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A Comparison between the Fehrenbacher-Rice and the Liechtenstein-Mazin models

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Unoccupied electronic states of $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (x = 0 - 1) thin films have been investigated using high-resolution polarization-dependent O K-edge x-ray absorption spectroscopy (XANES). After determining the hole distribution among different oxygen sites of the Pr-doped thin films, we compare the experimental data with the Fehrenbacher and Rice (FR) model and the Liechtenstein and Mazin (LM) model, both of which are based on the hybridization of Pr $4f_{z(x^2-y^2)}$ and O $2p_\pi$ orbitals in $PrBa_2Cu_3O_{7-y}$. Our experimental results are more consistent with the FR model.

Among the rare earth element-substituted isomorphic $YBa_2Cu_3O_{7-y}$ superconductors, $PrBa_2Cu_3O_{7-y}$ is an exception that fails to exhibit superconductivity. The suppression of superconductivity in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system is strongly related to the Pr concentration. A large number of theoretical models have been proposed to explain the absence of superconductivity in $PrBa_2Cu_3O_{7-y}$. However, Fehrenbacher and Rice (FR) proposed a localized Pr $4f_{z(x^2-y^2)}$-O $2p_\pi$ hybridized state which binds doped holes to Pr sites and causes a hole depletion in the CuO_2 planes [1]. The FR model also assumes that the O $2p_\pi$ orbitals rotate by an angle of about 45° and point toward the central Pr ion. Based on the idea of Pr $4f_{z(x^2-y^2)}$-O $2p_\pi$ hybridization (FR band), Liechtenstein and Mazin (LM) proposed another model in which the direct hopping between oxygen orbitals is taken into account [2]. They found that, in $PrBa_2Cu_3O_{7-y}$, there forms an additional hole-depleting band which crosses the Fermi level and consequently grabs holes from the CuO_2 band. However, in their model the O $2p_\pi$ holes are treated as planar (P_{xy}) character. It means that the rotation angle of O $2p_\pi$ orbitals is 0°. Since FR band may be closely related to the novel superconductivity in $PrBa_2Cu_3O_{7-y}$ which has been reported recently [3,4], it is of interest to put more stringent tests on these two competing models. To the rotation angle, denoted as γ, of O $2p_\pi$ orbitals to the CuO_2 plane, the predictions of the FR model and the LM model are quite different. In terms of the LM model, the rotation angle increases with Pr doping, while it decreases with Pr doping according to the FR model [4]. We derive the rotation angles for each Pr doping level from the O 1*s* XANES of $Y_{1-x}Pr_xBa_2Cu_3O_{6.9}$ thin films.

The well c-axis-oriented $Y_{1-x}Pr_xBa_2Cu_3O_{6.9}$ thin films with thickness of 400 nm were deposited on $SrTiO_3$ substrates by pulse laser deposition. The O K-edge x-ray absorption spectra were carried out using linearly polarized synchrotron radiation from 6-m high-energy spherical grating monochromator (HSGM) beamline located at SRRC, Taiwan. The in-plane spectra (**E**//ab, θ=0°, θ is the angle between the incoming beam and the sample surface normal) were obtained in a normal-incidence alignment. The samples were then rotated, with θ=60° and 75°, to obtain the polarized x-ray absorption spectra $I(\theta)$. According to $I(\theta)=I_{E//ab}\cos^2(\theta) + I_{E//c}\sin^2(\theta)$, we can obtain the out-of-plane spectra (**E**//c, θ=90°) spectra. The hole numbers can be obtained by integrating the cross sections of the spectra. The rotation angle γ for each sample with different Pr doping can be calculated by the following equations which are modified from those in Ref. [5],

$$\begin{aligned} &n_{Pr}=n_F(2-n_f),\\ &n_{FR}=n_F(n_f-1),\\ &2n_{E//ab}=n_{FR}\cos^2\gamma+n_{ZR}+n_{chain},\\ &n_{E//c}=n_{FR}\sin^2\gamma+n_{apex},\\ &n_{Pr}+n_{FR}+n_{ZR}+n_{apex}+n_{chain}=0.9 \end{aligned} \quad (1)$$

