



# Pr-induced superconductivity suppression in $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$ probed by soft-X-ray absorption spectroscopy: a comparative studies of $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$ and $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$

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## Abstract

The variation of hole states with Pr doping for  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  and  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  has been investigated by O K-edge X-ray absorption spectroscopy. Upon Pr substitution,  $T_c$  suppression rate in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is slower than that in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ . For both systems, hole carriers in the  $CuO_2$  planes and  $CuO$  chains decrease monotonically with increasing Pr doping level. The depletion rate of hole carriers in the  $CuO_2$  planes with Pr doping in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is considerably slower than that in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ . The oxygen content affects the depletion rate of hole carriers in cuprates with Pr doping.

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## 1. Introduction

After the discovery of high- $T_c$  cuprate superconductors, Pr substitution in  $YBa_2Cu_3O_7$  has stimulated much research interest [1]. The absence of superconductivity and the anomalously high-Neel temperature 17 K of  $PrBa_2Cu_3O_7$  have long remained controversial puzzles [2,3]. In contrast, it

has been recently reported that  $PrBa_2Cu_3O_7$  single crystals grown by the oxygen-annealed traveling-solvent floating-zone method show superconductivity at  $\sim 85$  K and  $T_c$  enhancement to more than 100 K under pressure [4,5]. These results contradict other reports on the insulating  $PrBa_2Cu_3O_7$  single crystals. However, these reports are still controversial due to the lack of reproducibility of data. The absence or occurrence of superconductivity in  $PrBa_2Cu_3O_7$  has reopened the field for discussion.

The substitution of Y by Pr in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  leads to a significant decrease in  $T_c$  with

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superconductivity disappearing for Pr content greater than 0.55 [6]. For  $Y_xPr_{1-x}Ba_2Cu_4O_8$ ,  $T_c$  decreases monotonically with increasing Pr doping level from  $T_c=80$  K for  $x=1$  to  $T_c=6$  K for  $x=0.3$  [7]. The critical Pr concentration required to quench superconductivity in  $Y_xPr_{1-x}Ba_2Cu_4O_8$  is estimated to be  $\sim 0.72$ , which is larger than that of  $\sim 0.55$  in  $Y_xPr_{1-x}Ba_2Cu_3O_7$ .  $PrBa_2Cu_3O_7$  is an insulator, while the  $PrBa_2Cu_4O_8$  compound exhibits the metallic behavior in the  $CuO_2$  planes at low temperature [8]. The crystal structure of  $YBa_2Cu_4O_8$  is composed of two  $Cu(2)O(2)O(3)$  layers separated by a Y plane. The unit of  $CuO_2$  and Y planes is separated by a  $Cu_2O_4$  ribbon consisting of a  $BaO(4)$  plane, two  $Cu(1)O(1)$  chains along the  $b$ -axis and another  $BaO(4)$  plane. Upon Pr substitution, the  $Y_xPr_{1-x}Ba_2Cu_4O_8$  compounds remain the orthorhombic structure isomorphic with  $YBa_2Cu_4O_8$ . The structure of  $Y_xPr_{1-x}Ba_2Cu_4O_8$  is thus very similar to that of  $Y_xPr_{1-x}Ba_2Cu_3O_7$  except the double  $CuO$  chains instead of a single  $CuO$  chain. Accordingly, the comparative studies of  $Y_xPr_{1-x}Ba_2Cu_4O_8$  and  $Y_xPr_{1-x}Ba_2Cu_3O_7$  would be helpful to improve the understanding on the mechanism of Pr-induced superconductivity suppression in  $PrBa_2Cu_3O_7$  and Pr-doped cuprates.

