

# Photoemission and x-ray absorption study of the two-dimensional triangular lattice superconductor $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$

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(Received 3 March 2004; published 30 July 2004)

We have investigated the electronic structure of a triangular lattice superconductor  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  ( $T_c \sim 5$  K) by photoemission and x-ray absorption spectroscopy. The Co  $2p$  x-ray absorption and Co  $2p-3d$  resonant photoemission clarified that the valence band near the Fermi level is mainly constructed by the narrow Co  $3d t_{2g}$  states at the binding energy of 1.0 eV with the low-spin configuration. In the resonant photoemission, Auger features coexist with the resonant enhancements, while the charge-transfer satellites are observed in the photoemission spectra of a Co  $2p$  core levels. It is also expected that the narrow  $t_{2g}$  band reflects on the importance of an electron-phonon coupling. Besides, O  $1s$  and Co  $1s$  x-ray absorption spectroscopy reveal that intercalated water condenses into a two-dimensional ice and showing no influence on a carrier doping.

DOI: 10.1103/PhysRevB.70.012508

PACS number(s): 74.25.Jb, 74.70.-b, 79.60.Bm

Since high- $T_c$  superconductivity is discovered in two-dimensional copper oxides, extensive efforts have been made to explore a layered transition-metal oxide superconductor. Takada *et al.* have recently discovered a superconductivity in the layered cobalt oxide  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ .<sup>1</sup> This compound has a two-dimensional triangular lattice of cobalt ions which forms a network of edge-sharing  $\text{CoO}_6$  octahedra. The enhancement of the two-dimensionality in the system is caused by the intercalation of  $\text{H}_2\text{O}$  between  $\text{CoO}_2$  layers to the mother compound  $\text{Na}_{0.7}\text{Co}_2\text{O}_4$ . It is expected that  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  shows an unconventional superconductivity. The triangular lattice of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  has attracted theoretical interest due to the possible realization of resonating valence bond (RVB) states predicted by Anderson.<sup>2</sup> The nature of superconductivity in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  has been intensively investigated. It is suggested that a spin-triplet superconductivity with  $p$ -symmetry appears.<sup>3,4</sup> In  $^{59}\text{Co}$  NMR measurements, the Knight shift showed an invariant behavior through  $T_c$ ,<sup>5</sup> while  $\mu\text{SR}$  study detected no outstanding change of an inner magnetic field between above and below  $T_c$ .<sup>6</sup> So far, there are controversial interpretations about the origin of superconductivity in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ .

An essential factor needed to reveal the driving force of superconductivity is an electronic structure. Although an electronic structure measurement such as photoemission (PES) and x-ray absorption spectroscopy (XAS) is indispensable, PES and XAS measurements have not been done, because of the difficult handling of the hydrated materials.<sup>7</sup> Motivated by the experimental elucidation of the electronic structure of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ , we have performed a high-resolution resonant photoemission and XAS measurements using synchrotron radiation. In the early days of research on high- $T_c$  superconductivity, many resonant photoemission studies have been carried out on high- $T_c$  superconductors to elucidate an electronic structure near the Fermi level.<sup>8</sup> Since there are considerable hybridization between Co  $3d$  and O  $2p$  states in Co oxides, Co  $2p-3d$  resonant photoemission is useful to elucidate the role of Co  $3d$  state.<sup>9</sup>

In this study, we have revealed that a  $t_{2g}$  state with the low-spin configuration dominates the valence-band near the Fermi level. The confined structure of water between Co triangular lattice layers in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  is also an intriguing physics in relation to a two-dimensional ice.<sup>10</sup>

The XAS and the photoemission measurements were carried out at the undulator beam line BL-2C of the Photon Factory in KEK. Gamdata SES-100 electron spectrometer

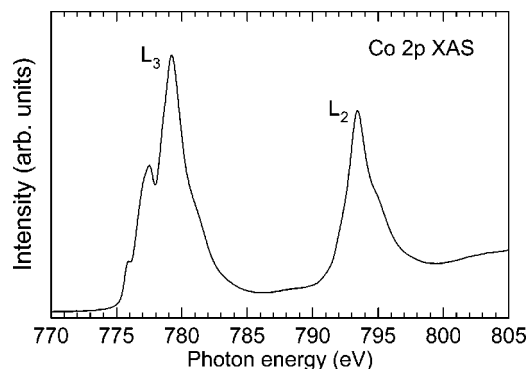


FIG. 1. X-ray absorption spectrum of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  at the Co  $L$ -edge at 11 K.  $L_3$  peak around 779 eV and the  $L_2$  peak around 793 eV are observed.

was used for the photoemission measurements. The total energy resolution of the photoemission determined from the Au Fermi edge is about 300 meV. XAS measurements were performed by a total electron yield method. All the measurements were performed at 11 K.

