PHYSICAL REVIEW B VOLUME 55, NUMBER 21 1 JUNE 1997-I

Origin of superconductivity suppression in $(Dy_{1-x}Pr_x)Ba_2Cu_3O_7$ studied by soft-x-ray absorption spectroscopy

J. M. Chen
Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan

R. S. Liu
Department of Chemistry, National Taiwan University, Taipei, Taiwan

J. G. Lin and C. Y. Huang
Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

J. C. Ho
Department of Physics and National Institute for Aviation Research, Wichita State University, Wichita, Kansas 67208

(Received 6 January 1997)

O K-edge and Cu L_{23}-edge x-ray-absorption near-edge structure (XANES) spectra for the series of $(Dy_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ compounds ($x=0-0.7$) were measured to investigate how the variation of hole states related to the superconductivity. Near the O $1s$ edge, prepeaks at ~527.6 and ~528.4 eV are assigned to transitions into O $2p$ holes located in the CuO_3 ribbons and CuO_2 planes, respectively. Both the O $2p$ hole concentration in the CuO_2 planes and CuO_3 ribbons decrease monotonically with increasing Pr doping, giving evidence in support of the hole depletion model proposed by Liechtenstein and Mazin. It clearly demonstrates that the suppression of superconductivity with Pr-doping results predominantly from the hole depletion effect. In the Cu $2p$ absorption edge, the high-energy shoulders originating from Cu $3d^9L$ defected states show a linear decrease in spectral weight as the Pr doping increases, where L denotes the ligand O $2p$ hole on the CuO_3 ribbons and the CuO_2 planes. [S0163-1829(97)07721-7]

I. INTRODUCTION

It is well known that $PrBa_2Cu_3O_7$ exhibits the same orthorhombic structure as $YBa_2Cu_3O_7$ ($Pmmm$) and other similar rare-earth compounds, however, it is nonsuperconducting.[1] Great research efforts have been carried out on the $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ system in an attempt to understand the origin of the depression of superconductivity in $PrBa_2Cu_3O_7$.[2–7] It has been experimentally shown that substitution of Pr for Y in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ depresses T_c with superconductivity disappearing for $x>0.55$.[8] Xu and Guan have systematically studied the suppression of T_c with Pr doping for several $(R\text{Pr})Ba_2Cu_3O_7$ compounds, where $R=$Y, Eu, Gd, and Dy. It has been found that the depression of T_c by Pr substitution in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ strongly depends on the rare-earth components. The smaller the atomic number of rare-earth elements in host compounds is, the greater the decrease in T_c.[9,10] In spite of an enormous number of experimental and theoretical investigations,[11] the dramatic suppression of superconductivity upon substituting Y by Pr in $YBa_2Cu_3O_7$ is still not well understood.

The models for explaining the quenching of superconductivity in the $PrBa_2Cu_3O_7$ compound include hole filling,[12] magnetic pair breaking,[12,13] hole localization,[14] percolation,[15] and hybridization.[16–18] However, no model allows for a consistent interpretation of all experimental data. As an example, the measurements of the Hall effect in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ showed a reduction of mobile carriers with increasing the Pr-doping level, supporting the hole-filling model which is based on Pr being in the +4 valence state. However, several experimental results have suggested that the valence of Pr is +3 and therefore that a Pr ion could not provide an electron to deplete the hole in the CuO_2 plane.[4,6,14,19,20] Recently, it has been proposed by Fehrenbacher and Rice (FR) that, in the $PrBa_2Cu_3O_7$ compound, the holes are localized in a hybridized state at the Pr sites with a mixture of $4f^2L$ (+3) and $4f^1$ (+4) configuration.[21] Here L is a ligand hole in the O $2p$ orbital around the Pr site and distributes 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. Hybridization of the Pr $4f$ electrons with those of copper and oxygen has also been proposed by Torrance and Metzger.[22] In their model, the presence of hybridization between the holes in the CuO_2 plane and the Pr $4f$ wave function could lead to a larger hopping barrier and consequently localize the hole, resulting in a loss of superconducting properties. The strong hybridization between Pr $4f$ states and conduction bands was supported on the basis of critical magnetic field,[13] x-ray-absorption measurement,[4] photoemission spectroscopy,[6] and spin-polarized electronic-structure calculations.[23] The FR model resolves the controversy on the different valence values of the Pr ion obtained from different measurements. However, it still cannot explain the R dependence on the suppression of T_c in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$. Liechtenstein and Mazin (LM) have recently modified the work of FR and proposed that, in $PrBa_2Cu_3O_7$, there forms an additional hole-depleting band which crosses the Fermi

© 1997 The American Physical Society

level and consequently snatches holes from the CuO_2 band.[24] On doping different rare-earth elements in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$, the position of this hole-depleting band shifts with the atomic number of the rare earth, through the energy level of $4f$ orbitals, resulting in the R dependence of destruction of T_c.

