

Hole State in Ladder-Compound (Sr,Ca)₁₄Cu₂₄O₄₁ by Soft X-ray Absorption and Emission Spectroscopies

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INTRODUCTION

Recent studies on low dimensional system have been focussed on the spin-ladder compound because of the theoretical respect which indicates a possibility of superconductivity on ladder system with even number legs.[1] Actually, two-leg ladder compound, SrCu₂O₃ shows spin-gap, while three-leg ladder compound, Sr₂Cu₃O₅, shows gapless spin excitation.[2,3] Unfortunately, SrCu₂O₃ has no holes and does not show superconductivity, but the compound Sr_{14-x}Ca_xCu₂₄O₄₁ shows superconductivity under high pressure with high Ca doping x . [4] This compound possesses both Cu₂O₃ two-leg ladder layer and edge-shared CuO₂ chain layer. The compound has six self-doped holes per chemical formula, and these holes are distributed on Cu-O sites in ladder and chain with an appropriate weights. The nominal hole number in the compound does not change with Ca doping x , but the conductivity in ambient pressure increases with an increase of x . In order to estimate the hole distribution between ladder and chain sites in the compound, spin-polarized neutron diffraction measurement was performed on Ca free compound, Sr₁₄Cu₂₄O₄₁, and the result suggests that almost holes (5 holes) exist in chain site.[5] The increase of electric conductivity might be due to a change of hole distribution between ladder and chain sites with Ca doping. High conductivity should originate from holes in ladder site because an impurity suspends the electronic transport in one dimensional Cu-O chain. In order to clarify the change of hole distribution (hole transfer from chain to ladder) in the compound, Ca-content dependent of the optical conductivity has been measured.[6] From the results, number of holes in ladder was estimated to increase with increase of x , although considerable amount of holes are still in chain site for high Ca content x . The purpose of our study is to estimate the hole distribution of O-2*p* state directly using X-ray absorption (XAS) and emission (XES) near O-K edge on single crystal which gives information on empty and occupied states of O-2*p* orbitals on selected crystalline sites, respectively.

EXPERIMENTS

The single crystalline samples, Sr_{14-x}Ca_xCu₂₄O₄₁ ($x=0.0$ and 11.5), were prepared by Traveling -Solvent Floating-Zone (TSFZ) method in an oxygen atmosphere, and were characterized by X-ray diffraction measurements. Before XAS and XES measurements, the samples were cut and polished. XAS and XES measurements were performed at KEK-PF BL19B and ALS BL8.0.1, respectively. The spectra were taken with the polarization vector of

the incident X-ray parallel to the crystalline a - and c -axes, i.e., perpendicular and parallel to the ladder, respectively.