The  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  sample was obtained as described in Ref. 1. Powder samples were pressed into a pellet with the diameter of 5 mm. It is known that the desorption of  $\text{H}_2\text{O}$  in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  is very crucial for the suppression of the superconductivity.<sup>11</sup> In this study, we have done the following special sample preparation to avoid the desorption of  $\text{H}_2\text{O}$ . The manipulator was cooled down to 11 K prior to the measurements. The sample was transferred very quickly (within 5 min) from the atmosphere to the ultrahigh vacuum measurement chamber. After the cooling of the sample, the sample was repeatedly fractured just before photoemission measurements to obtain a clean surface. The pressure of the chamber during the measurements is  $1 \times 10^{-9}$  Torr range. To confirm whether the sample preparation is adequate, we have measured the core-level and valence-band photoemission spectra of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  before and after each measurement. The C 1s peak due to the presence of carbon materials on the surface was not detected in the C 1s x-ray photoemission spectra, and the photoemission spectra were not changed before and after the measurements, indicating that the clean surface of the sample is obtained in the present study.

The XAS spectra bring reliable information on relevant unoccupied states at a specific atomic site. The Co  $2p$  XAS final states are characterized by the multiplet structure due to the Coulomb and exchange interactions between the Co  $2p$  core hole and the Co  $3d$  electrons, the crystal field splitting, and the spin-orbit interactions. Figure 1 shows the Co  $2p$  XAS spectra of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ . The spectra are split into two peaks that correspond to the  $L_3$  around 779 eV and the  $L_2$  around 793 eV separated by 14 eV. The Co  $2p$  XAS spectra are similar to that of the two-dimensional triangular lattice (Bi,Pb)-Sr-Co-O compounds accompanied with the low-spin states, in terms of peak position, the ratio of the magnitude of  $L_3$  to that of  $L_2$ , and the energy difference between  $L_2$  and  $L_3$ .<sup>12</sup> In addition, the multiplet calculations with the low-spin states accounts well for the Co  $2p$  spectra.<sup>13,14</sup> These suggest that the Co  $3d$  states in

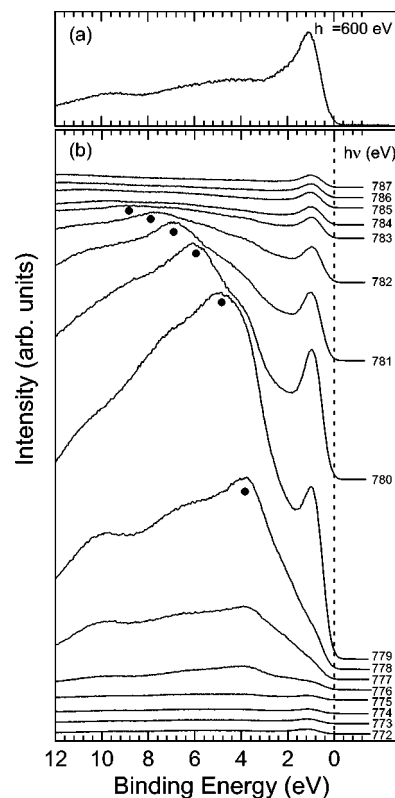


FIG. 2. Co  $2p$ - $3d$  resonant photoemission spectra of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  at 11 K: (a) overall spectral features taken at 600 eV; (b) resonant photoemission spectra. The solid circles indicate the position of Auger features.

$\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  have the low-spin configuration. There is extra features that are weak but observable in the XAS spectra in the energy region of 775–778 eV at the  $L_3$ -edge and the energy region of 790–793 eV at the  $L_2$  edge. It is noted that extra features indicate a possibility of the existence of extrinsic  $\text{Co}^{2+}$  components in XAS and PES spectra.

