Oxidation State of Cobalt in the $Na_xCoO_{2-\delta}\cdot yH_2O$ Superconductor

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Here we present results of accurate wet-chemical redox analyses revealing that the oxidation number of cobalt in the newly discovered CoO_2-layer superconductor, $Na_xCoO_2\cdot yH_2O$ ($x \approx 0.36$, $y \approx 1.3$) is ∼3.46. This value is significantly lower than the one (∼3.64) expected on the basis of the value determined for the Na to Co stoichiometry ratio, x. The "lower-than-expected" value for the Co oxidation state may be alternatively explained by the presence of oxygen vacancies or excess protons. Moreover, the result implies that rather than an electron-doped Co^{IV} lattice the phase should be considered as a hole-doped Co^{III} lattice.

Introduction

For the last one and a half decades unprecedented research efforts have been focused on layered strongly correlated electron oxide materials. These efforts were initially inspired by the discovery of high-T_c superconductivity[1] and more recently by discoveries of other spectacular phenomena such as large magnetoresistance[2] and high-efficiency thermoelectricity.[3] Very recently, superconductivity with the superconductivity transition temperature, T_c, at 4−5 K was discovered in CoO_2 layers[4] stacked together with layers of Na^+ ions and "iced"[5] water molecules. The superconducting phase, $Na_xCoO_2\cdot yH_2O$ ($x \approx 0.35$, $y \approx 1.3$), is obtained from its sodium-rich parent, Na_xCoO_2 ($x \approx 0.7$)[6] through oxidative deintercalation[7] of sodium and subsequent intercalation of water between each pair of adjacent CoO_2 layers. Neither the relatively low value of T_c nor the insufficient chemical stability of the new superconductor predicts good application at market. Nevertheless, the discovery has already gained considerable attention.[8] Here, the remarkable point is that the discovery made it possible for us to mirror the yet-puzzling high-T_c copper-oxide superconductor against another layered 3*d* transition metal oxide superconductor.

The similarities of the CoO_2- and the CuO_2-layer superconductors are evident: both are nonstoichiometric and possess crystal structures in which the nonsuperconducting or insulating layers that alternate with the CoO_2/CuO_2 layers play a dual role of a "spacing provider" and a "redox controller". On the other hand, an obvious difference is seen in the way the Co−O/Cu−O polyhedra are linked to each other: in $Na_xCoO_2\cdot yH_2O$ (despite the values of x and y) the "CoO_2 layer" is rather a three-layer block of triangular O, Co, and O layers (alternatively the same may be imagined as a thick layer of edge-sharing CoO_6 octahedra), whereas copper in the superconducting "CuO_2 layer" possesses square-planar coordination with a nearly 180° O−Cu−O bond angle. For Cu-based high-T_c superconductors the crucial importance of the oxidation state of Cu in the CuO_2 layers was established in an early stage of research, in both switching superconductivity on and off and controlling the value of T_c in the superconductivity regime.[9] For $Na_xCoO_2\cdot yH_2O$, no direct experimental data have been reported that would enable us to establish the oxidation state of Co in the CoO_2 layer. Given the Na content at $x = 0.30-0.35$, the phase has simply been considered as an electron-doped system of low-spin Co^{IV} with an electron density of 0.30−0.35 per Co atom, i.e. an oxidation number of 3.65−3.70 for Co.[4,10] The main conclusion of the present work—reached by means of accurate wet-chemical redox analysis—is that cobalt in the superconducting CoO_2 layer possesses an oxidation number markedly lower than what has been expected, that is, a value even somewhat lower than 3.5. An apparent implication of this is that rather than an electron-doped Co^{IV} lattice the phase should be considered as a hole-doped Co^{III} lattice. For comparison, we also report results of oxidation state analyses for a series of nonsuperconducting $Na_xCoO_2\cdot yH_2O$ samples with varying x and y.

