

## Soft x-ray absorption spectroscopy studies of doped Pr-containing cuprates

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Using high-resolution O *K*-edge x-ray absorption near-edge-structure (XANES) spectroscopy, unoccupied states of the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films and polycrystalline  $Pr_{1-x}Ca_xBa_2Cu_3O_7$  ( $x=0-0.3$ ) as well as  $R_{0.8}Pr_{0.2}Ba_2Cu_3O_7$  samples ( $R=Tm, Dy, Gd, \text{ and } Sm$ ) are investigated. In  $Y_xPr_{1-x}Ba_2Cu_3O_7$ , hole numbers in the  $CuO_2$  planes decrease significantly with increasing Pr doping level. Hole carriers generated via Ca doping in  $Pr_{1-x}Ca_xBa_2Cu_3O_7$  are directed predominantly into both the Zhang-Rice and Fehrenbacher-Rice (FR) states, while those in the  $CuO_3$  ribbons remain almost unchanged with Ca substitution. In  $R_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ , the hole content in the  $CuO_2$  planes decreases monotonically with increasing ionic size of the  $R^{3+}$  ions, confirming the hole depletion effect based on the Pr  $4f-O 2p$  hybridization. We demonstrate the spectroscopic evidence of the existence of the FR states. The present XANES results provide a deeper understanding of the nature of hybridization and the origin of the ionic size effect.

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### I. INTRODUCTION

One of the most controversial puzzles in the field of high- $T_c$  cuprates is the absence of superconductivity in  $PrBa_2Cu_3O_7$  (Pr123). In  $Y_xPr_{1-x}Ba_2Cu_3O_7$ ,  $T_c$  decreases monotonically with increasing Pr doping level, and superconductivity is completely quenched for a Pr content greater than 0.55.<sup>1</sup> In the  $R_xPr_{1-x}Ba_2Cu_3O_7$  series ( $R$  is a rare-earth element except for Ce, Tb, or Pm),  $T_c$  decreases with increasing ionic radius of the  $R$  ions at a fixed Pr concentration.<sup>2</sup> Furthermore, the Pr moments in  $PrBa_2Cu_3O_7$  order antiferromagnetically with a Neel temperature of 17 K.<sup>3</sup> This is in contrast to the other  $RBa_2Cu_3O_7$  compounds in which the rare-earth moments order at lower temperature ( $<2.5$  K). In spite of many experimental and theoretical investigations being undertaken, the mechanism of superconductivity suppression in  $PrBa_2Cu_3O_7$  is still the subject of controversial discussion.

Many models were proposed to explain the unique properties of Pr123 and related Pr-doped cuprates. These models include hole-filling,<sup>4</sup> hole localization,<sup>5</sup> percolation,<sup>6</sup> magnetic pair breaking,<sup>4,7</sup> hybridization,<sup>8-10</sup> disorder on the Ba site,<sup>11</sup> hole transfer from planes to chains,<sup>12</sup> etc. Among them, the existence of the Pr  $4f_{z(x^2-y^2)}-O 2p_{\pi}$  hybridized states proposed by Fehrenbacher and Rice (FR) is widely considered to be the most promising model, as it can explain many experimental results.<sup>8</sup> Based on this model, in  $PrBa_2Cu_3O_7$ , the hole carriers are localized in a hybridized state at the Pr sites with a mixture of  $4f^2L (+3)$  and  $4f^1 (+4)$  configurations.<sup>8</sup> Here  $L$  is a ligand hole in the O  $2p$  orbitals around the Pr sites, distributed over the eight nearest oxygen sites. They also proposed that the extra valence in addition to +3 for the Pr ion may not be detectable by some optical measurements.