Overall feature of a valence-band photoemission spectrum shows a narrow Co  $3d$  related peak around 1.0 eV of binding energy, while a broad bump around 6 eV corresponds to O  $2p$  state hybridized with Co  $3d$  state, as shown in Fig. 2(a). The information on Co  $3d$  states near the Fermi level was obtained from a Co  $2p$ - $3d$  resonant photoemission. Figure 2(b) exhibits the resonant photoemission spectra taken at the photon energy between 772 eV and 787 eV. Above the photon energy of 776 eV, the enhancement of O  $2p$  peak hybridized with Co  $3d$  state was observed and at 778 eV large Auger peak (closed circle) is also appeared. The resonant enhancement of the O  $2p$  region can be partially due to the extrinsic  $\text{Co}^{2+}$  component. The spectral intensity around 0–2 eV strongly increases above the photon energy of 779 eV, corresponding to the resonant enhancement. Further above 784 eV, the resonant photoemission peak remains in contrast with the vanishing of Auger features. The sharp peak at the binding energy around 1.0 eV can be assigned as the  $3d$  Co  $t_{2g}$  states. Similar local peak near the Fermi level ( $\sim 1$  eV) is also observed in (Bi,Pb)-Sr-Co-O.<sup>12</sup>

Figure 3 shows the PES spectra of a Co  $2p$  core level at the photon energy of 900 eV. The charge-transfer satellites

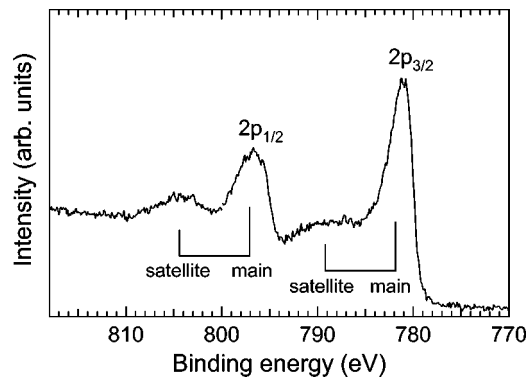


FIG. 3. Co  $2p$  photoemission spectrum of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  taken at 900 eV. The main peak as well as the satellite features are observed.

are observed with the 7 eV energy difference between the main peak and the satellite for both Co  $2p_{3/2}$  and  $2p_{1/2}$ , which reflects the localized character of Co  $3d$  electrons.<sup>12,15,16</sup> The intensity ratio of the satellite to the main peak  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  is much smaller than that in a representative charge-transfer-type compound CoO.<sup>15,17</sup> Combined with the resonant PES spectra, it is revealed that the electronic structure of  $t_{2g}$  state around Fermi level contains a rather localized character as well as an itinerant character. It is reported that the  $t_{2g}$  orbitals are split into  $a_{1g}$  orbitals and  $e'_g$  orbitals due to the trigonal crystal field and the  $a_{1g}$  mainly crosses the Fermi level and  $e'_g$ , which hybridized with the  $a_{1g}$ , also touches the Fermi level in  $\text{NaCo}_2\text{O}_4$ .<sup>18,19</sup> This scenario is consistent with the present photoemission study.

Figure 4 exhibits the O  $1s$  XAS of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ . Naturally, these spectra contain the information on which originated from the oxygen hybridized with Co  $3d$  and from the oxygen of intercalated  $\text{H}_2\text{O}$ . The spectral features below 532 eV are originated from the O states hybridized with the Co  $3d$  states, which are similar to the previous study.<sup>12</sup> Two distinctive peaks around 528 and 530 eV correspond to the transition from the O  $1s$  core level to the O  $2p$  states hybridized into the unoccupied Co states. However the spectra above 532 eV are totally different from those of typical Co oxides.<sup>20</sup> In the inset, previously reported XAS spectra of water in (a) gas, (b) ice, and (c) liquid phase are shown.<sup>21</sup> The gas-phase spectrum shows several conspicuous peaks, which corresponds to the excitation of O  $1s$  into the antibonding O–H molecular orbitals. On the other hand, the spectrum of ice and liquid water broadens due to the formation of the conduction band caused by a hydrogen bond network.<sup>21</sup> Overall features of the O  $1s$  XAS spectra above 532 eV in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  is analogous to that of ice. That is to say, the intercalated water forms two-dimensional ice structure between the Co layers.