Based on band-structure calculations[25–27] and x-ray-absorption measurements,[28,29] it has been shown that the O $2p$ holes near the Fermi level in $YBa_2Cu_3O_7$ are distributed between the CuO_2 planes and CuO_3 ribbons. If the LM model is valid, it is expected that, in the $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ system, both the hole concentration originating from CuO_2 planes and CuO_3 ribbons should decrease as the Pr doping increases. However, there is still a lack of direct experimental evidence in support of this hypothesis. Several methods have been used to obtain the hole concentration for high-temperature superconductors, including the Hall coefficient measurement, bond-valence-sum calculation,[30] idometric titration technique,[31] x-ray-absorption spectroscopy,[32] thermoelectric power (S) measurement,[33] etc. In measuring the hole states in cuprate compounds, x-ray-absorption spectroscopy has some advantages over other measurements. X-ray-absorption near-edge structure (XANES) using synchrotron radiation is a powerful tool for the investigation of the unoccupied electronic states in complex materials. XANES spectra can give the information on the local density and the distribution of hole states at both oxygen and copper sites in the cuprate superconductors.

While the enormous majority of research has been performed on the $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ system, there are few studies on the $(Dy_{1-x}Pr_x)Ba_2Cu_3O_7$ system. The superconducting properties for both systems are very similar. The chemical substitution of Pr for Dy in $(Dy_{1-x}Pr_x)Ba_2Cu_3O_7$ leads to a monotonical decrease of the superconducting temperature from $T_c=92$ K for $x=0$ to $T_c=10$ K for $x=0.6$.[34] The compound becomes semiconducting at $x>0.7$. To improve the understanding on the mechanism of T_c suppression, a detailed study on $(R_{1-x}Pr_x)Ba_2Cu_3O_7$would be helpful. The studies of the effect of the Pr ion on superconductivity may help our comprehensive understanding on the origin of the high-T_c superconductivity. We, therefore, measure systematically the variations of hole states related to the superconductivity for a series of $(Dy_{1-x}Pr_x)Ba_2Cu_3O_7$ compounds. In this study, we report the results on O $1s$-edge and Cu $2p$-edge x-ray-absorption measurements in the $(Dy_{1-x}Pr_x)Ba_2Cu_3O_7$ system with $x=0$, 0.2, 0.4, 0.6, and 0.7 using a bulk-sensitive x-ray fluorescence yield technique.

II. EXPERIMENT

The detailed procedures for the preparation of samples were reported elsewhere, so only pertinent details will be given here.[34] Samples of $(Dy_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ with $x=0$, 0.2, 0.4, 0.6, and 0.7 were prepared by a solid-state reaction method. Appreciate amounts of high-purity Dy_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO_2 were mixed and calcinated in air at 900 °C for 12 h. The product was then palletized for two successive sintering processes at 940 °C for 12 h each. Following the second sintering, the sample was slowly cooled to 600 °C in 3 h, annealed in flowing oxygen for 4 h, cooled again to 400 °C in 2 h, annealed for 8 h, and finally cooled to room temperature in 3 h. The oxygen content was determined by the idometric method. X-ray powder diffraction patterns show that samples are single phase corresponding to the orthorhombic structure. The homogeneity of each sample was also checked by the Messiner effect.

