Observation of Bulk Superconductivity in $Na_xCoO_2 \cdot yH_2O$ and $Na_xCoO_2 \cdot yD_2O$ Powder and Single Crystals

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Poly- and single-crystalline Na_xCoO_2 has been successfully intercalated with H_2O and D_2O as confirmed by x-ray diffraction and thermogravimetric analysis. Resistivity, magnetic susceptibility, and specific heat measurements show bulk superconductivity with T_c close to 5 K in both cases. The substitution of deuterium for hydrogen has an effect on T_c of less than 0.2 K. Investigation of the resistivity anisotropy of $Na_xCoO_2 \cdot yH_2O$ single crystals shows (a) almost zero resistivity below T_c, and (b) an abrupt upturn at $T^* \sim 52$ K in both the *ab* plane and the *c* direction. The implications of our results on the possible superconducting mechanism will be discussed.

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Sodium-cobalt oxide Na_xCoO_2 has been of interest for several years as a potential thermoelectric material, because it exhibits low resistivity coupled with a relatively large thermopower [1]. The crystal structure consists of layers of edge-sharing CoO_6 octahedra perpendicular to the *c* axis separated by Na layers. The Co ions are mixed valent with a formal oxidation state of $4 - x$. Qualitatively, this structure is similar to that of high-T_c cuprate superconductors, except that in each layer the Co atoms form a triangular (hexagonal) lattice rather than a square lattice. The dc magnetic susceptibility χ of Na_xCoO_2 is small and weakly temperature dependent, with no evidence of long-range magnetic order for $x < 0.75$. For $x = 0.75$, a weak magnetic transition at 21 K was reported by Motohashi and co-workers [2]. Magnetic frustration within the Co layers likely suppresses robust long-range magnetic order. The magnetic susceptibility and the in-plane (ρ_{ab}) and out-of-plane (ρ_c) resistivities of $Na_{0.5}CoO_2$ are, in fact, reminiscent of another layered metallic oxide, Sr_2RuO_4 [1,3], except for the absence of superconductivity at low temperatures. The recent discovery of superconductivity [4] in water-intercalated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ is very exciting, because it may be the first superconductor analogous to Sr_2RuO_4 as proposed by Singh as well as Tanaka and Hu [5].

Although ρ_{ab} is small, superconductivity has not been observed in Na_xCoO_2. Superconductivity also does not occur in $Na_{0.3}CoO_2 \cdot 0.6H_2O$ [6], indicating that sufficient hydration is crucial for the appearance of superconductivity in $Na_{0.3}CoO_2 \cdot yH_2O$. The relationship between the transition temperature T_c and the water content *y*, and the role that H_2O plays for the occurrence of superconductivity are central issues. In this Letter, we report that bulk superconductivity is observed not only in hydrated $Na_{0.3}CoO_2 \cdot yH_2O$ but also in deuterated $Na_{0.3}CoO_2 \cdot yD_2O$ with $T_c \sim 4.5$ K. By investigating the resistivity anisotropy of $Na_xCoO_2 \cdot yH_2O$ single crystals, we obtain, for the first time, almost zero resistivity below T_c along both the *ab* plane and the *c* axis, indicating fully three-dimensional superconductivity.

Superconducting sodium cobaltate was prepared following a procedure similar to that described in Ref. [4]. The parent compound Na_xCoO_2 was obtained via solid-state reaction. Starting materials Na_2CO_3 (Alfa Aesar 99.997%) and Co_3O_4 (Alfa Aesar 99.9985%) were mixed in a molar ratio of Na : Co = 0.7 : 1.0. After ball milling in a sealed chamber for 2 h, the mixture was put into a furnace that was preheated to 750 °C, i.e., the so-called rapid-heat-up technique [2]. After heating for 20 h, the powder was reground, pressed into pellets, and calcined at 830 °C for 16 h in flowing O_2 gas. X-ray diffraction results confirm the correct single phase with hexagonal crystal structure (lattice parameters are listed in Table I). For single crystal growth, both the floating-zone technique and flux method [7] were employed. In the latter case, thin platelike single crystals were obtained with surface areas up to 5×5 mm^2. Even larger single crystals could be grown using the floating-zone technique. Based on the values of the lattice parameters and high-temperature resistivity measurements, the actual Na content *x* is close to 0.6 for both poly- and single crystals [2,6]. It is worth mentioning that, in addition to forming Na_xCoO_2, the conventional slow-heat-up process often

