Structural and physical properties of the \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) superconducting system

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Abstract
The structural features and physical properties of \( \text{Na}_x \text{CoO}_2 \) and \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) materials have been investigated. The \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) samples, in general, undergo superconducting transitions at around 3.5 K. Energy dispersive x-ray analyses suggest that our samples have average compositions of \( \text{Na}_{0.65} \text{CoO}_2 \) for the parent compounds and \( \text{Na}_{0.26} \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) for the superconducting oxyhydrates. Transmission electron microscopy observations reveal a new superstructure with wave vector \( q = (1/2, 0, 0) \) in the parent material. This superstructure becomes very weak in the superconducting samples. Electron energy loss spectra analyses show that the Co ions have valence states of around +3.3 in \( \text{Na}_{0.65} \text{CoO}_2 \) and around +3.7 in \( \text{Na}_{0.26} \text{CoO}_2 \cdot y \text{H}_2 \text{O} \).

1. Introduction
Layered sodium cobalt oxyhydrate materials (\( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \)) have attracted considerable interest because of their similarity to high-\( T_c \) superconductors. Systematically, theoretical and experimental investigations on this new superconducting system are expected to shed light on the superconducting mechanism in high-\( T_c \) cuprates \([1–6]\). Like high-\( T_c \) superconductors, the \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) crystal structure consists of electronically active planes (edge sharing \( \text{CoO}_6 \) octahedra) separated by (Na–H\(_2\)O) layers, which act as charge reservoirs \([3]\). The Na content can be varied in the charge reservoir layers, which results in the same type of out-of-plane chemical doping control of in-plane electronic charge as found for cuprate superconductors. It has been confirmed that the structural and compositional alternations in this layered system could yield, evidently, a change of superconductivity \([3, 7, 8]\). Hence, a careful structural analysis, especially of the evolution of the microstructure along with oxyhydration, should play an important role in understanding the significant properties of this new material. In this paper, we report on the developments of our investigations on the structural and physical properties of the parent \( \text{Na}_x \text{CoO}_2 \) materials. We briefly discuss the \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) superconductors and the valence states of Co ions in several specific materials, as measured by electron energy loss spectra (EELS).

2. Experimental details
The polycrystalline samples of \( \text{Na}_{0.65} \text{CoO}_2 \) were prepared by conventional solid-state reactions \([9]\). Superconducting \( \text{Na}_x \text{CoO}_2 \cdot y \text{H}_2 \text{O} \) materials were prepared by \( \text{Na}_{0.65} \text{CoO}_2 \) in excessive bromine solved in acetonitrile at ambient temperature for 2–5 days to deintercalate sodium. The detailed process and treatments in sample preparation are similar to those reported previously in \([1]\). The product materials were washed several times with acetonitrile and water, and stored in a humidified atmosphere for 2 days. Then these were pressed into pellets and protected in liquid nitrogen. Specimens for transmission electron microscopy (TEM) observations were prepared simply by crushing the bulk material into fine fragments, which were then supported by a copper grid coated with a thin carbon film. The TEM investigations were performed on a H-9000NA transmission electron microscope operating at the voltage of 300 kV and a Tecnai F20 (200 kV) electron microscope with an atomic resolution of about 0.23 nm. The EELS measurements were performed on the Tecnai F20 transmission electron microscope (equipped with a post column Gatan imaging filter). The energy resolution in the EELS spectra was 0.7 eV under normal conditions.
operation conditions. In order to minimize the radiation damage under electron beam, the samples were cooled below 200 K during our TEM observations.

