Superconductivity, structural features and charge ordering in Na$_x$CoO$_2$$\cdot$yH$_2$O ($0 \leq y \leq 1.8$) system

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Received 14 March 2005; revised 15 June 2005; accepted 15 June 2005

Available online 13 September 2005

Abstract

Structural and physical properties of Na$_x$CoO$_2$ and superconducting Na$_x$CoO$_2$$\cdot$yH$_2$O hydrates have been systematically investigated. Raman scattering measurements reveal that the five active phonons in Na$_x$CoO$_2$$\cdot$yH$_2$O system change systematically with the H$_2$O intercalation and modification of superconductivity, in particular the A$_{1g}$ and E$_{1g}$ modes in correlation with oxygen movements. Incoherent inelastic neutron scattering (IINS) study on the local structure of H$_2$O-layers in Na$_x$CoO$_2$$\cdot$yH$_2$O ($0 \leq y \leq 1.8$) suggests the presence of three types of clusters, H$_3$O$^+$, H$_5$O$^+$ and ice-Ih like weakly bonded water, among CoO$_2$ sheets. Electron energy loss (EEL) analysis on Na$_{0.33}$CoO$_2$$\cdot$yH$_2$O ($0 \leq y \leq 1.3$) indicates certain notable changes in the electronic structure during hydration. Microstructure and structural phase transitions accompanied with local atomic ordering in the charge-ordered phase Na$_{0.5}$CoO$_2$ have been investigated along with the hexagonal–orthorhombic phase transition.

Keywords: Na$_x$CoO$_2$$\cdot$yH$_2$O; Superconductivity; Charge ordering; Phase transition

1. Introduction

The Na$_x$CoO$_2$ materials have attracted much attention in past several years due to its large thermoelectric power coexisting with low electric resistivity [1,2]. The discovery of superconductivity in water-intercalated Na$_{0.33}$CoO$_2$$\cdot$yH$_2$O immediately spurred a new round of intense interest in this system [3–18]. A phase diagram of Na$_x$CoO$_2$ for $0.3 < x < 0.75$ has demonstrated the existence of two distinct metallic regions separated by an insulating state at $x = 0.5$ with the remarkable charge-ordering phenomenon [4]. Theoretical investigations suggested that electron correlations among the Co-3d electrons are substantial for the presence of these significant properties in present system [5,6]. These materials, similar with the high-$T_c$ cuprates, have the layered structure consisting of the two-dimensional CoO$_2$ sheets and intercalated ions. Recent structural analysis revealed that the intercalations of either Na atoms or H$_2$O molecules could make the local structure much complex, the intercalated atoms can be random with high mobility or crystallized in certain ordered states [7–10]. Certain local ordered structures are demonstrated to have notable effects on physical properties. For instance, Na atoms in Na$_{0.5}$CoO$_2$ crystallize in a well-defined zigzag ordered pattern yielding an orthorhombic structure in which low temperature charge ordering is observed [7,10]. In this article, we will focus on the structural and physical properties of Na$_x$CoO$_2$ and superconducting Na$_x$CoO$_2$$\cdot$yH$_2$O materials; the correlation between local structure and physical properties is also discussed.

2. Experimental

Both ceramic and single-crystalline samples were used for the present study. Na$_x$CoO$_2$ ($0.5 < x \leq 0.85$) single crystalline samples were grown using a traveling-solvent floating zone method and polycrystalline samples were prepared via solid-state reactions [11,12]. The Na$_{0.5}$CoO$_2$ compound and Na$_x$CoO$_2$$\cdot$yH$_2$O hydrates were prepared by the method as described in previous publications [4,10,11]. The physical properties of all
samples have been well characterized. A H-9000NA and a Tecnai F20 transmission electron microscopes (TEM) both equipped with low-temperature sample stages were used for the microstructure investigations. Electron energy loss (EEL) spectroscopy analysis was carried out on the Tecnai F20 TEM with a post column Gatan imaging filter. Raman spectra were collected in back-scattering geometry using a Jobin-Yvon T64000 triple spectrometer equipped with a cooled charge-couple device. Incoherent inelastic neutron scattering (IINS) data was obtained using the HET spectrometer at ISIS, the UK spallation neutron source.

3. Results and discussion

3.1. The Na$_x$CoO$_2$·yH$_2$O hydrates

We will begin by considering the physical properties of superconducting Na$_x$CoO$_2$·yH$_2$O hydrates. Fig. 1(a) shows the experimental results of the magnetic susceptibility as a function of temperature for a series of Na$_x$CoO$_2$·yH$_2$O samples, demonstrating the superconducting transitions at different critical temperature ($T_c$) [13]. Systematical analysis reveals that the $T_c$ in present system could change notably with lattice parameters, certain physical properties, especially the superconductivity, are evidently in correlation with the distance between two adjacent CoO$_2$-sheets. The insert of Fig. 1(a) shows a monotonous decrease of $T_c$ with the increase of the c-axis parameter as measured in our Na$_x$CoO$_2$·yH$_2$O samples.