TABLE I. Room temperature lattice parameters and standard deviations for $Na_xCoO_2 \cdot yH_2O$ and $Na_xCoO_2 \cdot yD_2O$ (space group 194 $P6_3mmc$).

Composition	*a* (Å)	*c* (Å)
$Na_{0.6}CoO_2$	2.837(1)	10.878(2)
$Na_{0.3}CoO_2 \cdot 0.9H_2O$	2.825(2)	13.831(7)
$Na_{0.3}CoO_2 \cdot 1.4H_2O$	2.823(1)	19.696(1)
$Na_{0.3}CoO_2 \cdot 1.4D_2O$	2.821(1)	19.635(2)
$Na_{0.3}CoO_2 \cdot 1.8D_2O$	2.823(1)	19.660(4)

results in impurity phases including Co_3O_4 and perhaps $CoCO_3$.

To obtain superconductivity, it is necessary to first chemically extract additional Na from the structure. Both $Na_{0.6}CoO_2$ powder and small single crystals ($0.7 \times 0.7 \times 0.05$ mm^3) were placed in a 6.6 M Br_2/CH_3CN solution for 2–5 d. Careful filtering and washing in pure CH_3CN followed by a 50/50 mixture of CH_3CN/H_2O (or CH_3CN/D_2O) resulted in a single phase, intermediate state of hydration/deuteration first reported by Foo *et al.* [6]. Our thermogravimetric analysis measurements on this phase yield an approximate Na content $x = 0.3$ and H_2O/D_2O content of $y = 0.9$. This value of y is larger than $y = 0.6$ reported in Ref. [6]. This phase is stable as long as the powder is kept in a sealed bottle. As listed in Table I, the lattice parameter a remains virtually unchanged, while the c value is enlarged to 13.831 Å, a 26% increase compared to the parent compound. Superconductivity was obtained through further hydration/deuteration of the samples by stirring the powder or small crystals in distilled H_2O or D_2O for more than 12 h at room temperature. The exact time required to reach the optimum state of hydration/deuteration ($y \sim 1.4$) for superconductivity depends on the crystallite size. It is also possible to overhydrate the powder or to disorder the hydrated compound ($y \sim 1.4$–2.0) which strongly suppresses superconductivity but has little effect on the x-ray pattern. As may be seen in Table I, the lattice parameters for $Na_{0.3}CoO_2 \cdot 1.4H_2O$ are slightly larger than that for $Na_{0.3}CoO_2 \cdot 1.4D_2O$, consistent with the stronger D-O bond relative to the H-O bond [8].

