# Upper critical field of an aligned $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ superconductor from magnetization measurements

Zhi Ren,[1] Chunmu Feng,[2] Zhuan Xu,[1] Minghu Fang,[1] and Guanghan Cao[1,*]
[1]*Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China*
[2]*Test and Analysis Center, Zhejiang University, Hangzhou 310027, People's Republic of China*
(Received 17 April 2007; revised manuscript received 4 June 2007; published 1 October 2007)

We present magnetization measurements for the upper critical field $H_{c2}$ on aligned $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ superconductors with magnetic field parallel to $CoO_2$ layers. The temperature-dependent part of the normal-state magnetization $M(H,T)$ can be well scaled with Brillouin function, suggesting the existence of impurity moments. By subtracting the contribution of the magnetic impurity moments, a well defined onset of superconducting diamagnetism allows the in-field superconducting transition temperature $T_c(H)$ to be accurately determined. No superconducting transition was observed down to 1.9 K under an applied field of 8 T. The result suggests that the $H_{c2}^{\|ab}(0)$ value is just within the Pauli paramagnetic limit, supporting spin-singlet superconductivity in the cobalt oxyhydrate superconductor. Additionally, the upward curvature near $T_c$ in the $H_{c2}^{\|ab}$-$T$ phase diagram was confirmed to be intrinsic. Possible origin of the anomaly was discussed.

DOI: 10.1103/PhysRevB.76.132501 PACS number(s): 74.25.Ha, 74.25.Op, 74.70.Dd

## I. INTRODUCTION

Superconductivity in $Na_xCoO_2 \cdot yH_2O$ (Ref. 1) has attracted much attention in recent years. The new layered superconductor exhibits both similarities and differences with the well-known cuprate superconductors, shedding light on the challenging issue of understanding high-$T_c$ superconductivity.[2] At present, evidences of unconventional superconductivity in this material have been indicated or implied by experimental researches[3–9] as well as by theoretical studies.[10–12] However, some of the basic questions on the superconductivity remain open. For example, an unprecedented number of proposals have been suggested for the superconducting pairing symmetry.[13] Obviously, clarification of the spin state of Cooper pairs is crucial to this problem.

Upper critical field $H_{c2}$ is among the most important superconducting parameters since it not only directly correlates with the superconducting coherence length $\xi$, the size of Cooper pairs, but also gives a clue to the pairing symmetry. However, the determination of $H_{c2}(0)$ in $Na_xCoO_2 \cdot yH_2O$ superconductor remains controversial. Resistivity,[14] heat capacity,[9,15] and $^{59}$Co-NMR[16] measurements suggested that the $H_{c2}(0)$ value was within the Pauli paramagnetic limit[17,18] $H_P \approx 8.3$ T, implying spin-singlet state for the Cooper pairs. In contrast, a much larger $H_{c2}(0)$ value, far exceeding the Pauli paramagnetic limit, was inferred from magnetization measurements,[4,8] which favors spin-triplet superconductivity. Another issue is the observation of an abrupt slope change of $H_{c2}$ (or upward curvature) on the $H_{c2}$-$T$ curve near $T_c$,[8,9] which was explained in terms of field-induced pairing symmetry transition.[8,19] Since the anomalous curvature was observed on randomly oriented polycrystalline sample, the anomaly could be an extrinsic phenomenon due to the anisotropy of $H_{c2}$.[9]

In order to clarify these issues, we carried out magnetization measurements for $H_{c2}$ on *aligned* cobalt oxyhydrate superconductors. In principle, $H_{c2}$-$T$ phase diagram can be obtained by determining the superconducting transition temperature under different magnetic fields, i.e., $T_c(H)$. In the case of the cobalt oxyhydrate superconductor, however, determination of $T_c(H)$ becomes difficult especially at high field due to the susceptibility upturn in the normal state.[4] We found that the temperature-dependent part of the normal-state magnetization can be well scaled in terms of Brillouin function, suggesting that the susceptibility upturn above $T_c$ arises from impurity moments rather than spin fluctuation. The in-field superconducting transition temperature $T_c(H)$ was then accurately determined by subtracting the contribution of magnetic impurity. Consequently, the estimated $H_{c2}(0)$ was found to be just within the Pauli paramagnetic limit. Besides, the upward curvature near $T_c$ in the $H_{c2}$-$T$ phase diagram was confirmed to be intrinsic.

