Superconductivity in a layered cobalt oxyhydrate $Na_{0.31}CoO_2 \cdot 1.3H_2O$

Guanghan Cao,[1, *] Chunmu Feng,[2] Yi Xu,[1] Wen Lu,[1] Jingqin Shen,[1] Minghu Fang,[1] and Zhu'an Xu[1]

[1]*Department of Physics, Zhejiang University, Hangzhou 310027, P. R. China*
[2]*Test & Analysis Center, Zhejiang University, Hangzhou 310027, P. R. China*
(Dated: November 18, 2018)

We report the electrical, magnetic and thermal measurements on a layered cobalt oxyhydrate $Na_{0.31}CoO_2 \cdot 1.3H_2O$. Bulk superconductivity at 4.3 K has been confirmed, however, the measured superconducting fraction is relatively low probably due to the sample's intrinsic two-dimensional characteristic. The compound exhibits weak-coupled and extreme type-II superconductivity with the average energy gap $\Delta_a(0)$ and the Ginzburg-Landau parameter κ of ~ 0.50 meV and ~ 140, respectively. The normalized electronic specific heat data in the superconducting state well fit the T^3 dependence, suggesting point nodes for the superconducting gap structure.

The recent discovery of superconductivity in a two-dimensional cobalt oxyhydrate [1] has been spurring new round of intense interest in the field of superconductivity research. It was mentioned [1, 2] that the cobalt oxyhydrate superconductor resembles the high-T_c cuprates in the two-dimensional (2D) MO_2 (M=Co or Cu) layers and the existence of spin $1/2$ for Co^{4+} and Cu^{2+} ions, though their difference is obvious for the triangular CoO_2 sheets in contrast with the nearly tetragonal CuO_2 planes. The fact that the superconductivity is derived from the intercalation of H_2O into the host $Na_{0.35}CoO_2$, which itself is not a superconductor, suggests that strong two-dimensionality be important for the appearance of superconductivity [1].

The related theoretical work has been performed quickly, though some basic physical property characterizations of the new superconductors have not been reported yet. By employing the $t-J$ model on a planar triangular lattice, different kinds of superconducting states, such as time-reversal-symmetry-breaking $d_{x^2-y^2} + id_{xy}$ superconductivity [3, 4, 5], and spin triplet superconductivity [3, 6] have been proposed. Based on the density functional calculation, Singh [7] also speculates that a triplet superconducting state may exist in this kind of material. In a word, exotic superconductivity in the new system seems to be a consensus for theorists. To verify the theoretical result, therefore, the experimental investigations becomes very crucial on this topic.

Unfortunately, the development on the experimental aspect goes relatively slowly. One of the major reasons is that the preparation of samples is not optimized at present. The other reason concerns about the chemical instability of the oxyhydrate superconductor. It was reported [8] that the material is exceptionally sensitive to both temperature and humidity near ambient conditions, which makes the experimental reproducibility rather difficult. Consequently, only a few experimental results, such as the magnetic properties [9] and the hydrostatic pressure effect on T_c [10] have just been reported. Although some unconventional magnetic properties were revealed for the new superconductor [9], other basic properties such as the low-temperature specific heat have not been reported yet for this newly-discovered superconductor. We recently succeeded in preparing the cobalt oxyhydrate superconductor using a modified synthetic route [11]. The problem of the sample's instability was overcome to some extent by employing suitable experimental procedure. In this Letter, we report some superconducting and normal-state properties of this intriguing compound.

Our samples of $Na_{0.31}CoO_2 \cdot 1.3H_2O$ were prepared in four steps, briefly described as follows. First, single-phase hexagonal $Na_{0.74}CoO_2$ was prepared by a solid-state reaction at 1083 K in flowing oxygen with Na_2CO_3 and Co_3O_4 as the starting material. Second, partial sodium in $Na_{0.74}CoO_2$ was deintercalated by the excessive bromine solved in acetonitrile, similar to the treatment reported previously [1, 8]. Third, a hydration process was carried out by the direct reaction with distilled water. Last, the sample was slightly dehydrated and then "annealed" under ambient condition. Powder X-ray Diffraction (XRD) measurement indicates that the final product is a hexagonal single phase with the cell constants of a=2.820 Å and c=19.65 Å . The unit cell is slightly stretched along the c-axis, compared with that of the previous report [1]. This is probably due to the difference in the Na content. By employing the Atomic absorption spectroscopy, the atomic ratio of Na and Co was determined as 0.31 for the final product. Thermogravimetric analysis shows that the weight loss from 293 K to 693 K is 19.8 %, indicating that the content of H_2O is about 1.3 per formula. Therefore, the chemical formula of the final product is expressed as $Na_{0.31}CoO_2 \cdot 1.3H_2O$. Details of the sample's preparation and characterizations will be given elsewhere [11].

