X-ray absorption study of layered Co oxides with a Co-O triangular lattice

T. Mizokawa,^{1,2} L. H. Tjeng,³ H.-J. Lin,⁴ C. T. Chen,⁴ R. Kitawaki,⁵ I. Terasaki,⁵ S. Lambert,⁶ and C. Michel⁶

¹Department of Complexity Science and Engineering, University of Tokyo, Chiba 277-8581, Japan

²PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

³II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

⁴Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan

⁵Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan

⁶Laboratoire CRISMAT, ISMRA et Universite de Caen, UMR 6508, Boulevard du Maréchal Juin, 14050 Caen Cedex, France

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We have studied the electronic structure of the quasi-two-dimensional Co oxides NaCo₂O₄(Na_xCoO₂, $x \sim 0.5-0.6$), Ca₃Co₄O₉, and Bi₂Sr₂Co₂O₉ using O 1*s* and Co 2*p* x-ray absorption (XAS) spectroscopy. We found that these Co-O triangular lattice systems have in common that their Co³⁺ and Co⁴⁺ ions are all low-spin, supporting the Koshibae-Tsutsui-Maekawa theory to explain the enhanced thermopower at elevated temperatures. The concentration of holes in the Co 3*d* t_{2g} shell is estimated to be about 0.4, 0.6, and 0.33, respectively. The O 1*s* XAS spectra strongly depend on the direction of polarization vector of the incoming x-ray. The polarization dependence indicates that the t_{2g} orbital anisotropy of Na_xCoO₂ is different from that of Ca₃Co₄O₉ and Bi₂Sr₂Co₂O₉. We argue that the difference of the orbital anisotropy and hole concentration are essential to explain why Na_xCoO₂, Ca₃Co₄O₉, and Bi₂Sr₂Co₂O₉ have different electric and magnetic properties at low temperatures.

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The new family of quasi-two-dimensional Co oxides, $NaCo_2O_4(Na_xCoO_2, x \sim 0.5 - 0.6)$,^{1,2} $Ca_3Co_4O_9$,³⁻⁵ and Bi₂Sr₂Co₂O₉,^{6,7} has in common that these materials contain layers of Co-O in a triangular lattice and that they show enhanced thermoelectric properties at elevated temperatures. The Co-O triangular lattice consists of edge-sharing CoO_6 octahedra as shown in Fig. 1. A theoretical study by Koshibae, Tsutsui, and Maekawa successfully explains these properties based on the mixed-valence state of Co³⁺ and Co⁴⁺ in the Co-O triangular lattice with spin and orbital degeneracy.8 Koshibae, Tsutsui, and Maekawa proposed that hopping transport of Co^{3+} and Co^{4+} species provides entropy flow that contributes to the thermoelectric property. Since the magnitude of the entropy flow depend on the spin and orbital degeneracy of the Co³⁺ and Co⁴⁺ species, it is highly important to study the local electronic configuration of Co³⁺ and Co⁴⁺. While the theory predicts that the thermopower is enhanced for the combination of low-spin Co³⁺ and low-spin Co⁴⁺, the x-ray absorption and photoemission study of the misfit layered cobaltite $Bi_2Sr_2Co_2O_9$ (Ref. 9) has shown that the hole-doped Co-O triangular lattice indeed has spin- $1/2 \text{ Co}^{4+}$ (low-spin Co⁴⁺) species in the nonmagnetic Co³⁺ (low-spin Co³⁺) background (see Fig. 1), supporting the Koshibae-Tsutsui-Maekawa theory. In order to confirm that the origin of the enhanced thermoelectric properties is commonly explained by Koshibae-Tsutsui-Maekawa theory in the three Co oxides, the local electronic configuration of Co^{3+} and Co^{4+} should be clarified in Na_xCoO_2 and $Ca_3Co_4O_9$.