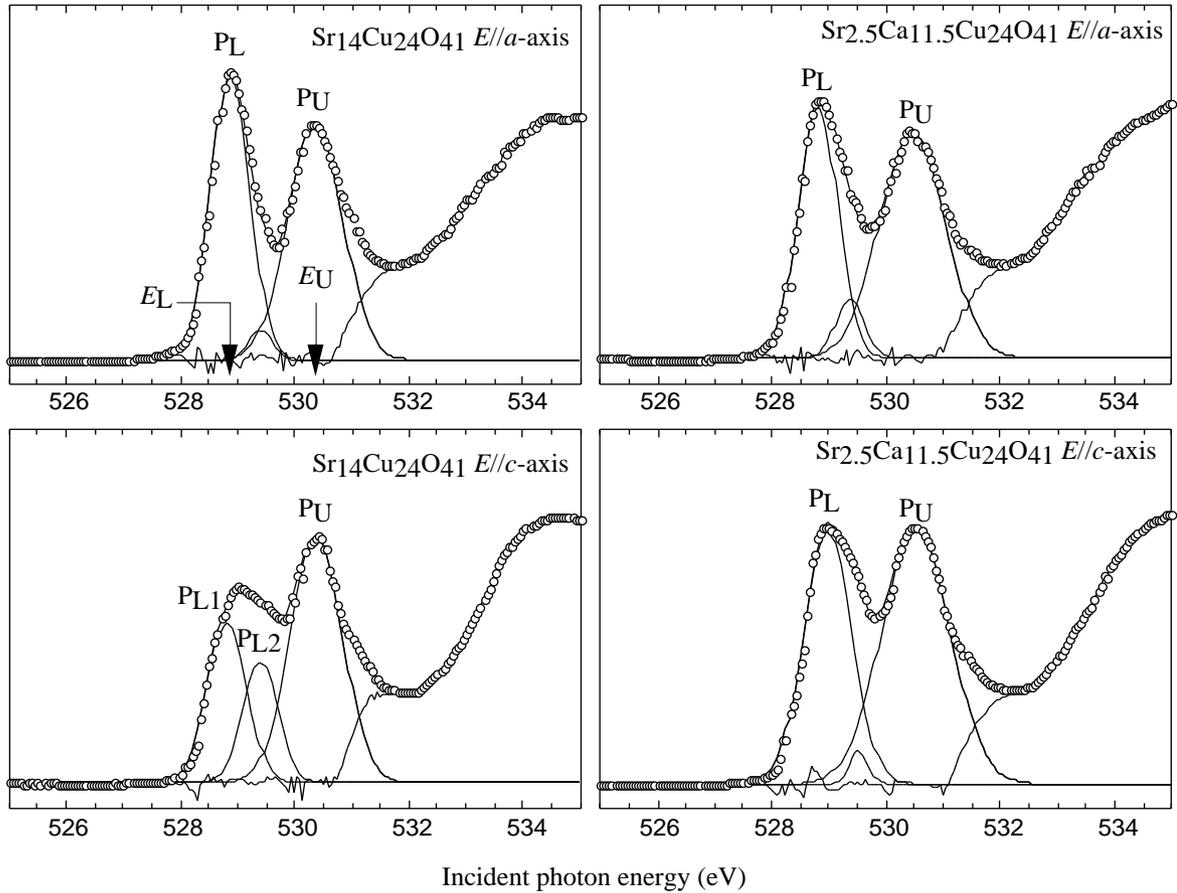


Fig. 1 XAS spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_{2.5}\text{Ca}_{11.5}\text{Cu}_{24}\text{O}_{41}$ at RT.

RESULTS AND DISCUSSIONS

Figure 1 shows the polarization dependence ($E//a$ - and c -axes) of XAS spectra of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($x=0.0$ and 11.5) at room temperature. The intensity is normalized by the intensity of the incident X-rays and scaled to unity at around $E=600$ eV. All the spectra contain two characteristic peaks (P_L and P_U) at the energy region, $E < 532$ eV. The total area intensity of the two peaks keeps being constant for all the spectra. The XAS spectrum of chain compound Li_2CuO_2 shows only one peak at around 530 eV (around E_U). This compound has no holes, then the P_U peak is assigned to upper Hubbard band (UHB) states of oxygen $2p$ on chain sites. Therefore, the P_L corresponds to hole state. For $x=0.0$ compound, there is large anisotropy between $E//a$ - and c -axes spectra. The large anisotropy observed in $x=0.0$ compound comes from holes on ladder sites because the angle between Cu-O-Cu in chain is close to 90 degrees, which shows isotropic hole distribution, i.e., isotropic XAS spectrum. But the possibility of holes in locally distorted chain remains. Furthermore, the peak P_L in $E//c$ spectrum of low-conductivity compound, $x=0.0$, seems to be composed of two peaks, P_{L1} and P_{L2} . When Ca content x increases, the conductivity increases, and the intensity of P_{L2} decreases, while that of P_{L1} increases. Because the conductivity along c -axis is larger than that along a -axis, holes in P_{L1} state contribute the conductivity. Figure 2 shows XES spectra of $x=0.0$ and 11.5 compounds with the excitation energy E_{ex} of E_L and E_U . The area intensity between E of 515 and 535 eV is

normalized to unity. These spectra show no Ca-content and crystalline-axis dependencies. But there is a difference between the spectra with $E_{\text{ex}}=E_{\text{L}}$ and $E_{\text{ex}}=E_{\text{U}}$. For all the hole-state excitation spectra, $E_{\text{ex}}=E_{\text{L}}$, a sharp non-bonding p state and relatively broadened bonding state are observed at about 525 and 523 eV, respectively. On the other hands, all the UHB-state excitation spectra are broad and not resolved to bonding and non-bonding states. These are similar profile of those of Li_2CuO_2 . To clarify the nature of the electronic structure of hole state, $\text{P}_{\text{L}1}$ and $\text{P}_{\text{L}2}$, observed in XAS spectra, it is necessary to measure XAS spectra with more high resolution to resolve $\text{P}_{\text{L}1}$ and $\text{P}_{\text{L}2}$, and to assign these two peaks by combining X-ray absorption and emission spectroscopies. This work was supported by a Grant-in-Aid for Science Research from the Japan Ministry of Education, Science and Culture.

