



Polarization analysis of x-ray absorption at the O 1s absorption edge in PrBa₂Cu₃O₇: Unusual electronic structure in CuO₂ plane

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The polarization dependence of x-ray absorption at the oxygen 1s absorption edge in untwinned LuBa₂Cu₃O₇ and PrBa₂Cu₃O₇ single crystal specimens was measured. The hole states of oxygen in the CuO₂ plane in PrBa₂Cu₃O₇ locate at higher energy position than those of the oxygen in the CuO₂ in superconducting LuBa₂Cu₃O₇, although the hole states of chain sites remain at the same energy position in both Pr123 and Lu123 samples. Although they are mainly of $p\sigma$ character rather than of $p\pi$ and were attributed as an upper Hubbard band, a possibility was pointed out that a trace of $p\pi$ character hole states in the CuO₂ plane exists in Pr123. The formation of Zhang-Rice singlet is suppressed by $p\pi$ holes in the CuO₂ plane on account of the strong Coulomb interaction on an oxygen site.

PrBa₂Cu₃O₇ is unique in being a semiconductor and not a superconductor having an isostructure with YBa₂Cu₃O₇(Y123), while all the other RBa₂Cu₃O₇ (R=rare-earth element) are superconductors with almost the same critical temperature 90 K. The suppression of the superconductivity by Pr in (Pr_xY_{1-x})Ba₂Cu₃O₇ has been discussed on the basis of three main mechanisms [1]. The first is that Pr is tetravalent, extra electrons are released and fill the holes in the CuO₂ plane. The second is that the magnetic moment of Pr suppresses superconductivity through the Cooper-pair breaking mechanism. The third is that the strong hybridization of Pr 4f and O 2p orbitals promotes the localization of mobile holes in the CuO₂ plane and reduces the superconducting transition temperature. Fehrenbacher and Rice [2] pointed out the unusual electronic structure which is composed of three independent components: insulating CuO₂ planes with oxidation state Cu^{II}, mixed-valent Pr ions with almost equal numbers of

Pr^{III} and Pr^{IV} and CuO₃ chains. They also argued that the difference from the high-Tc superconductors comes from an enhanced stability of the Pr^{IV} state due to the hybridization of Pr with O neighbors, and involves a transfer of holes from primarily O 2p σ to O 2p π states.

In order to detect the transfer of holes from primarily O 2p σ to O 2p π states in the CuO₂ plane, we made a polarization analysis of x-ray absorption spectra of oxygen 1s state. Using this technique, we could distinguish the electronic states of O(2) and O(3) in CuO₂ plane from the other oxygen states in x-ray absorption spectra [3] and could detect the electronic structure of CuO₂ in PrBa₂Cu₃O₇. In this paper we report on the site-selective x-ray absorption measurements on the untwinned PrBa₂Cu₃O₇ and LuBa₂Cu₃O₇ single crystals.

Samples were prepared using a self-flux growth, annealed in oxygen atmosphere and then detwinned by a thermal-mechanical method [4].

Polarized soft x-ray absorption at the O 1s edge was collected using polarized synchrotron radiation at the beam line BL-19B at Photon Factory, KEK, with the revolver undulator excitation light source. All measurements were made at 30 K and with resolution of 0.1 eV in a energy range from 520 eV through 540 eV and also with resolution of 0.2 eV from 520

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eV through 590 eV, using the VLM 19 monochromator with a varied-line spacing plane grating whose average groove density is 2400. Photon energy of the monochromator was calibrated within 0.1 eV by photo-electron spectroscopy for Au 4f peaks.

The absorption was monitored by the amount of the fluorescence light emitted from the sample using a photo-diode. The x-ray absorption measurement using the fluorescence yield is insensitive to the surface in contrast to the surface-sensitive total electron yield method. The primary intensity of light (I_0) was monitored by the total electron yield from the mirror of the monochromator. All spectra were normalized using the data between 580 and 590 eV.

