

Superconductivity suppression of $R(\text{Ba}_{1-z}\text{Pr}_z)_2\text{Cu}_3\text{O}_{7+\delta}$ ($R = \text{Nd}, \text{Pr}$) probed by soft-x-ray absorption spectroscopy

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O K -edge x-ray-absorption near-edge-structure (XANES) spectra of $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ for $x = 0-0.5$ and $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ for $z = 0-0.25$ were performed to search for microstructural features and hole distribution related to the superconducting properties. Near the O $1s$ edge, prepeaks at ~ 527.6 and ~ 528.3 eV are assigned to transitions into O $2p$ holes located in the CuO_3 ribbons and CuO_2 planes, respectively. As deduced from O $1s$ absorption spectra of $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ for $x = 0-0.5$, the hole concentrations in the CuO_2 planes and CuO_3 ribbons decrease monotonically with increasing Pr doping. The present XANES results clearly reveal that the suppression of superconductivity with Pr doping in $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ results predominantly from the hole depletion effect. The effect of Pr on the Ba site in $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ is to reduce the hole concentration in the CuO_2 planes and to create localized fivefold Cu chain sites. T_c of $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ is depressed upon Pr doping, primarily due to hole filling and hole localization. Compared to $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$, the enhanced suppression of T_c in $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ is primarily due to the hole localization. [S0163-1829(99)04505-1]

I. INTRODUCTION

It is well established that chemical substitution of Y in $\text{YBa}_2\text{Cu}_3\text{O}_7$ by rare-earth elements (Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu) neither affects its superconducting properties nor significantly changes the corresponding superconducting transition temperature (T_c) of ~ 92 K.^{1,2} The high- T_c cuprate superconductors $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = Y$ and rare-earth elements except Ce, Pr, and Tb) exhibit a wide range of oxygen stoichiometry ($0 \leq \delta \leq 1$) and undergo an orthorhombic-to-tetragonal transition as a result of variation in the oxygen content and oxygen distribution.³⁻⁶ In the fully oxygenated orthorhombic form of $R\text{Ba}_2\text{Cu}_3\text{O}_7$, all of the oxygen chain sites O(1) at $(0, \frac{1}{2}, 0)$ positions are occupied, while all of the oxygen antichain sites O(5) at $(\frac{1}{2}, 0, 0)$ positions are empty. As δ increases, the nearly full oxygen chain sites O(1) give away oxygen, while the nearly empty antichain sites O(5) take up oxygen. At higher values of δ , with more of the O(5) sites being occupied, the structural transformation to tetragonal symmetry occurs.⁴ Dramatic electronic and magnetic properties changes also accompany this structural transition. T_c is dramatically affected by oxygen content, oxygen distribution, and crystal symmetry.⁷⁻¹⁰

In addition to thermal treatments, the oxygen content and the crystal symmetry of the $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds may be changed by chemical substitution.¹¹ For the lighter rare-earth elements, the ionic radii approaches that of the Ba, allowing a large degree of substitution of the R for Ba without forming second phases. Thus the equilibrium phase diagram changes with rare-earth elements, and shows vary-

ing amounts of solid solution of the form $R_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$.¹²⁻¹⁴ In $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ [$\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123] compounds, the existence of a solid solution has been found in a range from $z = 0-0.3$.¹⁵ The superconducting properties in this system can be controlled via changing the substitution of divalent Ba by trivalent Pr in addition to changing the oxygen stoichiometry. For $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 samples with $z < 0.125$, the space group is $Pmmm$ (orthorhombic), while the structure collapsed to the tetragonal space group, $P4/mmm$, for higher substitution of the trivalent Pr ion for the divalent Ba ion.¹⁵ The chemical substitution of the Pr ion for the Ba ion in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 leads to a monotonic decrease of the superconducting transition temperature from $T_c = \sim 92$ K for $z = 0$ to nonsuperconducting for $z = 0.15$. Magnetization measurements show that $z = 0.15$ is paramagnetic down to 10 K. Although the physical properties in this system were reported by Kramer *et al.*,¹⁵ the relationship between the hole distribution, microstructural features, and superconductivity behavior was not established in detail.