It has been well established that a key parameter controlling the  $T_c$  value of the hole-doped superconducting cuprates is the carrier concentration in the  $CuO_2$  planes [9].  $T_c$  as a function of hole concentration in the  $CuO_2$  planes is found to follow a parabolic curve for many p-type high- $T_c$  cuprate superconductors [10]. Several methods have been applied to obtain the hole concentration for cuprate superconductors, including the Hall coefficient measurement [11], bond-valence-sum calculation [12], idometric titration technique [13], X-ray absorption spectroscopy [14,15], thermoelectric power measurement [16], etc. Among them, X-ray absorption spectroscopy using synchrotron radiation has some advantages over other measurements. X-ray absorption near-edge structure (XANES) measurements provide a direct probe on the local density of hole carriers at the distinct oxygen and copper sites in superconductive copper-oxide phases [9]. In particular, polarization-dependent X-ray absorption measurements

are able to provide detailed information on the orbital character of hole states and the distribution of hole carriers in the p-type cuprates [14].

While the enormous majority of research has been conducted on the  $R_xPr_{1-x}Ba_2Cu_3O_7$  systems ( $R$  = rare earth elements), no investigations on electronic structure of the  $Y_xPr_{1-x}Ba_2Cu_4O_8$  compounds have been performed. Utilizing high-resolution O K-edge X-ray absorption spectra, we report a comparative study on the variation of hole carriers over the different oxygen sites with Pr doping for the  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films and polycrystalline  $Y_xPr_{1-x}Ba_2Cu_4O_8$  ( $x=0-1$ ) samples.

## 2. Experimental

The detailed procedures for the preparation of samples were reported elsewhere. In brief, the polycrystalline  $Y_xPr_{1-x}Ba_2Cu_4O_8$  ( $x=0-1$ ) samples were prepared by the nitric pyrolysis method and oxalate coprecipitation method [17,18]. The annealing temperature is  $800^\circ\text{C}$  for  $0 \leq x \leq 0.4$  and  $870^\circ\text{C}$  for  $0.6 \leq x \leq 1$ . As confirmed by X-ray diffraction (XRD), all samples under study are single phase. The  $Y_xPr_{1-x}Ba_2Cu_3O_7$  ( $x=0-1$ ) thin films with thickness  $\sim 4000$  Å were deposited on the  $SrTiO_3$  substrates by pulsed laser deposition. These thin films are highly preferentially oriented with the  $c$ -axis perpendicular to the surface of thin films.

X-ray absorption measurements were performed at the 6-m high-energy spherical grating monochromator (HSGM) 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. X-ray fluorescence yield measurement is a strictly bulk-sensitive technique with a probing depth of thousands of angstrom. The absorption spectra were corrected for the energy-dependent incident photon intensity as well as for the self-absorption effects and normalized to tabulated standard absorption cross-section in the energy range of 600–620 eV. The polarization-dependent X-ray absorption spectra with several incidence angles  $\theta$  were measured by

rotating the sample around a vertical axis.  $\theta$  is the incident angle between the incoming synchrotron beam and 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 thin films. In order to obtain  $E//c$  spectra, the thin films were rotated to achieve different incidence angles of  $\theta = 0^\circ, 45^\circ, 60^\circ$  and  $75^\circ$ . According to  $I(\theta) = I_{E//ab} \sin^2(\theta) + I_{E//c} \cos^2(\theta)$ , the  $E//c$  absorption spectrum can be deduced. 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.

### 3. Results and discussion

In Fig. 1, polarized O K-edge X-ray absorption spectra of the  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  ( $x = 0-1$ ) thin films for  $E//ab$  polarization are reproduced. The O 1s X-ray absorption spectra for the  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  thin films can be divided into two regions. The low-energy pre-edge peaks with energy below 530 eV are attributed to transitions from the O 1s core electrons into hole states with mainly O 2p character on the oxygen sites. The strong rise in spectral weight of the absorption spectra above 535 eV may be due to continuum absorption of the Ba 4d, Cu 4s or Cu 4p states hybridized with O 2p states [9,14]. As noted, the X-ray absorption spectra with energy beyond 540 eV for all the thin films under study exhibit very similar features and are independent of Pr doping. 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 has been well established that, for  $YBa_2 Cu_3 O_7$ , the absorption feature at  $\sim 528.4$  eV is ascribed to hole states in the  $CuO_2$  planes (i.e., the Zhang–Rice (ZR) states), while the shoulder at  $\sim 527.8$  eV corresponds to unoccupied states in the CuO chains [9,14]. The absorption peak at  $\sim 529.5$  eV is attributed to the upper Hubbard band (UHB). Feature B shows an increase in intensity with increasing Pr doping level and is assigned to the Pr 5d states [19].