In order to get deep insight into the correlations between superconductivity and lattice vibrations, systematical Raman scattering measurements have been carried out on the parent material and Na$_x$CoO$_2$·1.3H$_2$O oxyhydrates. It is noted that there were several publications concerning with the structural features of Raman scattering spectra of this kind of materials, however, some reported results remain noticeably contradictory [13]. In our works, based on the calculated results for the relative scattering intensities associated with the $A_{1g}, E_{1g}, 3E_{2g}$ phonons, we unambiguously identified that five active phonons generally appear in the Raman spectra of this kind of materials at the position of around 663 cm$^{-1}$ ($A_{1g}$), 195 cm$^{-1}$ ($E_{1g}$) and 482, 522, 616 cm$^{-1}$($3E_{2g}$) by using a Na$_{0.75}$CoO$_2$ single crystal and a combination of different crystal orientations and polarizations [13].

Fig. 1(b) shows the Raman spectra for a parent and three superconducting samples. It can be seen that the Raman active modes appearing in these spectra show systematic alternations with superconductivity. All five peaks shift monotonously towards the lower frequencies with the $T_c$ increase. The $A_{1g}$ and $E_{1g}$ peaks, in connection with the movement of oxygen atoms, have much larger shifts than the three $E_{2g}$ modes. This result, therefore, directly demonstrates that the modification of oxygen motion in the crystal lattice plays an important role for understanding the superconductivity occurring in present system [13].

Now we go on to discuss the local structure of the intercalated water layers in the Na$_x$CoO$_2$·yH$_2$O superconducting hydrates. Recent theoretical and experimental investigations suggest that intercalated water layers during hydration have much complex structure rather than the simple ice-Ih state [14]; the water layers may not only just expand the crystal lattice and make the system more two-dimensional in nature, but also tune the oxidation states of Co by existing as H$_3$O$^+$ cluster [15]. IINS is a powerful tool for the structural characterization of hydrated inorganic compounds. The vibrations involving hydrogen dominate in the neutron spectroscopy with only negligible contribution from the inorganic framework of the host material due to the much greater scattering cross-section for hydrogen (80 barn) than for any other element (normally less than 5 barn).

We have collected IINS data in an energy range from 0 to 600 meV from the Na$_x$CoO$_2$·yH$_2$O of different hydration level. Fig. 2 shows an IINS result with the incident neutron energy of 250 meV, emphasizing O–H bending modes. The spectra, obtained, respectively, from Na$_x$CoO$_2$·yH$_2$O
In what follows we will briefly discuss our measurements of EEL spectra from the remarkable Na$_{0.33}$CoO$_2$·yH$_2$O (y = 0, 0.6 and 1.3) series to reveal changes of electronic structure along with hydration. Systematical analysis suggests that noticeable spectral changes appear in both the low energy range (<10 eV) and the high-energy core losses along with water intercalation. We have listed the main observed peaks in range of 0–80 eV from all Na$_{0.33}$CoO$_2$·yH$_2$O (y = 0, 0.6 and 1.3) samples in Table 1, and assigned the peaks based on the results of theoretical calculation [15]. It can be clearly recognized that the energy excitations below 10 eV change evidently with water intercalation.

Fig. 3 shows the oxygen K-edge core loss EEL spectra after background subtraction for Na$_{0.33}$CoO$_2$·1.3H$_2$O, and Na$_{0.33}$CoO$_2$ materials. Five peaks (a–e) ranging from 520 to 580 eV are observed on each spectrum. The peaks (labeled a) correspond to the transition from O1s towards Co3d-0.2p hybridized vacant states, it should be predominated by the $a_{1g}$ and $e_g$ bands [15]. It is noted that the relative weight of this contribution, as compared to the total intensity of the O–K edge, decreases evidently in the water intercalated superconducting Na$_{0.33}$CoO$_2$·1.3H$_2$O. This reflects a decrease of accessible vacant Co-3d states along with hydration. Peak c, at around $540$ eV, reflects a transition from O1s to O2p state hybridized with the more delocalized transition metal Co-4s and H-1s states. The structural feature of this peak can be understood based on intrashell multiple scattering within six-oxygen coordination shell as reported in Ref. [15]. Peak d lying to the high-energy-loss side of peak c and peak e at 570 eV arise clusters firstly resident in the Na site of the Na$_{0.33}$CoO$_2$ compound for Na$_{0.33}$CoO$_2$·0.3H$_2$O. When more water was introduced into crystal, it interacts with H$_2$O$^+$ clusters and leads to the formation of H$_2$O$_2^+$, these clusters still resident in same plane with the cation. When additional water was intercalated consecutively, it weakly interacts with the Na$^+$ and H$_2$O$_2^+$ to form the complex hydogentic water clusters. These clusters reside mostly in the voids of the crystal which behaves more like Ih ice. The detailed study on the structure of water sheets will be reported in a further coming paper [21].

