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Effects of water intercalation in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

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Abstract. Water intercalation is necessary for the occurrence of superconductivity in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. It is known that water insertion leads to the elongation of the c -axis. Beyond that, it remains controversial about the effects of water intercalation on the electronic structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. In this paper, we report the Co- K edge spectroscopy on $y=0.7$ and 1.4 samples, respectively. The spectra are compared with those of the reference samples. It is found that the variation of the Co valence can not be explained by the simple electron counting. These results are consistent with those of the previous chemical titration.

1. Introduction

Na_xCoO_2 has attracted much research interest recently due to its intriguing phase diagram [1]. By changing the Na content x , this system displays drastic changes of magnetic and transport properties. Meanwhile, for $x > 0.75$, the ground state of Na_xCoO_2 is largely unknown and still to be explored [2,3]. For applications, the combination of the relatively large thermoelectric power and small resistivity in Na_xCoO_2 makes this compound promising for the thermoelectric cooler and energy generation devices.

Na_xCoO_2 has further driven new excitement and surprise since superconductivity was discovered in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with $x \approx 0.35$ and $y \approx 1.3$ [4]. It has been the first superconductor among cobaltates. The theoretical interest has been high due to superconductivity in the trigonal CoO_2 planes, which is the ideal venue for the resonance bond valence (RVB) model. The pairing symmetry has been suggested to be with nodal lines [5,6]. Nevertheless, controversy remains due to the conflict experimental results [7]. Moreover, there has been no consensus on the microscopic superconducting mechanism in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$.

It is believed that the elongation of the c -axis due to water intercalation leads to the occurrence of superconductivity. In addition, it is interesting whether the water intercalation has other effects on the electronic structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. Reports from chemical titration suggested that the valence of Co ν was larger than the value determined by $\nu = 4 - x$ [8,9]. On the other hand, x-ray absorption spectroscopy (XAS) indicated no Co valence change due to the water intercalation [10]. Since the Co valence is crucial to determine the electronic structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ and probably to the occurrence of superconductivity, further clarification on this issue of the Co valence state in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is certainly desirable.

2. Experiments

Polycrystalline parent compounds of sodium cobaltates γ - $\text{Na}_{0.7}\text{CoO}_2$ were prepared using a rapid heat-up procedure. High purity powders of Na_2CO_3 and CoO were thoroughly mixed, ground, and calcined. The resulting powders were immersed in the $3\text{M Br}_2/\text{CH}_3\text{CN}$ solution for 5 days, followed by filtering and thorough washing with CH_3CN and DI water. The mono-layered $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ samples were prepared by placing $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ samples in the vacuum chamber of 10^{-9} torr for one week. X-ray diffraction (XRD) patterns indicated that all parent and hydrated samples were of single phase. T_c measurements were carried out in MPMS Quantum Design for $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$, and showed pronounced superconductivity with $T_c=4.5$ K before and after XAS experiments. To further characterize the samples, x-ray XAS was carried out for Co K -edge.

Special attention was paid to the sample quality of the hydrated samples during XAS experiments. Through the measurements, the hydrated samples were kept in the sealed capsules. Fig. 1 shows the XRD patterns for the as-prepared $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ sample and the same one after XAS measurements. It is clear that the sample has remained good quality during the experiments. T_c measurements were carried out in MPMS Quantum Design for $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$, and showed pronounced superconductivity with $T_c=4.5$ K both before and after XAS experiments.

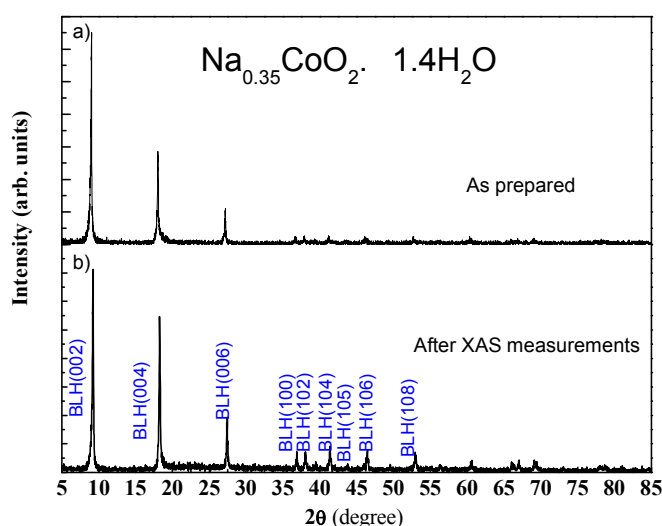


Figure 1. XRD patterns of the $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ sample before and after the XAS measurements. All the peaks can be indexed for both samples.

3. XAS results and discussions

Fig. 2 shows Co- K edge spectra of the anhydrous and hydrated samples together with those of the reference compounds. Two of the spectra were taken from Ref. [10]. An energy calibration of 0.57 eV was applied to both spectra from Ref. [10]. This 0.57 eV energy shift was to make coincident the main peaks in the spectra of the Co- K edge of the present CoO sample and that from Ref. [10].