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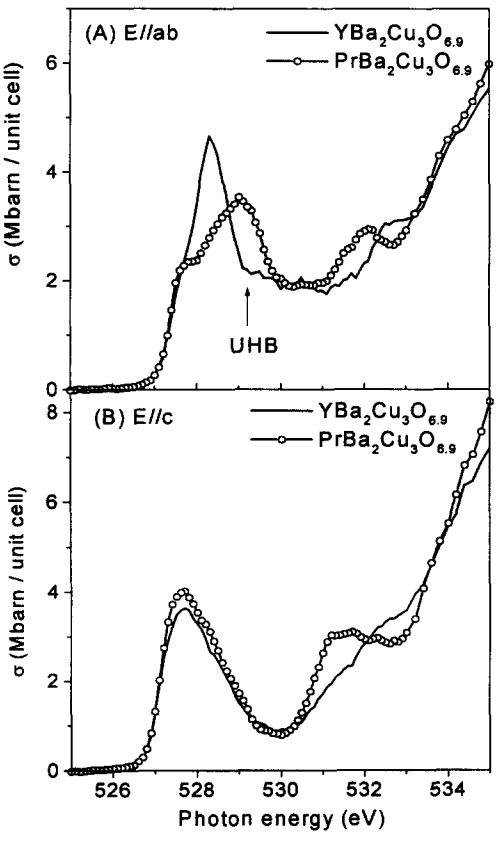

Fig. 1. O 1*s* absorption spectra of $YBa_2Cu_3O_{6.9}$ and $PrBa_2Cu_3O_{6.9}$ for polarization (A) E//ab and (B) E//c.

Where n_{Pr} denotes the number of holes transferred to Pr, n_{FR} the number of holes situated on the planar O $2p_\pi$ orbitals, n_F the density of Pr^{4+} ions, n_{ZR} the number of holes situated on the planar O $2p_\pi$ orbitals, n_{chain} the number of holes on the O sites in the CuO chains, n_{apex} the number of holes on the apical O sites, n_f the Pr^{4+} 4*f* electrons. The O K-edge XANES of $YBa_2Cu_3O_{6.9}$ and $PrBa_2Cu_3O_{6.9}$ for **E**//ab and **E**//c are plotted in Fig. 1. No spectrum contribution from the $SrTiO_3$ substrate was observed as reported in Ref. [6]. In the **E**//ab spectra, for $YBa_2Cu_3O_{6.9}$, the peak at about 528.5 eV is ascribed to the Zhang-Rice (ZR) band [4] and hole state in the CuO chains. However, for Pr-doped samples the peak also contains contributions from the FR state. In the **E**//c spectra, the peak at about 527.5 eV of $YBa_2Cu_3O_{6.9}$ is wholly attributed to hole state in the apical oxygen sites (n_{apex}). For Pr-doped samples, the peak also contains contributions from the FR state. In Fig. 2, the rotation angles of O $2p_\pi$ orbitals, γ, calculated by using equations (1) in which we take n_f=1.66, are plotted as a function of Pr concentration, *x*. It shows that γ decreases with increasing *x*.

Based on our measurements regarding the rotation angle of O $2p_\pi$ orbitals to the CuO_2 planes, our preliminary results are more consistent with the FR model than the LM model.

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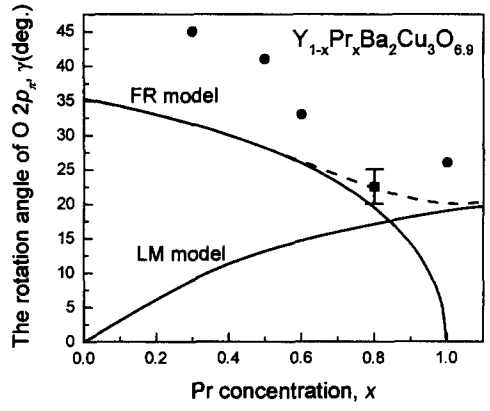

Fig. 2. The relation of the rotation angle of O $2p_\pi$, γ, and the Pr concentration, *x*. The possible value of γ for *x*=0.8 is from Ref. [5]. The two solid curves are predictions of the FR ($\sin^2\gamma=(2/3)(1-x)/(2-x)$) [4] and LM [7] models. The dash line indicates the argument that, because of dispersion of the FR band at large *x*, the FR model should give the same value of γ as the LM model at *x*=1 [4].

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