The substitution of Y by Pr in $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$ [$(\text{Y}_{1-x}\text{Pr}_x)$ -123] also leads to a significant decrease in T_c , with superconductivity disappearing for $x > 0.55$, whereas the orthorhombic structure remains unchanged.¹⁶ Furthermore, it has been observed that the depression of T_c by Pr is R radius dependent in $(R_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$ [$(R_{1-x}\text{Pr}_x)$ -123] with fixed x . The smaller the atomic number of rare-earth elements in host compounds is, the greater the decrease in T_c is.^{17,18} In spite of much experimental and theoretical work being undertaken, the mechanism of the superconductivity

suppression in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is still the subject of controversial discussion.^{19–21}

From studies by various methods on $(\text{Y}_{1-x}\text{Pr}_x)$ -123 samples, different mechanisms for the decrease in T_c with increasing Pr content have been suggested. Models for explaining the depression of superconductivity in $(\text{R}_{1-x}\text{Pr}_x)$ -123 include hole filling,²² hole localization,²³ percolation,²⁴ magnetic pair breaking,^{22,25} disorder on the Ba site,²⁶ and hole transfer from planes to chains.²⁷ However, no model allows for a consistent interpretation of all the experimental data. As an example, based on high-temperature susceptibility studies, $\text{PrBa}_2\text{Cu}_3\text{O}_7$ shows an effective Pr moment $\sim 2.7\mu_B$, comparable to that of the free Pr^{4+} ions ($2.5\mu_B$).²⁸ This supports the hole-filling model, which is based on Pr being in the +4 valence state. However, this proposal was criticized in view of experimental results based on structural investigation,²⁹ x-ray-absorption spectroscopy,^{21,30} and Raman spectroscopy,³¹ which were interpreted in terms of the simple Pr^{3+} ion.

To improve the understanding on the mechanism of T_c suppression, a detailed study on other $(\text{R}_{1-x}\text{Pr}_x)$ -123 systems would be helpful. Studies of the effect of the Pr ion on superconductivity may help in our comprehensive understanding of the origin of the high- T_c superconductivity. We therefore systematically measure the variation of electronic structure near the Fermi level for a series of $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ [$(\text{Nd}_{1-x}\text{Pr}_x)$ -123] compounds. The chemical substitution of the Pr ion for the Nd ion in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 depresses superconductivity in a systematic, linear fashion from $T_c \cong 92$ K for $x=0$ to $T_c \cong 20$ K for $x=0.3$. The compound becomes a semiconductor at $x \geq 0.4$.¹⁵

In this study, we investigate the role of nominally substituting Pr onto Ba sites, and R sites onto the superconductivity, in samples prepared with the nominal compositions of $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ ($z=0-0.25$) and $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ ($x=0-0.5$), respectively. There are two reasons for using a slightly overdoped rare earth in these systems. First, unlike $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, stoichiometric $\text{NdBa}_2\text{Cu}_3\text{O}_7$ does not form in 100% O_2 .³² Second, it has been shown that optimal doping occurs for 0.05 Nd on Ba sites in the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$ compounds.³³ For these reasons, all samples in this study were synthesized using 1.05 R atoms per formula unit.

It is well known that hole states play a pivotal role for superconductivity in p -type cuprate superconductors. Therefore, a knowledge of the electronic structure near the Fermi level of these compounds is an important step toward unveiling the mechanism of superconductivity. Soft-x-ray-absorption spectroscopy using synchrotron radiation has been widely applied to investigate the unoccupied states at the O and Cu sites in the high- T_c cuprates. In this study, O K -edge x-ray-absorption measurements in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0-0.5$ and $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 for $z=0-0.25$ were performed to search for microstructural features and hole distribution related to the superconducting properties.