## II. EXPERIMENT

Polycrystalline samples of the cobalt oxyhydrate superconductor were synthesized through three steps as described previously.[5,20] First, parent compound $Na_{0.7}CoO_2$ was prepared by a solid-state reaction from high purity $Na_2CO_3$ and $Co_3O_4$ powders. Second, the sodium was adequately deintercalated by employing $Br_2/CH_3CN$ solution as an oxidizing agent. Third, the resulted $Na_xCoO_2$ samples with $x \sim 0.33$ were then hydrated at room temperature in saturated NaCl solution for 10 days. X-ray diffraction confirmed that the obtained samples were single phase. The chemical composition of the sample was determined by the techniques described previously.[20] The sample used in the present study has the chemical composition of $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$.

We made use of the large anisotropy in magnetization[21] to align the powder samples. Since the easy magnetization direction is along the *ab* planes, the crystalline grains can be aligned with the *ab* planes parallel to the external field in a liquid medium by applying a high magnetic field. Upon cooling down under the field, the medium freezes; thus, the grain orientation is fixed. In our experiment, we chose the saturated NaCl solution as the medium in order to suppress the ion exchange between hydroniums and $Na^+$ ions.[20,22,23] Mix-

 

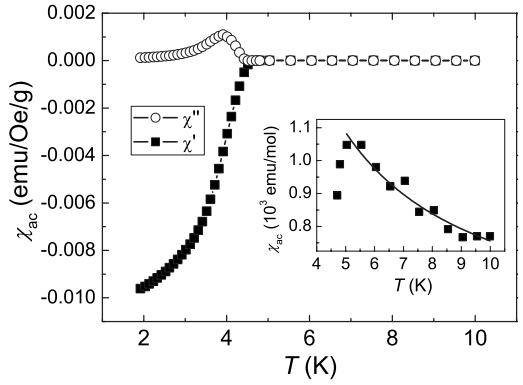


FIG. 1. Temperature dependence of ac magnetic susceptibility for aligned powder sample of $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ with an ac field of 10 Oe parallel to *ab* planes. $\chi'$ and $\chi''$ denote the real and imaginary parts, respectively. The inset is an expanded plot for displaying the normal-state susceptibility. The solid line is a Curie fit with the formula $\chi = \chi_0 + C/T$.

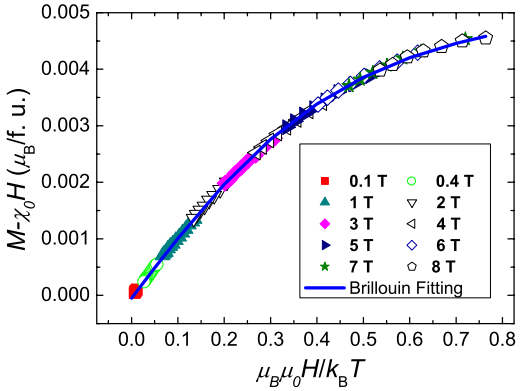


FIG. 2. (Color online) Scaling behavior of the normal-state magnetization for the aligned $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ superconductor.

ture of the powdered superconductor and saturated NaCl solution in a Teflon container was frozen below 250 K under an 8 T field. Magnetization measurement, performed on a Quantum Design physical property measurement system facility, showed that the aligned sample had relatively large magnetization compared with the nonaligned sample.

### III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of ac magnetic susceptibility for $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ sample with the field parallel to *ab* planes. Sharp superconducting transition can be seen at 4.5 K. The diamagnetic signal at 2 K is among the best results (for polycrystalline samples) in the literatures,[1,9,15] suggesting high quality of the present sample. The inset shows an expanded plot for the normal-state susceptibility. One can see an obvious susceptibility upturn with decreasing temperature. Similar phenomenon was previously reported.[4,8]

There exist at least two kinds of explanations about the susceptibility upturn behavior. One possibility is that the susceptibility enhancement above $T_c$ is relevant to spin fluctuations.[4,24,25] However, the enhancement was sample dependent.[26] Another explanation simply concerns the paramagnetic impurity.[4,21] The applied field lines up the impurity moments, hence inducing a magnetization, which can be expressed by the following equation:

$$M = n g_J \mu_B J B_J(\alpha), \tag{1}$$

where $n$ denotes the number of magnetic impurity per formula unit, $g_J$ the Landé $g$ factor, $J$ the angular moment, $\mu_B$ the Bohr magneton, $\alpha \equiv (g_J J \mu_B \mu_0 H)/(k_B T)$, $\mu_0$ the permeability in vacuum, and $B_J(\alpha)$ is called the Brillouin function,

$$B_J(\alpha) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\alpha\right) - \frac{1}{2J} \coth\frac{\alpha}{2J}. \tag{2}$$

For a large $\alpha$ (at very low $T$ and/or very high $H$), $M$ tends to saturate. For $\alpha \ll 1$ (at high $T$ and/or low $H$), the Brillouin function can be simplified and the susceptibility is given in the form of Curie law,

$$\chi = \frac{M}{H} \approx \frac{n\mu_0 \mu_{eff}^2}{3k_B T}, \tag{3}$$

where $\mu_{eff} = g_J \sqrt{J(J+1)}\mu_B$.