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Table 1. Chemical Characteristics of the Present $Na_xCoO_{2-\delta}\cdot yH_2O$ Samples, A−E, Together with Those of a $Na_{0.75}CoO_{2-\delta}$ Reference Sample[a]

sample	x	y	c [Å]	V(Co)	δ
$Na_{0.75}CoO_{2-\delta}$	0.77(2)	0	10.92(1)	3.26(1) [3.26(1)]	−0.02 [−0.02]
Sample A	0.72(2)	0	10.94(1)	3.26(1) [3.25(1)]	0.01 [0.01]
Sample B	0.36(2)	0	11.22(1)	3.48(1)	0.08
Sample C	0.36(2)	1.3(1)	19.61(1)	3.48(1) [3.44(1)]	0.08 [0.10]
Sample D	0.36[b]	0.5(1)	13.83(1)	3.48(1)	0.08
Sample E	0.36[b]	0	11.17(1)	3.37(1)	0.13

[a] Na content, x, from ICP analysis; water content, y, from TG analysis; c-axis lattice parameter from X-ray powder diffraction data; and the oxidation number of cobalt, V(Co), and the oxygen nonstoichiometry, δ, from cerimetric [iodometric] titration analysis. Note that only Sample C is superconducting ($T_c = 4.4$ K). [b] Used for the calculation of the values of V(Co) and δ from the titration data.

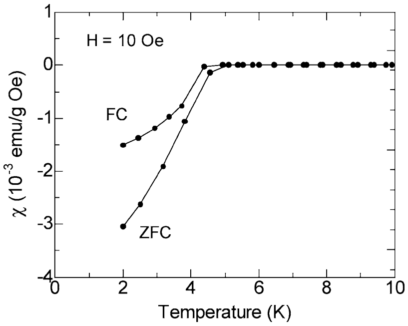

Figure 1. Magnetic susceptibility (χ) versus temperature as measured with a SQUID magnetometer in both field-cooled (FC) and zero-field-cooled (ZFC) modes for the Na-deintercalated, fully hydrated $Na_xCoO_{2-\delta}\cdot yH_2O$ sample (Sample C) showing the superconductivity transition at 4.4 K.

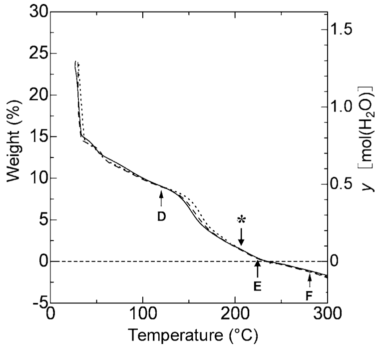

Figure 2. Thermogravimetric curves for dehydration of the $Na_xCoO_{2-\delta}\cdot yH_2O$ superconductor (Sample C). The curves are for three parallel experiments carried out (each time) in O_2 for a ~20-mg specimen with a heating rate of 0.25 °C/min. Indicated are the temperatures used to synthesize Samples D, E, and F from Sample C, and also the reflection point (∗) defining the onset temperature for the very last water-depletion step from the $Na_{0.36}CoO_{1.91}\cdot yH_2O$ structure (see text).

Experimental Section

Sample Synthesis and Basic Characterization. A single-phase sample of the γ-Na_xCoO_2 phase[6] with a nominal cation stoichiometry of $x = 0.70$ (thereafter referred to as Sample A) was first synthesized as a precursor utilizing a "rapid-heat-up" technique[11] in which a powder mixture of Na_2CO_3 and Co_3O_4 in an Al_2O_3 crucible is directly placed in a furnace preheated at 800 °C and fired for 12 h in air. Deintercalation of Na was performed following the precept given in a previous work,[12] i.e., stirring a 500-mg portion of Sample A in a 20 mL solution of 6 M Br_2 into CH_3CN at room temperature for 1 day. The resultant product was washed with CH_3CN several times and then dried in a fume box to obtain a Na-poor, nonhydrated Sample B. Finally, the fully hydrated, superconducting $Na_xCoO_{2-\delta}\cdot yH_2O$ phase (Sample C) was obtained from Sample B by keeping it in saturated humidity for a few days. To check the reproducibility of the results, Sample C was synthesized in triplicate; the three parallel samples turned out to be identical with respect to every characteristic measured.