The physical property measurements were performed at the temperature down to 1.8 K and under the field up to 8 Tesla, on a Quantum Design PPMS system. While

measured under "zero field", there still exists a remanent field of ~ 1 Oe. The precisions of ac magnetic susceptibility (χ_{ac}) and dc susceptibility (χ_{dc}) are better than $\sim 10^{-7}$ emu and $\sim 10^{-5}$ emu, respectively. The electrical resistivity (ρ) was measured in a standard four-probe configuration using a pressed sample bar. The heat capacity was measured using an automated relaxation technique with a square piece of ~ 20 mg sample. The contribution from the addenda has been subtracted. It is noted that the handling of the sample and the detailed measurement procedure sometimes affect the experimental result very much. So, we kept the same experimental condition for the different measurements.

Figure 1(a) shows the temperature dependence of magnetic susceptibility at low temperatures for the $Na_{0.31}CoO_2 \cdot 1.3H_2O$ sample. The real part of ac susceptibility χ' shows the onset of diamagnetism at 4.3 K, followed by a broad superconducting transition, similar to the original report [1]. The diamagnetic screening signal at 1.9 K is 9.2 % of the full shielding when the ac field amplitude (H_{ac}) is 2 Oe, suggesting relatively low superconducting fraction. Considering that the χ' value is not flat down to 1.9 K, the superconducting volume fraction will be over 10 % under the remanent field of ~ 1 Oe. The imaginary component of the ac susceptibility shows an incomplete dissipation peak, also suggesting that the superconducting transition is not finished yet at 1.9 K. The dc susceptibility under 30 Oe shows even low magnetic exclusion, which is primarily due to the very low H_{c1} value as well as the magnetic penetration (see the result below). An irreversible temperature can be noticed, like that observed in the high T_c cuprates [12].

From the structural and chemical bonding points of view, the present system should have very weak coupling between the CoO_2 layers, resulting in a strong 2D superconductivity. It is proposed that the relatively low superconducting fraction is mainly due to the sample's intrinsic 2D characteristic. The following observations are coincident with this point. First, the superconducting transition is broad. Second, zero resistance can never be achieved in our experiments as well as the previous report [1]. Third, the diamagnetic signal is enhanced when decreasing H_{ac}. Similar result was reported for a 2D organic superconductor $(BEDT-TTF)_2Cu(NCS)_2$ [13]. It should be pointed out that the low superconducting fraction is *not* mainly due to the sample's instability, because our XRD experiment shows that the sample contains no secondary phases before and *after* the magnetic susceptibility measurements.

Figure 2(a) shows the magnetization loop at 1.9 K for the $Na_{0.31}CoO_2 \cdot 1.3H_2O$ sample. Narrow field hysteresis was observed, superposed with a paramagnetic background which can be described by the Brillouin function. The amplificatory plot using the upper-right coordinates indicates the type-II superconductivity with H_{c1} of about 10 Oe at 1.9 K. By the data fitting
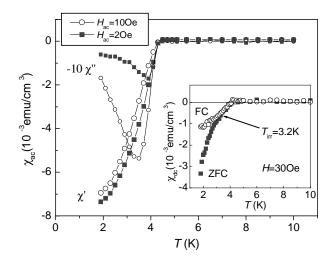

FIG. 1: Temperature dependence of ac magnetic susceptibility at zero field for $Na_{0.31}CoO_2 \cdot 1.3H_2O$ powdered sample. The inset shows the dc magnetic susceptibility under the field H=30 Oe. H_{ac}, T_{irr}, FC and ZFC refer to the ac field amplitude, irreversible temperature, field cooling and zero-field cooling, respectively.

