Tuning Co Valence State in Cobalt Oxyhydrate Superconductor by Postreduction

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We report a successful tuning of Co valence state in cobalt oxyhydrate superconductor via a facile postreduction using NaOH as reducing agent. The change in Co valence was precisely determined by measuring the volume of the released oxygen. The possible hydronium incorporation was greatly suppressed in concentrated NaOH solution, making the absolute Co valence determinable. As a result, an updated superconducting phase diagram was obtained, which shows that the superconducting transition temperature increases monotonically with increasing Co valence in a narrow range from +3.58 to +3.65.
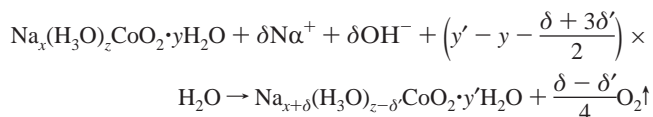
Introduction

One of the major challenges in the newly discovered Na_x-$CoO_2 \cdot yH_2O$ superconductor[1] is to establish experimentally the superconducting phase diagram (SPD), i.e., the dependence of the superconducting critical temperature T_c on the electron doping (or the Co valence state, V_{Co}). Schaak et al.[2] initially reported a narrow dome-shaped SPD with the optimal sodium content for the occurrence of superconductivity at $x = 0.3$, corresponding to the formal Co valence of +3.7. However, the SPD based on sodium content alone is not well reproducible.[3] Using redox titration, Milne et al.[4] proposed a revised SPD where the maximum T_c was achieved at $V_{Co} \sim +3.3$, which means that the superconductor is hole-doped rather than electron-doped. Very recently, Barnes et al.[5] suggested an asymmetric dome-like SPD where the optimal V_{Co} was about +3.5. Besides, Takada and co-workers[6] showed that T_c was also significantly affected by the isovalent exchange between Na^+ and H_3O^+, which further complicates the situation. In a word, the SPDs proposed by different groups are far from consistent.

The above controversial results basically come from the uncertainty in determining V_{Co}. First of all, the initial assumption that V_{Co} is determined by sodium content alone is not strictly correct because subsequent experimental results[7,8] indicated inevitable incorporation of hydronium ions

during the hydration process. The possible existence of oxygen vacancies in CoO_2 layers also results in the "lower-than-expected" value of V_{Co}.[9] Second, wet-chemical redox analysis[3,9] is an alternative way to determine the Co oxidation state; however, complex side reactions and uncertainty of water content may introduce a large error for V_{Co}.[10] Third, the incorporation of hydronium ions probably leads to phase separation (into Na-rich domains and Na-poor domains), which brings further uncertainty for establishing a reliable SPD.

To minimize the measurement errors, we developed a new strategy to tune V_{Co} utilizing soft-chemical reduction *after* the superconductor is synthesized. Based upon previous experimental results,[7,8] the postreduction in aqueous NaOH solution at room temperature can be expressed as follows:

$$Na_x(H_3O)_zCoO_2 \cdot yH_2O + \delta Na^+ + \delta OH^- + \left(y' - y - \frac{\delta + 3\delta'}{2}\right) \times$$
$$H_2O \rightarrow Na_{x+\delta}(H_3O)_{z-\delta'}CoO_2 \cdot y'H_2O + \frac{\delta - \delta'}{4}O_2\uparrow$$

Note that oxygen vacancy is ignored due to the following reasons: (1) both powder neutron diffraction[11] and recent redox titration analysis[12] indicate that the oxygen content of unhydrous $Na_{0.38}CoO_2$ is stoichiometric to a precision of 1 and 2%; (2) even if there are some oxygen vacancies in $Na_{0.38}CoO_2$, they will be filled up by the oxygen from the intercalated H_2O.[10] From the above chemical equation, the change in V_{Co} can be determined precisely by measuring the volume of the released oxygen, regardless of the extent of

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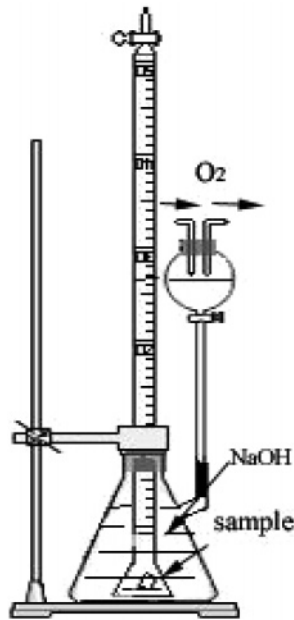(12) Choi, J.; Manthiram, A. *Phys. Rev. B* **2006,** *74,* 205114.