However, we have noticed that the shape of the pre-edge peak around 535 eV is different from that of ice. Considering that the pre-edge peak reflects on the defect of hydrogen

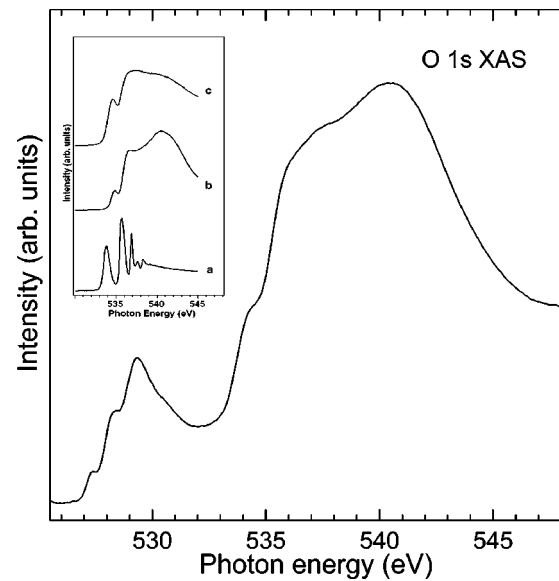


FIG. 4. X-ray absorption spectrum of  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  at the O  $K$ -edge at 11 K. The inset shows previously reported XAS spectra of water in (a) gas, (b) ice, and (c) liquid phase (Ref. 21).

bonds,<sup>21</sup> the formation of a characteristic hydrogen bonding network is different from that in a conventional ice, and has a possible influence on the superconductivity in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ . To explore the role of intercalated water on the electronic structure, we have performed Co  $1s$  XAS measurements in a hard x-ray region at 2 and 300 K for  $\text{Na}_{0.35}\text{CoO}_2$ ,  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.65\text{H}_2\text{O}$ , and  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ .<sup>11,22</sup> No energy shift of the Co  $1s$  XAS spectra indicates that the intercalated water gives no outstanding contribution to the Co layers in terms of a carrier doping, and a charge neutrality of water remains. However, for further discussion on a subtle change of electronic structure by intercalated water, we think that further high-resolution photoemission study is indispensable on a single crystal of the sample.

In summary, we have performed PES and XAS studies on  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ . In the Co  $2p$  PES spectra, the charge-transfer satellites are clearly observed, while in the resonant photoemission study, the resonant photoemission process and the Auger process comparably coexist with each other. It is revealed that the  $t_{2g}$  state with the low-spin configuration stays near the Fermi level. Considering the Co–O–Co bond angle, the hopping to the Co sites is expected to be small. In fact, the width of the  $t_{2g}$  related peak is comparatively narrow to the energy scale of an electron–lattice interaction. As a result, there is a possibility that the electron–phonon coupling predominantly works and gives rise to reducing  $T_c$  such as 5 K due to the formation of small polarons in the Co triangular lattice.

This work was done under Project No. 02S2-002 at the Institute of Materials Structure Science at KEK.