of $H_{c1}(T)$ using the well-known equation: $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2]$, $H_{c1}(0)$ can be obtained as 13 Oe. The H_{c2} value is difficult to be measured by the $M - H$ curve due to the very narrow hysteresis. Nevertheless, by measuring the electrical resistance at fixed temperatures, one can basically obtain the $H_{c2}(T)$ data, as shown in figure 2(b). $H_{c2}(T)$ is here determined as the point where the resistance deviates from the linearity in the $R - H^2$ curves [14]. The slope of H_{c2} at T_c, $dH_{c2}/dT \mid_{T_c}$, is obtained as -34 kOe/K. $H_{c2}(0)$ can thus be estimated to be 1×10^5 Oe, using the WHH formula [15]. Then, the average Ginzburg-Landau (GL) coherent length $\xi_{GL}(0)$=57 Å can be calculated using the formula $\xi_{GL}(0)=(\Phi_0/2\pi H_{c2}(0))^{1/2}$. On the other hand, by solving the equation $H_{c1} = \Phi_0 \ln(\lambda/\xi)/4\pi\lambda^2$, the average penetration depths can also be obtained: $\lambda(0)$=7900 Å . Therefore, the Ginzburg-Landau parameter $\kappa = \lambda/\xi_{GL}$ is estimated as ~ 140, indicating that the cobalt oxyhydrate is an extreme type-II superconductor, like the high-T_c cuprates. This conclusion has also been drawn in a very recent report [9], in which different method was employed to determine the $H_{c2}(T)$. It is worth while to note that, compared with the previous result, the values of $H_{c1}(0)$ and $H_{c2}(0)$ in the present sample are remarkably smaller, which is possibly resulted from the differences in the carrier-doping level and/or the water content.

The result of low-temperature specific heat measurement is shown in figure 3. At temperatures much below the Debye temperature Θ_D, and if neglected the possible magnetic contribution, the specific heat can be expressed as the sum of electron and phonon contributions: $C = \gamma T + \beta T^3$, where the coefficient γ is generally called
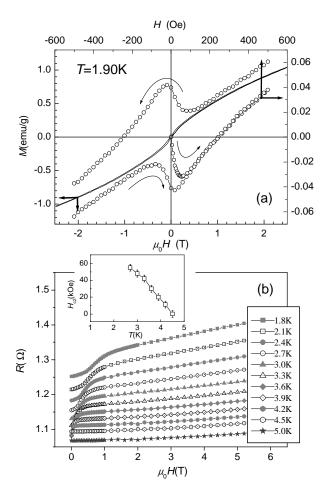
FIG. 2: Magnetic field dependence of magnetization (a) and electrical resistance (b) at certain temperatures. Note that the upper-right axes are employed for the amplificatory plot in (a). The inset of (b) shows the temperature dependence of the upper critical field H_{c2}.

Sommerfeld parameter. The phonon contribution can be separated by employing the T^2 vs C/T plot. It can be seen that good linearity is satisfied in the temperature range of 4.5 K< T <11 K. We thus obtained $\gamma = 15.9$ mJ/K^2·mol-f.u. (f.u. denotes formula unit) and $\beta = 0.235$ mJ/K^4· mol-f.u. Θ_D is then calculated to be 391 K using the formula $\Theta_D = ((12/5)N\pi^4 R/\beta)^{1/3}$, where N=7.21 for Na$_{0.31}CoO_2$·1.3H$_2$O and R=8.314 J/mol·K. The γ value is significantly smaller than that of the parent compound Na$_{0.5}$CoO$_2$ ($\gamma \sim 40$ mJ/K^2·mol-Co [16]). Since the Sommerfeld parameter γ is related to the density of state (DOS) at Fermi level, $N(E_F)$, by the relation $\gamma = \frac{1}{3}k_B^2\pi^2 N(E_F) = \frac{1}{3}k_B^2\pi^2 N(0)(1+\lambda_{ep})$, where $N(0)$ is the bare, or band-structure electronic DOS at E_F, λ_{ep} an electron-phonon interaction parameter [17], one can obtain that $N(E_F)$=6.7 states/eV·f.u. On the other hand, λ_{ep} can be calculated to be 0.57 using the formula

$$\lambda_{ep} = \frac{1.04 + \mu^* ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*)ln(\Theta_D/1.45T_c) - 1.04}, \quad (1)$$

where Coulomb repulsion parameter μ^* is assumed to be 0.13 empirically [17]. Therefore, $N(0)$ is derived to be 4.3 states/eV·f.u. We note that this value is almost identical to the band calculation result (4.4 states/eV·Co) for the parent compound Na$_{0.5}$CoO$_2$ [18].