II. EXPERIMENT

Details on the preparation of samples were reported elsewhere.¹⁵ In brief, $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0-0.5$ was prepared by mixing and heating appropriate amounts of

Nd_2O_3 , Pr_6O_{11} , BaCO_3 , and CuO powders at $\sim 880^\circ\text{C}$ in air for 24 h. This was repeated, with grinding of the sample between calcinations (up to four times). Samples were then annealed at 950°C for 48 h in 100% O_2 , and ground again. X-ray diffraction (XRD) showed that all samples were single phase with an orthorhombic structure.

$\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 was prepared by mixing and heating appropriate amounts of Nd_2O_3 , Pr_6O_{11} , BaCO_3 , and CuO powders at 880°C in air twice, then annealing at 940°C in 100% O_2 three times, with grinding in between. Oxygenation was performed on ground powders at 450°C for 24 h. Heat treatments were repeated until (XRD) and differential thermal analysis confirmed the formation of a single-phase solid solution. For the x-ray-absorption measurements, 400-mg aliquots from the larger 10-g batches were pressed into 6-mm pellets, and annealed as described above but with an additional oxygenation step of 450°C for 48 h.

Using the 6-m high-energy spherical grating monochromator beamline, the x-ray-absorption measurements were performed at the Synchrotron Radiation Research Center with an electron-beam energy of 1.5 GeV and a maximum stored current of 240 mA. X-ray-absorption spectra recorded by total x-ray fluorescence yield were measured using a microchannel plate (MCP) detector.³⁴ This MCP detector consists of a dual set of MCPs with an electrically isolated grid mounted in front of them. The x-ray fluorescence yield measurement is strictly bulk sensitive with a probing depth of thousands of Å. During the x-ray fluorescence yield measurements, the grid was set to a voltage of 100 V while the front of the MCPs was set to -2000 V and the rear to -200 V. The negative MCP bias was applied to expel electrons before they entered the detector, while the grid bias insured 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 sample normal. The incident photon intensity (I_0) was measured simultaneously by a Ni mesh located after the exit slit of the monochromator. All the absorption spectra were normalized to I_0 . The photon energies were calibrated using the known O K -edge absorption peaks of CuO . The O K -edge x-ray-absorption spectra of both series of compounds for different Pr dopings were normalized to the integrated area between 535 and 555 eV with respect to the number of O atoms per unit cell. The energy resolution of the monochromator was set to ~ 0.22 eV for the O K -edge x-ray-absorption measurements. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

A. XANES of $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$

The x-ray-absorption spectra of materials are determined by electronic transitions from a selected atomic core level to the unoccupied states. Based on dipole selection rules, only local unoccupied states with major O $2p$ character are probed in the oxygen K -edge x-ray-absorption near edge spectra (XANES). Therefore, if the hole states near the Fermi level in the p -type cuprates are primarily of O $2p$ character, a pre-edge peak should be visible in the O K -edge

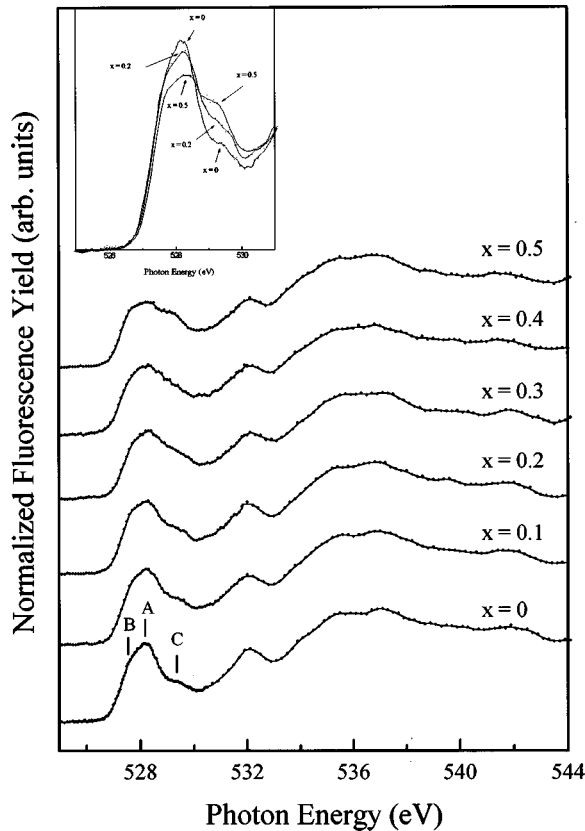


FIG. 1. O K -edge x-ray-absorption spectra for a series of $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ samples for $x=0-0.5$. The O K -edge x-ray absorption spectra of various compounds of different Pr content were normalized to the integrated area between 535 and 555 eV.