The precise Na to Co cation ratio was determined for the three samples, A, B, and C, by inductively coupled plasma atomic-emission spectroscopy (ICP-AES; Hitachi P-5200) at x = 0.72(2), 0.36(2), and 0.36(2), respectively (Table 1). From the X-ray diffraction patterns for the samples, the c-axis lattice parameter was respectively determined at 10.94(1), 11.22(1), and 19.61(1) Å. Bulk superconductivity with $T_c = 4.4$ K was confirmed for Sample C with a large volume fraction as judged from a zero-field-cooled magnetization curve measured upon heating (starting from 2 K) under an applied magnetic field of 10 Oe in a SQUID magnetometer (Quantum Design MPMS-XL), see Figure 1. The values presently revealed for T_c (4.4 K), Na content ($x = 0.36$), and c-axis parameter (19.61 Å) of Sample C well agree with those assigned in the original report by Takada et al.[4] for the novel $Na_xCoO_2\cdot yH_2O$ superconductor, i.e. 4−5 K, 0.35, and 19.62 Å, respectively. The c-axis parameter of 10.94 Å for Sample A (with $x = 0.72$) may be compared to that of 10.88 Å reported for $Na_{0.71}CoO_2$.[13]

To determine the precise water content of the superconducting phase, we subjected a portion of Sample C to thermogravimetric (TG) annealing in which the water accommodated in it is gradually but completely removed. The TG annealing was carried out in a high-sensitivity thermobalance (Perkin-Elmer Pyris 1) by heating a specimen of ca. 20 mg in O_2 up to 300 °C with a rate of 0.25 °C/min. Owing to the slow heating rate the resultant TG curve should represent a nearly equilibrium state at each temperature. To warrant the result, the experiment was repeated several times. In Figure 2, three representative TG curves are shown to demonstrate the fact that the dehydration process was highly reproducible. Another confirmation of the data is that the present TG curves are almost identical to that reported previously by Foo et al.[12] From Figure 2, the dehydration occurs in several distinct steps by 230 °C resulting in an overall loss of 1.3(1) H_2O molecules per formula unit. In other words, we determined the magnitude of y at 1.3(1) for Sample C.

We further utilized the TG data given in Figure 2 to consider the dehydration and decomposition characteristics of the $Na_xCoO_{2-\delta}\cdot yH_2O$ system in more detail. About 130 °C a clear change is seen in the slope of the TG curve, indicating that a relatively stable intermediate phase is formed at temperatures somewhat below 130 °C. To obtain a specimen of this phase (Sample D) we annealed a portion of Sample C in air at 120 °C for 1 h: a single-phase sample was obtained with the c-axis lattice parameter at 13.83(1) Å (and the value of y at 0.5(1) on the basis of the TG data). The c-axis parameter for our partially dehydrated phase is close to the 13.84 Å value reported by Takada et al.[14] for their "monolayer hydrate" sodium cobalt oxide. Upon further heating beyond 130 °C, the

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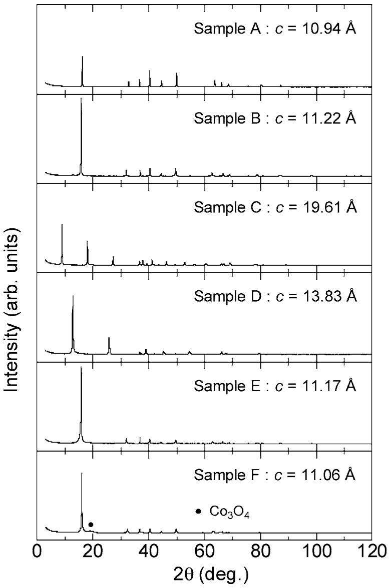

Figure 3. X-ray diffraction patterns for $Na_xCoO_{2-\delta}\cdot yH_2O$ samples with different Na and H_2O contents: Sample A ($Na_{0.72}CoO_{1.99}$ precursor), Sample B ($Na_{0.36}CoO_{1.92}$), Sample C ($Na_{0.36}CoO_{1.91}\cdot 1.3H_2O$ superconductor), Sample D ($Na_{0.36}CoO_{1.92}\cdot 0.5H_2O$), Sample E ($Na_{0.36}CoO_{1.87}$), and Sample F (a mixture of $Na_xCoO_{2-\delta}$ and Co_3O_4).

water which remained in the original Sample C is lost (in two or three fairly distinguishable steps) by 230 °C. Guided by this observation, 220 °C was selected for the annealing temperature to synthesize (in air for 1 h) a specimen of the completely dehydrated $Na_{0.36(2)}CoO_{2-\delta}$ phase (Sample E) starting again from another portion of Sample C. For Sample E the *c*-axis parameter was determined at 11.17(1) Å. The further weight loss seen in TG curves above 230 °C (Figure 2) is apparently due to partial reductive decomposition of the completely dehydrated phase of $Na_{0.36(2)}CoO_{2-\delta}$. Accordingly, peaks due to Co_3O_4 (besides those for the main phase of $Na_xCoO_{2-\delta}$) were clearly seen in the X-ray diffraction pattern recorded for a sample obtained by annealing a portion of Sample C in air at 280 °C for 1 h (Sample F). For the $Na_xCoO_{2-\delta}$ phase contained in Sample F the *c*-axis parameter was determined at 11.06(1) Å. Figure 3 shows X-ray diffraction patterns for all the six samples, A, B, C, D, E, and F.