Many efforts have been devoted to converting the Pr123 samples into superconductors. One common way to recover the superconductivity is to introduce additional holes into the

$CuO_2$  planes and thus induce superconductivity. It has been shown that Ca doping into the  $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$  samples leads to a substantial increase of hole numbers in the  $CuO_2$  planes and thus induces the superconductivity with  $T_c \sim 46$  K for  $x=0.2$  and  $y=0.98$ .<sup>13,14</sup> However, no superconductivity has been found in any bulk  $Pr_{1-x}Ca_xBa_2Cu_3O_7$  samples for  $x \leq 0.4$ . Recently, superconductivity around 90 K in Pr123 was reported in some low-temperature pulsed-laser deposited thin films and oxygen-annealed traveling-solvent floating-zone (TSFZ) grown single crystals.<sup>15,16</sup>  $T_c$  of the TSFZ Pr123 samples can be enhanced from 85 to 105 K under pressure.<sup>15</sup> In addition, superconductivity in sintered-polycrystalline Pr123 has also been reported.<sup>17</sup> These results are in contrast to earlier works. However, these reports are still debatable due to the lack of reproducibility of data and the existence of an anomalously long  $c$  axis for the structure of the superconducting Pr123 samples.<sup>15</sup> In order to account for the peculiar properties of superconducting Pr123, the possibility of superconductivity due to the FR states in Pr123 was recently proposed.<sup>18</sup> In addition, the FR model cannot explain the  $R$  dependence on the suppression of  $T_c$  in  $R_xPr_{1-x}Ba_2Cu_3O_7$ . Thus further experiments are needed to provide a deeper understanding of the nature of hybridization and the origin of the ionic size effect.

There is a general consensus that the hole states play a pivotal role for superconductivity in the  $p$ -type cuprate superconductors. Therefore, an understanding of the unoccupied electronic states near the Fermi level of cuprate superconductors is a crucial step toward unveiling the mechanism of superconductivity. Soft x-ray absorption spectroscopy using synchrotron radiation has been widely applied to probe the unoccupied states in materials and molecules. In particular, polarization-dependent x-ray absorption measurements are able to provide detailed information about the orbital character of hole states in the  $p$ -type cuprates.<sup>19,20</sup> In this study, utilizing high-resolution O *K*-edge x-ray absorption

near-edge-structure (XANES) spectra, unoccupied electronic states near the Fermi level of the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films and polycrystalline  $Pr_{1-x}Ca_xBa_2Cu_3O_7$  ( $x=0-0.3$ ) as well as  $R_{0.8}Pr_{0.2}Ba_2Cu_3O_7$  samples ( $R=Tm, Dy, Gd, \text{ and } Sm$ ) have been investigated. We demonstrate the spectroscopic evidence of the existence of FR states. The present XANES results help in understanding some recently controversial findings of Pr-doped cuprates, and shed light on the origin of the ionic size effect.

## II. EXPERIMENTS

The detailed procedures for the preparation of samples were reported elsewhere.<sup>21,22</sup> In brief, polycrystalline  $Pr_{1-x}Ca_xBa_2Cu_3O_7$  ( $x=0-0.3$ ) and  $R_{0.8}Pr_{0.2}Ba_2Cu_3O_7$  samples were prepared by the standard solid-state reaction method.  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films, with a thickness of  $\sim 4000$  Å, were deposited on the SrTiO<sub>3</sub> substrates by pulsed laser deposition. As checked by x-ray diffraction, all the samples under study are single phase and the thin films are highly preferentially oriented with the  $c$  axis perpendicular to the surface of the thin films.

X-ray absorption measurements were performed at the 6-m high-energy spherical grating monochromator beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. The x-ray absorption spectra were recorded by the x-ray-fluorescence yield mode using a microchannel plate detector. In contrast to the electron-yield measurement, the x-ray-fluorescence yield measurement is a bulk-sensitive technique with a probing depth of thousands of Å. The absorption spectra were corrected for the energy-dependent incident photon intensity as well as for self-absorption effects and normalized to tabulated cross sections in the energy range of 600–620 eV. The photon energy was calibrated using the known O  $K$ -edge absorption peaks of CuO. The energy resolution of the monochromator was set to  $\sim 0.2$  eV for the O  $K$ -edge energy range. The linear polarization of the monochromatic beam is estimated to be greater than 95%. In order to obtain  $E||c$  spectra, the polarized x-ray absorption spectra were recorded with different incidence angles of  $\theta = 0^\circ, 45^\circ, 60^\circ$  and  $75^\circ$  with respect to the surface normal. The absorption spectrum for  $\theta = 0^\circ$  corresponds to the normal incidence geometry where the electric-field vector  $E$  of the linearly polarized synchrotron light is parallel to the  $ab$  plane of the thin film. According to  $I(\theta) = I_{E||ab} \sin^2(\theta) + I_{E||c} \cos^2(\theta)$ , the  $E||c$  absorption spectrum can be deduced.

