2 \text{ eV}$, which is a factor of 7 smaller than the LDA bandwith. We therefore conclude that there is a mass enhancement of ~ 7 compared with band theory.

By assuming g=2, we find that the measured χ_c of 3.5×10^{-4} cm³/Co-mole corresponds to a free electron DOS of 10.86 states/eV. This gives a Wilson ratio $(4\pi^2k^2/3(g\mu_B)^2)\chi/\gamma$ of 1.53. In case a significant portion of χ comes from the van Vleck term, the Wilson ratio will be even smaller. The combination of susceptibility and specific heat measurements indicate that Na_{0.3}CoO₂·yH₂O may be viewed as a Fermi liquid with strong mass enhancement due to correlations. The occurrence of superconductivity in such a narrow band mate-

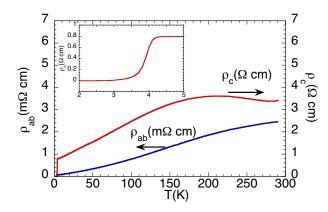


FIG. 4: Resistivity in the ab plane and along the c axis. Low temperature results for ρ_c are shown in an expanded scale in the inset.

rial 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 ρ_c and ρ_{ab} at low temperatures below $T_c \simeq 4.2 \text{ K}$ (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 ρ_c and ρ_{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 hours. Even though partial dehydration may have occurred during this process, it appears that superconductivity in the single crystal sample, with its smaller surface-to-volume ratio, is more robust than in the 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} vs. 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. The value of H_{c2} for $H \parallel ab$ is consistent with the Pauli paramagnetic limit for pair breaking. From the H_{c2} vs. 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 ξ_o can be expressed in terms of the DOS $\rho(\epsilon_F)$ in the following way: $\xi_o = \frac{v_F}{\pi \Delta_o} = \frac{\sqrt{3}k_F a^2}{2\pi^2 \rho(\epsilon_F)\Delta_o}$. Using $\rho(\epsilon_F) = 7.09 \text{ eV}^{-1}$ extracted from specific heat and assuming $2\Delta_o = 3.52 \text{ kT}_c$, we obtain $\xi_o \approx 27a \approx 76 \text{ Å}$,

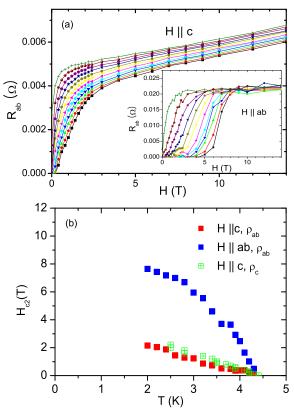


FIG. 5: (a) The in-plane resistance curves $R_{ab}(H)$ measured for temperatures ranging from 2.0 K to 4.2 K. Field orientations with $H \parallel c$ and $H \parallel ab$ (inset) are measured. (b) H_{c2} vs T for both field orientations.

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 many microscopic probes (such as x-ray and neutron scattering studies) which should help achieve an understanding of this strongly correlated material.

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[†]Permanent address: RCDAMP and Department of Physics, Pusan National University, Pusan 609-735, Korea

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