Contrary to the common behavior at elevated temperatures, Na_xCoO_2 , $Ca_3Co_4O_9$, and $Bi_2Sr_2Co_2O_9$ have very different electric and magnetic properties at low temperatures. Among this family of Co oxides, only Na_xCoO_2 shows a good metallic behavior at low temperatures¹ while the other two Co oxides have relatively high resistivity.^{3,4,6} Very recently, it has been found that Na_xCoO_2 intercalated by H₂O molecules even shows superconductivity.¹⁰ Since then, the superconductivity in the Co-O triangular lattice has been attracting much interest and the mechanism of the superconductivity is under debate. $Ca_3Co_4O_9$ (Refs. 3,4) and $Bi_2Sr_2Co_2O_9$,⁶ on the other hand, show ferromagnetism or ferrimagnetism at low temperatures and the origin of the magnetism may be related to the geometry of Fermi surface of the Co-O triangular lattice.^{11,12} In order to understand the origin of the superconductivity and magnetism, it is very useful and important to study the electronic structure of these Co oxides using x-ray absorption spectroscopy (XAS) and reveal what is common and what is different in this family of



FIG. 1. A schematic drawing of the Co-O triangular lattice in Na_xCoO_2 , $Ca_3Co_4O_9$, and $Bi_2Sr_2Co_2O_9$. The Co-O triangular lattice consists of edge-sharing CoO_6 octahedra. The low-spin configurations for Co^{3+} and Co^{4+} ions are also indicated.



FIG. 2. O 1s XAS and Co 2p XAS spectra of Na_xCoO₂ as a function of incidence angle.

Co oxides. In particular, XAS can provide information on the concentration and orbital symmetry of the doped holes in the Co-O triangular lattice.

In the present work, using O 1s and Co 2p XAS measurements, we have studied the electronic structures of Na_xCoO₂ and Ca₃Co₄O₉, and compared them with that of Bi₂Sr₂Co₂O₉. XAS spectra of the layered compounds can depend on the direction of polarization vector of incoming x-ray, providing information on orbital symmetry of the carriers and important clues to reveal origins of the superconductivity in Na_xCoO₂ and the ferromagnetism or ferrimagnetism in Ca₃Co₄O₉.

The experiments were performed at the Dragon beamline, National Synchrotron Radiation Research Center in Taiwan. The XAS data were taken in the total electron yield mode as a function of the angle θ between the surface normal and the Poynting vector of the linearly polarized incoming light. The pressure of the chamber was 1×10^{-9} mbar during the measurements. Single crystals of Na_xCoO₂ ($x \sim 0.5$ –0.6) and Ca₃Co₄O₉ were cleaved *in situ* with the cleaved surfaces parallel to the *ab* or the CoO₂ planes. The misfit layered cobaltite Ca₃Co₄O₉ consists of the Ca(Co)-O rock-salt layer and the CoO₂ layer. The actual composition of the present Ca₃Co₄O₉ sample is approximately given by [Ca₂CoO₃][CoO₂]_{1.62}.⁵

Figure 2 shows the O 1s and Co 2p XAS spectra of Na_xCoO₂ for the incident angle θ of 0° and 60°. The data for θ =30° is almost identical to that for θ =0°. In the O 1s XAS

spectra, structure α is due to transitions from the O 1s core level to the O 2p orbitals that are mixed into the unoccupied Co t_{2g} states. Structures β and γ are transitions to the O 2p orbitals mixed into the unoccupied Co e_g states. The line shape of the Co 2p XAS spectra is rather peculiar in that the $2p_{3/2}$ and $2p_{1/2}$ peaks are very sharp with relatively small multiplet splitting. In fact, not only the line shape but also the integrated area ratio of the $2p_{3/2}$ and $2p_{1/2}$ peaks is quite similar to that found for EuCoO₃, a low spin system, and quite different from that of Sr₂CoO₃Cl, a high spin system.¹³ These results on the Co 2p XAS spectra indicate that the Co ions have the low-spin state character, i.e. t_{2g}^6 for Co³⁺ and t_{2g}^5 for Co⁴⁺ ions,^{14–17} implying also that the e_g states are fully unoccupied. This is supported by the fact that structures β and γ in the O 1s XAS show little angular dependence, consistent with the e_g states being fully unoccupied. The peak area of structure α in the O 1s XAS spectra increases in going from $\theta = 0^{\circ}$ to 60° . Structure α in the Co 2p XAS spectra is primarily due to the transition from the Co 2p core level to the unoccupied Co t_{2g} states. The intensity of structure α' in the Co 2p XAS spectra also increases in going from $\theta = 0^{\circ}$ to 60° which is consistent with the angular dependence of structure α .