The x-ray-absorption measurements were recorded using the 6-m high-energy spherical grating monochromator (HSGM) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. X-ray-fluorescence-yield (XFY) spectra were recorded using a microchannel plate (MCP) detector. This MCP detector is composed of a dual set of MCP's with an electrically isolated grid mounted in front of them. XFY measurement is strictly bulk sensitive with a probing depth of thousands of Å. During the XFY measurement, the grid was set to a voltage of 100 V while the front of the MCP's was set to -2000 V and the rear to -200 V. The negative MCP bias was applied to expel negatively charged particles before they entered the detector, while the grid bias ensured that no positive ions were detected. The MCP detector was located at ~ 2 cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45° with respect to the normal direction of the sample. The incident photon flux (Io) was measured simultaneously by the photocurrent from an 80% transmission Ni mesh located after the exit slit of the monochromator. All the absorption measurements were normalized to Io. The energy calibration was carried out by a measurement of the known O K-edge and Cu L_3-edge absorption peaks of CuO. The energy resolution of the monochromator was set to approximately 0.22 and 0.45 eV for the O K-edge and Cu L-edge x-ray-absorption measurements, respectively. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

In Fig. 1 are displayed O K-edge x-ray-absorption spectra for a series of $(Dy_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ samples with $x=0$, 0.2, 0.4, 0.6, and 0.7 obtained using the XFY technique. The conspicuous features in the O $1s$ x-ray-absorption spectrum for samples with $x=0$, as shown in Fig. 1(a), are two prepeaks at ~ 528.4 eV and ~ 529.6 eV with a shoulder at ~ 527.6 eV, and a broad peak at ~ 537 V. The low-energy prepeaks with energy below 532 eV are ascribed to transitions from the O $1s$ core electrons to holes with predominant $2p$ character on the oxygen sites. The strong rise in spectral weight above 532 eV is related to O $2p$ states hybridized with a Ba $4d$, Pr $5d$, or Pr $4f$ state.[14] The O K-edge x-ray-absorption spectra for various compounds with different x values in Fig. 1 were normalized to have the same height at the main peak of ~ 537 eV.

In the crystal structure of $(Dy_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$,there exists four nonequivalent oxygen sites—O(2) and O(3) within the Cu(2) O_2 layers, O(4) in the BaO planes, and O(1) in the Cu(1) O chains along the b axis. The observed multiple prepeaks in Fig. 1 may be related to chemical shifts of O $1s$ binding energies for different oxygen sites. The differences in chemical shifts of O $1s$ core levels can be estimated using local-density-approximation (LDA) band-structure calculations. According to the calculations in $YBa_2Cu_3O_{7-\delta}$ by Krakauer *et al.*,[35] the O $1s$ energy levels of the O(2) and

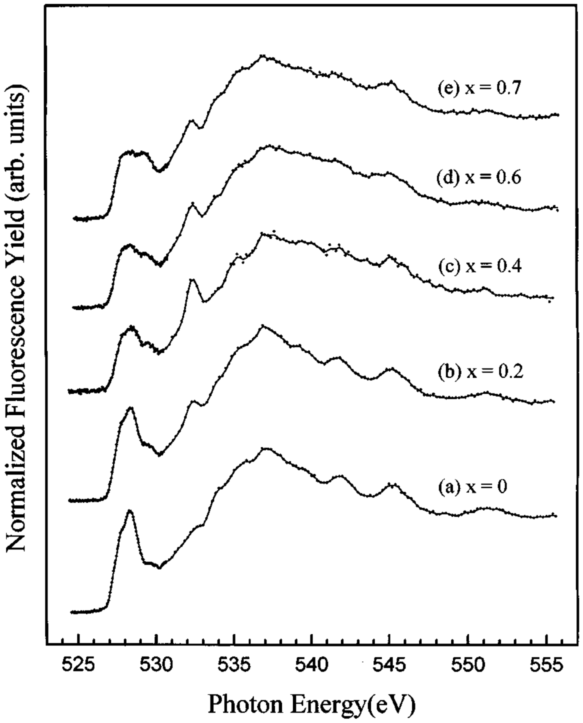

FIG. 1. O K-edge x-ray-absorption spectra for the series of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ samples with $x=0$, 0.2, 0.4, 0.6, and 0.7. The absorption spectra for various compounds with different x values were normalized to have the same height at the main peak of ~537 eV.

