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Orbital symmetry and electron correlation in Na_xCoO_2

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Abstract

We present measurements of polarization-dependent soft X-ray absorption on Na_xCoO_2. The results reveal that the electronic states determining the low-energy excitations of Na_xCoO_2 have predominantly a_{1g} symmetry with significant O 2p character. A large transfer of spectral weight observed in O 1s X-ray absorption provides spectral evidence for strong electron correlations in Na_xCoO_2 with the Na doping higher than half. For the Na concentration less than half, our measurements of O 1s absorption suggest that Na_xCoO_2 exhibits band-like electronic character.

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Keywords: Orbital polarization; Soft X-ray absorption

Sodium cobalt oxides (Na_xCoO_2) have attracted renewed interest because of their exceptionally large thermoelectric power [1] and the discovery of superconductivity in their hydrated counterparts [2]. Despite intensive experimental and theoretical works, there remain many unresolved issues concerning the electronic structure of Na_xCoO_2, including the orbital character of the valence electrons responsible for low-energy excitations and the Coulomb correlations of Co 3d electrons [3].

The lattice of Na_xCoO_2 exhibits a trigonal distortion, leading to a splitting of t_{2g} states into e_g' and a_{1g} states. The e_g' states spread over the *ab* plane, whereas the a_{1g} state extends to the *c*-axis [4]. Band-structure calculations in the local-density approximation (LDA) show that the a_{1g} state has a one-particle energy higher than that of e_g' and is most relevant to low-energy excitations [5]. These calculations are however, different from a crystal-field approach in which the compressed trigonal distortion stabilizes the a_{1g} state [6].

Many microscopic models with strong electron correlations explicitly included have been proposed to explain the spectacular properties of Na_xCoO_2 [6–9]. To comprehend the effect of electron correlations is imperative for an understanding of the electronic structure of Na_xCoO_2. On the other hand, a recent LDA + U study (LDA including the on-site Coulomb energy *U*) [10] explains the Fermi surface measured by angle-resolved photoemission [11,12] and concludes that Na_xCoO_2 is a moderately correlated system. One, therefore, requires further spectral evidence for strong electron correlations to justify microscopic models of correlated electrons for Na_xCoO_2.

Here, we report measurements of soft X-ray absorption spectroscopy (XAS) on Na_xCoO_2 pertinent to its orbital character of the electronic states determining the low-energy physics. We discuss the spectral character of strongly correlated electrons of Na_xCoO_2 with various Na concentrations. We measured XAS of Na_xCoO_2 with the Dragon beamline at the National Synchrotron Radiation Research Center in Taiwan. Details of XAS measurements and sample preparation are discussed elsewhere [13,14].

In order to determine the symmetry of electronic states in the low-energy excitations, we resorted to measurements of polarization-dependent O 1s XAS of $Na_{0.5}CoO_2$, as plotted in Fig. 1. The O 1s XAS shows that

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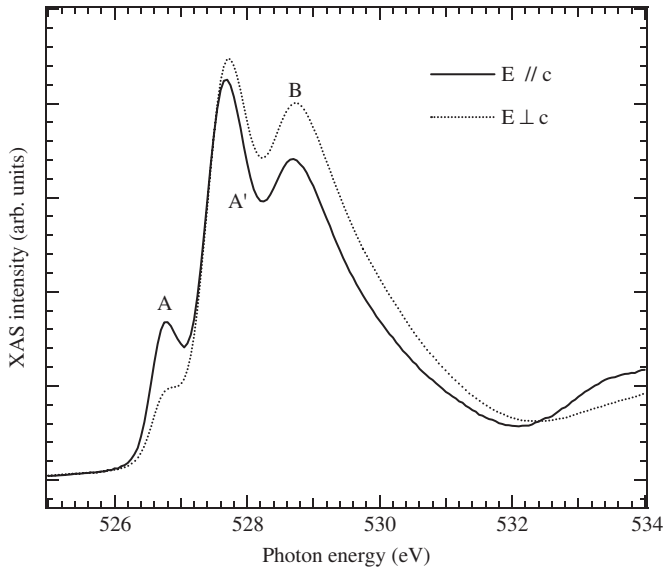

Fig. 1. Polarization-dependent O 1s XAS of $Na_{0.5}CoO_2$ with the **E** vector of the light perpendicular (dotted line) and parallel (solid line) to the *c*-axis.