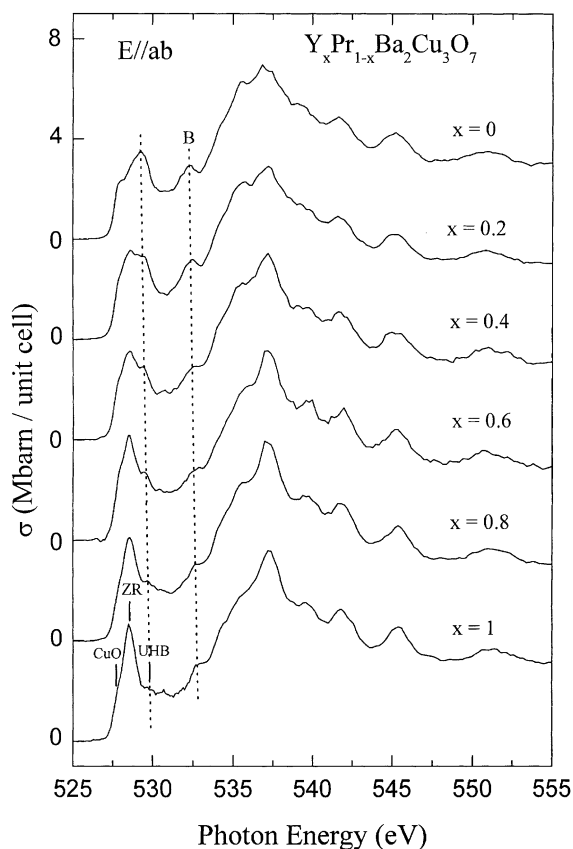


Fig. 1. Polarized O K-edge X-ray absorption spectra of the  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  ( $x = 0-1$ ) thin films for  $E//ab$  polarization.

As noted from Fig. 1, upon Pr substitution, spectral weight of the ZR states is strongly reduced, but 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. Furthermore, the peak positions of the UHB and feature B are shifted to lower energies with increasing Pr content. This implies that the O 1s core level and Fermi level are shifted to higher energies with increasing dopant concentration of Pr [14].

Many models were proposed to explain the superconductivity suppression in  $PrBa_2 Cu_3 O_7$  and related Pr-doped cuprates. These models include hole-filling [20], hole localization [21], percolation [22], magnetic pair-breaking [20,23], hybridization [24], disorder on Ba site [25], hole transfer from

planes to chains [26], etc. Among them, the existence of  $\text{Pr } 4f_{z(x^2-y^2)}-\text{O } 2p_{\pi}$  hybridized states proposed by Fehrenbacher and Rice (FR) is considered to be the most promising model [24]. Based on this model, the  $\text{Pr } 4f_{z(x^2-y^2)}-\text{O } 2p_{\pi}$  hybridized state is competitive in energy to hole states in the  $\text{CuO}_2$  planes. The FR model proposed that hole depletion in the  $\text{CuO}_2$  planes with Pr doping is due to transfer of hole carriers from the  $\text{CuO}_2$  planes into the FR states which bind doped holes to the Pr sites. However, there is no direct evidence in support of the existence of the FR states.

Fig. 2 presents the O K-edge X-ray absorption spectra of the  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $x=0-1$ ) thin