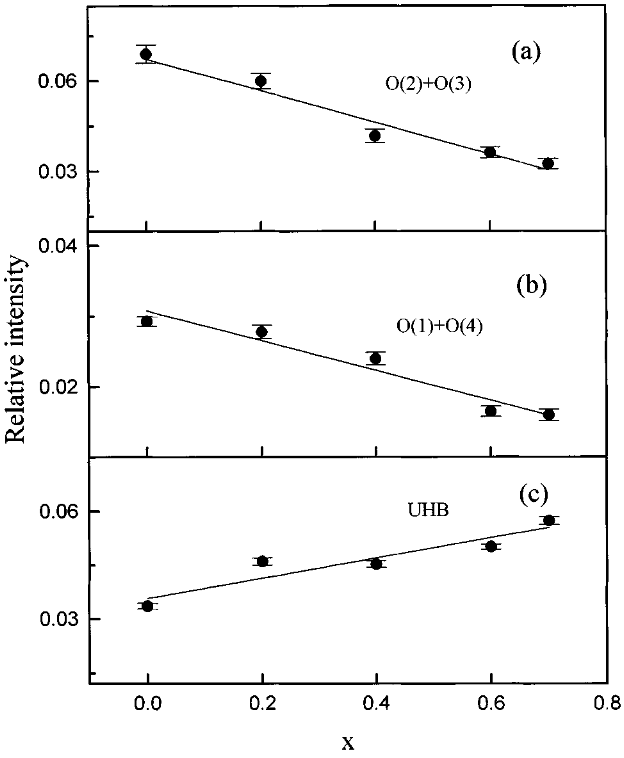

FIG. 2. X dependence of the relative intensity of hole states in $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ on oxygen sites originating from the (a) CuO_2 planes, (b) CuO_3 ribbons, and (c) upper Hubbard band (UHB). The solid curves are drawn as a guide for the eyes.

O(3) atoms in the CuO_2 planes are expected to be very close to each other and predicted to be about 0.29 eV higher than that of the O(1) atoms. The O 1s binding energy of the O(1) atom in the CuO chains is 0.4 eV higher than that of the O(4). In addition, the lowest O 1s binding energy is also assigned to the O(4) atom in the apical sites by Zaanen *et al.*[36] In O K-edge x-ray-absorption spectra of $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$, the prepeaks at ~527.8 eV are attributed to transitions into O 2p holes in the apical oxygen sites and CuO chains. The high-energy prepeak at ~528.5 eV is ascribed to transitions into O 2p hole states within the CuO_2 planes.[28,32] The orthorhombic $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ $(Pmmm)$compound is isomorphic with $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$.[34] In addition, the O 1s x-ray-absorption spectrum of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ with $x=0$ shows similar features as seen in $\mathrm{YBaCu}_3\mathrm{O}_{7-\delta}$ with $\delta=0$.[28,32] When oxygen is removed from $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ compounds, a strong reduction of the prepeak structure due to charge transfer is realized,[14] as observed for the $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ compound.[28] Furthermore, the low-energy loss function of $\mathrm{PrBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (δ~0.3) is very similar to that measured for the $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (δ~0.2) compound. We therefore adopt the same assignment scheme for the O 1s absorption spectrum of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$. The low-energy prepeaks at ~527.6 eV, as shown in Fig. 1, are due to the superposition of O 2p hole states originating from the apical oxygen sites and CuO chains. The high-energy prepeak at ~528.4 eV is ascribed to transition into O 2p holes in the CuO_2 planes. According to recent studies on $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$, the absorption peak at ~529.6 eV can be ascribed to transitions into the conduction band (upper Hubbard band) which is predominantly formed by Cu 3d states with some admixture of O 2p states.[37,38] As a consequence of the strong on-site correlation effects on the copper sites in the cuprate superconductors, the upper Hubbard band has always been assumed to exist.[39] As noted from Fig. 1, the prepeak at ~528.4 eV originating from the O 2p hole states in the CuO_2 layers decreases in spectral weight with increasing the dopant concentration of Pr. This clearly demonstrates that the chemical substitution of the Pr ion for the Dy ion in the $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ system results in a decrease in hole concentration in CuO_2 planes. The present x-ray-absorption data are consistent with the heat-capacity measurement which indicates continuous hole reduction with increasing x in the $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ system.[40]

In order to quantify the amount of reduction in the hole concentration on different oxygen sites as a function of the Pr doping, Gaussian functions were used to estimate the spectral weight of each feature in the spectrum. In Fig. 2 the integrated intensity of each prepeak, normalized against the intensity of main peak at ~537 eV, is plotted as a function of compositional parameter x in $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$. It can be seen from Figs. 2(a) and 2(b) that both the hole concentration from the CuO_2 planes and CuO_3 ribbons decrease monotonically with increasing Pr doping. According to the LM model, the hole depletion upon substituting R by Pr in $(R_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ is due to the charge transfer from holes in the CuO_2 planes and CuO_3 ribbons into the LM band. The hole reduction observed in $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ gives evidence in support of the