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- <sup>1</sup>K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, *Nature (London)* **422**, 53 (2003).
- <sup>2</sup>P. W. Anderson, *Mater. Res. Bull.* **8**, 153 (1973).
- <sup>3</sup>A. Tanaka and X. Hu, *Phys. Rev. Lett.* **91**, 257006 (2003).
- <sup>4</sup>G. Baskaran, *Phys. Rev. Lett.* **91**, 097003 (2003).
- <sup>5</sup>T. Waki, C. Michioka, M. Kato, K. Yoshimura, K. Takada, H. Sakurai, E. Takayama-Muromachi, and T. Sasaki, *cond-mat/0306036*.
- <sup>6</sup>W. Higemoto, K. Ohishi, A. Koda, R. Kadono, K. Ishida, K. Takada, H. Sakurai, E. T. Muromachi, and T. Sasaki, *cond-mat/0310324*.
- <sup>7</sup>The related compounds are studied recently by angle-resolved photoemission spectroscopy; M. Z. Hasan, Y.-D. Chuang, A. Kuprin, Y. Kong, D. Qian, Y. W. Li, B. Mesler, Z. Hussain, A. V. Fedorov, R. Kimmerling, E. Rotenberg, K. Rossnagel, H. Koh, N. S. Rogado, M. L. Foo, and R. J. Cava, *Phys. Rev. Lett.* **92**, 246402 (2004); H.-B. Yang, S.-C. Wang, A. K. P. Sekharan, H. Matsui, S. Souma, T. Sato, T. Takahashi, T. Takeuchi, J. C. Campuzano, R. Jin, B. C. Sales, D. Mandrus, Z. Wang, and H. Ding, *ibid.* **92**, 246403 (2004).
- <sup>8</sup>See, for example, R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, *Phys. Rev. B* **35**, 8818 (1987); Z.-X. Shen, J. W. Allen, J. J. Yeh, J.-S. Kang, W. Ellis, W. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, *ibid.* **36**, 8414 (1987); J. W. Allen, C. G. Olson, M. B. Maple, J. S. Kang, L. Z. Liu, J. H. Park, R. O. Anderson, W. P. Ellis, J. T. Markert, Y. Dalichaouch, and R. Liu, *Phys. Rev. Lett.* **64**, 595 (1990).
- <sup>9</sup>In a resonant photoemission for  $3d$  transition-metal compounds, a more drastic enhancement of resonant, photoemission is expected in the case of the  $2p \rightarrow 3d$  absorption threshold, than that in  $3p \rightarrow 3d$  absorption threshold.
- <sup>10</sup>See, for example, J. Hu, X.-D. Xiao, D. F. Ogletree, and M. Salmeron, *Science* **268**, 267 (1995); M. Odelius, M. Bernasconi, and M. Parrinello, *Phys. Rev. Lett.* **78**, 2855 (1997); Y. Zhu and S. Granick, *ibid.* **87**, 096104 (2001); S.-H. Park and G. Sposito, *ibid.* **89**, 085501 (2002).
- <sup>11</sup>K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, *J. Solid State Chem.* **177**, 372 (2004).
- <sup>12</sup>T. Mizokawa, L. H. Tjeng, P. G. Steeneken, N. B. Brookes, I. Tsukada, T. Yamamoto, and K. Uchinokura, *Phys. Rev. B* **64**, 115104 (2001).
- <sup>13</sup>R. H. Potze, G. A. Sawatzky, and M. Abbate, *Phys. Rev. B* **51**, 11 501 (1995).
- <sup>14</sup>M. Abbate, J. C. Fuggle, A. Fujimori, L. H. Tjeng, C. T. Chen, R. Potze, G. A. Sawatzky, H. Eisaki, and S. Uchida, *Phys. Rev. B* **47**, 16 124 (1993).
- <sup>15</sup>Z.-X. Shen, J. W. Allen, P. A. P. Lindberg, D. S. Dessau, B. O. Wells, A. Borg, W. Ellis, J. S. Kang, S.-J. Oh, I. Lindau, and W. E. Spicer, *Phys. Rev. B* **42**, 1817 (1990).
- <sup>16</sup>T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, *Phys. Rev. B* **56**, 1290 (1997).
- <sup>17</sup>The energy difference between the main peak and the satellite is  $\sim 5$  eV in CoO and  $\sim 10$  eV in (Bi,Pb)-Si-Co-O and (La,Sr)CoO<sub>3</sub>.
- <sup>18</sup>D. J. Singh, *Phys. Rev. B* **61**, 13 397 (2000).
- <sup>19</sup>T. Yamamoto, K. Uchinokura, and I. Tsukada, *Phys. Rev. B* **65**, 184434 (2002).
- <sup>20</sup>F. M. F. de Groot, M. Abbate, J. van Elp, G. A. Sawatzky, Y. J. Ma, C. T. Chen, and F. Sette, *J. Phys.: Condens. Matter* **5**, 2277 (1993).
- <sup>21</sup>S. Myneni, Y. Luo, L. A. Naslund, M. Cavalleri, L. Ojamaa, H. Ogasawara, A. Pelmenchikov, Ph. Wernet, P. Vaterlein, C. Heske, Z. Hussain, L. G. Pettersson, and A. Nilsson, *J. Phys.: Condens. Matter* **14**, L213 (2002).
- <sup>22</sup>K. Ono, M. Kubota, K. Takada, T. Sasaki, H. Kumigashira, J. Okabayashi, M. Oshima, M. Suzuki, N. Kawamura, M. Takagaki, and K. Fukuda (unpublished).