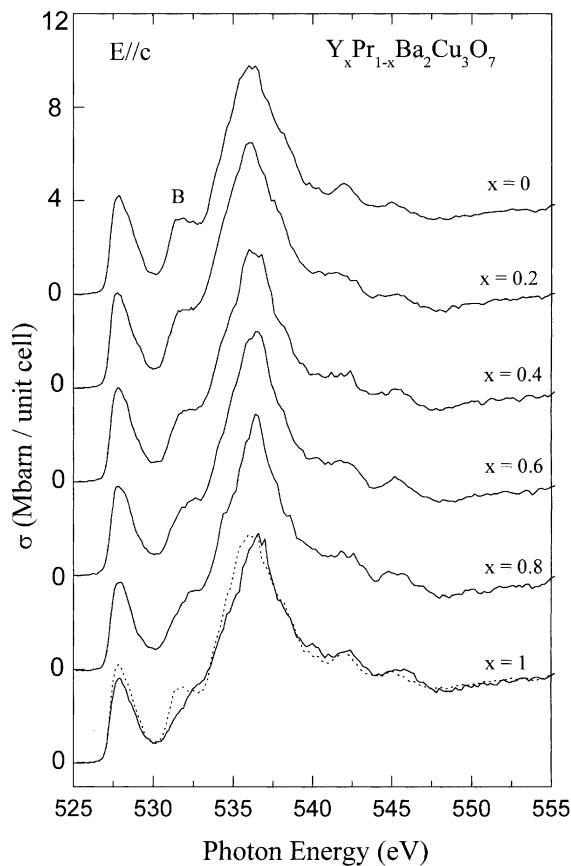


Fig. 2. Polarized O K-edge X-ray absorption spectra of the  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $x=0-1$ ) thin films for E//c polarization. The absorption spectrum of  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  is plotted as a dashed curve for comparison.

films for E//c polarization. For  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the absorption peak at  $\sim 527.8$  eV is assigned to the O  $2p_z$  hole states in the apical oxygen sites. Upon Pr substitution, an additional small band around 527.8–529.5 eV is observed. If this additional band is attributed to hole transfer from planes and chains to the apical oxygen sites, it is expected that the reduction of hole carriers within the  $\text{CuO}_2$  planes and CuO chains in Fig. 1 should be approximately equal to the increase of hole numbers in the apical oxygen sites in Fig. 2. In contrast, the increase in the absorption peak at  $\sim 527.8$  eV in Fig. 2 is significantly smaller than the reduction of spectral weight in the ZR states and CuO chains in Fig. 1 for a fixed Pr content. It is thus ascribed the additional spectral weight in the E//c spectra of  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  to the Pr  $4f$ -O  $2p$  hybridized states or FR states [14,27]. As noted, this band lies in the almost same energy range as the ZR states observed for the E//ab spectra below the UHB. Accordingly, the substitution of Y by Pr in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  induces a transfer of hole carriers from the ZR states to the energetically favored FR states, as evidenced in Fig. 1. The experimental results provide direct spectroscopic evidence in support of the FR model.

In Fig. 3, the O K-edge X-ray absorption spectra for the series of  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  samples with  $x=0-1$  are presented in the energy range of 525–560 eV. The major features in the O 1s X-ray absorption spectra for those samples are two distinct pre-edge peaks at  $\sim 528.5$  eV and  $\sim 529.6$  eV with a shoulder at  $\sim 527.8$  eV, and a broad peak at  $\sim 537$  eV. According to the local-density approximation (LDA) band-structure calculations in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the O(2,3) atoms in the  $\text{CuO}_2$  planes and the O(1) atom in the CuO chain are predicted to have the largest and the lowest binding energy of the O 1s level, respectively [28]. In contrast, in  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , the O(1) atom in the CuO chain is predicted to have the largest binding energies of the O 1s level [29]. This is due to the fact that in  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , the O(1) atom is coordinated with three Cu atoms while in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  there exist only two next-nearest Cu atoms. These predications are consistent with the experimental results [29].