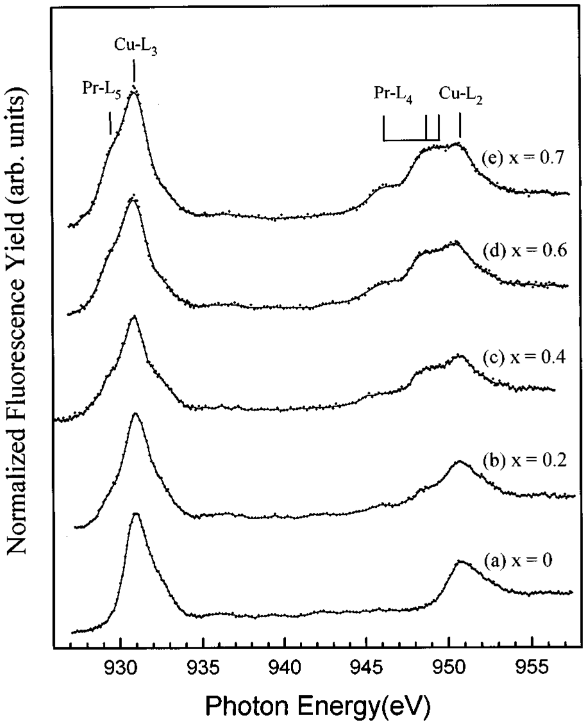

FIG. 3. Pr M_{45}-edge and Cu L_{23}-edge x-ray-absorption spectra of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ with $x=0$, 0.2, 0.4, 0.6, and 0.7.

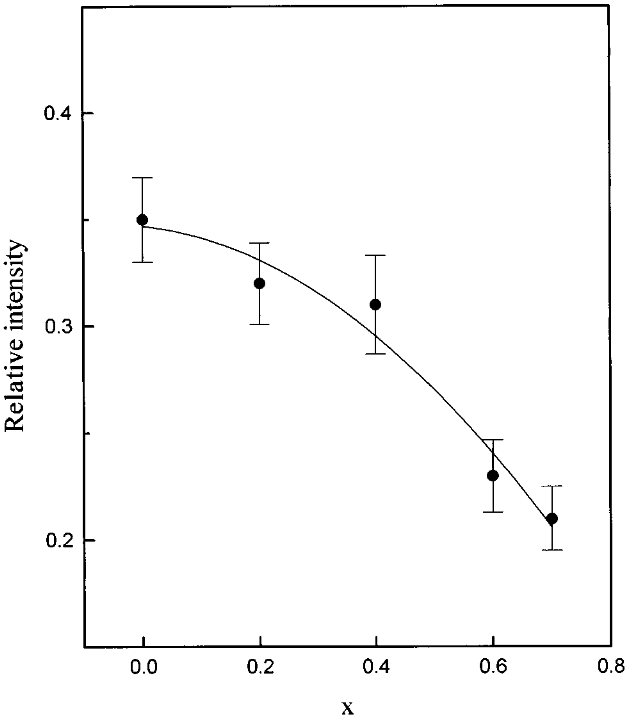

FIG. 4. Relative intensity of defect state at ~932.6 eV on the Cu sites as a function of the compositional parameter x in $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$. The solid curve is drawn as a guide for the eyes.

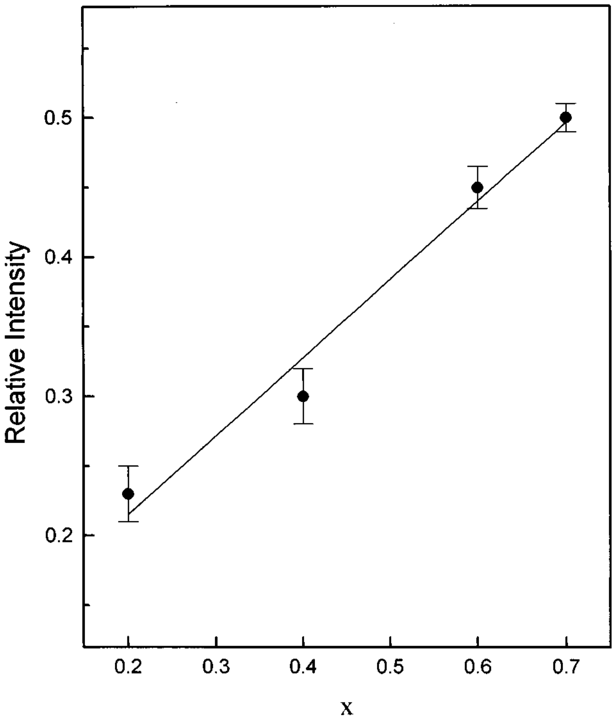

FIG. 5. Relative intensity at peak ~929.4 eV originating from the excitations of Pr $3d_{5/2}$ electrons as a function of x in $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$. The solid line is drawn as a guide for the eyes.