It is noted that the sample's magnetic susceptibility ($\sim 2.0\times10^{-3}$ emu/mol-f.u) is almost temperature independent from 30 K to 300 K (not shown here). In order to obtain the Pauli susceptibility χ^{Pauli}, the $\chi(T)$ data were fitted using the equation $\chi = \chi_0 + AT^2 + C/(T - \theta)$ [9]. We obtained that χ_0, A, C and θ are 0.0019 emu/mol, 2.6×10^{-9} emu/mol·K^2, 0.0024 emu·K/mol and 1.7 K, respectively. The parameter C gives the small effective magnetic moment of 0.14 μ_B. The small positive θ value suggests the existence of weak ferromagnetic correlations. The unusually large χ_0 value should be dominantly contributed by χ^{Pauli}, which is probably enhanced by the Stoner-type ferromagnetic correlation. The Wilson ratio, $R_W = \pi^2 k_B^2 \chi^{Pauli}/3\gamma\mu_B^2$, is calculated to be 11, in sharp contrast with the case of heavy fermion superconductor [19].

At 4.3 K, specific heat anomalies can be seen, which is ascribed to the superconducting transition. The specific heat jump at the T_c under zero field, ΔC_{obs}, is 6.9 mJ/K·mol-f.u, further confirming the bulk superconductivity. When applying magnetic field, both the ΔC_{obs} and T_c decrease as expected. It is noted that the T_c (H) values are basically consistent with the $H_{c2}(T)$ result described above.

The specific jump at T_c , ΔC, can be calculated using an approximate formula $\Delta C = H_c(0)^2/2\pi T_c$, where $H_c(0)$ is the thermodynamic critical field. $H_c(0)$ is found to be 505 Oe by using the formula $H_c(0) = H_{c2}(0)/\sqrt{2}\kappa$, where $H_{c2}(0)$ and κ are 1×10^5 Oe and 140, respectively. Then, ΔC should be 38.2 mJ/K·mol-f.u. Therefore, the superconducting fraction is estimated to be $\Delta C_{obs}/\Delta C$=18.1 %, which is basically consistent with the magnetic susceptibility measurement result. In addition, the average superconducting gap at zero temperature, $\Delta_a(0)$, can be obtained using the relation [20],

$$\frac{2\Delta_a(0)}{k_B T_c} = \frac{4\pi}{\sqrt{3}}[\frac{H_c(0)^2 V_m}{8\pi\gamma T_c^2}]^{1/2}. \quad (2)$$

$\Delta_a(0)$ is then obtained to be 0.50 meV. The value of $2\Delta_a(0)/k_B T_c$ is found to be 2.71, suggesting that the system belongs to the weak coupling limit.

A further data-analysis was carried out as follows. The lattice specific-heat contribution, $C_L = \beta T^3$, was first deducted, obtaining the electronic specific heat term: $C_{el} = C - C_L$. If the superconducting fraction is η, the electronic specific heat of the full superconductor can be normalized as C_{es}=[$C_{el} - (1-\eta)\gamma T]/\eta$. Figure 3(b) shows the result with η=18.1 %. The Sommerfeld-parameter jump at the T_c, $\Delta C/T_c$, becomes 9 mJ/K^2·mol-f.u. So, the dimensionless parameter $\Delta C/\gamma T$ value is about 0.57, which is remarkably lower than the expected value 1.43
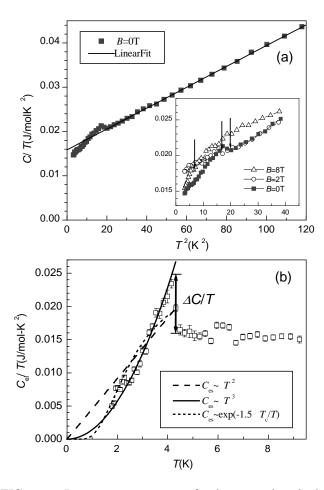
FIG. 3: Low-temperature specific heat result of the $Na_{0.31}CoO_2 \cdot 1.3H_2O$ superconductor. (a) plot of C/T vs T^2. The arrows in the inset point to the T_c under different field. (b) temperature dependence of the normalized Sommerfeld parameter. The electronic specific heat data in the superconducting state, $C_{es}(T)$, was fitted using different formula containing just one fitting parameter (the coefficient).

for an isotropic gap. This suggests that the superconducting order parameter is basically not a s-wave.

