Observation of Bulk Superconductivity in Na₃CoO₂·yH₂O and Na₃CoO₂·yD₂O Powder and Single Crystals

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Poly- and single-crystalline Na₃CoO₂ has been successfully intercalated with H₂O and D₂O as confirmed by X-ray diffraction and thermogravimetric analysis. Resistivity, magnetic susceptibility, and specific heat measurements show bulk superconductivity with Tc close to 5 K in both cases. The substitution of deuterium for hydrogen has an effect on Tc of less than 0.2 K. Investigation of the resistivity anisotropy of Na₃CoO₂·yH₂O single crystals shows: (a) almost zero resistivity below Tc, and (b) an abrupt upturn at T* ~ 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 Na₃CoO₂ 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 CoO₆ 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-Tc 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 Na₃CoO₂ 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 Na₀.₅CoO₂ are, in fact, reminiscent of another layered superconductor, Sr₂RuO₄ ¹, ², except for the absence of superconductivity at low temperatures. The recent discovery of superconductivity ¹ in water-intercalated Na₀.₃₅CoO₂·1.₃H₂O is very exciting, because it may be the first superconductor analogous to Sr₂RuO₄ as proposed by Tanaka and Hu ².

Although ρ_ab is small, superconductivity has not been observed in Na₃CoO₂. Superconductivity also does not occur in Na₀.₃CoO₂·0.₆H₂O ², indicating that sufficient hydration is crucial for the appearance of superconductivity in Na₀.₃CoO₂·yH₂O. The relationship between the transition temperature Tc and the water content y, and the role that H₂O plays for the occurrence of superconductivity are central issues. In this Letter, we report that (a) the results reported in Ref. ¹ can be reproduced, (b) the superconducting volume may be enhanced or suppressed, depending on the water content, (c) superconductivity is observed in deuterated Na₀.₃CoO₂·1.₄D₂O with Tc ~ 4.5 K, and (d) the superconductivity is observed in both the ab-plane and the c-axis resistivities (ρ_ab and ρ_c) of Na₃CoO₂·yH₂O single crystals.

Superconducting sodium cobaltate was prepared following a procedure similar to that described in Ref. ¹. The parent compound Na₃CoO₂ was obtained via solid-state reaction. Starting materials Na₂CO₃ (Alfa Aesar 99.997%) and Co₃O₄ (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 re-ground, pressed into pellets, and calcined at 830 °C for 16 h in flowing O₂ gas. X-ray diffraction results confirm the correct single phase with hexagonal crystal structure (lattice parameters are listed in Tab. 1). For single crystal growth, both the floating-zone technique and flux method ² were employed. In the latter case, thin plate-like single crystals were obtained with surface areas up to 5×5 mm². 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, ³. It is worth mentioning that, in addition to forming Na₃CoO₂, the conventional slow-heat-up process often results in impurity phases including Co₃O₄ and perhaps CoCO₃.

To obtain superconductivity, it is necessary to first chemically extract additional Na from the structure. Both Na₀.₆CoO₂ powder and small single crystals (1×1×0.1 mm³) were placed in a 6.6 molar Br₂/CH₃CN solution for 2-5 days. Careful filtering and washing in pure CH₃CN followed by a 50/50 mixture of CH₃CN/H₂O (or CH₃CN/D₂O) resulted in a single phase, intermediate state of hydration/deuteration first reported by Foo et al. ⁴. Our TGA measurements on this phase give an approximate Na content x = 0.3 and H₂O/D₂O content of y = 0.9. This value of y is larger than y = 0.6 reported in Ref. ⁴. This phase is stable as long as the powder is kept in a sealed bottle. As