hole-depletion model proposed by LM. It has been demonstrated that the concentration of O $2p$ holes in the CuO_2 planes is strongly correlated with T_c.[41] As a result, the superconducting transition temperature in the $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ system should decrease with increasing the Pr doping. Our experimental results demonstrate that the suppression of superconductivity with Pr doping is caused predominantly by the hole depletion.

Furthermore, as shown in Fig. 2(c), the peak at ~529.6 eV originating from the upper Hubbard band shows a linear increase in intensity as the Pr doping increases. The change in the intensity of the structure at ~529.6 eV is related to the transfer of spectral weight from the upper Hubbard band to the doping-induced low-energy prepeaks.[42] The same behavior has also been observed in O $1s$ absorption spectra of other p-type cuprates.[37,38,43]

The peak at ~532.4 eV may be due to surface contamination since this peak changes its intensity from sample to sample and exhibits a greater intensity in surface-sensitive total-electron yield spectra. Existence of surface contamination has been reported by many researchers. Based on the photoemission studies by Iqbal *et al.*, it is suggested that this peak arises from the absorption of hydrides, water, and CO_2 on surface.[44]

The Pr M_{45}-edge and Cu L_{23}-edge x-ray-absorption near-edge-structure x-ray-fluorescence-yield spectra for a series of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ compounds in the energy range 925–960 eV are shown in Fig. 3. For samples with $x=0$ shown in Fig. 3(a), the Cu L_{23}-edge absorption spectrum is asymmetric and two shoulders exhibit at the high-energy side of the main peak. Based on the curve-fitting analyses, the high-energy features are found to center at ~932.6 and ~952.4 eV, respectively. The spectral shape in the Cu L_3 absorption edge of $(\mathrm{Dy}_{1-x}\mathrm{Pr}_x)\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ with $x=0$ is analogous to that of single-crystal $\mathrm{YBaCu}_3\mathrm{O}_{7-\delta}$ for $\delta=0$.[45]

The excitonic peaks at 930.9 and 950.7 eV shown in Fig. 3 are ascribed to transitions from the Cu($2p_{3/2,1/2}$)$3d^9$-O $2p^6$ ground states (formal Cu^{+2} state) into the Cu$(2p_{3/2,1/2})^{-1}3d^{10}$-O $2p^6$ excited states, respectively, where $(2p_{3/2,1/2})^{-1}$ denotes a $2p_{3/2}$ or $2p_{1/2}$ hole. The high-energy shoulders, first reported by Bianconi *et al.* for YBa$_2$Cu$_3$O$_{7-\delta}$, are assigned as transitions from the Cu($2p_{3/2,1/2}$)$3d^9L$ ground state (formal Cu^{+3} state) into the Cu$(2p_{3/2,1/2})^{-1}3d^{10}L$ excited state, where L denotes a ligand hole in the O $2p$ orbital.[46] Because there exists two different Cu sites in the unit cell for the series of (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ compounds, these high-energy shoulders can be identified as the holes in the CuO$_2$ layers and the CuO$_3$ ribbons. In Fig. 4 the integrated intensity under the high-energy shoulder at ~932.6 eV, normalized against that under the Cu L_3 peak at 930.9 eV, is plotted as a function of the compositional parameter x in (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$. The integrated intensity was estimated by fitting the Cu L_3 peak and the shoulders centered at ~929.4 eV and ~932.6 eV with Gaussian functions. As seen from Fig. 4, the normalized intensity of the high-energy shoulder shows a linear decrease with increasing the Pr concentration. This indicates that the total hole content originating from the CuO$_2$ planes and CuO$_3$ ribbons in (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ decreases as the Pr doping increases.