Co Valence State in Cobalt Oxyhydrate Superconductor

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Table 1. Characterizations of the As-Prepared $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ Superconductor as Well as Those Post-treated in NaOH Solutions

C_{NaOH}	x	y	z	ΔV_{Co}	a (Å)	c (Å)	T_c (K)
0	0.325	1.44	0.02	0	2.8239	19.642	4.5
0.1	0.33	1.19	0.04	−0.018(2)	2.8255	19.732	3.8
0.33	0.38	1.00	0.00	−0.028(3)	2.8260	19.558	3.2
1	0.387	0.93	0.00	−0.037(3)	2.8267	19.540	3.0
3.3	0.40	0.89	0.00	−0.050(3)	2.8273	19.538	2.5
10	0.42	0.90	0.00	−0.072(4)	2.8281	19.533	2.4

Once the sample contacted the NaOH solution, small bubbles formed on the sample's surface, and they were released to the top of the buret. The postreduction was carried out for enough time (24−48 h) to ensure a complete reaction. The final reading of the liquid level was recorded as V_2 (mL). After the postreduction, the powder sample was filtered and washed with deionized water several times until the pH value of the filtered solution was below 9. The resultant powder was then preserved below 263 K in a refrigerator. According to the reaction equation, the change in Co oxidation state could be calculated directly from the volume of the released oxygen by the following equation,

$$\Delta V_{Co} = 4 \times \frac{M}{m} \times \frac{P \times (V_1 - V_2)}{RT}$$

where m is the mass of the as-prepared superconductor, M the molecular weight of the initial $Na_x(H_3O)_zCoO_2 \cdot yH_2O$, P the oxygen pressure (equal to the ambient pressure because the two liquid surfaces were kept at the same level while reading V_1 and V_2), T the ambient temperature, and R the gas constant. M could be calculated after x, y, and z were determined by the inductively coupled plasma atomic emission spectroscope (ICP-AES) technique and the thermogravimetric (TG) analysis.[13] The dominant error of ΔV_{Co} comes from the volume measurement which was at most 0.04 mL. Considering that the M value was 125 ± 4 (this large uncertainty mainly comes from the variation of hydronium incorporation and the absorbed free water), the precision of ΔV_{Co} was still better than 0.004.

Sample's Characterization. Each sample was investigated by powder X-ray diffraction using a D/Max-rA Diffractometer with the Cu Kα radiations. Lattice parameters were refined by a least-squares fit with the consideration of the zero shifts. The Na:Co molar ratio of each sample was analyzed by the ICP-AES technique. The measurement precision was better than 2%. The thermogravimetric analysis was carried out on a WCT-2 differential thermal balance, operating at a heating rate of 10 K/min from 298 to 1373 K. The temperature dependence of ac magnetization (M_{ac}) was measured on a Quantum Design PPMS facility. The applied ac magnetic field was $H_{ac}=10$ Oe; thus, the ac susceptibility could be calculated by $\chi_{ac} = M_{ac}/H_{ac}$.

Results and Discussion

In our postreduction experiments the concentration of NaOH was respectively set to be 0.1, 0.33, 1, 3.3, and 10 M, as listed in Table 1. After the reduction, each sample was examined by XRD and compositional measurements. Figure 2 shows the XRD pattern for the as-prepared superconductor as well as the post-treated specimens. As can be seen, the reduced samples show an almost identical XRD pattern to that of the as-prepared superconductor, indicating that the postreduction maintains the crystal structure with

Figure 1. Experimental apparatus for measuring the amount of the released oxygen in the postreduction for the as-prepared cobalt oxyhydrate superconductor.

hydronium incorporations. It is emphasized that, in the presence of concentrated NaOH, the incorporated hydronium is mostly removed. Therefore, V_{Co} of the heavily reduced specimen can be determined merely by the sodium content, and the absolute V_{Co} values of other successive samples can thus be given. By measurement of the superconducting transition temperatures, as a result, an updated SPD for the cobalt oxyhydrate superconductor has been established.