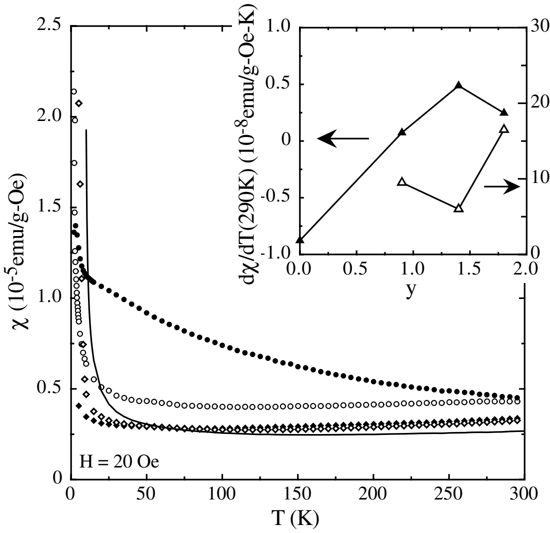

FIG. 1. Temperature dependence of the dc magnetic susceptibility for the parent compound $Na_{0.6}CoO_2$ (filled circles), intermediate phase $Na_{0.3}CoO_2 \cdot 0.9H_2O$ (unfilled circles), superconducting $Na_{0.3}CoO_2 \cdot 1.4H_2O$ (filled diamonds), and $Na_{0.3}CoO_2 \cdot 1.4D_2O$ (unfilled diamonds) above the superconducting transition T_c, and overdeuterated $Na_{0.3}CoO_2 \cdot 1.8D_2O$ (solid line). All measurements were carried out by applying $H = 20$ Oe using a commercial SQUID magnetometer by quantum design. The inset shows the H_2O/D_2O content y dependence of the room-temperature magnetic susceptibility slope $d\chi/dT$ (290 K) (filled triangles) and crossover temperature T_x (unfilled triangles) (see the definition in the text). Note that both $d\chi/dT$ (290 K) and T_x exhibit extrema at $y = 1.4$, indicating that the susceptibility data correlate with both the Na content (Co valence) and the degree of hydration/deuteration.

In Fig. 1, we present the temperature dependence of the dc magnetic susceptibility χ of $Na_{0.6}CoO_2$, $Na_{0.3}CoO_2 \cdot yH_2O$ ($y = 0.9, 1.4$), and $Na_{0.3}CoO_2 \cdot yD_2O$ ($y = 1.4, 1.8$). Note that for the parent compound χ is positive and increases with decreasing temperature. Although the Curie-Weiss–like tail remains below a particular temperature T_x, the oxidation and hydration/deutration process results in qualitative changes in the magnetic susceptibility of $Na_{0.3}CoO_2 \cdot yH_2O$ and $Na_{0.3}CoO_2 \cdot yD_2O$ at high temperatures. Above T_x, χ increases with T, in contrast to that of the parent compound. As shown in the inset of Fig. 1, the smaller T_x, the larger the slope $d\chi/dT$ determined at $T = 290$ K. However, both T_x and $d\chi/dT$(290 K) vary nonmonotonically with y, exhibiting extrema at $y = 1.4$. This demonstrates that the qualitative change in χ depends on the sodium content (cobalt valence) as well as the degree of hydration/deuteration. For fixed y, the substitution of deuterium for hydrogen results in little effect on the high-temperature magnetic susceptibility.

As mentioned previously, superconductivity does not occur until the water content y is close to 1.4. Presented in Fig. 2 is the temperature dependence of the

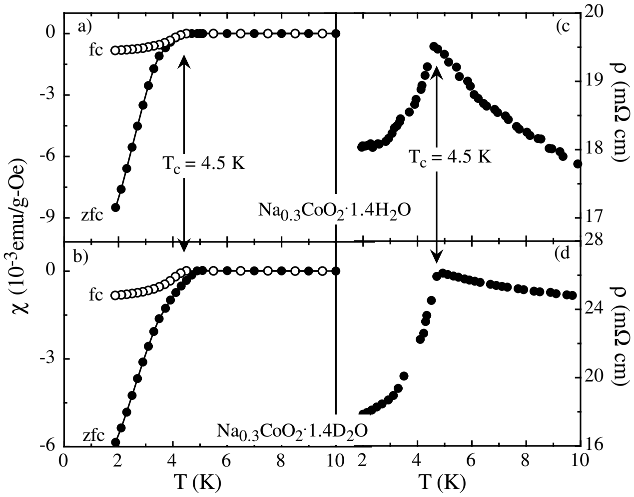

FIG. 2. Temperature dependence of the magnetic susceptibility χ of $Na_{0.3}CoO_2 \cdot 1.4H_2O$ (a) and $Na_{0.3}CoO_2 \cdot 1.4D_2O$ (b) between 1.9 and 10 K at $H = 20$ Oe. The measurements were performed under both zero-field-cooling (ZFC) (filled circles) and field-cooling (FC) (unfilled circles) conditions. Shown in the right panels are the temperature dependences of the electrical resistivity of polycrystalline $Na_{0.3}CoO_2 \cdot 1.4H_2O$ (c) and $Na_{0.3}CoO_2 \cdot 1.4D_2O$ (d).