The peak at ~929.4 eV is related to transitions from Pr $3d_{5/2}$ electrons into $4f$ states. As shown in Fig. 5, the spectral weight of peak at ~929.4 eV increases linearly with increasing the Pr doping in the compounds. This confirms that the Dy atoms in the (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ system are partially substituted by Pr atoms.

IV. CONCLUSION

X-ray-absorption spectra at the O $1s$ and Cu $2p$ edges of (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ with $x=0$–0.7 were carried out to understand the variation of hole states related to the superconductivity. Near the O $1s$ edge, the low-energy prepeaks at ~527.6 eV are attributed to O $2p$ holes in the apical oxygen sites and CuO chains. The high-energy prepeak at ~528.4 eV is ascribed to transitions into O $2p$ hole states within the CuO$_2$ planes. The distribution of holes on the different oxygen sites has been derived for (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$. The chemical substitution of Pr ion for Dy ion in the (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ system results in a decrease in hole concentration in the CuO$_2$ planes and the CuO$_3$ ribbons. This result is consistent with the prediction by the LM model. The high-energy shoulders in the Cu L_{23}-edge x-ray-absorption spectra are attributable to the electronic transitions from Cu$3d^9L$ defected states into Cu$2p^{-1}3d^{10}L$ excited states, where L denotes the ligand O $2p$ hole on the CuO$_3$ ribbons and the CuO$_2$ planes. The spectral weight of the high-energy shoulder shows a linear decrease with increasing the Pr doping, indicating that the total hole concentration in (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ decreases as the Pr doping increases. Based on the present XANES studies, it is concluded that the suppression of superconductivity with Pr doping in (Dy$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ results predominantly from the hole-depletion effect.

ACKNOWLEDGMENTS

We would like to thank all the members at SRRC for their technical support. This research is financially supported by SRRC and the National Science Council of the Republic of China under Grant Nos. NSC 86-2112-M002-011 and NSC 86-2613-M-213-010.

---

[1] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature (London) **328**, 604 (1987).

[2] H. B. Radousky, J. Mater. Res. **7**, 1917 (1992), and references therein.

[3] J. Zaanen, A. T. Daxton, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **60**, 2685 (1988).

[4] F. W. Lytle, G. van der Laan, R. B. Greegor, E. M. Larson, C. E. Violet, and J. Wong, Phys. Rev. B **41**, 8955 (1990).

[5] I. S. Yang, A. G. Schrott, and C. C. Tsuei, Phys. Rev. B **41**, 8921 (1990).

[6] S. Horn, J. Cai, S. A. Shaheen, Y. Jeon, M. Croft, C. L. Chang, and M. L. den Boer, Phys. Rev. B **36**, 3895 (1987).

[7] J. J. Neumeier, M. B. Maple, and M. S. Tarikachvili, Physica C **156**, 574 (1988).

[8] J. J. Neumeier and M. B. Maple, Physica C **191**, 158 (1992).

[9] Y. Xu and W. Guan, Appl. Phys. Lett. **59**, 2183 (1991); Y. Xu and W. Guan, Solid State Commun. **80**, 105 (1991).

[10] S. K. Malik, C. V. Tomy, and P. Bhargava, Phys. Rev. B **44**, 7042 (1991).

[11] D. Khomskii, J. Supercond. **6**, 69 (1993).

[12] J. J. Neumeier, T. Bjornholm, M. B. Maple, and I. K. Schuller, Phys. Rev. Lett. **63**, 2516 (1989).

[13] J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn, and L. Bernardez, Phys. Rev. B **40**, 4517 (1989).

[14] J. Fink, N. Nücker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumeier, and J. W. Allen, Phys. Rev. B **42**, 4823 (1990).

[15] C. Infante, M. K. El Mousky, R. Dayal, M. Husain, S. A. Siddiqi, and P. Ganguly, Physica C **167**, 640 (1990).

[16] J. B. Torrance and R. M. Metzger, Phys. Rev. Lett. **63**, 1515 (1989).

[17] J. J. Neumeier, M. B. Maple, and M. S. Tarikachvili, Physica C **156**, 574 (1988).

[18] A. P. Goncalves, I. C. Santos, E. B. Lopes, R. T. Henriques, and M. Almeida, Phys. Rev. B **37**, 7476 (1988).

[19] A. Kebede, C. S. Jee, J. Schwegler, J. E. Crow, T. Henriques, M. Almeida, and M. O. Figueiredo, Phys. Rev. B **37**, 7476 (1988).