## III. RESULTS AND DISCUSSION

In Fig. 1, polarized O  $K$ -edge x-ray absorption spectra of the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films for  $E||ab$  and  $E||c$  polarization are depicted. The O  $1s$  x-ray-absorption spectra of the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  thin films can be divided into two regions. The low-energy pre-edge peaks are attributed to transitions from the O  $1s$  core electrons into the hole states with mainly O  $2p$  character on the oxygen sites. The strong rise in the spectral weight of the absorption spectra above 533 eV may be due to continuum absorption of the Ba  $4d$ , Cu  $4s$ , or Cu  $4p$  states hybridized with O  $2p$  states.<sup>23</sup>

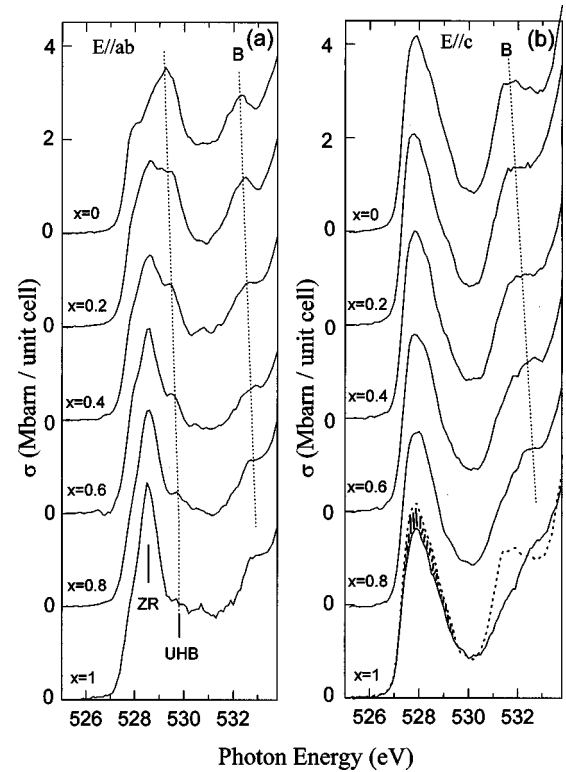


FIG. 1. Polarized O  $K$ -edge x-ray absorption spectra of the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films for (a)  $E||ab$  and (b)  $E||c$  polarizations. For comparison, the absorption spectrum of Pr123 is plotted as a dashed curve. The additional FR band is observed, as indicated by the hatched lines.

The x-ray absorption spectra, with energies beyond 540 eV for all the thin films, under study exhibit very similar features and are independent of Pr substitution (not shown). According to dipole selection rules, for  $E||ab$ , only the unoccupied electronic states with O  $2p_{xy}$  symmetry are accessible for the O  $1s$  transition, and, in the  $E||c$  case, the empty O  $2p_z$  states are probed. It is well established that, for  $E||ab$  spectra in Fig. 1(a), the absorption feature at  $\sim 528.4$  eV in  $YBa_2Cu_3O_7$  (Y123) is ascribed to the hole states in the  $CuO_2$  planes [i.e., Zhang-Rice (ZR) states], while the shoulder at  $\sim 527.8$  eV corresponds to the unoccupied states in the CuO chain.<sup>23</sup> The absorption peak at  $\sim 529.5$  eV is associated with an upper Hubbard band (UHB) with major Cu  $3d$  character. Feature B shows an increase in intensity with increasing Pr concentration and is assigned to the Pr  $5d$  states.<sup>24</sup>