absorption spectrum with an intensity proportional to the total number of holes on the O sites, which includes both mobile and localized holes.

In Fig. 1, the O K -edge x-ray-absorption spectra for a series of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 samples for $x=0-0.5$ are shown in the energy range of 525–544 eV, obtained using a bulk-sensitive x-ray fluorescence yield method. The predominant features in the O $1s$ x-ray-absorption spectrum of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0$ are two distinct prepeaks at ~ 528.3 and ~ 529.3 eV, with a shoulder at ~ 527.6 eV, and a broad peak at ~ 537 eV. As shown, beyond 535 eV, the x-ray-absorption spectra of these samples are virtually indistinguishable and independent of Pr concentration. The low-energy prepeaks with energy below 532 eV are ascribed to photoexcitation of the O $1s$ core electrons to hole states with major O $2p$ character. The enhanced peaks above 535 eV in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 may originate from unoccupied states related to the Ba $4d$, Cu $4s$, or Cu $4p$ states hybridized with O $2p$ states.^{23,35}

The crystal structure of $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is composed of two $\text{Cu}(2)\text{O}(2)\text{O}(3)$ layers separated by a Nd plane. The unit of CuO_2 and Nd planes are separated by a CuO_3 ribbon consisting of a $\text{BaO}(4)$ plane, a $\text{Cu}(1)\text{O}(1)$ chain along the b axis, and another $\text{BaO}(4)$ plane. Therefore, there exist four nonequivalent oxygen sites in $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$: O(2), and O(3) within the $\text{Cu}(2)\text{O}_2$ layers, O(4) in the BaO planes, and O(1) in the $\text{Cu}(1)\text{O}$ chains. With respect to the O $1s$ edge,

the observed different O $1s$ thresholds in Fig. 1 may be due to chemical shifts originating from the influence of charges on the oxygen sites and the site-specific neighborhood.³⁶ Based on the polarization-dependent x-ray-absorption measurements on single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$,⁷ it was found that O(2) $1s$ level is about 0.8 eV lower in energy than the O(4) $1s$ level. The O(1) $1s$ binding energy is in between those of O(4) and O(2,3). These results are consistent with the theoretical predictions.³⁷ In the O K -edge x-ray-absorption spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the prepeaks at ~ 527.8 eV are attributed to transitions into O $2p$ holes in the CuO_3 ribbons (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.^{7,38}

The orthorhombic $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound is isomorphic with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (space group $Pmmm$). When oxygen is removed from the $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds, the system behaves analogously to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a reduction in total hole concentrations and T_c .³³ In addition, when oxygen is removed from $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a strong reduction of the prepeak structure in the O $1s$ x-ray-absorption spectrum is observed,²³ as seen for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds.⁷ The low-energy loss function of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta\sim 0.3$) is very similar to that measured for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta\sim 0.2$) compound. As shown in Fig. 1, the O $1s$ x-ray-absorption spectra of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 exhibit similar features to these observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for $\delta=0$.^{7,38} We therefore adopt the same assignment scheme for the O $1s$ x-ray-absorption spectra of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 ($x=0-0.5$). The high-energy prepeak at ~ 528.3 eV, as marked by A in Fig. 1, is attributed to the excitation of O $1s$ electrons to O $2p$ holes in the CuO_2 planes. The low-energy prepeaks at ~ 527.6 eV, as marked by B in Fig. 1, are due to the superposition of O $2p$ hole states in the apical oxygen sites and the CuO chains. As shown in the inset of Fig. 1, the prepeak at ~ 528.3 eV, originating from the O $2p$ hole states in the CuO_2 layers, shows a decrease in spectral weight with an increasing dopant concentration of Pr. This clearly demonstrates that the chemical substitution of the Pr ion on the R site in the $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 system leads to a decrease in the hole concentration within the CuO_2 planes. Based on x-ray-absorption studies in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the absorption peak at ~ 529.3 eV, as marked by C in Fig. 1, can be ascribed to transitions between O $1s$ core states and the empty upper Hubbard Cu $3d$ conduction band.^{39,40} This kind of pre-edge structure is a result of hybridization in the ground state of the Cu $3d^9$ and Cu $3d^{10}L$ states, where L is a ligand hole from the O $2p$ band.⁴¹ Due to the strong on-site correlation effects on the copper sites in the cuprate superconductors, an upper Hubbard band (UHB) has always been assumed to exist.⁴¹