magnetic susceptibility and resistivity between 1.9 and 10 K for polycrystalline $Na_{0.3}CoO_2 \cdot 1.4\,H_2O$ and $Na_{0.3}CoO_2 \cdot 1.4D_2O$. Under both zero-field-cooling (ZFC) and field-cooling (FC) conditions, χ becomes negative below $T_c = 4.5$ K in both materials. Correspondingly, the electrical resistivity measured on pressed pellets departs from high-temperature behavior and drops rapidly below T_c (see Figs. 2(c) and 2(d)), indicating that the system undergoes a superconducting transition. The substitution of deuterium for hydrogen has no apparent effect on T_c. While $\chi_{\rm ZFC}$ is much larger than that reported previously [4,6], $\chi_{\rm FC}$ is still small for both $Na_{0.3}CoO_2 \cdot 1.4H_2O$ and $Na_{0.3}CoO_2 \cdot 1.4D_2O$. Note that the electrical resistivity of the polycrystalline samples does not vanish down to 1.9 K, similar to the results reported in Ref. [4]. These observations imply that the superconducting volume fraction may be improved.

Specific heat C_p was measured on gently compacted pellets. In inset (b) of Fig. 3, we present C_p versus T between 2 and 60 K. No obvious anomaly is visible. However, the superconducting anomaly can be clearly seen when the data are replotted as C_p/T versus T^2 as shown in the main panel of Fig. 3. Note C_p/T varies more or less linearly with T^2 between ~5.5 and 10 K, suggesting that the electron and phonon contributions dominate C_p in this region. The normal electronic specific heat coefficient may thus be estimated via a linear fitting procedure. We obtain $\gamma \sim 16.4$ mJ/mol K^2 for $Na_{0.3}CoO_2 \cdot 1.4D_2O$ and 16.1 mJ/mol K^2 for $Na_{0.3}CoO_2 \cdot 1.4H_2O$, close to that reported in Ref. [9]. Below ~5 K, C_p/T deviates from linearity in both systems, however. By subtracting the phonon contribution (T^2 term in C_p/T), one may clearly see that the electronic specific heat $C_p^{\rm el}$ exhibits a peak centered around 4.5 K as displayed in inset (b) of Fig. 3. This indicates bulk superconductivity in both $Na_{0.3}CoO_2 \cdot 1.4D_2O$ and $Na_{0.3}CoO_2 \cdot 1.4H_2O$. The detailed analysis of $C_p^{\rm el}/T$ below T_c will be described elsewhere [10].

For a system with bulk superconductivity, one may expect that the electrical resistivity reaches zero below T_c. So far, zero resistivity has not be reported in superconducting sodium-cobalt oxide. Similar to what is shown in Ref. [4], the resistivity of our best polycrystalline $Na_{0.3}CoO_2 \cdot 1.4H_2O$ tends to saturate after 10–50% reduction compared to the normal-state value (see Figs. 2(c) and 2(d)). Is this intrinsic? From the structural point of view, the present system may have very weak coupling between adjacent CoO_2 layers, as they are separated by two layers of H_2O/D_2O and one layer of Na. If the superconductivity were confined within the CoO_2 layers, the zero-resistivity state may never be observed in polycrystals, due to the contribution of nonzero ρ_c.

