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LETTER TO THE EDITOR

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

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Abstract

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 an average energy gap $\Delta_a(0)$ and a Ginzburg–Landau parameter κ of $\sim$0.50 meV and 140, respectively. The temperature dependence of the normalized electronic specific heat in the superconducting state gives a clue to the superconducting gap structure.

1. Introduction

The recent discovery of superconductivity in a two-dimensional cobalt oxyhydrate [1] has been spurring a new round of intense interest in the field of superconductivity research. It has been 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 with the triangular CoO_2 sheets in contrast to 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 is not a superconductor itself, suggests that strong two-dimensionality is 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 state, such as time-reversal-symmetry-breaking $d_{x^2-y^2}+id_{xy}$ superconductivity [3–5] and spin triplet superconductivity [3, 6], have been proposed. Based on the density functional calculation [7], it is also speculated that a triplet superconducting state may exist in this kind of material.

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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 become crucial on this topic.

Unfortunately, the development of the experimental aspect is proceeding relatively slowly. One of the major reasons is that the preparation of samples is not optimized at present. The other reason concerns 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 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 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 a suitable experimental procedure. In this letter, we report the superconducting properties of this intriguing compound.

2. Experimental details

Our samples of $Na_{0.31}CoO_2{\cdot}1.3H_2O$ were prepared in three 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 materials. Second, partial sodium in $Na_{0.74}CoO_2$ was deintercalated by excessive bromine dissolved in acetonitrile, similar to the treatment reported previously [1, 8]. Third, a hydration process was carried out by direct reaction with distilled water. Powder x-ray diffraction (XRD) measurement indicates that the final product is a hexagonal single phase with the cell constants of $a = 2.824$ Å and $c = 19.68$ 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 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 293–693 K is 19.8%, indicating that the content of H_2O is about 1.3/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 characterization will be given elsewhere [11].

The physical property measurements were performed at temperature down to 1.8 K and under field up to 8 T, on a Quantum Design PPMS system. The electrical resistance was measured in a standard four-probe configuration. The heat capacity was measured using an automated relaxation technique with a square piece of ∼20 mg sample. The contribution from the addenda was pre-measured and then subtracted. It is noted that the handling of the sample and the detailed measurement procedure sometimes affect the experimental result very much. Therefore, we kept the same experimental conditions for the different measurements.

3. Results and discussion

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 the 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 a relatively low superconducting fraction. Considering that the χ' value is not flat down to 1.9 K, the superconducting volume

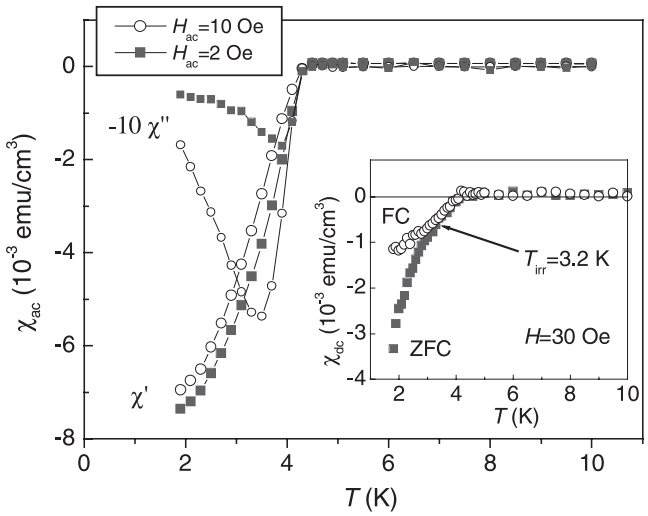

Figure 1. Temperature dependence of ac magnetic susceptibility at zero field for the $Na_{0.31}CoO_2 \cdot 1.3H_2O$ powdered sample. The inset shows the dc magnetic susceptibility under field $H = 30$ Oe. T_{irr}, FC and ZFC refer to the irreversible temperature, field cooling and zero-field cooling,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

fraction will be over 10% under the remanent field of ∼1 Oe. The imaginary component of the ac susceptibility χ'' shows an incomplete dissipation peak, also suggesting that the superconducting transition is not yet finished at 1.9 K. The dc susceptibility under 30 Oe even shows 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 in the previous report [1]. Third, the diamagnetic signal is enhanced when decreasing H_{ac}. A 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 the XRD experiment shows that the sample contains no secondary phase before or *after* the magnetic susceptibility measurement.

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 10 Oe at 1.9 K. By data fitting on $H_{c1}(T)$ 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 measure 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 linearity in the $R–H^2$ curves[4]. The slope

[4] The transverse magneto-resistance in the normal state is found to be proportional to the applied magnetic field, i.e., $\Delta R = R(H) - R(0) \propto H^2$.