For the present study, the total molar magnetization above $T_c$ can be expressed as

$$M_{tot}(H,T) = \chi_0 H + M(H/T), \tag{4}$$

where $\chi_0$ includes the contribution from Pauli paramagnetism as well as core diamagnetism, which is independent of both temperature and magnetic field. Experimentally, $\chi_0$ value was obtained by the Curie fit shown in the inset of Fig. 1. Therefore, $(M_{tot}\text{-}\chi_0 H)$ should be scaled in terms of $H/T$. As shown in Fig. 2, the $T$-dependent part of the normal-state $M(H,T)$ $(0.1\ \text{T} \leqslant H \leqslant 8\ \text{T},\ 5\ \text{K} \leqslant T \leqslant 10\ \text{K})$ data actually falls on the same curve. Furthermore, Eq. (1) gives a satisfactory fit of the curve. The fitting parameters are $n = 0.0014$, $g_J = 2.4 \pm 0.1$, and $J = 1.6 \pm 0.2$. We have also checked validity of the scaling behavior on different samples. The $g_J$ and $J$ values are almost identical for all the samples. However, the $n$ value varies from sample to sample, even for the samples with nearly the same $T_c$. This sample-dependent behavior strongly suggests that the $T$-dependent part of the normal-state magnetization is not intrinsic.

As we know, $Co^{2+}$ in the high spin state has $J = S = 3/2$ and $g = 2.5$, which is very close to the fitting result. Thus, the susceptibility upturn probably arises from the magnetic ion $Co^{2+}$ formed through charge disproportionation reaction.[23] Since the effective moments of $Co^{2+}$ is 4.8 $\mu_B$, according to the Curie fit in the inset of Fig. 1, the $Co^{2+}$ concentration would be 0.13(2)%, consistent with the above Brillouin fitting.

Bearing in mind that the $T$-dependent part of the normal-state magnetization $M(H,T)$ can be well described by the Brillouin function, we can subtract the magnetic impurity contribution from the total magnetization. After this correction, the superconducting diamagnetism is linear with temperature near the transition region. According to the criterion

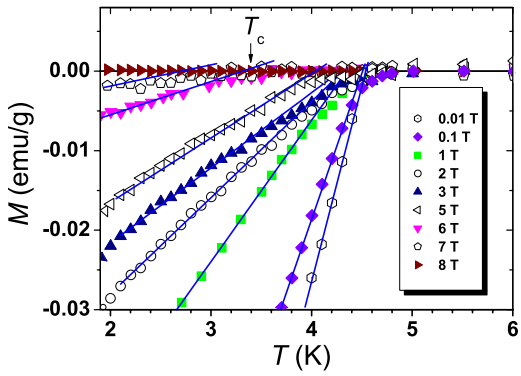


FIG. 3. (Color online) Temperature dependence of the magnetization (after subtracting the contribution from impurity magnetic moments) under different magnetic fields for the aligned $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ superconductor.

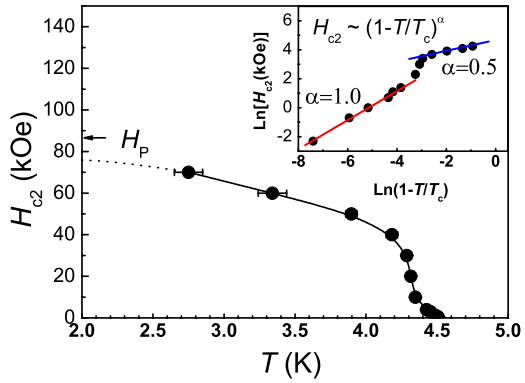


FIG. 4. (Color online) Temperature dependence of upper critical field $H_{c2}^{\|ab}(T)$ for the aligned $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ superconductor.

of the superconducting transition,[27] the $T_c(H)$ values were determined as the intersection of linear extrapolation of the magnetization with the base line, as shown in Fig. 3. The result shows that $T_c$ is gradually suppressed with increasing applied field. It is noted that no superconducting transition can be observed under 8 T down to the lowest temperature of 1.9 K. This is in sharp contrast with the previous magnetization measurements.[8] At high fields and low temperatures, in fact, the impurity moments tend to saturate, which could be mistaken for a superconducting transition.