In order to investigate the variation of the hole states among different oxygen sites as a function of the Pr doping, these pre-edge features shown in Fig. 1 were analyzed by fitting Gaussian functions to each spectrum. In Fig. 2 the relative intensity of each prepeak is plotted as a function of Pr content x in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123. As noted from Figs. 2(a) and 2(b), the hole content from the CuO_2 planes decreases dramatically with increasing Pr doping, while that from apical oxygen sites and CuO chains decreases slowly. In addition, as shown in Fig. 2(c), the peak at ~ 529.3 eV originat-

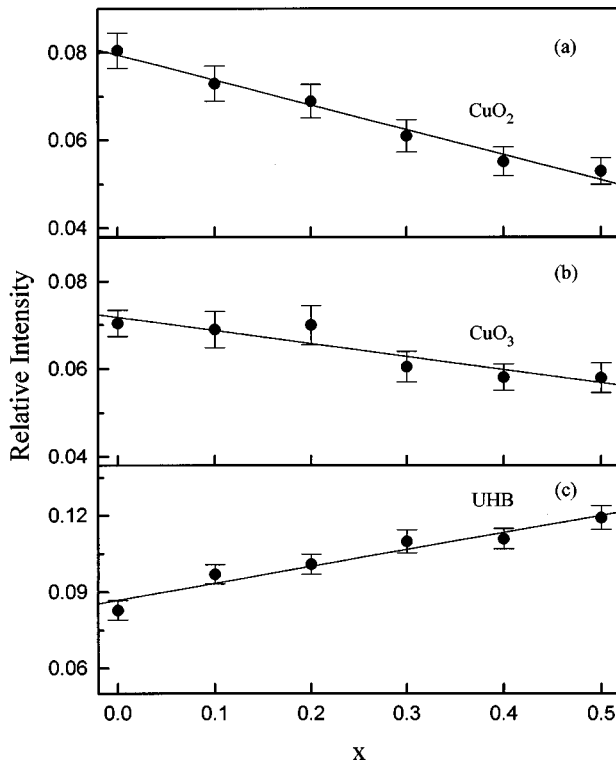


FIG. 2. Doping dependence of the relative intensity of hole states in $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ on oxygen sites originating from the (a) CuO_2 planes, (b) CuO_3 ribbons, and (c) upper Hubbard band (UHB). The solid curves are drawn as a guide for the eyes.

ing from the UHB shows a monotonic increase in spectral weight as the Pr doping increases. This change is related to a spectral weight transfer of states from the UHB to doping-induced hole states near the Fermi level.⁴² A similar behavior has also been observed in the O $1s$ absorption spectra of other p -type cuprate superconductors.^{38,39,43}

It has been proposed by Fehrenbacher and Rice (FR) that, in the $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compound, the holes are localized in a hybridized state at Pr sites with a mixture of $4f^2L(+3)$ and $4f^1(+4)$ configurations.⁴⁴ Here L denotes the ligand hole in the O $2p$ orbital around the Pr site, and is distributed over the eight nearest oxygen sites. This hybridized state is competitive in energy with the hole states in the CuO_2 planes. The FR model assumes hole depletion in the CuO_2 planes, not because of higher Pr valence but because of transfer of the holes from the CuO_2 planes into the FR state which binds doped holes to the Pr sites. The strong hybridization between Pr $4f$ states and conduction bands was supported on the bases of critical magnetic field,²⁵ x-ray-absorption measurement,^{21,35} photoemission spectroscopy,³⁰ and spin-polarized electronic-structure calculations.⁴⁵ 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 $(R_{1-x}\text{Pr}_x)$ -123.