3. Results and discussion

The basic crystal structures of the parent materials Na$_x$CoO$_2$ and the superconducting materials Na$_x$CoO$_2$·yH$_2$O have been measured by x-ray diffraction (XRD). Figure 1(a) shows an XRD pattern obtained from a parent Na$_x$CoO$_2$ sample; all diffraction peaks in this pattern can be well indexed by a hexagonal cell with lattice parameters $a = 2.839$ Å and $c = 10.804$ Å. Figure 1(b) shows XRD data obtained from a typical superconducting sample of Na$_x$CoO$_2$·yH$_2$O with $T_c = 3.5$ K. It can be recognized that the crystal lattice has a longer $c$-axis in the superconducting samples, which results from the intercalation of additional H$_2$O sheets between the CoO$_2$ layers. The basic parameters for the superconducting crystal are $a = 2.821$ Å and $c = 19.807$ Å with the space group of $P6_3/mmc$. After careful analysis, we also find some weak diffraction peaks in the diffraction pattern from some other impurity phases.

Figure 2 shows the zero-field-cooling direct current (dc) magnetization data measured in a field of 20 Oe for selected samples prepared under slightly different conditions. The superconducting transition occurs at around 3.5 K for both samples. Strong diamagnetic signals appearing in these measurements provide direct evidence for bulk superconductivity in the Na$_x$CoO$_2$·yH$_2$O samples.
Alternations of Na concentration from one area to another and the resultant structural inhomogeneities are likely to be the essential causes for the rounding of the superconducting transitions.

Microstructural features of sodium cobalt oxyhydrate materials depend essentially on the synthesis process. Figures 3(a)–(d) show scanning electron microscopy (SEM) images illustrating the typical microstructure of the Na_{0.65}CoO_{2} and Na_{x}CoO_{2}·yH_{2}O samples; both materials show clearly layered structural features. The grain sizes range from 0.1 to 10 µm in the Na_{0.65}CoO_{2} materials and from 3 to 30 µm in the superconducting samples. The crystal structure of this type of material is based on the close-packed layers of the edge-sharing CoO_{2} octahedra perpendicular to the c-axis, separated by intercalent layers consisting of Na and H_{2}O sheets. The crystals can be cleaved easily between the CoO_{2} layers and give rise to noticeable layered crystalline pieces, as displayed in the SEM images of figures 3(c) and (d). In the superconducting materials, in general, we can find the perfect crystal with a thickness of less than 1 µm along the c-direction. We also note that the superconducting crystals are very unstable under electron beam illumination. Lowering the sample temperature to 200 K by using a low-temperature stage can effectively prevent the crystal modification from the decomposition of H_{2}O molecules. Energy dispersive x-ray analysis (EDAX) has been used to measure the compositions of the crystal grains prepared under different conditions. The composition of the parent materials is estimated as Na_{0.65}CoO_{2}, and in some cases it is likely that additional oxygen, intercalated among the structural layers, can be detected. In the superconducting materials, the EDAX measurements revealed that the Na concentration could change slowly from one grain to another. The composition is estimated in the range Na_{0.25}CoO_{2}·yH_{2}O to Na_{0.3}CoO_{2}·yH_{2}O for our superconducting samples. Moreover, EDAX confirms the presence of a few impurity phases in the superconducting materials, which is consistent with the XRD results.

TEM observations reveal that the crystal structures, for both the parent compound and the superconducting phase, have a hexagonal lattice with the space group of P6_{3}/mmc in agreement with the reported data. The basic properties of the crystal structure can be clearly illustrated by convergent-beam electron diffraction (CBED) patterns and TEM images obtained along several relevant zone-axis directions. Figure 4(a) shows the [001] zone CBED pattern, illustrating the 6-mm symmetry with the systematical mirror planes located in the [100] and [210] crystal planes. A sixfold axis is along the c-direction. The most striking feature revealed in our TEM observations is the presence of a superstructure within the ab crystal plane. This superstructure is strong and clearly visible in the parent Na_{0.65}CoO_{2} material, and becomes weaker, even invisible, in the Na_{0.3}CoO_{2}·yH_{2}O
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Figure 4. (a) CBED pattern of Na_{x}CoO_{2}·yH_{2}O along the c-axis direction, showing the 6 mm symmetry. (b) Electron diffraction pattern showing the presence of superstructure in Na_{0.65}CoO_{2}. (c) High-resolution TEM image from an area with clear superstructure fringes. (d) High-resolution TEM image showing the hexagonal sublattice for the superconducting phase.