The $H_{c2}^{\|ab}$-$T$ phase diagram obtained is shown in Fig. 4. Our phase diagram is basically in agreement with the measurements from resistivity,[14] thermodynamics,[9,15] and $^{59}$Co-NMR.[16] Although the upper critical field at zero temperature $H_{c2}^{\|ab}(0)$ could not be directly measured in the present work, the rapid decrease of $T_c$ at high magnetic field suggests that $H_{c2}^{\|ab}(0)$ is much smaller than those of the previous results by magnetic measurements.[4,8] In fact, the specific-heat measurement shows no superconducting transition down to 0.6 K at 8 T.[15] That is to say, the $H_{c2}^{\|ab}(0)$ value is very close to the Pauli paramagnetic limit $H_P \sim 8.3$ T, supporting spin-singlet superconductivity in $Na_x(H_3O)_zCoO_2 \cdot yH_2O$. It is noted that recent $^{59}$Co Knight-shift measurement[28] also indicated that the electron pairing in the superconducting state is in the spin-singlet form.

Figure 4 also shows an upward curvature or a slope change near $T_c$. Since our measurements were performed on aligned samples, the effect of anisotropy of $H_{c2}$ can be ruled out. Therefore, the slope change of $H_{c2}^{\|ab}(T)$ should be an intrinsic phenomenon.

There were theoretical explanations for the $H_{c2}(T)$ anomaly in terms of pairing symmetry transition.[8,19] Considering the two dimensionality of the present superconductor, here we propose another possibility: a field-induced three-dimensional (3D) to two-dimensional (2D) crossover. As can be seen from the inset of Fig. 4, $H_{c2}^{\|ab}(T)$ is proportional to $(1-T/T_c)$ near $T_c$, as expected from 3D Ginzburg-Landau theory. On the other hand, $H_{c2}^{\|ab}(T)$ is proportional to $(1-T/T_c)^{1/2}$ for $0.6T_c \leqslant T \leqslant 0.95T_c$, which is a signature of decoupled 2D behavior.[29] Deutscher and Entin-Wohlman[30] have shown that a layered superconductor built up by alternating superconducting and insulating layers shows a dimensional crossover characterized by an upturn in $H_{c2}^{\|ab}(T)$ at the temperature where interlayer coherence length $\xi_{\perp}(T)$ is of the order of the sum of single superconducting and insulating layers. The $\xi_c(0)$ value of $\sim$13 Å (Ref. 14) is comparable to the interlayer spacing of 9.8 Å, indicating that the dimensional crossover is probable for the present superconductor. In order to clarify this issue, the measurement of the angular dependence of the upper critical field on high quality single crystal is highly desired. As is known, in the 3D regime, $H_{c2}^{\|ab}(\Theta)$ shows a rounded maximum around $\Theta=0$, while in the 2D case, it exhibits a cusp.[31]

## IV. CONCLUSION

In summary, we have carried out a detailed magnetization measurement on aligned $Na_{0.33}(H_3O)_{0.02}CoO_2 \cdot 1.4H_2O$ superconductors with magnetic field parallel to *ab* planes. The temperature-dependent part of the normal-state magnetization was revealed to arise from paramagnetic impurity rather than spin fluctuations. The onset of superconductivity was characterized by the deviation from the normal-state magnetization governed by the Brillouin function. The result suggested that the $H_{c2}^{\|ab}(0)$ value for the cobalt oxyhydrate superconductor was just within the Pauli paramagnetic limit $H_P \approx 8.3$ T, which supports spin-singlet superconductivity. Besides, the slope change near $T_c$ in the $H_{c2}^{\|ab}$-$T$ phase diagram was confirmed to be intrinsic. A field-induced 3D to 2D dimensional crossover is an alternative explanation for this anomaly, which needs further investigations.

## ACKNOWLEDGMENTS

We acknowledge the support from the National Basic Research Program of China (No. 2006CB601003) and the National Science Foundation of China (Projects No. 10674119 and No. 10634030).