Chemical Analysis for the Oxidation State of Cobalt. The oxidation state of cobalt, *V*(Co), was determined for the five single-phase samples, A, B, C, D, and E, utilizing two independent wet-chemical redox analysis methods, i.e. cerimetric and iodometric titration, which are known to accurately detect the amount of Co^{III} and/or Co^{IV} in layered cobalt oxides.[15] Additionally, a "$Na_{0.75}CoO_{2-\delta}$" sample of the γ-Na_xCoO_2 phase was synthesized (using the same synthesis conditions as for Sample A) for a reference. Note that ICP-AES analysis revealed a cation stoichiometry of $Na_{0.77(2)}CoO_{2-\delta}$ for this sample (Table 1). The titration experiments were carried out by dissolving ~20 mg of the sample in oxygen-freed 3 M HCl solution containing an excess of the reductant, Fe^{2+} (cerimetric titration) or I^- (iodometric titration). After the complete reduction of high-valent Co species to divalent state, the amount of left-over Fe^{2+}/liberated I_2 was determined volumetrically using $Ce(SO_4)_2/Na_2S_2O_3$ solution as a titrant. The experimental details were the same as those given elsewhere.[15] For both the methods parallel experiments revealed the value of *V*(Co) with a reproducibility better than ±0.01. Moreover, the two independent methods gave highly agreeable results. The values for *V*(Co) as summarized in Table 1 are all average values of more than four parallel experiments. Knowing the precise value of *V*(Co) from the titration analysis as well as the precise Na content, *x*, from ICP-AES analysis, and assuming charge neutrality, the degree of oxygen nonstoichiometry, δ, was calculated for each sample (Table 1).

The two sodium-rich samples, $Na_{0.77(2)}CoO_{2-\delta}$ (reference) and $Na_{0.72(2)}CoO_{2-\delta}$ (precursor; Sample A), were found nearly stoichiometric in terms of oxygen, i.e. δ was determined at $-0.02(1)$ for the former and at 0.01(1) for the latter. Upon oxidative deintercalation of Na^+ ions, Co species get oxidized as expected, i.e., *V*(Co) increases from 3.26(1) (for Sample A) to 3.48(1) (for Sample B). On the other hand, intercalation of neutral H_2O molecules into the Na-poor $Na_{0.36(2)}CoO_{2-\delta}$ phase maintains the oxidation state of cobalt essentially constant: cerimetric titrations reveal *V*(Co) at 3.48(1) and iodometric titrations reveal *V*(Co) at 3.44(1) for the superconducting $Na_{0.36(2)}CoO_{2-\delta}\cdot 1.3(1)H_2O$ phase (Sample C). Partial dehydration of Sample C to obtain the $Na_{0.36(2)}CoO_{2-\delta}\cdot 0.5(1)H_2O$ phase (Sample D) does not change the value of *V*(Co) either. For the completely dehydrated $Na_{0.36(2)}CoO_{2-\delta}$ (Sample E), the *V*(Co) value was slightly lower, i.e. 3.37(1). This may originate from small amounts (nondetectable by X-ray diffraction) of Co_3O_4 impurity with Co at an oxidation state of 2.67. (Sample E was obtained under conditions that are close to those causing decomposition of the Na-deficient $Na_xCoO_{2-\delta}$ phase, cf. Sample F.)

