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X-ray spectroscopy study on the electronic structure of hole-doped edge-shared chains in $Ca_{2+x}Y_{2-x}Cu_5O_{10}$

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Abstract

X-ray absorption (XAS) and emission (XES) spectroscopy near O K edge has been performed on edge-shared CuO chain compounds $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ ($0.0 \le x \le 2.0$) using poly- and single-crystalline samples. Two large peaks are observed at 528 eV (P_H) and 530 eV (P_U) in the XAS spectra. The intensity of the P_H peak monotonically increases and that of the P_U monotonically decreases with hole doping. The two characteristic peaks in the XAS spectra at P_H and P_U, which are assigned for the polycrystalline samples to the hole and upper Hubbard band (UHB) states, respectively. The theoretical calculations reproduce the experimental XAS results, especially that the P_U peak decreases by hole doping. The spectral weight transfer from the P_U peak to the P_H peak of the edge-shared chain by hole doping is strongly suppressed in comparison with that of the CuO_2 plane. From the single crystal measurements of undoped $Ca_2Y_2Cu_5O_{10}$, the spectra of XAS and XES are interpreted in terms of a square-like CuO_4 plaquette for the compound. As for the hole-doped $Ca_3YCu_5O_{10}$ sample, the plaquette containing a doped hole is found to be square-like, and the plaquettes with no doped holes are found to be rectangle-like. We concluded that the doped hole is localized associated with the lattice deformation. The electric properties are discussed based on our result.

Keywords: XAS; XES; Edge-shared chain; One-dimensional cuprate; Localized hole

1. Introduction

It has been about 18 years since the first report on high T_c superconductors (HTSCs) by Bednorz and Müller [1], but the origin of high T_c superconductivity is controversial even now. The issue is related to the highly correlated electron systems in the two-dimensional CuO_2 plane. Recently, ladder compounds composed of one-dimensional Cu–O chains have been focused on experimentally and theoretically in the context of superconductivity of a highly correlated electron system, because an even-leg ladder system has a spin-gap. This gives the possibility of superconductivity in the spin-gap system as pointed out by Dagotto and Rice, who have predicted a spin-gap in even-leg ladder compounds and superconductivity in these compounds with hole doping [2].

Superconductivity has been not found in pure ladder compounds, but Uehara et al. have reported that the compound $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$ shows superconductivity under high pressure [3]. This discovery has motivated research in low-dimensional systems [4–6], but unfortunately, the spin-ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ contains both the two-

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leg ladder structure and the edge-shared chain structure. Thus there is ambiguity regarding the hole distribution between these two structures. Although the theoretical prediction of superconductivity in the hole-doped even-leg ladder system seems to be realized in this compound, the electronic properties of the ladder structure have not been clarified because of its complex crystal structure mentioned above. Therefore, the study of simple structure compounds which contain only chains or ladders, is important in order to clarify the electronic structure of low-dimensional cuprates.

The compound $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ contains only edge-shared CuO chain structure, and has a solid solution range of $0.0 \leq x \leq 2.0$. This compound is suitable for research into the electronic properties of chain structures because of its simple crystal structure and the control of hole concentration provided by changing the trivalent Y ion content x. The crystal structure of the compound is closely related to that of $NaCuO_2$ and contains one-dimensional edge-shared CuO chains along the a-axis [7–10]. Miyazaki et al. [11] have analyzed the crystal structure of $(Ca_{1-x}Y_x)_{0.82}CuO_2$ ($0 \leq x \leq 0.435$) by means of the Rietveld method using powder X-ray diffraction. They have discussed the dependence of the Cu─O inter-atomic distance and the angle of O─Cu─O along the a-axis on the hole concentration per Cu ion, n. Thereafter, Isobe et al. [12] have studied the crystal structure of $Ca_{0.824}CuO_2$ ($n = 0.35$) by the Rietveld refinement of X-ray diffraction data using a super-space group. They have determined the hole distribution by bond-valence sum (BVS) calculation. Hayashi et al. [13] have reported electric and magnetic properties of the compound $Ca_{2+x}Y_{2-x}Cu_5O_{10}$. The hole-doped compound $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ ($x > 0$) is not metallic in sharp contrast with the HTSCs containing CuO_2 plane which becomes metallic by hole doping. The temperature dependence of the electrical conductivity σ indicates variable range hopping in the low-hole-doped compound $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ ($0 \leq x \leq 1.5$) and the heavily hole-doped compound $Ca_4Cu_5O_{10}$ shows resistivity of thermal activated type [13].