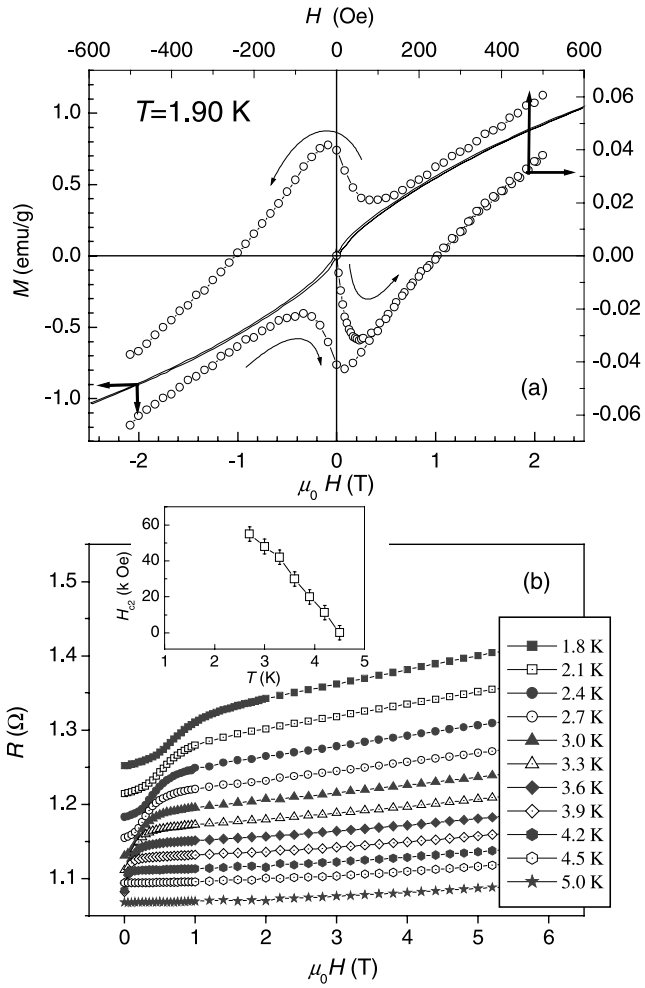

Figure 2. Magnetic field dependence of magnetization (a) and electrical resistance (b) at certain temperatures. Note that the upper right axes are employed for the amplificatory plot in (a). The inset of (b) shows the temperature dependence of the upper critical field H_{c2}.

of H_{c2} at T_c, $dH_{c2}/dT|_{T_c}$, is obtained as -34 kOe K^{-1}. $H_{c2}(0)$ can thus be estimated to be 1×10^5 Oe, using the WHH formula [14]. 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 $H_{c1}(0) = \Phi_0 \ln(\lambda/\xi)/4\pi\lambda^2$, the average penetration depths can also be obtained: $\lambda(0) = 7900$ Å. Therefore, the GL parameter $\kappa = \lambda/\xi_{GL}$ is estimated as $\sim$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 a different method was employed to determine $H_{c2}(T)$. It is worthwhile 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 possibly results 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 neglecting the possible magnetic contribution, the specific heat can be expressed as the sum of electron and phonon contributions:

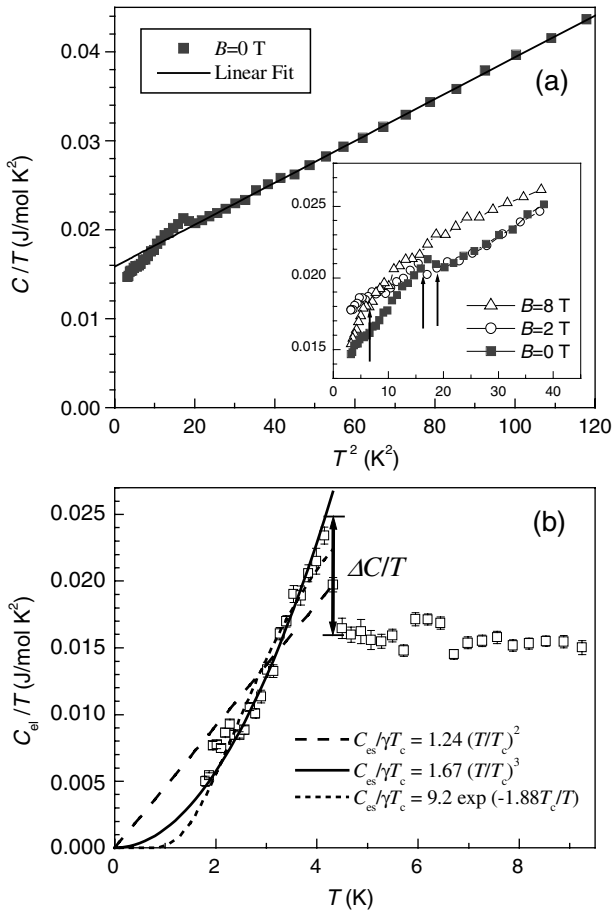

Figure 3. Low-temperature specific heat result of the $Na_{0.31}CoO_2{\cdot}1.3H_2O$ superconductor. (a) Plot of C/T versus T^2. The arrows in the inset point to T_c under different fields. (b) Plot of $C_{el}/T - T$ (for $\eta = 18.1\%$). The electronic specific heat data in the superconducting state, $C_{es}(T)$, were fitted using a different formula.