Upon Pr substitution, the spectral weight of the ZR states is strongly reduced, while the UHB intensity is significantly enhanced at the same time. This change is attributed to the well-known transfer of spectral weight from the ZR states to the UHB due to strong correlation effects in the  $CuO_2$  planes. As noted from Fig. 1, the peak positions of the UHB and feature B are shifted to lower energies with increasing Pr doping level. This implies that the O  $1s$  core level along with Fermi level is shifted to higher energies with increasing Pr concentration.<sup>25</sup>

For the  $E||c$  spectra in Fig. 1(b), the absorption peak at  $\sim 527.8$  eV in Y123 is assigned to O  $2p_z$  hole states in the

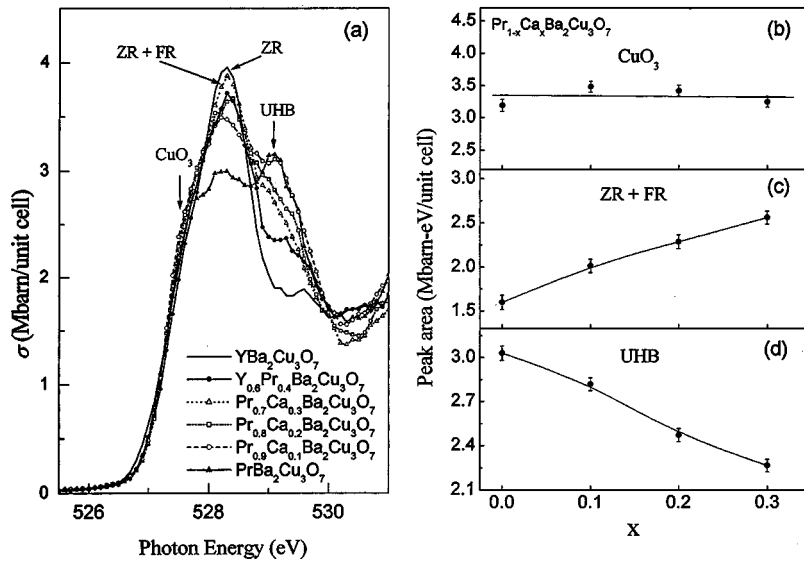


FIG. 2. (a) O  $K$ -edge x-ray absorption spectra of  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $x=0-0.3$ ), together with spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Y}_{0.6}\text{Pr}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_7$  for comparison. Integrated cross section of the (b)  $\text{CuO}_3$  ribbons, (c) ZR+FR states, and (d) upper Hubbard band (UHB) as a function of Ca doping ( $x$ ) in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ . The solid curves are drawn as a guide for the eyes.

apical oxygen sites.<sup>23</sup> Upon Pr substitution, an observed increase in the spectral weight indicates the existence of additional small band around 527.8–529.5 eV, as indicated by hatched lines. If this additional band is attributed to hole transfer from planes and chains to the apical oxygen sites, the reduction of hole carriers within the  $\text{CuO}_2$  planes and  $\text{CuO}$  chain in Fig. 1(a) should be approximately equal to the increase of hole numbers in the apical oxygen sites in Fig. 1(b), assuming that the O  $1s$  absorption cross section for the hole states in the apical oxygen sites is equal to that in the  $\text{CuO}_2$  planes (and  $\text{CuO}$  chain). In contrast, the increase of peak intensity at  $\sim 527.8$  eV in Fig. 1(b) is significantly smaller than the reduction of the spectral weight in the ZR states and  $\text{CuO}$  chain in Fig. 1(a) for a fixed Pr content. The additional spectral weight in the  $E\parallel c$  spectra of  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  is thus ascribed to the  $\text{Pr}4f\text{-O}2p$  hybridized states, otherwise known as the FR states for lack of another model.<sup>25,26</sup> Especially noteworthy is that this band lies in almost the same energy range as the ZR states observed for the  $E\parallel ab$  spectra below the UHB. Accordingly, the substitution of Y by Pr in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  triggers a transfer of hole carriers from the ZR states to energetically favored FR states, as evidenced in Fig. 1(a). It is clear that without the polarization-dependent XANES spectroscopy, there is no way to distinguish between the FR and ZR states. The experimental results provide the spectroscopic evidence in support of the FR model.