Under trigonal crystal field, the t_{2g} orbitals are split into a_{1g} and e'_g orbitals which have primarily out-of-plane and in-plane characters, respectively. The hole population in the a_{1g} and e'_g orbitals can be estimated from the angular dependence of structure α . In the O 1s spectra of Bi₂Sr₂Co₂O₉, the peak area of structure α is strongly reduced at $\theta=0^{\circ}$ and rapidly increases with θ . The strong angular dependence indicates that holes are mainly located in the a_{1g} band in Bi₂Sr₂Co₂O₉.⁹ On the other hand, in Na_xCoO₂, structure α is already intense at $\theta=0^{\circ}$ and gains its intensity slightly in going from $\theta=0^{\circ}$ to 60°. The weak angular dependence in Na_xCoO₂ indicates that the orbital polarization of the holes is rather weak in Na_xCoO₂ compared to that in Bi₂Sr₂Co₂O₉. In other words, the holes in Na_xCoO₂ are located both in the a_{1g} band.

In order to quantitatively analyze the O 1s XAS data, we have fitted the O 1s XAS spectra using two Gaussians for structures α and β , and the tail of another Gaussian to represent the tail of structure γ . The area ratio of structure α at $\theta = 60^{\circ}$ to that at $\theta = 0^{\circ}$ is thus estimated to be 1.5. Since the peak area of O 1s XAS is determined by the dipole matrix element of the O 1s-2p transition, the transitions to the O $2p_x/2p_y$ and $2p_z$ orbitals have θ dependencies of $\cos^2 \theta$ and $\sin^2 \theta$, respectively. The a_{1g} orbital has the form of $(1/\sqrt{3})$ $\times (|x'y'\rangle + |y'x'\rangle + |z'x'\rangle) = |3z^2 - r^2\rangle$ and the two e'_g orbitals have the form of $1/\sqrt{3}(|x'y'\rangle + e^{\pm(2\pi/3)i}|y'x'\rangle + e^{\pm(4\pi/3)i}|z'x'\rangle)$, where the x', y', and z' axes are the three axes through the center and the corners of the CoO_6 octahedron. For the a_{1g} orbital, the transfer integral with $2p_z$ is $\frac{2}{3}(pd\pi)$ and the average transfer integral with $2p_x/2p_y$ is given by $\frac{1}{3}(pd\pi)$. For the e'_g orbitals, the average transfer integral with $2p_z$ is $\frac{1}{3}(pd\pi)$ and that with $2p_x/2p_y$ is $\sqrt{10/6(pd\pi)}$. Therefore, the intensity of structure α is expected to have the angular dependence of $((2n_a+5n_e)/18)\cos^2\theta + ((4n_a+n_e)/9)\sin^2\theta$. Here, n_a and n_e are the number of holes in the a_{1e} and e'_a states, respectively. The area ratio of structure α at $\theta = 60^{\circ}$ to



FIG. 3. O 1s XAS and Co 2p XAS spectra of Ca₃Co₄O₉ as a function of incidence angle.

that at $\theta = 0^{\circ}$ is given by $(26n_a + 11n_e)/(8n_a + 20n_e)$ that is estimated to be 1.5 experimentally. The analysis of the angular dependence shows that the ratio n_a/n_e is ~1.5. Since the t_{2e} hole concentration in Na_xCoO₂, namely $n_a + n_e$, is estimated to be 0.4 as explained later, 0.24 holes/Co are located in the a_{1g} band and 0.16 holes/Co are located in the e'_{g} band. Since the LDA calculation for Na_xCoO₂ predicts that the e'_g band is much wider than the a_{1g} band,¹¹ the holes in the e'_g band would be responsible for the well-developed metallic behavior in Na_rCoO₂ which is in contrast to the bad metallic behavior in $Bi_2Sr_2Co_2O_9$. Probably, the holes in the a_{1g} band are almost localized and are responsible for the enhanced magnetic susceptibility commonly observed in these Co oxides. Apparently, the holes in the e'_{g} band gives the difference between Na_xCoO₂ and the other two Co oxides. This picture agrees with the model proposed by Maignan et al.18 and would give an important insight that the e'_{a} band is playing essential role in the superconductivity found in Na_xCoO₂ intercalated by H₂O molecules.

Figure 3 shows the O 1s and Co 2p XAS spectra of $Ca_3Co_4O_9$ as a function of incidence angle. The line shape of the Co 2p XAS indicates that Co^{3+} and Co^{4+} ions have also the low-spin configurations as in Na_xCoO_2 and $Bi_2Sr_2Co_2O_9$.⁹ We note that the Co 2p XAS of $Ca_3Co_4O_9$ does not show any Co^{2+} component. This is important since it indicates that the Co-O rock-salt layers also present in this compound have the similar low spin Co^{3+} (or Co^{4+}) configuration as the Co-O triangular layers. In the O 1s spectra of



FIG. 4. Co 2p XAS spectra of Bi₂Sr₂Co₂O₉, Na_xCoO₂, and Ca₃Co₄O₉ as a function of incidence angle.