Discussion

The present study showed that the value of *V*(Co) is essentially the same for the three Na-poor samples, the superconducting $Na_{0.36(2)}CoO_{1.91(1)}\cdot 1.3(1)H_2O$ sample (Sample C), and the nonsuperconducting samples of $Na_{0.36(2)}CoO_{1.92(1)}$ (Sample B) and $Na_{0.36(2)}CoO_{1.92(1)}\cdot 0.5(1)H_2O$ (Sample D). This confirms previous suggestions that the proper oxidation state of cobalt alone does not facilitate superconductivity, but that proper spacing between the CoO_2 layers is simultaneously required.[4,12,14] The most profound result, however, is that the value of *V*(Co) for Sample C, i.e. ~3.46, is markedly lower than the value of ~3.64 expected on the basis of the Na content ($x = 0.36$) only. The fact that *V*(Co) for this sample is even lower than 3.5 provides us with the basis to consider the superconducting $Na_{0.36(2)}CoO_{1.91(1)}\cdot 1.3(1)H_2O$ phase as a hole-doped Co^{III} lattice. Note that in terms of the oxidation state of Co the CoO_2 layer in Sample C is not very far from that in the parent *p*-type thermoelectric compounds, Na_xCoO_2 ($0.57 \le x \le 0.75$)[3,11,16] having holes as charge carriers and *V*(Co) in the range of 3.25 to 3.43 (assuming oxygen stoichiometry). To confirm the type of charge carriers in the $Na_xCoO_{2-\delta}\cdot yH_2O$ superconductor Seebeck measurements are highly demanded.

The "lower-than-expected" *V*(Co) value for the superconducting $Na_xCoO_{2-\delta}\cdot yH_2O$ phase (Sample C) is compatible with the presence of oxygen vacancies with the concentration of $\delta \approx 0.09(1)$. For the $Na_xCoO_{2-\delta}$ system presence of oxygen vacancies is not a totally new fact, but already mentioned in the 1980s was that samples with reduced Na contents may be nonstoichiometric.[17,18] For a related system, $Li_xCoO_{2-\delta}$, quantitative data based on iodometric titration analysis were recently reported, showing that upon ambient-temperature extraction of Li using NO_2PF_6 in acetonitrile medium as an oxidant,

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the phase started to deplete oxygen when the Li deficiency exceeded a level of $(1 - x) \approx 0.35$.[19,20] The maximum of V(Co) for $Li_xCoO_{2-\delta}$, i.e. ~3.45, appeared for $0.3 < x < 0.5$ with δ at 0.10−0.15. For the fully delithiated ($x = 0$) metastable $CoO_{2-\delta}$ phase of the CdI_2 structure, δ and V(Co) were determined at ~0.33 and ~3.34, respectively.[19] Qualitatively, the presence of oxygen vacancies in the $CoO_{2-\delta}$ phase was also concluded from in-situ synchrotron X-ray diffraction data.[21] Recognizing the situation in $Li_xCoO_{2-\delta}$, the presently obtained results for the $Na_xCoO_{2-\delta}\cdot yH_2O$ superconductor appear highly plausible.

Assuming an analogy to the CuO_2-layer superconductors, it may sound somewhat amazing that the CoO_2 layer in $Na_xCoO_{2-\delta}\cdot yH_2O$ would be oxygen deficient and at the same time superconducting. Recently Rivadulla et al.[22] discussed the same subject hypothetically and proposed a model which assumes that—if existing—the CoO_2-layer oxygen vacancies would, during the water intercalation, be filled with the O^{2-} heads of the intercalated water molecules. As a consequence, extra protons would be created in the structure. It may thus not be "O^{2-} vacancies" but rather "excess H^+" to account for the "lower-than-expected" value of V(Co) for the superconducting phase, i.e. "$Na_xCoO_2\cdot yH_2O_{1-\delta/y}$" or "$Na_xCoO_2\cdot 2\delta H^+\cdot(y - \delta)H_2O$". Keeping this in mind we look back at the TG curves shown in Figure 2. Among the H_2O molecules, those that have participated in filling the CoO_2-layer oxygen vacancies should be most strongly bound. Therefore they would be the last water molecules to be depleted from the structure upon heating. It is thus tempting to assign the very last step of weight loss seen in the TG curves at 200−230 °C to these water molecules. This step corresponds to ca. 0.1 H_2O molecules per formula unit, which well agrees with the estimated δ value of 0.09(1) for Sample C. However, we emphasize that the present study on the novel $Na_xCoO_{2-\delta}\cdot yH_2O$ superconductor, which clearly concludes that the oxidation state of Co is lower than expected on the basis of stoichiometric oxygen content and the Na content being at $x \approx 0.36$, does not allow us to judge whether the obtained result is due to oxygen vacancies or excess protons. Hence, further careful studies by proper analytical tools are definitely required and warranted to clarify this point.

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