Figure 2(a) shows the O  $K$ -edge absorption spectra of  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $x=0-0.3$ ). For comparison, the absorption spectra of the polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Y}_{0.6}\text{Pr}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_7$  samples are also included. As discussed, the absorption feature around 527.8 eV corresponds to the unoccupied states in the  $\text{CuO}_3$  ribbons. It is clearly seen from Fig. 2(a) that Ca doping leads to a significant increase in the spectral weight of the pre-edge peak at  $\sim 528.4$  eV, indicating an increase in hole numbers. It is intriguing to compare the absorption spectra of  $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  and  $\text{Y}_{0.6}\text{Pr}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_7$ . As noted, the peak intensity at  $\sim 528.4$  eV in  $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  is comparable to that in  $\text{Y}_{0.6}\text{Pr}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_7$ , while the former shows a much higher

intensity in the UHB than the latter. It should be pointed out that the former is not superconducting, while the latter exhibits a  $T_c$  of  $\sim 45$  K. As demonstrated, an increase of hole carriers in the ZR states would be accompanied by a decrease of the spectral weight in the UHB. On the other hand, since the O  $2p_\pi$  orbital is not hybridized with the Cu  $3d$  states, it is presumed that the FR states have no correlation with the UHB.<sup>25</sup> Thus the experimental results clearly infer that some of the Ca-doped holes in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  reside on the FR states, and the other part of the doped holes are introduced into the ZR states at the expense of the UHB. The observed increase of the Pr valence in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  with Ca substitution can be interpreted in terms of additional doped holes into the FR states.<sup>27</sup>

The Ca-doped holes in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ , introduced into both the ZR and FR states, also suggest that the low-energy states of the ZR band overlap with the high-energy states of the FR band, as demonstrated in Fig. 1. This observation naturally explains why 20% Ca doping is not enough to induce Pr123 into being superconducting, as well as explaining why  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_7$  is still not superconducting, even though it has an amount of hole carriers comparable to Y123 [see Fig. 2(a)]. If all Ca-doped holes were directed into ZR states,  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_7$  would probably be a superconductor. However, the share of additional Ca-doped hole carriers with FR states leads only to the brink of superconductivity, up to 50% Ca doped into Pr123.

To quantify the results in Fig. 2(a) the spectral weight of the pre-edge peaks was analyzed by fitting with Gaussian functions. In order to define the peak widths for those three peaks, the results from related single crystals were referenced.<sup>13,25</sup> The energy shift of the UHB upon hole doping was also taken into consideration. The obtained hole distributions are consistent with those obtained from corresponding single crystals in the literature.<sup>13,25</sup> The resultant hole distributions and the spectral weight of the UHB for several compounds are shown in Figs. 2(b)–2(d), and listed in Table I. As noted from Fig. 2(b), hole carriers in the  $\text{CuO}_3$  ribbons remain almost unchanged with Ca substitution. Similar results were observed in the Ca-doped Y123 system.<sup>13</sup>

TABLE I. The normalized hole distributions and spectral weight of the UHB for various related compounds. We fix the number of holes in Y123 to one as in Ref. 13.

	ZR+FR (holes/ unit cell)	CuO <sub>3</sub> ribbon (holes/ unit cell)	UHB (Mbarn eV/ unit cell)
Pr <sub>0.7</sub> Ca <sub>0.3</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.43	0.55	2.27
Pr <sub>0.8</sub> Ca <sub>0.2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.38	0.57	2.47
Pr <sub>0.9</sub> Ca <sub>0.1</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.34	0.58	2.82
Y <sub>0.4</sub> Pr <sub>0.6</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.34	0.52	2.25
Y <sub>0.6</sub> Pr <sub>0.4</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.39	0.50	2.06
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.45	0.55	1.67
PrBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	0.26	0.53	3.03

Accordingly, hole carriers induced by Ca doping in Pr<sub>1-x</sub>Ca<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> are directed predominantly into the FR and ZR states [Fig. 2(c)] at the expense of the UHB [Fig. 2(d)]. Based on the theoretical calculations in Ref. 8 and Table I, it is estimated that at least 30% of Ca-doped holes in Pr<sub>0.7</sub>Ca<sub>0.3</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> are introduced into FR states.