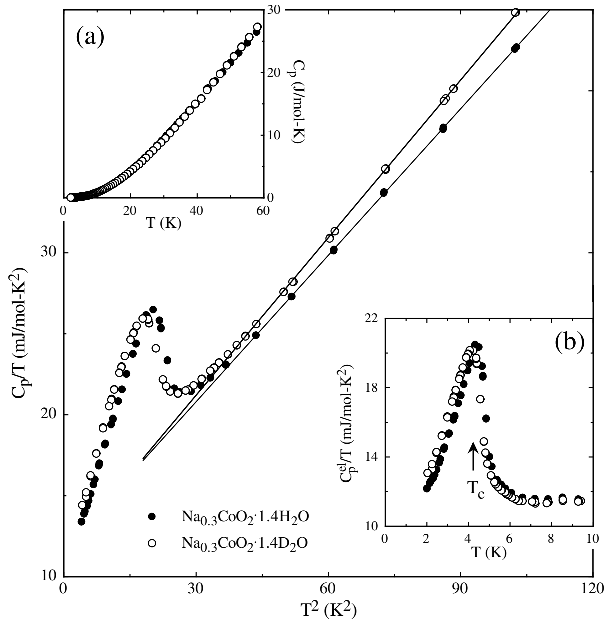

FIG. 3. Temperature dependence of specific heat C_p of $Na_{0.3}CoO_2 \cdot 1.4H_2O$ (filled circles) and $Na_{0.3}CoO_2 \cdot 1.4D_2O$ (unfilled circles) plotted as C_p/T versus T^2 between 2 and 10 K. The solid lines are the fit to experimental data between 5.5 and 10 K using $C_p/T = \gamma + \beta T^2$ (β and γ are constants). The insets show the temperature dependence of (a) C_p between 2 and 60 K and (b) electronic specific heat $C_p^{\rm el}$ plotted as $C_p^{\rm el}/T$ versus T^2 between 2 and 10 K.

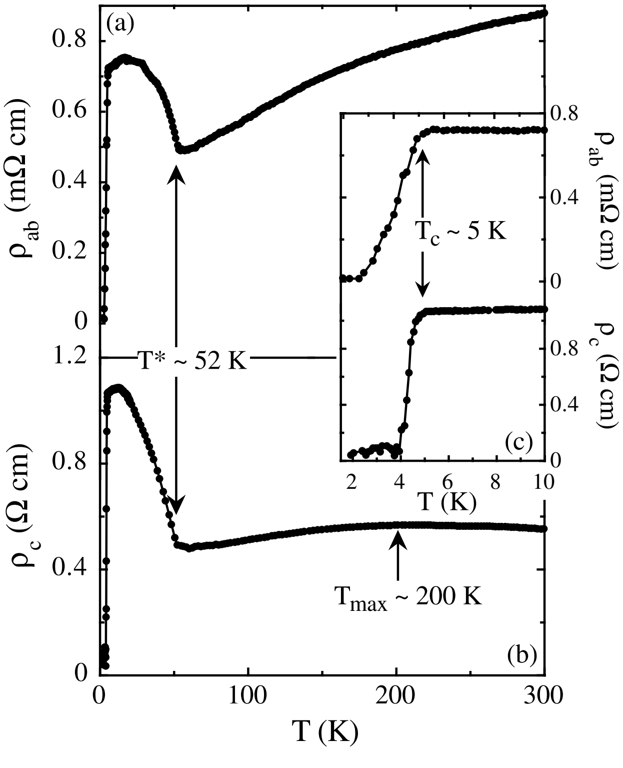

FIG. 4. Temperature dependence of the in-plane and out-of-plane resistivity ρ_{ab} (a) and ρ_c (b) of $Na_{0.3}CoO_2 \cdot yH_2O$ single crystals. The inset (c) is an enlargement of the low-temperature data, showing a superconducting transition in both ρ_{ab} and ρ_c at $T_c = 5$ K.