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the optimum state of hydration/deuteration (at room temperature. The exact time required to reach the superconducting transition $T_c$ and overdeuterated Na$_2$CoO$_2$·1.8D$_2$O (dashed line). All measurements were carried out by applying $H = 20$ Oe using a commercial SQUID magnetometer by Quantum Design. The inset shows the $H_2$O/D$_2$O content $y$ dependence of the room-temperature magnetic susceptibility slope $dy/dT(290K)$ (filled triangles) and crossover temperature $T_x$ (unfilled triangles) (see the definition in the text). Note that, both $dy/dT(290K)$ and $T_x$ exhibit extrema at $y = 1.4$, indicating that the susceptibility data correlates with both the Na content (Co valence) and the degree of hydration/deuteration.

listed in Tab. 1, 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 $H_2$O or $D_2$O 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 ($y \sim 1.8-2.0$) which strongly suppresses superconductivity but has little effect on the X-ray pattern. As may be seen in Tab. 1, the lattice parameters for Na$_2$CoO$_2$·1.4H$_2$O are slightly larger than that for Na$_2$CoO$_2$·1.4D$_2$O, consistent with the stronger D - O bond relative to H - O bond.

In Fig. 1, we present the temperature dependence of the DC magnetic susceptibility $\chi$ of Na$_2$CoO$_2$, Na$_2$CoO$_2$·yH$_2$O ($y = 0.9, 1.4$), and Na$_2$CoO$_2$·yD$_2$O ($y = 1.4, 1.8$). Note that for the parent compound $\chi$ is positive and increases with decreasing temperature. Although the Curie-Weiss-like tail remains below a particular temperature $T_x$, the oxidation and hydration/deuteration process results in qualitative changes in the magnetic susceptibility of Na$_2$CoO$_2$·yH$_2$O and Na$_2$CoO$_2$·yD$_2$O at high temperatures. Above $T_x$, $\chi$ increases with $T$, in contrast to that of the parent compound. As shown in the inset of Fig. 1, the smaller $T_x$ of both Na$_2$CoO$_2$·yH$_2$O and Na$_2$CoO$_2$·yD$_2$O (space group no. 194 P6$_3$mnmc).

![FIG. 1: Temperature dependence of the DC magnetic susceptibility for the parent compound Na$_2$CoO$_2$ (filled circles), intermediate phase Na$_2$CoO$_2$·0.9H$_2$O (unfilled circles), superconducting Na$_2$CoO$_2$·1.4H$_2$O (filled diamonds) and Na$_2$CoO$_2$·1.4D$_2$O (unfilled diamonds) above the superconducting transition $T_c$, and overdeuterated Na$_2$CoO$_2$·1.8D$_2$O (dashed line). All measurements were carried out by applying $H = 20$ Oe using a commercial SQUID magnetometer by Quantum Design. The inset shows the $H_2$O/D$_2$O content $y$ dependence of the room-temperature magnetic susceptibility slope $dy/dT(290K)$ (filled triangles) and crossover temperature $T_x$ (unfilled triangles) (see the definition in the text). Note that, both $dy/dT(290K)$ and $T_x$ exhibit extrema at $y = 1.4$, indicating that the susceptibility data correlates with both the Na content (Co valence) and the degree of hydration/deuteration.](image)

| composition          | $a$ (Å)  | $c$ (Å)  |
|-----------------------|----------|----------|
| Na$_2$CoO$_2$         | 2.837(1) | 10.878(2) |
| Na$_2$CoO$_2$·0.9H$_2$O | 2.825(2) | 13.831(7) |
| Na$_2$CoO$_2$·1.4H$_2$O | 2.823(1) | 19.696(1) |
| Na$_2$CoO$_2$·1.4D$_2$O | 2.821(1) | 19.635(2) |
| Na$_2$CoO$_2$·1.8D$_2$O | 2.823(1) | 19.660(4) |

TABLE I: Room temperature lattice parameters and standard deviations for Na$_2$CoO$_2$·yH$_2$O and Na$_2$CoO$_2$·yD$_2$O.
FIG. 2: Temperature dependence of the magnetic susceptibility χ of Na0.3CoO2·1.4H2O (a) and Na0.3CoO2·1.4D2O (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 right panels are the temperature dependences of the electrical resistivity of polycrystalline Na0.1CoO2·1.4H2O (c) and Na0.3CoO2·1.4D2O (d).