superconducting materials. Figure 4(b) shows an electron diffraction pattern taken from the parent material Na_{0.65}CoO_{2}, exhibiting superstructure spots at the systematic (h + 1/2, k, l) positions. Detailed analyses suggest that this superstructure results possibly from the mismatch between the CoO_{2} layer and the Na(H_{2}O) sheets. On the other hand, this superstructure is likely to be in correlation with chemical inhomogeneity commonly occurring in this type of material, e.g. the alteration of the Na concentration. In situ cooling TEM observations indicate that this superstructure is very stable within the temperature range from room temperature down to 100 K. No structural phase transition is observed. A further investigation of the origin of this superstructure, by means of XRD and high-resolution electron microscopy, is still under progress.

Figure 4(c) shows a high-resolution electron micrograph of a Na_{x}CoO_{2}·yH_{2}O crystal taken along the [001] zone-axis direction; the superstructure fringes with the space of 2d_{100} are indicated by arrows. It is commonly observed that the areas with clear superstructure show up complex domain structure corresponding to different orientation variants. In the superconducting samples, this superstructure becomes very weak and, as a result, only the hexagonal sublattice structure feature of the sublattice is revealed in the high-resolution TEM images, as shown in figure 4(d).

EELS analyses have been performed on both the parent material Na_{0.65}CoO_{2} and the superconducting material Na_{x}CoO_{2}·yH_{2}O. Figure 5(a) shows an EELS spectrum of a superconducting crystal taken from an area of about 100 nm in diameter. In this spectrum the typical peaks, i.e. the collective plasmon peak as well as core edges for Co, O and Na elements, are displayed.

Figure 5. (a) EELS spectrum of the Na_{x}CoO_{2}·yH_{2}O superconductor showing the zero-loss peak, plasmon resonance and ionization edges arising from the elements of O, Co and Na. (b) An EELS spectrum acquired from a crystal in the superconducting sample, schematically illustrating the method used to extract the intensities of white lines.

EELS, a powerful technique for material characterization at a nanometre spatial resolution, has been widely used in
chemical microanalysis [10]. For transition metals with unoccupied 3d states, the transition of an electron from the 2p state to 3d levels leads to the formation of white lines. The L3 and L2 lines are the transitions from 2p3/2 to 3d3/2,5/2 and from 2p1/2 to 3d3/2, respectively. Their intensities are related to the unoccupied states in the 3d bands. In Na0.3CoO2·yH2O materials, we have made a series of measurements in association with quantitative analyses using the method as reported by Wang et al [10]. Figure 5(b) shows a typical spectrum for the Co L2 and L3 peaks obtained from an area of about 20 nm in size, in which we schematically illustrate the extraction of the intensities for the white lines of Co for a superconducting sample. As pointed out previously in the literature, the ratio of L3/L2 is very sensitive to the valence state of Co [10, 11]. A series of relevant experimental data and some well-established empirical models are also reported in the studies of the related materials. These results provide a basis for our measurement of the Co valence in Na0.65CoO2·yH2O materials.

Our first analysis was performed on the parent sample Na0.65CoO2. The results indicate that the ratio of L3/L2 in general is around 2.4, which could yield the Co valence of about 3.3–3.4 in the parent sample. The analyses of the superconducting sample give rise to L3/L2 at around 2.2; these data could change slightly from one grain to another. Our systematical analyses conclude that the Co valence state ranges from 3.6 to 3.8 for superconducting samples. This result is in good agreement with the data from other experiments [4–6].

4. Conclusion

In summary, we have prepared a series of layered sodium cobalt oxyhydrates with evident superconducting transitions at around 3.5 K. SEM observations clearly show the layered structural feature of this type of material. A TEM investigation reveals a superstructure with wave vector $q = \langle 1/2, 0, 0 \rangle$ appearing in the parent materials, which becomes weak and even invisible in the superconducting samples. EELS analyses of Co valence states suggest that the Co ions have valence states ranging from +3.3 to +3.4 in the Na0.65CoO2 materials and from +3.6 to +3.8 in the superconducting materials.

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