Experimental Section

Preparation of $Na_xCoO_2 \cdot yH_2O$. First, unhydrous compound Na_xCoO_2 was prepared by a solid-state reaction method. High-purity Na_2CO_3 (99.99%) and Co_3O_4 (99.99%) powders with the Na:Co ratio of 0.74:1 were mixed thoroughly and then pressed into pellets. The pellets were rapidly heated to 1073 K under flowing oxygen, holding for 12 h. This process was repeated twice with intermediate grindings. Consequently, pure γ-Na_xCoO_2 was obtained, as checked by powder X-ray diffractions (XRD). Second, partial sodium was deintercalated from the γ-Na_xCoO_2 phase using Br_2/CH_3CN as oxidizing agent. To ensure a deep oxidation, the amount of bromine used was 30 times excess. The topotactic reaction was carried out in a sealed container at 313 K for 5 days. The resultant black powder was filtered, washed with acetone several times, and then dried in vacuum. Finally, the powder was placed in a chamber with the relative humidity of 100% at 300 K for 2 weeks for the thorough hydration. The resultant (hereafter called as-prepared superconductor) was preserved below 263 K in a refrigerator for the succeeding experiments.

Postreduction in Aqueous NaOH solutions. Postreduction was carried out using the apparatus shown in Figure 1. Before the experiment, NaOH solution was saturated with oxygen by flowing oxygen gas for 24 h. The buret and the flask were washed with oxygen gas before the oxygen-saturated NaOH solution was infused into the flask and the buret. The as-prepared superconductor powder (about 0.5 g) was carefully wrapped with plastic film and then placed on the top of the modified buret. After the sample had been immersed, the valve of the buret was shut down immediately. The reading of the liquid level of the buret was recorded as V_1 (mL).

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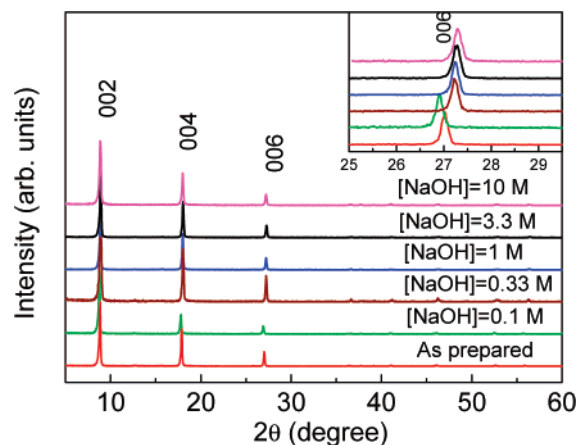
Figure 2. Powder X-ray diffraction for the as-prepared cobalt oxyhydrate superconductor as well as those post-treated in aqueous NaOH solutions. The inset shows an enlarged view of the (006) reflections.

bilayers of water.[1] At the same time, the sodium content in the postreduced samples also increases with the concentration of NaOH (see Table 1), suggesting that partial Na^+ ions intercalate back into the layered structure. This result is consistent with the chemical equation proposed above. One can see in Table 1 that the water content surprisingly decreases with increasing Na content. A possible explanation is that, in the case of high Na content, one water molecule may serve as the ligand for two Na^+ ions. Detailed structural determination is called for with this issue.

As shown in Table 1, the change of V_{Co}, $|\Delta V_{Co}|$, increases with increasing the concentration of NaOH, indicating a successful tuning of Co valence state. It is noted that ΔV_{Co} is not exactly equal to the value inferred from the sodium content alone. This is due to the variations of hydronium incorporation. In fact, ΔV_{Co} is determined by the changes of both sodium content and hydronium content, i.e., $\Delta V_{Co} = \delta' - \delta$. The hydronium content was measured by TG analysis, which shows that the sample treated in relatively concentrated NaOH ($c_{NaOH} \geq 1$ M) is almost free of hydronium (see Supporting Information). This is not surprising since Na^+ and OH^- *cooperatively* suppress the hydronium incorporation. Therefore, the hydronium content is negligible in the presence of concentrated, e.g., 10 M, NaOH.