Based on polarization-dependent X-ray absorption measurements on the  $\text{YBa}_2\text{Cu}_4\text{O}_8$  single

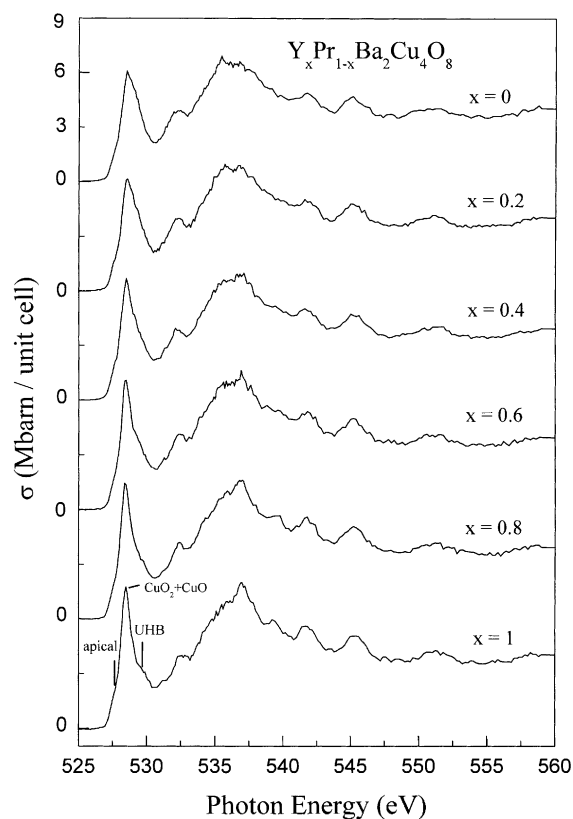


Fig. 3. O K-edge X-ray absorption spectra of the polycrystalline  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  ( $x=0-1$ ) samples.

crystals, the pre-edge peaks at  $\sim 528.7$  eV are ascribed to transitions into the O 2p hole states within the  $CuO_2$  planes and CuO chains [29]. The orthorhombic  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  compounds are isomorphic with  $YBa_2 Cu_4 O_8$ . We therefore adopt the same assignment scheme for the O 1s X-ray absorption spectra of  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$ . The low-energy pre-edge peak at  $\sim 527.8$  eV in Fig. 3 corresponds to excitations of the O 1s electrons to the O 2p hole states in the apical oxygen sites. The high-energy pre-edge peaks at  $\sim 528.5$  eV are due to the superposition of the O 2p hole states in the  $CuO_2$  planes and CuO chains. The absorption peak at  $\sim 529.6$  eV is ascribed to transitions between the O 1s core electrons and the upper Hubbard Cu 3d conduction band. This kind of pre-edge structure is a result of hybridization in the ground state of the  $Cu3d^9$  and  $Cu3d^{10}L$  states,

where L is ligand hole from the O 2p band. Due to the strong on-site correlation effects on the copper sites in the cuprate superconductors, an UHB has always been assumed to exist. As noted from Fig. 3, the pre-edge peaks at  $\sim 528.5$  eV originating from the O 2p hole states in the  $CuO_2$  layers and CuO chains show a slight decrease in spectral weight with increasing the dopant concentration of Pr. This result clearly reveals that chemical substitution of Pr for Y in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  causes a reduction in hole concentration within the  $CuO_2$  planes and CuO chains.

To quantify the variation of hole carriers over the different oxygen sites as a function of Pr content, the pre-edge peaks shown in Figs. 1 and 3 were analyzed by fitting each spectrum with Gaussian functions. In order to define peak width for those three peaks, the results from the single crystals were referenced [14,15,29]. The energy shift of the UHB upon Pr substitution was also taken into account. The hole distribution and spectral weight of the UHB as a function of Pr content for  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  are presented in Figs. 4a and b. It can be seen from Fig. 4a that hole carriers within the  $CuO_2$  planes and CuO chains in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  decrease significantly with increasing Pr doping level. Accordingly, the UHB shows a monotonic increase in intensity as Pr content increases, as presented in Fig. 4b. In Figs. 4c–e, the integrated intensity of each pre-edge peak is plotted as a function of Pr content in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$ . As noted from Figs. 4c and d, the hole content in the  $CuO_2$  planes and CuO chains reduces slowly with increasing Pr doping level, while that in the apical oxygen sites remains nearly constant. In contrast, spectral weight of the UHB increases moderately as Pr doping level increases, as shown in Fig. 4e.