ported in Ref. [9]. In the lower temperature region, Cp/T deviates from linearity in both systems, however. By subtracting the phonon contribution (T2 term in Cp/T), one may clearly see that the electronic specific heat Cpe exhibits a hump centered around 6.0 K as displayed in the inset (b) of Fig. 3. In combination with the magnetic susceptibility and resistivity data, we believe that the hump in Cpe/T results from the superconducting transition. The lack of a sharp specific heat peak may be due to the distribution of Tc from H2O/D2O deintercalation during pellet pressing process.

We recall that there is no specific heat anomaly at Tc in the optimally doped Nd1.85Ce0.15CuO4 superconductor, while its electrical resistivity reaches zero just below Tc. [10] So far, zero-resistivity has not been reported in superconducting sodium-cobalt oxide. Similar to what is shown in Ref. [4], the resistivity of our best polycrystalline Na0.3CoO2·1.4H2O tends to saturate after 10 - 50% reduction compared to the normal-state value (see Fig. 2c-2d). Is this intrinsic? From the structural point of view, the present system may have very weak coupling between adjacent CoO2 layers, as they are separated by two layers of H2O/D2O and one layer of Na. If the superconductivity were confined within the CoO2 layers, the zero-resistivity state may never be observed in polycrystals, due to the contribution of non-zero ρc.

Bearing this issue in mind, we have investigated the resistivity anisotropy of superconducting Na0.3CoO2·1.3H2O single crystals. To reduce the loss of H2O, 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 minutes.

FIG. 3: Temperature dependence of specific heat Cp of Na0.3CoO2·1.4H2O (filled circles) and Na0.3CoO2·1.4D2O (unfilled circles) plotted as Cpe/T versus T2 between 1.9 and 12 K. The solid lines are the fit to experimental data between 7.5 and 12 K using Cpe/T = γ + βT2 (β and γ are constants). The inset shows the temperature dependence of (a) Cpe between 1.9 and 60 K and (b) electronic specific heat Cpe plotted as Cpe/T versus T2 between 1.9 and 12 K.

Shown in Fig. 4 is the temperature dependence of the electrical resistivity of Na0.3CoO2·1.3H2O in the ab plane (a) and along the c direction (b). Compared to the parent compound, both ρab and ρc 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 1×1×0.1 mm3. Nevertheless, both ρab and ρc exhibit very similar behavior as that of the parent compound above T* = 52 K. While ρab decreases with T, ρc reveals a broad maximum near 200 K as indicated in Fig. 4b. Strikingly, below T*, both ρab and ρc increase with decreasing T before entering the superconducting state. Although the resistivity of polycrystalline Na0.35CoO2·1.3H2O 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 only be observed in single crystals, where ρab and ρc exhibit an abrupt decrease at Tc. 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 show an anomaly in this temperature range.

Owing to the inaccurate geometric factor, the absolute value of ρab and ρc should be further examined. However, it is unambiguous that both ρab and
FIG. 4: Temperature dependence of the in-plane and out-of-plane resistivity $\rho_{ab}$ (a) and $\rho_c$ (b) of Na$_{0.3}$CoO$_2\cdot$$\gamma$H$_2$O single crystals. The inset (c) is an enlargement of the low-temperature data, showing a superconducting transition in both $\rho_{ab}$ and $\rho_c$ at $T_c = 5$ K.

$\rho_c$ 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 $\rho_{ab}$ and $\rho_c$ saturate with a small but non-zero value (see Fig. 4c).

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$_2$O/D$_2$O content at room temperature. Most prominent is that $d\chi/dT(290K)$ exhibits a maximum at $\gamma = 1.4$, 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 Tanaka and Hu [5].

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