As the Na content of the sample treated in 10 M NaOH in Table 1 is 0.42, it is easy to see that the absolute value of V_{Co} is +3.58. Accordingly, V_{Co} values of the other samples were determined in the range from +3.6 to +3.65 using the ΔV_{Co} data. The result is in reasonable agreement with recent ARPES,[14] NMR,[15] and XAS[16] studies. With the use of obtained V_{Co} data, as a matter of fact, the hydronium content of the samples can be calculated by the formula $z = 4 - x - V_{Co}$. The calculated z-value is in good agreement with the TG analysis within experimental errors.

Figure 3 shows the lattice parameters as a function of ΔV_{Co}. On one hand, the a-axis reasonably expands slightly
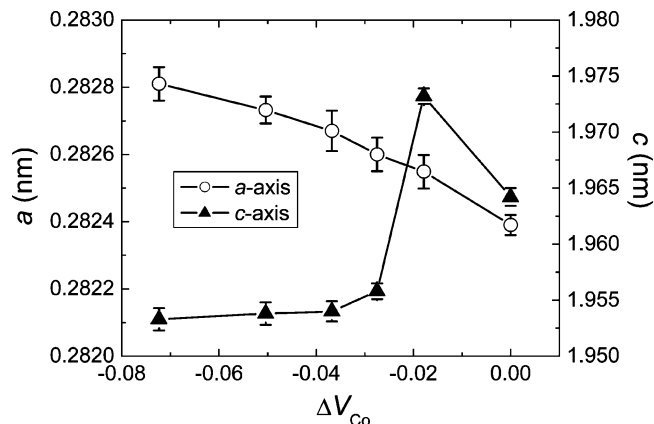
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Figure 3. Lattice parameters plotted as a function of change in Co valence (ΔV_{Co}).
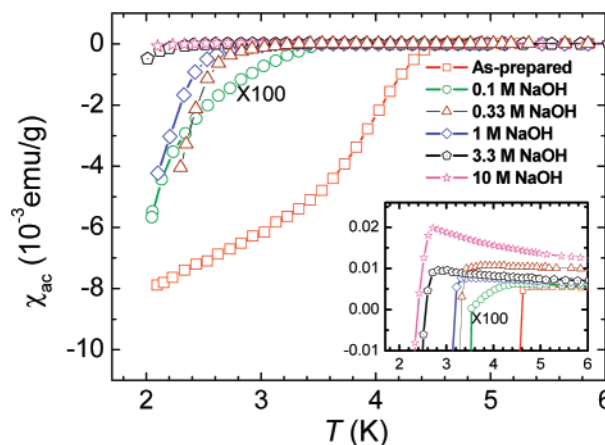

Figure 4. Temperature dependence of ac magnetic susceptibility for the cobalt oxyhydrate superconductors. As labeled, different concentrations of NaOH solution were used to reduce the Co valence. The inset shows an enlargement of the superconducting transitions.

as V_{Co} decreases. On the other hand, the c-axis tends to shrink with the decrease of V_{Co}, in agreement with the strengthening of the interlayer Coulomb attraction between Na^+-ion layers and the negatively charged CoO_2 layers. However, there is one exception: the c-axis of the second sample surprisingly increases. We attribute this increase of c-axis to the increase of hydronium content as shown in Table 1. Previous studies[7,8,13] demonstrated that the c-axis became unusually large when the hydronium content was comparable to the sodium content. In contrast, we found that the c-axes were almost identical and particularly short for the last three samples in Table 1. This fact further supports that the hydronium content becomes nearly zero under the circumstance of concentrated NaOH.