It is intriguing to compare the depletion rate of hole carriers with Pr doping for  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  and  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ . Fig. 5 presents the change rates of hole carriers in the ZR states and CuO chains and spectral weight of the UHB for  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  and  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  relative to the undoped parent cuprates for  $x=1$ . As noted from Fig. 5a, upon Pr substitution, the reduction rate of hole carriers within the ZR states and CuO chains in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is considerably slower

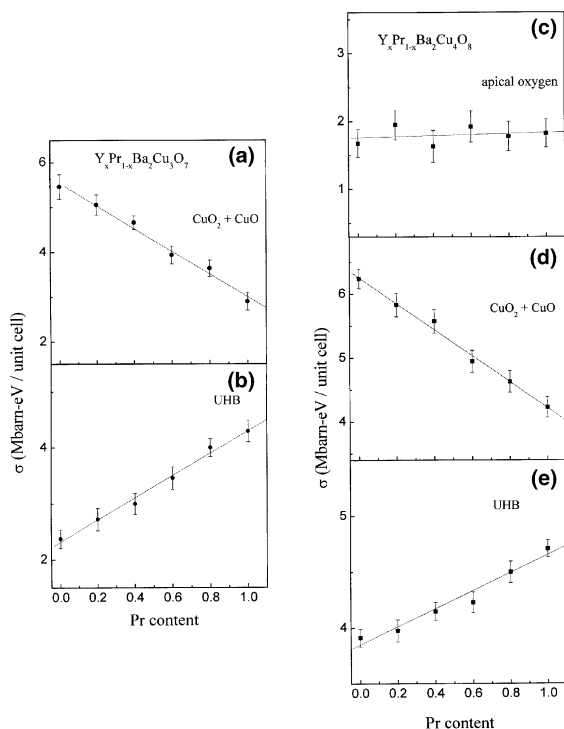


Fig. 4. Integrated cross-sections of (a) hole states in the  $\text{CuO}_2$  planes +  $\text{CuO}$  chains and (b) the upper Hubbard band (UHB) as a function of Pr concentration in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ . Integrated cross-sections of (c) hole states in the apical oxygen sites, (d) hole states in the  $\text{CuO}_2$  planes +  $\text{CuO}$  chains, and (e) the upper Hubbard band (UHB) as a function of Pr content in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$ . The solid curves are drawn as a guide for the eyes.

than that in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ . Moreover, the increased rate of spectral weight in the UHB with Pr doping in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  is significantly higher than that in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ , as shown in Fig. 5b. It is known that the UHB is strongly correlated with the ZR states and presumed to have no correlation with hole states in the  $\text{CuO}$  chains [9]. Thus, the results in Fig. 5b confirm that the hole depletion rate in the ZR states with Pr substitution in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  is slower than that in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ . As well established, the hole concentration in the ZR states is strongly correlated with  $T_c$ . Thus, the  $T_c$  suppression rate with Pr doping in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  should be in principle slower than that in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ , which is indeed found to be the case.

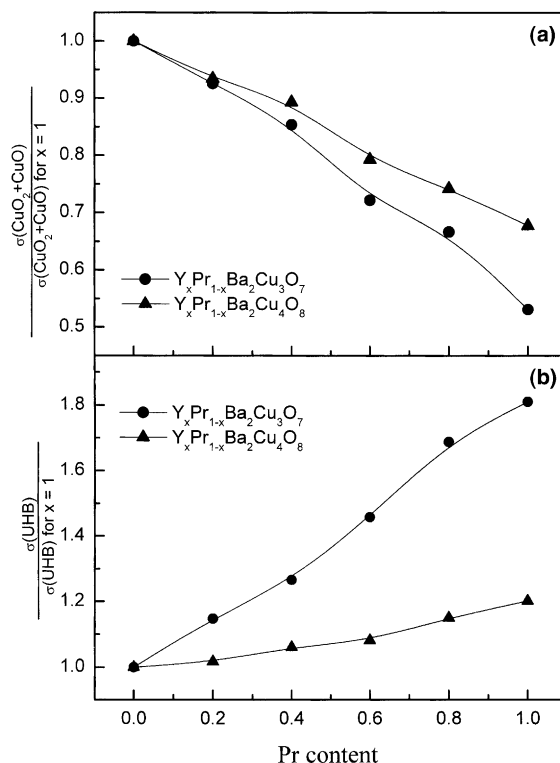


Fig. 5. Variation rates of (a) hole carriers in the  $\text{CuO}_2$  plane +  $\text{CuO}$  chain and (b) spectral weight of the UHB for  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  and  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  relative to the undoped parent cuprates for  $x = 1$ .