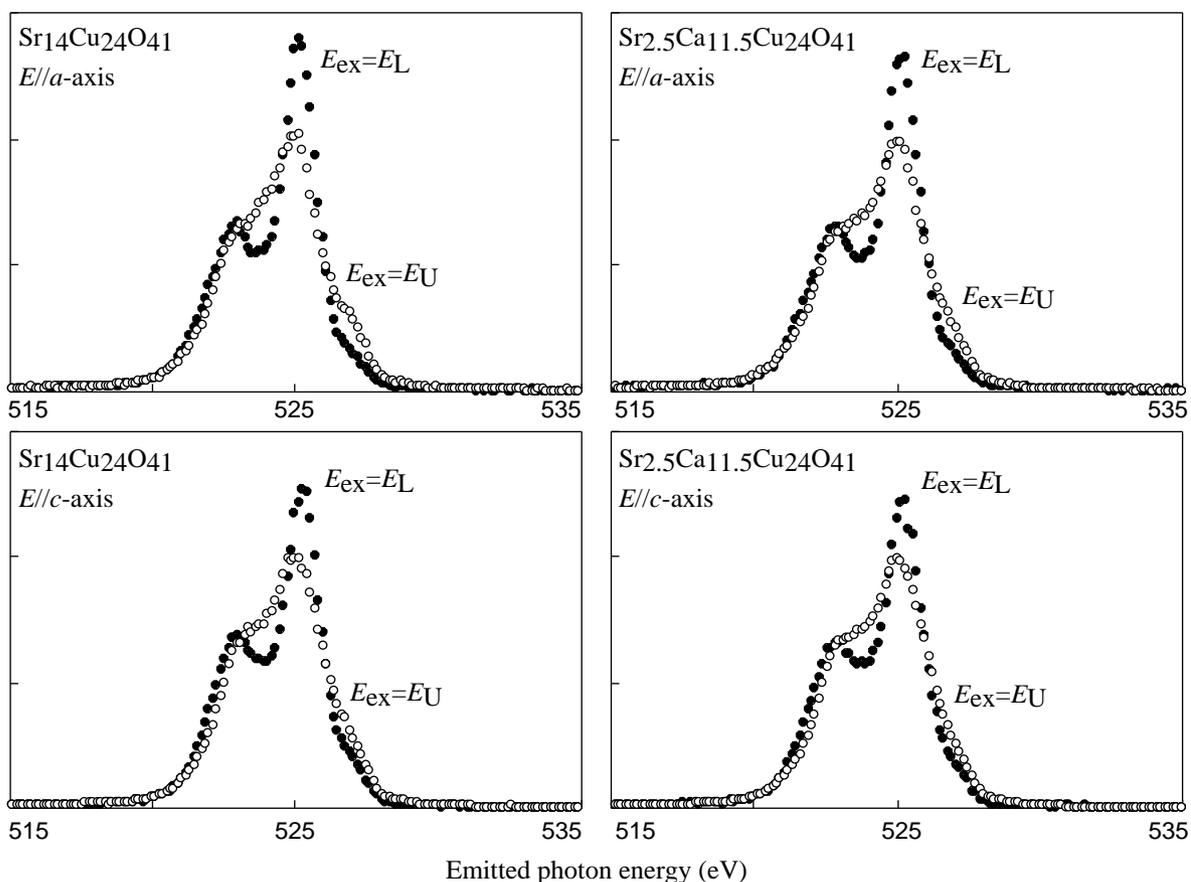


Fig. 2 XES spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_{2.5}\text{Ca}_{11.5}\text{Cu}_{24}\text{O}_{41}$ at RT.

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