Unconventional upper- and lower-critical fields and normal-state magnetic susceptibility of the superconducting compound $Na_{0.35}CoO_2 \cdot 1.3H_2O$

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Magnetic properties of the layered superconductor, $Na_{0.35}CoO_2 \cdot 1.3H_2O$ have been investigated. From the temperature dependence and field dependence of the magnetization, the superconducting transition temperature, as well as upper- and lower-critical fields have been estimated to be $T_C = 4.6$ K, $H_{C2}(0) = 61.0$ T and $H_{C1}(0) = 28.1$ Oe, respectively. These values give quite unusual phenomenological parameters, i.e., coherent length, penetration depth and Ginzburg-Landau parameter of $\xi = 2.32$ nm, $\lambda = 5.68 \times 10^2$ nm, and $\kappa \equiv \lambda/\xi = 244$, respectively, suggesting an unconventional nature of superconductivity. Additionally, the magnetic susceptibility above T_C and the magnetization curve up to 54 T are also reported.

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Very recently, a Co oxide, $Na_{0.35}CoO_2 \cdot 1.3H_2O$, was found to be a superconductor with $T_C \simeq 5$ K.[1] This compound is the first to be discovered superconducting Co oxide and moreover, it has been claimed that there is a marked resemblance between this compound and high T_C cuprates.[1,2] The first similarity is that the compound has a layered structure composed of two-dimensional (2D) CoO_2 layers separated by a thick insulating layer of Na ions and water molecules. As is widely known, high T_C cuprates have also layered structures with 2D CuO_2 planes, which play an essential role in the high T_C superconductivity. The second similarity is related to valence and spin states of the transition metals. The Cu ions of the high T_C cuprates are of mixed-valence states by hole doping; Cu^{2+} ($S = 1/2$) ions are partially oxidized to Cu^{3+} ($S = 0$) ions. In a similar way, the Co ion in the Co oxide is either Co^{4+} (d^5) or Co^{3+} (d^6) with a spin state of $S = 1/2$ or $S = 0$, respectively, assuming low-spin configurations.

It is also worth noting that there is an obvious difference between the two systems. In a high T_C cuprate, the Cu atoms form a square lattice, whereas the Co atoms form a triangular lattice in the present material. This geometric difference appears to be quite important because the triangular lattice can cause the geometric frustration. An additional difference is that the holes of a high T_C cuprate exist in the e_g orbitals, while the electrons of the Co oxide exist in the t_{2g} orbitals.

Studies of the present Co oxide have just begun, and its fundamental superconducting and normal-state properties still need to be investigated. In particular, magnetic properties seem to be of primary importance. Such investigation may lead to the understanding of superconductivity, not only of the Co oxide but also of high T_C cuprates. Here, we report upper- and lower-critical fields and normal-state magnetic susceptibilities up to 54 T for the superconducting Co oxide and they are discussed in comparison with those of conventional superconductors and the high T_C cuprates.

A powder sample was synthesized as described in the previous report.[1] The sample was shown by powder x-ray diffraction to be in single phase with $Na_{0.35}CoO_2 \cdot 1.3H_2O$. The magnetic data below 7 T were collected with a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL7). All the measurements were done under zero-field-cooling condition. The high-field magnetization measurements were performed by using a pulse magnet at KYOKUGEN in Osaka University.

Typical magnetization/magnetic field (M/H) data are shown as a function of temperature in Fig. 1(a). For $H \geqslant 7$ kOe, magnetic susceptibility was not negative down to 1.8 K but the superconducting transition was observed as a downturn of M/H. The transition temperature T_C could be determined by the simple straight line fit as shown in Fig. 1(a), for given H of 0.02, 0.1, 0.5, 1, 2, 4, 7, 10, 15, 20, 30, and 40 kOe. For $H \geqslant 50$ kOe, however, the superconducting transition became quite broad and T_C could not be determined without seriously large uncertainty. This procedure gives an upper-critical field H_{C2} versus temperature relation of $H_{C2}(T) = 88.0 - 19.3T$, as shown in Fig. 1(b). From this equation, T_C at $H = 0$ and $dH_{C2}/dT|_{T_C}$ are calculated to be 4.56 K and 19.3 T/K, respectively. The value of T_C obtained at $H = 0$ agrees well with the onset T_C determined from the susceptibility data at $H = 20$ Oe [see the insert of Fig. 1(b)] but slightly lower than that in the previous report.[1] The initial slope $dH_{C2}/dT|_{T_C}$ is much larger than the ~ 7.5 T/K of a molybdenum chalcogenide which had been known to have the highest initial slope before the discovery of high T_C cuprates.[3]