It has been shown that the extent of the Pr 4f–O 2p hybridization in Pr-doped cuprates is determined predominantly to the Pr–O(2,3) bond length as well as the O(2,3)–Pr–O(2,3) bond angle and the energy level difference between the Fermi level  $E_F$  and the Pr 4f level [30,31]. As compared to  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ , the corresponding  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  compounds exhibit a longer  $c$ -axis parameter due to the double  $\text{CuO}$  chains. Based on X-ray diffraction studies, the Pr–O(2,3) bond length in  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  is slightly shorter than that in  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  [32,33]. It is thus expected that the hybridization between the Pr 4f states and O 2p orbitals in  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_4\text{O}_8$  is less pronounced than that in corresponding  $\text{Y}_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ . It has been proposed that the energy of the hole-depletion band (or FR states) may depend on the extent of the Pr 4f–O 2p hybridization [34]. In other words, the enlarged

lattice in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  reduces the extent of the Pr 4f–O 2p hybridization and in turn leads to the decrease in position of the hole-depletion band (or FR states) relative to the ZR states. Accordingly, as compared to  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ , the resultant hole depletion rate in corresponding  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is mitigated and the remaining hole content in the ZR states is higher, as evidenced in Fig. 5.

It has been demonstrated that hole depletion in cuprates upon Pr doping arises from not only the ZR states but also hole states in the CuO chains [14]. For  $R_x Pr_{1-x} Ba_2 Cu_3 O_7$ , the hole reduction with Pr substitution originates predominantly from the ZR states [14,35]. However, due to double CuO chains in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ , the energy level of hole states in the CuO chains might be more overlapped with the ZR states [29]. Thus, another possibility for slow reduction rate in the ZR states with Pr doping in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  compared to  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  is that the transfer of hole carriers in the CuO chains to the FR states in the former system may make a significant contribution. Here, we assumed that the total reduction of hole carriers from the ZR states and CuO chains in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  is the same as that in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  for a fixed Pr content. Accordingly, the hole depletion in the ZR states with Pr doping in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is less than that in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ . The high content of hole carriers in the ZR states might be the possible reason for metallic properties of the  $CuO_2$  planes in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  for Pr content greater than 0.72 at low temperature [7,8]. In other words, due to the significant decrease of hole carriers in the ZR states with Pr doping in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ , it is expected that  $PrBa_2Cu_3O_7$  should be an insulator. The monotonic depletion of hole carriers in the  $CuO_2$  planes and CuO chains with increasing Pr content in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  and  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  provides evidence in support of hole-depletion effect based on the Pr 4f–O 2p hybridization [35].

#### 4. Conclusion

We have studied the variation of hole states with Pr doping related to the  $T_c$  suppression for

$Y_x Pr_{1-x} Ba_2 Cu_3 O_7$  and  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  by O K-edge X-ray absorption spectroscopy. We demonstrate spectroscopic evidence of the existence of FR states. For both systems, hole carriers in the  $CuO_2$  planes and CuO chains decrease monotonically with increasing Pr doping level, which are caused by the transfer of hole carriers from the ZR band and CuO chains to the localized FR band. The depletion rate of hole carriers in the ZR states with Pr substitution in  $Y_x Pr_{1-x} Ba_2 Cu_4 O_8$  is slower than that in  $Y_x Pr_{1-x} Ba_2 Cu_3 O_7$ . The experimental results provide clear evidence in support of hole-depletion effect based on the Pr 4f–O 2p hybridization. Based on present XANES studies, the oxygen content affects the hole depletion rate of cuprates with Pr doping.

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