Figure 4 shows temperature dependence of ac magnetic susceptibility (χ_{ac}) for each powder sample. The as-prepared superconductor does show bulk superconductivity at 4.5 K. The χ_{ac} value at 2 K achieves -8×10^{-3} emu/g, corresponding to a volume fraction of magnetic shielding as high as ~30% (this is among the best results ever reported for powder samples). The postreduced samples also show superconducting transitions with clearly different T_c ranging from 2.4 to 3.8 K. One may note that the superconducting transition is much broader for the second sample, suggesting a high degree of inhomogeneity. As discussed above, the sample noticeably contains hydronium ions, which possibly
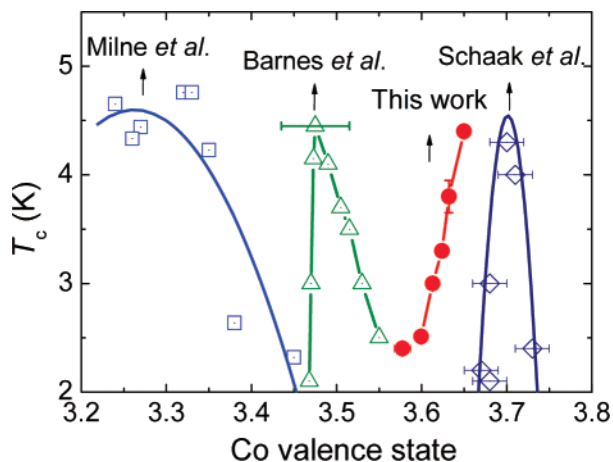
Figure 5. Updated superconducting phase diagram for cobalt oxyhydrate superconductors. For comparison, previous results proposed by some other groups are also presented.

leads to a kind of phase separation. Nevertheless, other samples show sharp superconducting transition, as can be seen in the inset of Figure 4.

Barnes et al.[5] recently reported time-dependent superconducting properties for the cobalt oxyhydrate superconductor, which was, however, not observed in the present study. The difference may arise from the different way in synthesizing the superconductor. They employed aqueous Br_2 solution to deintercalate the sodium from the parent compound γ-Na_x-CoO_2. Since the aqueous Br_2 solution is acidic, the hydronium content of the synthesized cobalt oxyhydrate superconductor would be considerably high.[13] So the reported "time-dependent superconductivity" seems to be due to the phase separation induced from the remarkable incorporation of hydronium. Besides, our samples were kept below 263 K, which slowed down the possible redox reaction that could alter V_{Co} in the cobalt oxyhydrate superconductors.

Figure 5 shows our updated SPD plotted as a function of Co valence state. The superconducting region in our SPD is between those of Schaak et al.[2] and Barnes et al.[5] As can be seen, superconductivity appears in the vicinity of the quarter filling, which show charge ordering in the unhydrous Na_x-CoO_2 system.[17] The striking feature of our phase diagram is that T_c decreases monotonously with decreasing V_{Co}. Actually, based on the neutron diffraction study, Lynn et al.[18] has also suggested that T_c increased as electrons transferred

off the cobalt in the cobalt oxyhydrate superconductor, which is in agreement with our result. However, it is stressed that this is not a definitive conclusion for the shape of the SPD since we are unable to increase the V_{Co} from the as-prepared superconductor. Moreover, synthesis of the "overdoped" superconductors is very difficult because such superconductor could be reduced by itself (the intercalated water) at room temperature.

According to the analysis by Shaak et al.,[2] $Na_xCoO_2 \cdot yH_2O$ would be a Mott-Hubbard insulator and a band insulator for $x = 0$ (Co^{4+}) and $x = 1$ (Co^{3+}), respectively, concerning the splitting of the Co 3d band due to the crystal field effect. Assuming a simple rigid band, in this scenario, each added Na above $x = 0$ in $Na_xCoO_2 \cdot yH_2O$ results in the addition of one electron per cobalt to the upper Hubbard band. For $V_{Co} > 3.5$ as in the present result, the system will be electron-doped. One expects some careful experiments such as Hall measurement to make a definite conclusion on this issue.

Conclusion

In summary, we have presented a facile route to tune and measure the Co valence state in the cobalt oxyhydrate superconductor by a topotactic postreduction using NaOH as reducing agent. The remarkable advantage of this method lies in that the disturbance of hydronium incorporation can be eliminated to a great extent for the sample treated in concentrated NaOH, which makes the absolute Co valence determinable. Magnetic susceptibility measurement indicates that the superconducting transition temperature decreases monotonically with Co valence state in the range from +3.58 to +3.65. Further study is needed to clarify the doping dependence of T_c for Co valence larger than +3.65. We expect that this approach of valence tuning can also be applied to other related systems in the future.

Supporting Information Available: Thermal analysis of the specimens treated in 0.1 and 1 M NaOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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