Figure 1 shows the polarization dependence of the x-ray absorption spectra of $\text{LuBa}_2\text{Cu}_3\text{O}_7$ between 526 and 539 eV. The spectrum for $E \parallel a$ has a sharp peak of the Lorentzian shape with $\text{FWHM}=0.6\text{eV}$ at 529.0 eV. The spectrum exhibits the hole states of O(2) of the CuO_2 plane. The spectrum $E \parallel b$ in the corresponding energy range instead is apparently composed of two parts: a broad spectrum in the lower energy side is that of the chain site O(1) and a sharp spectrum in the higher energy side is that of plane site O(3). The latter is very similar to the one for $E \parallel a$. The spectrum for $E \parallel c$ is broad and of a trapezoidal shape of apical O(4).

Figure 2 shows the spectrum for untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$. The spectrum for $E \parallel a$ has a broad and gaussian peak. The peak position and the lower half maximum position of the peak shift by 0.8eV and 0.3eV higher in energy compared with those of $\text{LuBa}_2\text{Cu}_3\text{O}_7$, respectively. The spectrum for $E \parallel b$ is also apparently composed of two parts, a lower energy broad spectrum and a higher energy broad spectrum. The latter is very similar to the one for $E \parallel a$. The spectrum for $E \parallel c$ is almost the same as that of $\text{LuBa}_2\text{Cu}_3\text{O}_7$. The hole states of the chain sites remain the same in fundamental structure in both Pr123 and Lu123 samples.

The sharp spectra for oxygen (2) and (3) of the CuO_2 plane in $\text{LuBa}_2\text{Cu}_3\text{O}_7$ have the symmetry of $p\sigma$ in the CuO_2 plane and are thought to be the Zhang-Rice singlet. We should note that the narrow hole states near the Fermi surface are reproduced theoretically around the extended saddle points for the doping 2D Hubbard system [5]. The spectra for O(2) and O(3) of the CuO_2 plane in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ are not of $p\pi$ character which Fehrenbacher and Rice predicted but of $p\sigma$ character in the CuO_2 plane. The spectra are rather broad and located at higher energy than those of $\text{LuBa}_2\text{Cu}_3\text{O}_7$. Therefore, the main

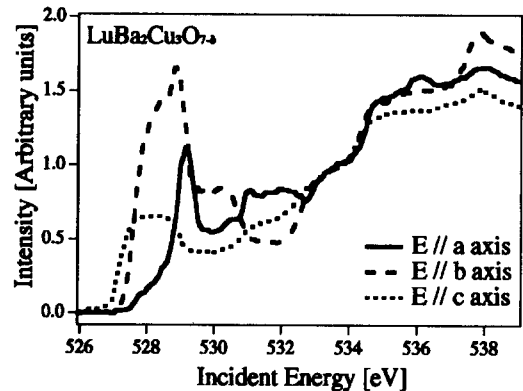


Fig. 1 Polarization dependence of x-ray absorption spectra of $\text{LuBa}_2\text{Cu}_3\text{O}_7$.

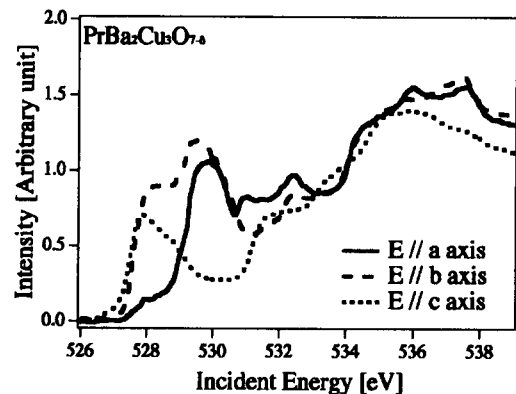


Fig. 2 Polarization dependence of x-ray absorption spectra of $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

spectra for O(2) and O(3) of the CuO_2 plane in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ are not due to the hole of $p\pi$ but to that of the upper Hubbard band. However, there is a possibility that a trace of a $p\pi$ symmetry spectrum in the CuO_2 plane is still present. When the $p\pi$ hole state is once formed, the intra-atomic Coulomb interaction between $p\sigma$ and $p\pi$ holes on an oxygen site suppresses the formation of the Zhang Rice singlet state and only the upper Hubbard states would be observed in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

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