According to the Werthamer-Helfand-Hohenberg (WHH) formula,[4]

$$H_{C2}(0) = 0.693 \left(\left. \frac{dH_{C2}}{dT} \right|_{T_C} \right) T_C , \qquad (1)$$

$H_{C2}(0)$ is calculated to be 61.0 T. In high T_C cuprates, H_{C2} does not always have a strictly defined meaning. This may also be the case for the present system. Corresponding to the

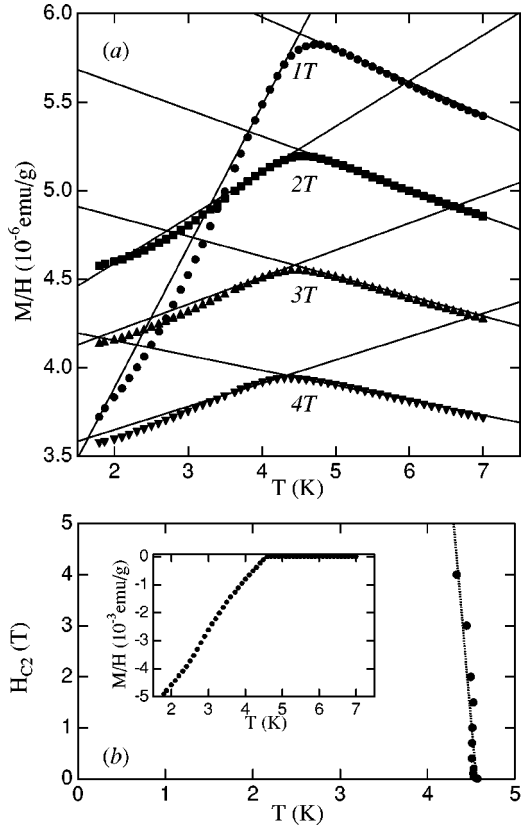

FIG. 1. (a) Temperature dependence of the magnetization under various fields. Each curve except that under 1 T is offset for clarity. (b) Field dependence of T_C. The dotted line is the result when fitted by a linear function. The inset shows M/H data at 20 Oe.

high H_{C2} value, a quite small coherent length $\xi = 2.32$ nm is obtained according to the formula $H_{C2} = \Phi_0/2\pi\xi^2$ (Φ_0: fluxoid quantum). This length is comparable to those of high T_C cuprates but far smaller than those of conventional superconductors. The present compound has highly 2D structure with a hexagonal lattice and strong anisotropy is expected for the superconducting properties. In the above procedure, we determine onset T_C and which should correspond to higher H_{C2} value. Namely, since $H_{C2}^{H//c} < H_{C2}^{H//ab}$ by structural analogy of high T_C cuprates, H_{C2} determined above reflects $H_{C2}^{H//ab} (= \Phi_0/2\pi\xi_{ab}\xi_c)$ and $\xi = 2.32$ nm is an average of $\sqrt{\xi_{ab}\xi_c}$ (ξ_i: the coherent length of i direction). For further discussion of the anisotropy, we need single crystal data though single crystal growth seems quite hard for the present system.

