Orbital symmetry and electron correlation in Na$_x$CoO$_2$

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Abstract

We present measurements of polarization-dependent soft X-ray absorption on Na$_x$CoO$_2$. The results reveal that the electronic states determining the low-energy excitations of Na$_x$CoO$_2$ 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$_x$CoO$_2$ with the Na doping higher than half. For the Na concentration less than half, our measurements of O 1s absorption suggest that Na$_x$CoO$_2$ exhibits band-like electronic character.

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Sodium cobalt oxides (Na$_x$CoO$_2$) 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$_x$CoO$_2$, 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$_x$CoO$_2$ 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$_x$CoO$_2$ [6–9]. To comprehend the effect of electron correlations is imperative for an understanding of the electronic structure of Na$_x$CoO$_2$. 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$_x$CoO$_2$ is a moderately correlated system. One, therefore, requires further spectral evidence for strong electron correlations to justify microscopic models of correlated electrons for Na$_x$CoO$_2$.

Here, we report measurements of soft X-ray absorption spectroscopy (XAS) on Na$_x$CoO$_2$ 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$_x$CoO$_2$ with various Na concentrations. We measured XAS of Na$_x$CoO$_2$ 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 Ni$_{0.5}$CoO$_2$, as plotted in Fig. 1. The O 1s XAS shows that
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 a1g symmetry, whereas peaks A and B correspond to adding electrons to states of eg symmetry. In other words, the symmetries of the transitions associated with peaks A, A' and B correspond mainly to (a1g) \( ^1 \rightarrow (a_1g)^2 \), (a1g) \( ^1 \rightarrow (a_1g)^1(e_g)^1 \), and (a1g) \( ^2 \rightarrow (a_1g)^2(e_g)^1 \), respectively. O 1s XAS of Na\(_{x}\)CoO\(_2\) with final states of a1g symmetry has a large out-of-plane polarization, whereas that with eg symmetry has an in-plane polarization.

We plot doping-dependent isotropic O 1s XAS of Na\(_{x}\)CoO\(_2\) 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 a1g and eg symmetries (Co\(^{3+}\) of eg symmetries, respectively). Such a spectral-weight transfer of the one-electron addition observed in Na\(_{x}\)CoO\(_2\) is a general feature of strongly correlated systems [15]. In contrast, the doping-dependent XAS spectra of Na\(_{x}\)CoO\(_2\) when Na concentration less than 0.5 do not exhibit a spectral weight transfer as observed in Na\(_{x}\)CoO\(_2\) 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\(_{x}\)CoO\(_2\) with low Na doping, e.g., x = 0.3 and 0.33, suggesting a band-like electronic character.

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