Researches on the electronic structure of low-dimensional cuprates and nickelates (included corner-shared chain and edge-shared chain) were performed using photoemission spectroscopy (PES) on valence band and 2p core-level of Cu and Ni atom in conjunction with detailed many-body calculation including full multiplet interactions [14–17]. Systematic changes in the electronic structure with lowering of the dimensionality have been found to be driven by two factors: (1) a suppression of the non-local contribution to screening and (2) a systematic decrease of the charge-transfer energy Δ.

The doped holes in cuprates locate mainly on the oxygen sites rather than the copper sites, as the undoped cuprate is a charge-transfer insulator. Soft X-ray absorption (XAS) and emission (XES) spectroscopy near the O K edge is useful tool in order to clarify the electronic structure of a hole-doped CuO chain. XAS and XES near the O K edge give direct information of the partial density of states (PDOS) of oxygen, i.e., the hole (empty) and electron (occupied) states of oxygen are directly measured. Because of the dipole transition between O 1s and O 2p orbitals, XAS and XES of single crystals provide direct information on the PDOS of oxygen on selective p-orbitals. However, for interpretation of XAS and XES spectra, we must take into consideration of p–d hybridization and the crystalline configuration of Cu and O. Chen et al. [20] first pointed out the relationship between the hole-number in the CuO_2 plane and the intensity of the hole and upper Hubbard band (UHB) states in XAS for polycrystalline $La_{2-x}Sr_xCu_2O_4$ (LSCO). That is, with increasing holes in the CuO_2 plane, the hole-state spectral weight increases and UHB states decrease, respectively. They have reported that the intensity of UHB in the $n = 0.2$ sample decreases to about one-half of that of the undoped sample. Thereafter, Eskes et al. [18] have discussed the hole-number dependence of the total-spectral weight of X-ray photoemission spectroscopy (XPS) and inverse X-ray photoemission spectroscopy (IXPS) taking the p–d hybridization into consideration. They have pointed out that the hole-state spectra strongly depend on the p–d hybridization, i.e. for low-doped region, the intensity of the hole state for the p–d hopping integral $t_{pd} = 2.0\,eV$ is about three times than that of $t_{pd} = 0.0\,eV$. However, they only discussed XPS and IXPS results, and did not explore XES and XAS. Thus the p–d hybridization dependence of the spectral weight for XES and XAS remains to be carefully considered. Hu et al. [19] have discussed the O K XAS spectrum for the several polycrystalline samples with edge-shared chain structures in wide hole-doped region ($n = 0.0$–1.0). They have reported that the spectral weight transfer from the UHB state to the hole state by hole doping is strongly suppressed in comparison with that of the CuO_2 plane discussed by Chen et al. [20]: the UHB feature of the edge-shared chain is observed even up to $n = 0.67$. They have studied the XAS intensity of the one-dimensional edge-shared chain of various elements ($Ca_{0.83}CuO_2$, $Sr_{0.73}CuO_2$, and $Ba_{0.67}CuO_2$) with high hole-doping levels, but the elements with low-hole-doping levels (cf. HTSC and the spin-ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$) have not been studied in detail. The purpose of the present study is to observe the hole-number dependence of the electronic structure of oxygen by XAS and XES in a one-dimensional edge-shared chain system with low-hole concentration using the unique crystal system $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ ($0.0 \leq x \leq 2.0$). We discuss the hole state in the edge-shared chain from the polarization dependence between the XAS (XES) spectra of $\vec{E}//a$-axis and $\vec{E}//c$-axis.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ ($0.0 \leq x \leq 2.0$) were prepared by solid-state reaction. Appropriate amounts of $CaCO_3$ (99.99%), Y_2O_3 (99.99%) and CuO (99.99%) powders were mixed and calcined at 900 °C in air