The temperature dependence of the lower-critical field H_{C1} is shown in Fig. 2. The H_{C1} values were determined from M-H curves below 100 Oe at various temperatures. The magnetization decreases as $M = \chi H$ with increasing applied field below H_{C1} and starts to deviate from the straight line at H_{C1}. According to Bean's critical-state model,[5] the deviation ΔM from the linear function may be calculated as $\sqrt{\Delta M} \propto -H_{C1} + H$.[6] However, $\sqrt{\Delta M}$ of our data did not obey well with this linear relation. This might be due to the shape effect which is not taken into account in the model. The simple straight line fit used in the H_{C2} determination

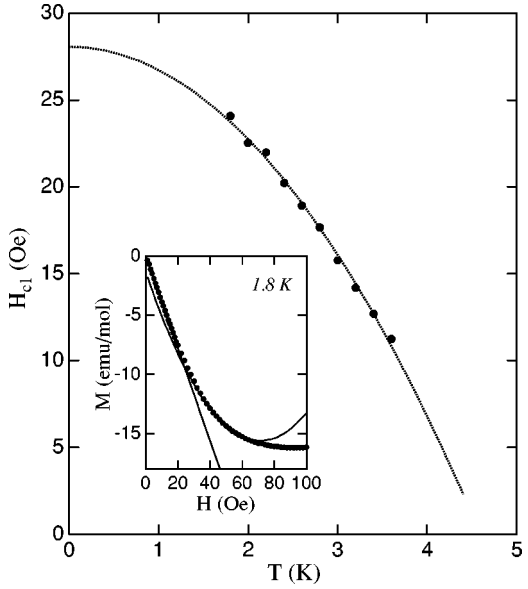

FIG. 2. Temperature dependences of H_{C1}. The dotted line is the result when fitted by Eq. (2). The inset shows the magnetization curve at 1.8 K. The solid lines are the linear function and the parabola for the estimation of H_{C1} (see the text).

was not appropriate to estimate H_{C1} because the result depended largely on the range of fitting for the data above H_{C1}. Instead, we represented the M-H curve above H_{C1} by a quadratic function and $H_{C1}(T)$ was determined from the intersection point of the quadratic curve and the straight line which was obtained for the low field data. The $H_{C1}(T)$ values obtained were fitted by the function

$$H_{C1}(T) = H_{C1}(0)[1 - (T/T_C)^2], \tag{2}$$

where $H_{C1}(0)$ and T_C were fitting parameters, resulting in $H_{C1}(0) = 28.1$ Oe and $T_C = 4.59$ K. The T_C thus calculated agrees very well with that determined from H_{C2}.

From $H_{C1}(0)$ and ξ, the penetration depth can be calculated to be $\lambda = 5.68 \times 10^2$ nm by the formula

$$H_{C1} = \frac{\Phi_0}{4\pi\lambda^2} \ln\left(\frac{\lambda}{\xi}\right). \tag{3}$$

The Ginzburg-Landau (GL) parameter $\kappa \equiv \lambda/\xi = 244$ is much larger than the parameters of conventional superconductors (it is even larger than those of high T_C cuprates), suggesting that the present compound belongs to an extreme type II family. Since $H_{C1}^{H//c} > H_{C1}^{H//ab}$ is expected by analogy of high T_C cuprates, H_{C1} in Fig. 1 reflects mainly $H_{C1}^{H//ab}$ and both λ and κ values should be considered as some averages of those along the c axis and along the ab plane as in the case of ξ. However, even taking into account this limitation, the phenomenological parameters obtained in the present study are quite unusual. It is strongly suggested that the present compound is an unconventional superconductor as expected by theoreticians.[7,8]

The magnetic susceptibility measured under 10 kOe is shown in Fig. 3. The susceptibility decreases first with decreasing temperature and then increases between T_C and 130

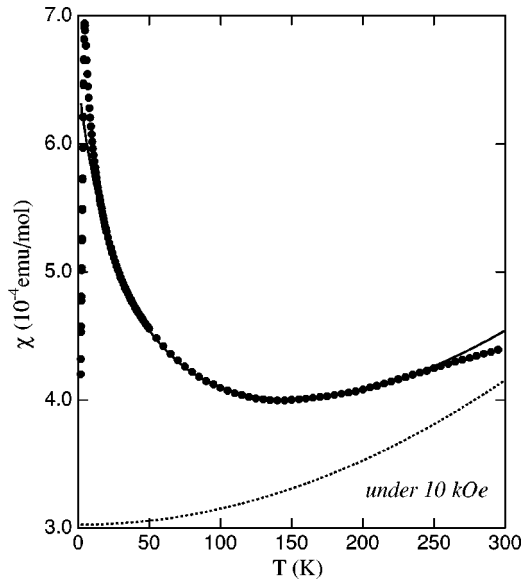

FIG. 3. Temperature dependence of the magnetic susceptibility measured under 1 T. The solid line is the result when fitted by Eq. (4). The dotted lines represent the Pauli paramagnetic terms of Eq. (4).