| Na$_{0.33}$CoO$_2$ | Na$_{0.33}$CoO$_2$·0.6H$_2$O | Na$_{0.33}$CoO$_2$·1.3H$_2$O ($T_c$ = 4.6 K) |
|-----------------|-----------------|-----------------|
| Peak (eV)       | Description     | Peak (eV)       | Description               | Peak (eV)       | Description               |
| 5.8             | O2p to $a_{1g}$ | 5.5 (±0.2)      | O2p to $a_{1g}$          | 4.0             | Co t$_{2g}$ to e$_g$     |
| 7.9 (±0.3)      | Plasmon         | 7 (±0.3)        | Plasmon                  | 6 (±0.3)        | Plasmon                   |
| 19              | O–L$_1$         | 24.8 (±0.4)     | Bulk plasmon             | 13.8            | H–K                       |
| 25.5 (±0.4)     | Bulk plasmon    |                |                          | 19.2            | O–L$_1$                   |
| 33.3            | Na–L$_{2,3}$    | 33.5            | Na–L$_{2,3}$             | 24.5 (±0.4)     | Bulk plasmon              |
|                 |                 |                |                           | 33.5            | Na–L$_{2,3}$              |

Fig. 2. IINS data from Na$_{0.33}$CoO$_2$·yH$_2$O samples using incident neutron energy of 250 meV on HET, the Na$_{0.75}$CoO$_2$ and ice-Ih data is also measured for comparison.

Table 1
The peak positions and brief descriptions of the nature of the transitions in EEL spectra obtained from Na$_{0.33}$CoO$_2$·yH$_2$O (y = 0, 0.6, and 1.3). The uncertainty in the energy positions is partial given in parentheses.
The structure of the phase transitions in Na$_{0.5}$CoO$_2$ is well characterized by the Raman scattering measurements. The susceptibility and resistivity changes with temperature, highlighting the phase transitions at 87, 53, and 20 K. The low-temperature phase transitions at 87 K is mainly due to the charge ordering, while the transitions at 53 K and 20 K are related to the structural changes. The high-temperature phase transitions at 470 K are associated with the incommensurate modulated structure. Upon in-situ heating, the Na$_{0.5}$CoO$_2$ material transforms into a high-temperature hexagonal structure (Fig. 5a). Upon in-situ cooling, the Na$_{0.5}$CoO$_2$ material undergoes a transformation at 200 K towards an orthorhombic structure (Fig. 5d) with space group $Pnmm$ in which a charge-ordered state is observed at the lower temperatures. This low temperature orthorhombic symmetry can be well interpreted by the zigzag-type Na order among the CoO$_2$ sheets. Raman scattering
measurements considering the hexagonal to orthorhombic structure transition also reveal notable spectrum alternations. Fig. 6 displays the Raman spectra taken in the temperature range of 80–300 K. The changes of active modes along with phase transition can be clearly recognized. A further analysis illustrates that, from 300 to 200 K, the $E_{2g}$ mode at 474 cm$^{-1}$ and the $A_{1g}$ mode at 681 cm$^{-1}$ shift progressively to higher frequencies. Moreover, the line width of the $A_{1g}$ mode becomes substantially narrower. These transformations can be considered to be correlated with confined sodium motion and ordering with lowering temperature [10].

4. Summary

In summary, we have investigated the Raman spectra of the single crystal Na$_{0.75}$CoO$_2$ and superconducting Na$_x$CoO$_2$-1.3H$_2$O materials. Five active phonons are commonly observed at the position of about 663 cm$^{-1}$ ($A_{1g}$), 195 cm$^{-1}$ ($E_{1g}$) and 482, 522, 616 cm$^{-1}$($3E_{2g}$). The Raman active modes, in particular the $A_{1g}$ and $E_{1g}$ modes in correlation with oxygen movement, change apparently along with the H$_2$O intercalation and the modification of superconductivity. We have present an INS measurement on the local structure of water sheets in numerous Na$_x$CoO$_2$-yH$_2$O samples with different hydration levels. Three kinds of clusters, i.e. H$_3$O$^+$, H$_2$O$^+$ and ice, have been found to exist in present system. Measurements of EEL spectra from the notable Na$_{0.33}$CoO$_2$-yH$_2$O ($y=0$, 0.6 and 1.3) series revealed evident changes in both the low energy range (<10 eV) and the high-energy core losses along with water intercalation. Microstructure and structural phase transitions in connection with Na-ordering in the charge-ordered phase Na$_{0.2}$CoO$_2$ have been investigated in the temperature range from 100 to 100 K, structural changes along with numerous phase transitions, such as the hexagonal–orthorhombic transition, have been well analyzed by a combined electron diffraction and Raman spectroscopy investigation.

Acknowledgements

We would like to thank Professor N.L. Wang for providing single crystal of Na$_x$CoO$_2$, Miss Y. Li, G. Zhu for the assistance in preparing samples and measuring Raman spectra and H.C. Yu for the help with TEM experiment. We are grateful to CCLRC for provision of beam time at ISIS. The work reported here is supported by National Natural Foundation and by the ‘Outstanding Youth Fund’ (JQL) with Grant No 10225415 of China.

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