Ca₃Co₄O₉, the intensity of structure α is reduced at θ =0° and rapidly increases with θ as observed in Bi₂Sr₂Co₂O₉.⁹ The intensity ratio of structure α at θ =60° to that at θ =0° is estimated to be 3.

The strong angular dependence has several implications concerning the location of the doped holes and their orbital character. If there is hole doping in the Co-O rock-salt layer, then one would expect to see an intensity for $\theta = 0^{\circ}$ due to holes transferred via π -bonding to the p_x or p_y orbitals of the in-plane oxygen or to the p_x or p_y orbitals of the out-of-plane oxygen, with the latter case being more likely since the structure study has shown that the out-of-plane Co-O bond in the Co-O rock-salt layers is the shortest one.⁴ However, we do not observe a significant intensity at $\theta = 0^{\circ}$. Therefore, we can safely conclude that the hole doping does not take place in the Co-O rock-salt layers and that most of the hole doping occurs in the Co-O triangular layers. The strong angular dependence can then be taken as an indication that holes are mainly located in the a_{1g} band of the Co-O triangular layers in Ca₃Co₄O₉. The area ratio of structure α at θ =60° to that at $\theta = 0^{\circ}$ is given by $(26n_a + 11n_e)/(8n_a + 20n_e)$. Since the ratio $(26n_a+11n_e)/(8n_a+20n_e)$ is estimated to be 3 for Ca₃Co₄O₉ from the angle dependence of the peak area, the ratio n_e/n_a is calculated to be ~ 0.04 . This value is very similar to that of the Bi₂Sr₂Co₂O₉, suggesting strongly that the magnetic transitions found in Bi₂Sr₂Co₂O₉ and Ca₃Co₄O₉ have a similar origin.

Figure 4 shows the Co 2p XAS spectra of Bi₂Sr₂Co₂O₉, Na_rCoO_2 , and $Ca_3Co_4O_9$ taken at an incidence angle of 60°. The Co 2p XAS spectra are normalized using the peak height of the main peak. The relative intensity of structure α' is 1, 1.2, and 1.8 for $Bi_2Sr_2Co_2O_9$, Na_rCoO_2 , and $Ca_3Co_4O_9$, respectively. Since the transition matrix elements for the a_{1g} and e'_{q} orbitals are similar at the angle of 60°, it is reasonable to assume that the area of structure α' reflects the amount of the hole concentration. In the previous photoemission and x-ray absorption study of Bi₂Sr₂Co₂O₉, the hole concentration in the CoO_2 layer is estimated to be 0.33.⁹ Assuming that the amount of holes is 0.33/Co in Bi₂Sr₂Co₂O₉, those in Na_rCoO_2 and $Ca_3Co_4O_9$ are estimated to be 0.4/Co and 0.6/Co, respectively. The obtained result is summarized in Table I. The obtained value for $Ca_3Co_4O_9$ is consistent with the estimation from the chemical composition in that the CoO₂ layer in Ca₃Co₄O₉ is heavily hole-doped¹⁹ although

TABLE I. Hole population in the $a_{1g}(n_a)$ and that in the $e'_g(n_e)$ orbitals in the Co-O triangular lattice for Bi₂Sr₂Co₂O₉, Na_xCoO₂, and Ca₃Co₄O₉ obtained from the present XAS study.

	Bi ₂ Sr ₂ Co ₂ O ₉	Na _x CoO ₂	Ca ₃ Co ₄ O ₉
n _a	0.33	0.24	0.6
n _e	0	0.16	0

the obtained value for Ca₃Co₄O₉ is higher than the hole concentration of 0.5/Co estimated from the chemical composition of Ca₃Co₄O₉. Also the obtained values are consistent with the estimation from the magnetic susceptibility of Bi₂Sr₂Co₂O₉ and Ca₃Co₄O₉. Probably, holes in the a_{1g} band are responsible for the enhanced magnetic susceptibility observed in these Co oxides although the hole concentration in the a_{1g} band is ranging from 0.3 to 0.6.