K. Assuming that this upturn is due to a magnetic impurity and/or crystal defects, we fit the data between 20 K and 250 K by the equation

$$\chi = \chi_0 + AT^2 + \frac{C}{T-\theta}, \tag{4}$$

where the first and the second terms are due to Pauli paramagnetism. The parameters obtained are $\chi_0 = 3.02 \times 10^{-4}$ emu/mol, $A = 1.25 \times 10^9$ emu/K^{2}mol, $C = 1.31 \times 10^{-2}$ emu K/mol, and $\theta = -37.6$ K. The solid line in Fig. 3 represents Eq. (4) and seems to reproduce the data well.

On the other hand, as seen in Fig. 4, high-field magnetization increases linearly with increasing field above 15 T and there is no anomaly up to 50 T. The slope of magnetization curve between 15 T and 50 T is 4.9×10^{-4} emu/mol, which is different from 3.02×10^{-4} ($=\chi_0 + A \times 4.2^2$) emu/mol obviously beyond experimental uncertainty. There are two possible scenarios to explain this discrepancy. First, the sample contained a magnetic impurity phase, though it was not detected by the x-ray diffraction, and its magnetization was not saturated up to 50 T at 4.2 K. Second, the upturn in question

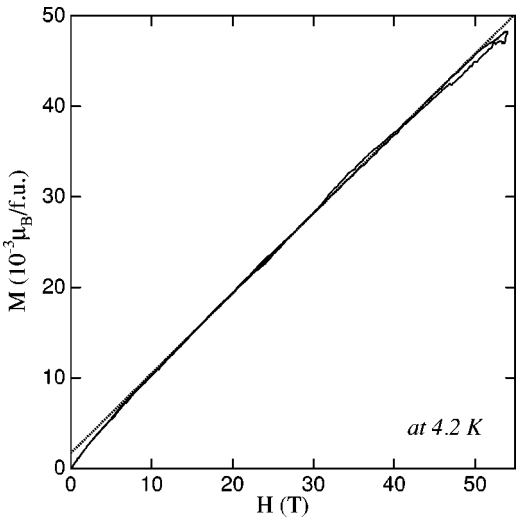

FIG. 4. Magnetization curve at 4.2 K. The dotted line is the result when fitted by a linear function.

reflects the intrinsic nature of the compound. Related to the second scenario, previous reports for $Na_{0.5}CoO_2$ and La-doped Sr_2RuO_4 may be worth noting. The magnetic susceptibility of $Na_{0.5}CoO_2$ increases with decreasing temperature owing to a kind of spin fluctuation.[9] The La-doped Sr_2RuO_4 has been reported to show an enhancement of the susceptibility.[10] Although we need further studies to rule out the first scenario, the enhancement of the magnetic susceptibility may have relevance to the mechanism of the Cooper pair formation[7]

In summary, from M-T and M-H curves, superconducting transition temperature, as well as upper- and lower-critical fields are estimated to be $T_C = 4.6$ K, $H_{C2} = 61.0$ T and $H_{C1} = 28.1$ Oe, for the Co oxide superconductor of $Na_{0.35}CoO_2 \cdot 1.3H_2O$. The coherent length, penetration depth and GL parameter are calculated to be $\xi = 2.32$ nm, $\lambda = 5.68 \times 10^2$ nm, and $\kappa = 244$, respectively. These phenomenological parameters are quite unusual and strongly suggest that the superconductivity is unconventional. The normal-state magnetic susceptibility is also presented. The normal-state magnetic behavior may have relevance to the mechanism of the Cooper pair formation.

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