In Fig. 3, the O *K*-edge x-ray absorption spectra of R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> for R=Tm, Dy, Gd, and Sm, are reproduced. As shown, the spectral weight of the pre-edge peak at ~528.4 eV decreases monotonically with increasing ionic size of the R<sup>3+</sup> ions. In contrast, the peak intensity at ~527.8 eV, corresponding to hole carriers in the CuO<sub>3</sub> ribbons, is nearly the same for all of the samples. Simulta-

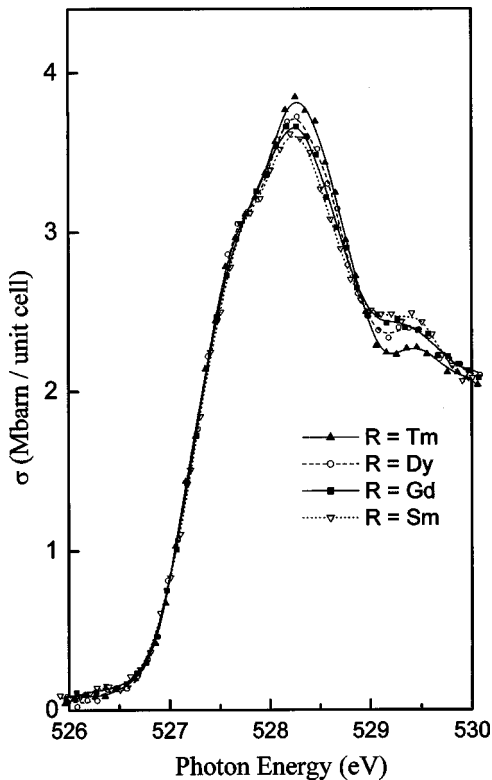


FIG. 3. O *K*-edge x-ray absorption spectra of R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> for R=Tm, Dy, Gd, and Sm.

neously, an increase of the spectral weight in the UHB at ~529.5 eV is observed from smaller to larger ionic radii of the rare-earth hosts ( $r_{Sm} > r_{Gd} > r_{Dy} > r_{Tm}$ ). This confirms that hole carriers are reduced mainly from the ZR states, not from the FR states. From the Hall measurements in R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, the Hall number (mobile hole) decreases roughly linearly with increasing the R<sup>3+</sup> ionic radius at a constant temperature,<sup>28</sup> in accordance with the present observation.

It has been demonstrated that the extent of the Pr 4*f*-O 2*p* hybridization in Pr-doped cuprates is determined predominantly to the Pr-O(2,3) bond length as well as O(2,3)-Pr-O(2,3) bond angle and the energy-level difference between the Fermi level  $E_F$  and the Pr 4*f* level ( $E_f$ ).<sup>29-31</sup> The larger ionic size of the R ions in R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> gives rise to strong steric effects, leading to a distortion of the local environment around the rare-earth ions. For example, x-ray-diffraction studies showed that an increase of *c*-axis lattice constant from 11.689 Å for Tm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> to 11.746 Å for Sm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is less than that of the ionic radius from 0.871 Å for Tm<sup>3+</sup> to 0.964 Å for Sm<sup>3+</sup> (Ref. 32). This trend is generally valid for the whole series of R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.<sup>28</sup> The lattice thus undergoes a monotonic compression with a larger ionic radius of the rare-earth hosts. This implies that the separation between the Pr ions and CuO<sub>2</sub> planes in Sm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is less than that in Tm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. It is thus expected that the hybridization between the Pr 4*f* states and O 2*p* orbitals in Sm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is more pronounced than that in Tm<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. This result may be associated with the increase of the Pr 4*f*-O 2*p* hybridization in R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> with an enlargement of the R<sup>3+</sup> ionic radius.