Very recently, Wu *et al.* has reported XAS study of Na_xCoO_2 .²⁰ The reported polarization dependence of structure α is more or less consistent with the present result for Na_xCoO_2 and is much smaller than the present result for $Ca_3Co_4O_9$. If the carriers in Na_xCoO_2 is dominated by a_{1g} character as argued by Wu *et al.*,²⁰ it is impossible to explain the larger angle dependence observed in $Ca_3Co_4O_9$. Since the analysis in the present work can provide a systematic description of the three systems, the obtained orbital popula-

tion would be more reliable. In future, the polarization dependence of the O 1s XAS spectra should be analyzed using more realistic and sophisticated models to resolve this discrepancy.

In conclusion, we have studied the electronic structure of quasi-two-dimensional Co oxides Na_xCoO₂ and Ca₃Co₄O₉ using O 1s and Co 2p x-ray absorption spectroscopy. We found that the Co-O triangular layers in Na_xCoO₂, Ca₃Co₄O₉, and Bi₂Sr₂Co₂O₉ are hole doped and commonly take the low-spin Co^{3+} and Co^{4+} configurations. The present result supports the theory by Koshibae, Tsutsui, and Maekawa to explain the enhanced thermopower at elevated temperatures. On the other hand, the incidence-angle dependence of the O 1s XAS spectra indicates that the t_{2g} orbital anisotropy of Na_xCoO₂ is small compared with those of Ca₃Co₄O₉ and Bi₂Sr₂Co₂O₉. We suspect that this difference is essential to explain why Na_xCoO₂, Ca₃Co₄O₉, and Bi₂Sr₂Co₂O₉ have different electric and magnetic properties at low temperatures.

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- ¹I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12 685 (1997).
- ²K. Fujita, T. Mochida, and K. Nakamura, Jpn. J. Appl. Phys., Part 1 **40**, 4644 (2001).
- ³A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, Phys. Rev. B 62, 166 (2000).
- ⁴Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, and T. Tajitani, Jpn. J. Appl. Phys., Part 1 **39**, L531 (2000).
- ⁵S. Lambert, H. Leligny, and D. Grebille, J. Solid State Chem. **160**, 322 (2001).
- ⁶T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsubone, M. Ichihara, and K. Kobayashi, Jpn. J. Appl. Phys., Part 1 **39**, L747 (2000).
- ⁷H. Leligny, D. Grebille, O. Pérez, A. Masset, M. Hervieu, C. Michel, and B. Raveau, C. R. Acad. Sci. Paris, Série IIc. 2, 409 (1999).
- ⁸W. Koshibae and S. Maekawa, Phys. Rev. Lett. **87**, 236603 (2001); W. Koshibae, K. Tsutsui, and S. Maekawa, Phys. Rev. B **62**, 6869 (2000).
- ⁹T. Mizokawa, L. H. Tjeng, P. G. Steeneken, N. B. Brookes, I. Tsukada, T. Yamamoto, and K. Uchinokura, Phys. Rev. B 64, 115104 (2001).
- ¹⁰K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A.

Dilanian, and T. Sasaki, Nature (London) 422, 53 (2003).

- ¹¹D. J. Singh, Phys. Rev. B **61**, 13 397 (2000).
- ¹²R. Asahi, J. Sugiyama, and T. Tani, Phys. Rev. B 66, 155103 (2002).
- ¹³Z. Hu, Hua Wu, M. W. Haverkort, H. H. Hsieh, H.-J. Lin, T. Lorenz, J. Baier, A. Reichl, I. Bonn, C. Felser, A. Tanaka, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. **92**, 207402 (2004).
- ¹⁴J. van Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F. de Groot, and T. S. Turner, Phys. Rev. B 44, 6090 (1991).
- ¹⁵ 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).
- ¹⁶M. 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).
- ¹⁷T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B 56, 1290 (1997).
- ¹⁸A. Maignan, S. Hébert, M. Hervieu, C. Michel, D. Pelloquin, and D. Khomskii, J. Phys.: Condens. Matter **15**, 2711 (2003).
- ¹⁹J. Shimoyama, S. Horii, K. Otzschi, M. Sano, and K. Kishio, Jpn. J. Appl. Phys., Part 1 42, 1194 (2003).
- ²⁰W. Wu, D. Huang, J. Okamoto, A. Tanaka, H. Lin, F. Chou, A. Fujimori, and C. Chen, cond-mat/0408467.