$C = \gamma T + \beta T^3$, where the coefficient γ is generally called the Sommerfeld parameter. The phonon contribution can be separated by employing the T^2 versus 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 fu (fu denotes formula unit) and $\beta = 0.235$ mJ K^{-4}/mol fu. 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 $Na_{0.31}CoO_2{\cdot}1.3H_2O$ and $R = 8.314$ J mol^{-1} K^{-1}. The γ value, which is close to that of an unpublished result [15], 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 states (DOS) at the 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 band-structure electronic DOS at E_F and λ_{ep} an electron–phonon interaction parameter [17], one can obtain that $N(E_F) = 6.7$ states/eV fu. On the other hand, λ_{ep} can be calculated to be 0.57 using the formula

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

where the Coulomb repulsion parameter μ^* is assumed to be 0.13 empirically [17]. Therefore, $N(0)$ is derived to be 4.3 states/eV fu. 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 ($\sim 2.0 \times 10^{-3}$ emu/mol fu) is almost temperature independent from 30 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^{-1}, 2.6×10^{-9} emu mol^{-1} K^{-2}, 0.0024 emu K^{-1} mol^{-1} 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 due to the Stoner-type enhancement. The Wilson ratio, $R_W = \pi^2 k_B^2 \chi^{\text{Pauli}}/3\gamma\mu_B^2 = 11$, is in sharp contrast with the case of a heavy-fermion superconductor [19]. One notes that the weak itinerant ferromagnetic state is predicted in the parent compound Na_xCoO_2, especially for relatively small x [7].

At 4.3 K, specific heat anomalies can be seen, which is ascribed to the superconducting transition. The specific heat jump at T_c under zero field, ΔC_{obs}, is 6.9 mJ K^{-1}/mol fu, further confirming the bulk superconductivity. When applying magnetic field, both 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 for the full superconductor, 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^{-1}/mol fu. Therefore, the superconducting fraction is estimated to be $\Delta C_{\text{obs}}/\Delta C = 18.1\%$, which is roughly consistent with the magnetic susceptibility measurement result. In addition, the average superconducting gap at zero temperature, $\Delta_a(0)$, can be obtained to be 0.50 meV using the conventional relation [20],

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

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 scenario.

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 $C_{\text{el}} = C - C_L$. If the superconducting fraction is η, the electronic specific heat of the full superconductor can be normalized as $C_{\text{es}} = [C_{\text{el}} - (1-\eta)\gamma T]/\eta$. Figure 3(b) shows the result for $\eta = 18.1\%$. The Sommerfeld-parameter jump at T_c, $\Delta C/T_c$, becomes 9 mJ K^{-2}/mol fu. So, the dimensionless parameter $\Delta C/\gamma T$ value is 0.57, which is remarkably lower than the expected value, 1.43, for an isotropic gap. This suggests that the superconducting order parameter is basically not an s wave.

As we know, the temperature dependence of C_{es} may give important information on the structure of the superconducting gap. At temperatures far below T_c, the exponential dependence of $C_{\text{es}}(T)$ indicates fully gapped superconducting states, while the power-law dependence suggests nodal structures for the gap topology. The latter case is basically divided into three categories: $C_{\text{es}}(T) \propto T^3$, $C_{\text{es}}(T) \propto T^2$ and $C_{\text{es}}(T) \propto T$ represent point nodes, line nodes and non-gap for the superconducting gap structure, respectively [21]. Though the extra-low-temperature data are absent here, fitting on the present data may give a clue to the superconducting gap structure. Figure 3(b) presents the data fitting on $C_{\text{es}}(T)$ using the three formulae $C_{\text{es}}/\gamma T_c = a_1(T/T_c)^2$, $C_{\text{es}}/\gamma T_c = a_2(T/T_c)^3$ and $C_{\text{es}}/\gamma T_c = a_3 \exp(-bT_c/T)$.

It can be seen that the T^3 dependence best fits the $C_{es}(T)$ data; however, the exponential fitting also gives a fairly good result. It should be mentioned that the η value, which is difficult to precisely determine, affects the fitting result. For $13\% \leqslant \eta \leqslant 15\%$, the exponential relation best fits the data (when $\eta \leqslant 12\%$, C_{es} becomes an unreasonable negative value at 1.8 K), but the fitted parameters a_3 and b tend to be even larger. For $15\% < \eta \leqslant 20\%$, T^3 dependence most favours the data. Only when $\eta > 20\%$ does the T^2 relation become suitable for the data. Therefore, as a preliminary conclusion, both the fully gapped and the point-node state are probable. Meanwhile, the isotropic s wave and the line–node structure are not supported by the present experiment.

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 likely. Considering the long cylindrical Fermi surface [7, 18], the p-wave axial state $\Delta(\boldsymbol{k}) = \hat{\boldsymbol{x}}k_x + \hat{\boldsymbol{y}}k_y$ will have no point nodes on the poles. Therefore, a fully gapped p wave seems to be most probable in the present system.

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Note added in proof. Since completion of this letter we note that p-wave pairing with the fully-gapped superconducting state has been supported by a Co NMR study [22].

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