Since the Co valence of Na_xCoO_2 is known to $\nu=4-x$. It is seen that the edge of the main peak shifts to higher energy with increasing ν . This general trend is useful to further discussions of the Co valence state in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. It is clear that the edge energy of both $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ and $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ do not coincident with that of $\text{Na}_{0.3}\text{CoO}_2$ with $\nu=3.7$. Without the effects of the water intercalation, ν of both samples should have been $4-x=3.65$. This implies that the valence state of Co is changed due to water intercalation. Actually, the spectrum of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ is close to that of $\text{Na}_{0.7}\text{CoO}_2$ with $\nu=3.3$.

To discuss in a more quantitative way, the edge energy of the main peak for Co-K edge was determined by the first inflection and plotted in Fig. 3 with respect to the Co valence ν . Fig. 3 further shows that ν of both $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ and $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ deviates from the relation of $\nu=4-x$. Interpolation of the data in Fig. 3 between $\nu=3.3$ and 3.7 leads to an estimate of $\nu \approx 3.4$ for $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$, consistent with $\nu=3.42$ from chemical titration [9].

The present Co-K edge XAS demonstrates the effects of water intercalation on the Co valence state in $\text{Na}_x\text{CoO}_2 \cdot \gamma\text{H}_2\text{O}$. Possible existence of H_3O^+ in $\text{Na}_x\text{CoO}_2 \cdot \gamma\text{H}_2\text{O}$ has been proposed as one of the mechanisms for this intriguing decrease in the value of ν . However, this issue is still sort of under debate [10, 11]. The alternative explanation with oxygen deficiency was proposed in Ref. [8]. It is noted that the results of the present work is different from those of Ref. [10]. This discrepancy could be due to different sample preparation and processing. Indeed, different physical properties were observed in $\text{Na}_x\text{CoO}_2 \cdot \gamma\text{H}_2\text{O}$ with nominally the same composition (see references in Ref. [7]).

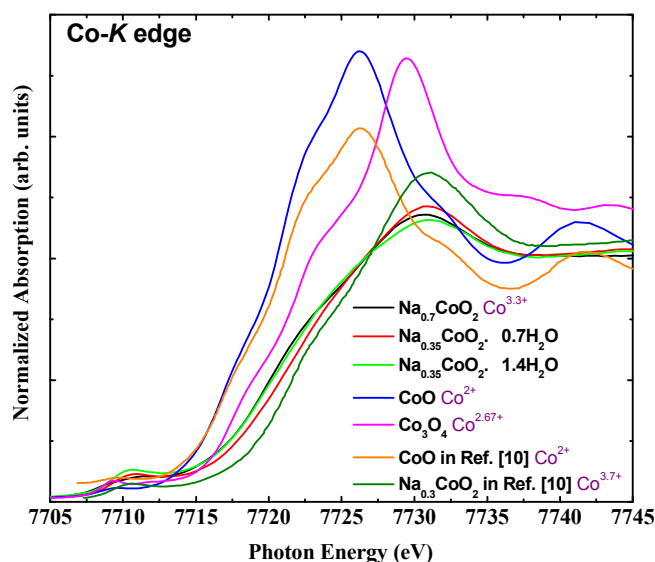


Figure 2. Co-K edge XAS for the anhydrous and hydrated samples together with the reference compounds. See test for the details.

4. Conclusion

In the present work, XAS clearly indicates the change of the Co valence state of $\text{Na}_x\text{CoO}_2 \cdot \gamma\text{H}_2\text{O}$ due to water intercalation. It is found that $\nu \approx 0.4$ for the superconducting sample. This information is of importance to reveal the electronic structure of $\text{Na}_x\text{CoO}_2 \cdot \gamma\text{H}_2\text{O}$, and is crucial to the investigation of superconductivity mechanism. These results are different from those in some of the literature, and the discrepancy could result from the subtle differences in samples.

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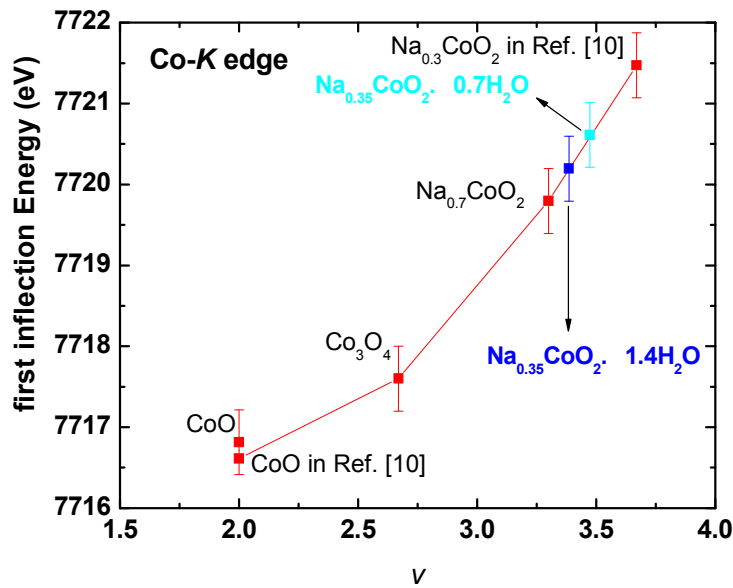


Figure 3. The Co-K edge energy vs. the Co valence v .

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