Based on the concept of the Pr-CuO<sub>2</sub> hybridization, Liechtenstein and Mazin calculated the electronic structure of R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> using an *ab initio* local-density approximation plus a Hubbard parameter and the Coulomb correlation in the Pr 4*f* shell.<sup>33</sup> They found that, in Pr123, an additional hole-depleting band forms, which crosses the Fermi level and consequently grabs the mobile holes from the ZR states. Upon doping different rare-earth elements in R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, the position of this hole-depleting band shifts with the ionic size of the R<sup>3+</sup> ions. In other words, the energy of the hole-depleting band (or FR states) may depend on the extent of the Pr 4*f*-O 2*p* hybridization.<sup>34</sup> Smaller ions on the R site in R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> reduce the extent of the Pr 4*f*-O 2*p* hybridization (as discussed above), leading to the lowering in position of the hole-depletion band (or FR states) relative to the ZR band. Accordingly, for smaller R<sup>3+</sup> ions in R<sub>x</sub>Pr<sub>1-x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, the resultant hole depletion is mitigated and the hole content in the ZR states is higher. The monotonic reduction of hole numbers in the CuO<sub>2</sub> planes with increasing ionic radius of the R<sup>3+</sup> ions in R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> provides clear evidence in support of hole-depletion effect based on the Pr 4*f*-O 2*p* hybridization.<sup>35,36</sup> Accordingly, the variations of the superconducting properties in R<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> may originate from the difference in the hybridization strength which is

caused by the local structural changes associated with different ionic radius of the  $R$  ions. The present results shed light on the origin of the ion size effect.

Our results also have implications on the recently reported superconductivity in  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  and the TSFZ Pr123 single crystals. It has been shown that  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  exhibits a  $T_c$  of  $\sim 52$  K in the orthorhombic phase, while it has a  $T_c \sim 97$  K in the tetragonal phase.<sup>37</sup> As compared to the orthorhombic phase, the tetragonal  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  phase exhibits a longer  $c$ -axis lattice constant, which may reduce the extent of the  $\text{Pr} 4f\text{-O} 2p$  hybridization. Accordingly, more Ca-doped holes in the tetragonal  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  phase are directed into the ZR states, which lead to a higher  $T_c$  value. Furthermore, it has been proposed that one possible mechanism for rendering the TSFZ Pr123 samples superconducting is due to Ba doping on the Pr sites.<sup>16</sup> The O  $K$ -edge absorption spectra of the Ba-rich  $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$  crystals show a slight increase of the hole carriers in the ZR states,<sup>26</sup> similar to the results for Ca doping in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  presented above. Correspondingly, the additional holes in the ZR states may induce the TSFZ Pr123 samples to become superconducting. On the other hand, an anomalously long  $c$ -axis lattice constant for the structure of superconducting Pr123 was reported.<sup>15</sup> As demonstrated, the extent of the  $\text{Pr-CuO}_2$  hybridization is very sensitive to the local structural changes around the rare-earth hosts. The enlarged lattice in the TSFZ Pr123 samples gives rise to a longer  $\text{Pr-CuO}_2$  distance, as well as a smaller  $\text{O}(2,3)\text{-Pr-O}(2,3)$  bond angle, and thus reduces the extent of hybridization significantly. This might lead to the localized FR states being pushed below the Fermi

level, and accordingly to a transfer of the doped holes from the FR states back to the ZR states, generating a metallic and superconducting sample.

#### IV. CONCLUSION

We have studied the unoccupied states of some doped Pr-containing cuprates by O  $K$ -edge x-ray absorption spectroscopy. In  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ , hole numbers in the  $\text{CuO}_2$  planes decrease significantly with increasing Pr doping level, which are caused by the transfer of hole carriers from the ZR states to the localized FR states. Hole carriers generated via Ca doping in  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  are directed predominantly into both the ZR and FR states, while those in the  $\text{CuO}_3$  ribbons remain almost unchanged with Ca substitution. In  $\text{R}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$ , the hole concentration in the  $\text{CuO}_2$  planes decreases monotonically with increasing ionic size of the  $R^{3+}$  ions, confirming the hole depletion effect arising from the hybridization of the O  $2p_\pi$  orbitals and  $\text{Pr} 4f_{z(x^2-y^2)}$  states. Although these measurements do not constitute proof of FR states, the observations demonstrate clear evidence of their existence. The present XANES results help understand some recently controversial findings of Pr-doped cuprates and shed light on the origin of the ionic size effect.

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