[20] H. J. Rosen, R. M. MacFarlane, E. M. Engler, V. Y. Lee, and R. D. Jacowitz, Phys. Rev. B **38**, 2460 (1988).

[21] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[22] J. B. Torrance and R. M. Metzger, Phys. Rev. Lett. **63**, 1515 (1989).

[23] G. Y. Guo and W. M. Termerman, Phys. Rev. B **41**, 6372 (1990).

[24] A. I. Liechtenstein and I. I. Mazin, Phys. Rev. Lett. **74**, 1000 (1995).
[25] A. M. Olés and W. Grzelka, Phys. Rev. B **44**, 9531 (1991).
[26] C. J. Mei and G. Stollhoff, Phys. Rev. B **43**, 3065 (1991).
[27] W. M. Temmerman, Z. Szotec, and G. Y. Guo, J. Phys. C **21**, L867 (1988).
[28] N. Nücker, E. Pellegrin, P. Schweiss, J. Fink, S. L. Molodtsov, C. T. Simmons, G. Kaindl, W. Frentrup, A. Erb, and Müller-Vogt, Phys. Rev. B **51**, 8529 (1995).
[29] A. Krol, Z. H. Ming, Y. H. Kao, N. Nücker, G. Roth, J. Fink, G. C. Smith, K. T. Park, J. Yu, J. Yu, A. J. Freeman, A. Erb, G. Müller-Vogt, J. Karpinski, E. Kaldis, and K. Schönmann, Phys. Rev. B **45**, 2581 (1992).
[30] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).
[31] M. W. Shafer, T. Penney, and B. L. Olson, Phys. Rev. B **36**, 4047 (1987).
[32] J. Fink, N. Nücker, E. Pellegrin, H. Romberg, M. Alexander, and M. Knupfer, J. Electron Spectrosc. Relat. Phenom. **66**, 395 (1994).
[33] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).
[34] J. G. Lin, Y. Y. Xue, C. W. Chu, X. W. Cao, and J. C. Ho, J. Appl. Phys. **73**, 5871 (1993).
[35] H. Krakauer, W. E. Pickett, and R. E. Cohen, J. Supercond. **1**, 111 (1988).
[36] J. Zaanen, F. J. Himpsel, G. V. Chandrashekhar, and M. W. Shafer, Phys. Rev. B **39**, 837 (1989).
[37] H. Romberg, M. Alexander, N. Nücker, P. Adelmann, and J. Fink, Phys. Rev. B **42**, 8768 (1990).
[38] C. T. Chen, F. Sette, Y. Ma, M. S. Hybertsen, E. B. Stechel, W. M. C. Foulkes, M. Schluter, S. W. Cheong, A. S. Cooper, L. W. Rupp, Jr., B. Batlogg, Y. L. Soo, Z. H. Ming, A. Krol, and Y. H. Kao, Phys. Rev. Lett. **66**, 104 (1991).
[39] D. Vaknin, S. K. Shiha, D. E. Moneton, D. C. Johnston, J. M. Newsam, C. R. Safiva, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).
[40] Z. J. Huang, L. G. Lin, J. J. Lin, C. Y. Huang, X. L. Cheng, and J. C. Ho, Chin. J. Phys. **34**, 505 (1996).
[41] A. Krol, C. S. Lin, Y. L. Soo, Z. H. Ming, Y. H. Kao, Jui H. Wang, Min Qi, and G. C. Smith, Phys. Rev. B **45**, 10 051 (1992).
[42] M. B. J. Meinders, H. Eskes, and G. A. Sawatzky, Phys. Rev. B **48**, 3916 (1993).
[43] J. Van Elp, H. Eskes, P. Kuiper, and G. A. Sawatzky, Phys. Rev. B **45**, 1612 (1992).
[44] Z. Iqbal, E. Leone, R. Chin, A. J. Signorelli, A. Bose, and H. Eckhardt, J. Mater. Res. **2**, 768 (1987).
[45] N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B **39**, 6619 (1989).
[46] A. Bianconi, M. DeSantis, A. Di Ciccio, A. M. Flank, A. Fronk, A. Fontaine, P. Legarde, H. K. Yoshida, A. Kotani, and A. Marcelli, Phys. Rev. B **38**, 7196 (1988); Physica C **153-155**, 1760 (1988).