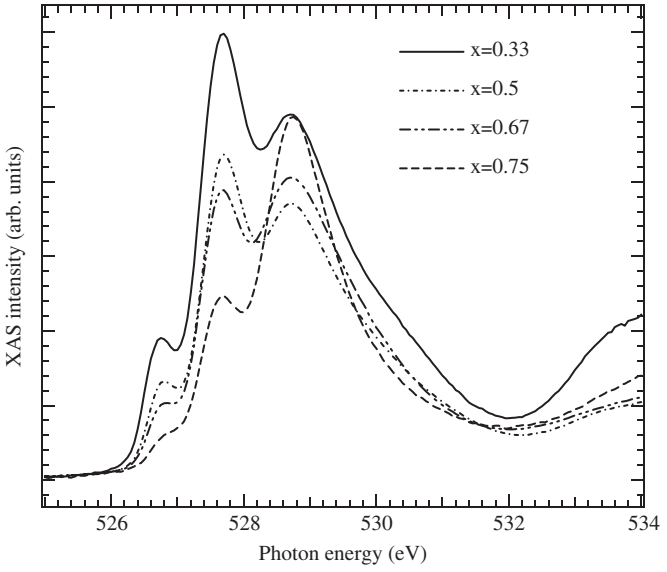

Fig. 2. Doping-dependent isotropic O 1s XAS spectrum of $Na_{0.5}CoO_2$, i.e., $(I_{\parallel} + I_{\perp})/2$.

the lowest-energy peak at 526.8 eV (labelled as A) has a strong *z* component, indicating an out-of-plane electronic state. The in-plane components of two other peaks at 527.6 and 528.7 eV (labelled as A′ and B, respectively) are slightly larger than their corresponding out-of-plane components. Because peak A and A′ (or B) have opposite polarizations, peak A results predominantly from adding an electron to a state of a_{1g} symmetry, whereas peaks A′ and B correspond to adding electrons to states of e_g symmetry. In other words, the symmetries of the transitions associated with peaks A, A′ and B correspond mainly to $(a_{1g})^1 \rightarrow (a_{1g})^2$, $(a_{1g})^1 \rightarrow (a_{1g})^1(e_g)^1$, and $(a_{1g})^2 \rightarrow (a_{1g})^2(e_g)^1$, respectively. O 1s XAS of $Na_{0.5}CoO_2$ with final states of a_{1g} symmetry has a large out-of-plane polarization, whereas that with e_g symmetry has an in-plane polarization.

We plot doping-dependent isotropic O 1s XAS of Na_xCoO_2 in Fig. 2. As the doping *x* increases from 0.5 to 0.67 and 0.75, the intensities of peaks A and A′ decrease, but peak B increases in intensity. These variations of XAS peaks are derived from the change in the relative concentration of Co^{4+} and Co^{3+}, because a fraction *x* of Co^{4+} changes to Co^{3+} when the mother compound CoO_2 is doped with Na. The peaks A and A′ (peak B) originate from O 2p hybridized with Co^{4+} (Co^{3+}) 3d states and correspond to adding one electron to the Co^{4+} states of a_{1g} and e_g symmetries (Co^{3+} of e_g symmetries), respectively. Such a spectral-weight transfer of the one-electron addition observed in Na_xCoO_2 is a general feature of strongly correlated systems [15]. In contrast, the doping-dependent XAS spectra of Na_xCoO_2 when Na concentration less than 0.5 do not exhibit a spectral weight transfer as observed in Na_xCoO_2 with high Na doping and other correlated oxides. We found that the unoccupied O 2p density of states in the vicinity of the Fermi level obtained from LDA + U calculations [16] are consistent with the measured XAS spectra of Na_xCoO_2 with low Na doping, e.g., $x = 0.3$ and 0.33, suggesting a band-like electronic character.

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References

[1] I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B 56 (1997) R12685.
[2] K. Takada, et al., Nature 422 (2003) 53.
[3] Ref. [13] and references therein.
[4] If the *z*-axis is along the *c*-axis, a_{1g} is $d_{3z^2-r^2}$; e'_g are $1/\sqrt{3}(d_{yz} + \sqrt{2}d_{xy})$ and $1/\sqrt{3}(d_{zx} - \sqrt{2}d_{x^2-y^2})$.
[5] D.J. Singh, Phys. Rev. B 61 (2000) 13397.
[6] W. Koshibae, S. Maekawa, Phys. Rev. Lett. 91 (2003) 257003.
[7] G. Baskaran, Phys. Rev. Lett. 91 (2003) 097003.
[8] Q.-H. Wang, D.-H. Lee, P.A. Lee, Phys. Rev. B 69 (2004) 092504.
[9] B. Kumar, B.S. Shastry, Phys. Rev. B 68 (2003) 104508; O.I. Motrunich, P.A. Lee, Phys. Rev. B 69 (2004) 214516.
[10] P. Zhang, et al., Phys. Rev. Lett. 93 (2004) 236402.
[11] M.Z. Hasan, et al., Phys. Rev. Lett. 92 (2004) 246402.
[12] H.-B. Yang, et al., Phys. Rev. Lett. 92 (2004) 246403.
[13] W.B. Wu, et al., Phys. Rev. Lett. 94 (2005) 146402.
[14] F.C. Chou, et al., Phys. Rev. Lett. 92 (2004) 157004.
[15] H. Romberg, et al., Phys. Rev. B 42 (1990) 8768; C.T. Chen, et al., Phys. Rev. Lett. 66 (1991) 104; P. Kuiper, et al., Phys. Rev. Lett. 62 (1989) 221.
[16] P. Zhang, et al., Phys. Rev. B 70 (2004) 085108.