As we know, the temperature dependence of C_{es} may give important information on the structure of the superconducting gap. At the temperatures far below T_c, the temperature dependences of $C_{es}(T) \propto \exp(-bT_c/T)$ with $b \sim 1.5$, $C_{es}(T) \propto T^3$ and $C_{es}(T) \propto T^2$ indicate an isotropic BCS gap, point nodes and gap-zeroes along lines in the superconducting gap structure, respectively [21]. Though the extra-low temperature data is absent here due to the experimental limitation, fitting on the present data may give a preliminary clue. In figure 3(b), it can be seen that the T^3 dependence best fits the $C_{es}(T)$ data, suggesting point nodes for the superconducting gap. It should be mentioned that the T^3 dependence most favors the data in the wide range of 13 % $\le \eta \le$ 20 % (When $\eta \le 12$ %, C_{es} becomes a negative value at 1.8 K).

Based on symmetry and some preliminary experimental results, Tanaka and Hu [6] proposed spin triplet superconductivity in the cobalt oxyhydrate. The p-wave superconductivity was also suggested by Baskaran [3] for the higher doping level. Owing to the ferromagnetic correlation in the normal state, as stated above, spin-triplet p-wave pairing is very probable. Considered the point nodes for the superconducting gap, therefore, the gap function will be $\Delta(\mathbf{k}) = \hat{\mathbf{x}}k_x + \hat{\mathbf{y}}k_y$, which shows the difference from the conclusion in the strontium ruthenate superconductor [22]. Obviously, further experiments such as NMR, neutron scattering, and μ SR will be needed to make clearer picture for the symmetry of the superconducting order parameters.

---

* Author to whom correspondence should be addressed; Electronic address: ghcao@zju.edu.cn
[1] K. Takada *et al.*, Nature **422**, 53 (2003).
[2] J. V. Badding, Nature Materials **2**, 208 (2003).
[3] G. Baskaran, cond-mat/0303649.
[4] B. Kumar and B. S. Shastry, cond-mat/0304210.
[5] Q. H. Wang, D. H. Lee, and P. A. Lee, cond-mat/0304377.
[6] A. Tanaka and X. Hu, cond-mat/0304409.
[7] D. J. Singh, cond-mat/0304532.
[8] M. L. Foo *et al.*, cond-mat/0304464.
[9] H. Sakurai *et al.*, cond-mat/0304503.
[10] B. Lorenz *et al.*, cond-mat/0304537.
[11] G. Cao *et al.*, unpublished.
[12] K. A. Müller *et al.*, Phys. Rev. Lett. **58**, 408 (1987).
[13] P. A. Mansky, P. M. Chaikin, and R. C. Haddon, Phys. Rev. B **50**, 15929 (1994).
[14] The transverse magneto-resistance in the normal state is found to be proportional to the applied magnetic field, i.e., $\Delta R = R(H) - R(0) \propto H^2$. See: J. Callaway, *Quantum Theory of Solid State*, (Academic Press, NewYork, 1991), p. 650.
[15] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966)/R. R. Hake, Appl. Phys. Lett. **10**, 189 (1967)/T. P. Orlando *et al.*, Phys. Rev. B **19**, 4545 (1979).
[16] Y. Ando *et al.*, Phys. Rev. B **60**, 10580 (1999).
[17] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[18] D. J. Singh, Phys. Rev. B **61**, 13397 (2000).
[19] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).
[20] B. B. Goodman, C. R. Acad. Sci. **246**, 3031 (1958).
[21] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).
[22] Y. Maeno, T. M. Rice, and M. Sigrist, Physics Today **54**, 42 (2001).