Bearing this issue in mind, we have investigated the resistivity anisotropy of superconducting $Na_{0.3}CoO_2 \cdot yH_2O$ single crystals. To reduce the loss of H_2O, a silver paint that dries at room temperature was used to adhere four leads onto each crystal. The contact resistance was about 5–20 Ω, after drying at room temperature for 30 min. Shown in Fig. 4 is the temperature dependence of the electrical resistivity of $Na_{0.3}CoO_2 \cdot yH_2O$ in the *ab* plane (a) and along the *c* direction (b). Compared to the parent compound, both ρ_{ab} and ρ_c are somewhat large at room temperature. We believe this is due to the error involved in estimating the geometric factor from small superconducting single crystals with a typical size of $0.7 \times 0.7 \times 0.05$ mm^3. Nevertheless, both ρ_{ab} and ρ_c exhibit very similar behavior as that of the parent compound above $T^* = 52$ K. While ρ_{ab} decreases with T, ρ_c reveals a broad maximum near 200 K as indicated in Fig. 4(b). Strikingly, below T^*, both ρ_{ab} and ρ_c increase with decreasing T before entering the superconducting state. Although the resistivity of polycrystalline $Na_{0.35}CoO_2 \cdot 1.3H_2O$ also increases with decreasing T below T^* (see Fig. 4 in Ref. [4]), the change is much smoother and less pronounced. It should be emphasized that such a sharp upturn at T^* can be observed only in single crystals, where ρ_{ab} and ρ_c exhibit an abrupt decrease at T_c. This strongly suggests that the resistivity upturn at T^* is an intrinsic property of the superconducting phase. At present, it is unclear whether this new feature is associated with a phase transition, since neither magnetic susceptibility nor the specific heat data obtained on polycrystalline samples shows an anomaly in this temperature range.

Owing to the inaccurate geometric factor, the absolute value of ρ_{ab} and ρ_c should be further examined. However, it is unambiguous that both ρ_{ab} and ρ_c drop spontaneously below $T_c \sim 5$ K. This indicates three-dimensional (3D) superconductivity, despite an extremely high anisotropy ($\rho_c/\rho_{ab} \sim 10^3$). Surprisingly, the transition is sharper along the *c* axis than in the *ab* plane, though at low temperatures both ρ_{ab} and ρ_c saturate with a small but nonzero value [see Fig. 4(c)].

Based on the above results, we believe that the coupling mechanism between the CoO_2 layers is the key to understanding superconductivity in this unique system. As shown in Fig. 1, the magnitude of magnetic susceptibility tends to decrease with increasing H_2O/D_2O content at room temperature. Most prominent is that $d\chi/dT$ (290 K) exhibits a maximum at $y = 1.4$, a value that also results in the highest T_c. Correspondingly, the low-temperature tail is almost suppressed as reflected by the smallest T_x. This indicates an intimate relationship between the normal-state magnetism and superconductivity as proposed by Singh as well as Tanaka and Hu [5].

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[1] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, 12 685 (1997).

[2] T. Motohashi, M. Karppinen, and H. Yamauchi, *Oxide Thermoelectrics* (Research Signpost, India, 2002).

[3] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).

[4] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).

[5] D. J. Singh, Phys. Rev. B **68**, 20503 (2003); A. Tanaka and X. Hu, cond-mat/0304409 (unpublished).

[6] M. L. Foo, R. E. Schaak, V. L. Miller, T. Klimczuk, N. S. Rogado, Y. Wang, G. C. Lau, C. Craley, H. W. Zandbergen, N. P. Ong, and R. J. Cava, Solid State Commun. **127**, 33 (2003).

[7] K. Fujita, T. Mochida, and K. Nakamura, Jpn. J. Appl. Phys. **40**, 4644 (2001).

[8] D. F. Shriver, P. Atkins, and C. H. Langford, *Inorganic Chemistry* (W. H. Freeman and Company, New York, 1994), 2nd ed.

[9] G. Cao, C. Feng, Y. Xu, W. Lu, J. Shen, M. Fang, and Z. Xu, J. Phys. Condens. Matter 15, L519 (2003).

[10] R. Jin *et al.* (unpublished).