*Author to whom correspondence should be addressed; ghcao@zju.edu.cn

[1] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).
[2] J. V. Badding, Nat. Mater. **2**, 208 (2003).
[3] R. E. Schaak, T. Klimczuk, M. L. Foo, and R. J. Cava, Nature (London) **424**, 527 (2003).
[4] H. Sakurai, K. Takada, S. Yoshii, T. Sasaki, K. Kindo, and E. Takayama-Muromachi, Phys. Rev. B **68**, 132507 (2003).
[5] G. H. Cao, C. M. Feng, Y. Xu, W. Lu, J. Q. Shen, M. H. Fang, and Z. A. Xu, J. Phys.: Condens. Matter **15**, L519 (2003).
[6] T. Fujimoto, G. Q. Zheng, Y. Kitaoka, R. L. Meng, J. Cmaidalka, and C. W. Chu, Phys. Rev. Lett. **92**, 047004 (2004).
[7] F. C. Chou, J. H. Cho, P. A. Lee, E. T. Abel, K. Matan, and Y. S. Lee, Phys. Rev. Lett. **92**, 157004 (2004).
[8] M. M. Maska, M. Mierzejewski, B. Andrzejewski, M. L. Foo, R. J. Cava, and T. Klimczuk, Phys. Rev. B **70**, 144516 (2004).
[9] H. D. Yang, J.-Y. Lin, C. P. Sun, Y. C. Kang, C. L. Huang, K. Takada, T. Sasaki, H. Sakurai, and E. Takayama-Muromachi, Phys. Rev. B **71**, 020504(R) (2005).
[10] G. Baskaran, Phys. Rev. Lett. **91**, 097003 (2003).
[11] A. Tanaka and X. Hu, Phys. Rev. Lett. **91**, 257006 (2003).
[12] Q. H. Wang, D. H. Lee, and P. A. Lee, Phys. Rev. B **69**, 092504 (2004).
[13] I. I. Mazin and M. D. Johannes, Nat. Phys. **1**, 91 (2005), and references therein.
[14] T. Sasaki, P. Badica, N. Yoneyama, K. Yamada, K. Togano, and N. Kobayashi, J. Phys. Soc. Jpn. **73**, 1131 (2004).
[15] N. Oeschler, R. A. Fisher, N. E. Phillips, J. E. Gordon, M.-L. Foo, and R. J. Cava, Chin. J. Phys. (Taipei) **43**, 574 (2005).
[16] Y. Kobayashi, H. Watanabe, M. Yokoi, T. Moyoshi, Y. Mori, and M. Sato, J. Phys. Soc. Jpn. **73**, 1297 (2004).
[17] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[18] B. S. Chandrasekhar, Appl. Phys. Lett. **1**, 7 (1962).
[19] J. T. Kao, J. Y. Lin, and C. Y. Mou, Phys. Rev. B **75**, 012503 (2007).
[20] G. H. Cao, X. M. Tang, Y. Xu, M. Zhong, X. Z. Chen, C. M. Feng, and Z. A. Xu, Solid State Commun. **131**, 125 (2004).
[21] F. C. Chou, J. H. Cho, and Y. S. Lee, Phys. Rev. B **70**, 144526 (2004).
[22] K. Takada, K. Fukuda, M. Osada, I. Nakai, F. Izumi, R. A. Dilanian, K. Kato, M. Takata, H. Sakurai, E. Takayama-Muromachi, and T. Sasaki, J. Mater. Chem. **14**, 1448 (2004).
[23] Z. Ren, Y. W. Wang, S. Liu, J. Wang, Z. A. Xu, and G. H. Cao, Chem. Mater. **17**, 1501 (2005).
[24] M. Mochizuki, Y. Yanase, and M. Ogata, Phys. Rev. Lett. **94**, 147005 (2005).
[25] K. Ishida, Y. Ihara, Y. Maneo, C. Michioka, M. Kato, K. Yoshimura, K. Takada, T. Sasaki, H. Sakurai, and E. Takayama-Muromachi, J. Phys. Soc. Jpn. **72**, 3041 (2003).
[26] Y. Ihara, K. Ishida, K. Yoshimura, K. Takada, T. Sakaki, H. Sakurai, and E. Takayama-Muromachi, J. Phys. Soc. Jpn. **74**, 2177 (2005).
[27] U. Welp, W. K. Kwok, G. W. Crabtree, K. G. Vandervoort, and J. Z. Liu, Phys. Rev. Lett. **62**, 1908 (1989).
[28] Guo-qing Zheng, Kazuaki Matano, D. P. Chen, and C. T. Lin, Phys. Rev. B **73**, 180503(R) (2006).
[29] S. T. Ruggiero, T. W. Barbee, Jr., and M. R. Beasley, Phys. Rev. B **26**, 4894 (1982).
[30] G. Deutscher and O. Entin-Wohlman, Phys. Rev. B **17**, 1249 (1978).
[31] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).