Recently, taking correlation effects on the rare-earth site into account, Liechtenstein and Mazin (LM) calculated the electronic structure of $(R_{1-x}\text{Pr}_x)$ -123 using an *ab initio* local-density approximation plus a Hubbard parameter including Coulomb correlation in the f shell.^{46,47} They found that, in $\text{PrBa}_2\text{Cu}_3\text{O}_7$, there forms an additional hole-depleting

band which crosses the Fermi level and consequently “grabs” holes from the CuO_2 band. On doping different rare-earth elements in $(R_{1-x}\text{Pr}_x)$ -123, the position of this hole-depleting band shifts with the atomic number of the rare earth, through the energy level of $4f$ orbitals, leading to the R dependence of the suppression of T_c .⁴⁶

Taking consideration of Madelung potentials in $\text{YBa}_2\text{Cu}_3\text{O}_7$, a simple estimation indicates that the energy of the hole states in CuO_3 chains is slightly higher than the holes in the CuO_2 planes. In addition, based on band-structure calculations^{48,49} and x-ray-absorption measurements,^{7,50} it has been shown that the holes near the Fermi level in $\text{YBa}_2\text{Cu}_3\text{O}_7$ are distributed between the CuO_2 planes and CuO_3 ribbons. If the LM model is valid, it is therefore expected that, in the $(R_{1-x}\text{Pr}_x)$ -123 system, the hole concentrations in the CuO_2 planes and the CuO_3 ribbons should decrease with increasing Pr doping.

As shown in Figs. 1 and 2, the reduction in hole concentration upon Pr doping observed in the $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 system provides evidence in support of the LM model. It has been experimentally shown that the concentration of O $2p$ holes in the CuO_2 planes is strongly correlated with T_c in the p -type cuprates.^{7,51} Accordingly, the T_c value in the $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 system should decrease with increasing Pr content. Our experimental results clearly demonstrate that the quenching of superconductivity with Pr doping in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 results predominantly from the hole depletion.⁵² The present results are consistent with those obtained for $(\text{Y}_{1-x}\text{Pr}_x)$ -123 by Merz *et al.*³⁵ However, the hole depletion rate in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 with Pr doping is greater than that in $(\text{Y}_{1-x}\text{Pr}_x)$ -123. This may be related to the fact that superconductivity disappears at $x > 0.55$ in $(\text{Y}_{1-x}\text{Pr}_x)$ -123, while $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 becomes a semiconductor at $x \geq 0.4$.¹⁵

B. XANES of $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$

Figure 3 shows O K -edge x-ray fluorescence-yield spectra of the $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 compounds for $z = 0-0.25$. The prominent features in the O $1s$ absorption edge for samples with $z = 0.05$ are two strong prepeaks at ~ 528.3 and ~ 529.3 eV with a shoulder at ~ 527.6 eV, and a broad peak at ~ 537 eV.

The $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 compounds for $z < 0.125$ are isomorphic with orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (space group $Pmmm$). With the increase of Pr content in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123, the compound becomes tetragonal for $z > 0.125$ (space group $P4/mmm$) for fully oxygenated samples. The tetragonal structure is isomorphic with $\text{YBa}_2\text{Cu}_3\text{O}_6$.⁴ We therefore adopt the same scheme in the assignment of present O $1s$ absorption spectra discussed above. Near the O $1s$ edge, prepeaks at ~ 527.6 and ~ 528.3 eV are assigned to transitions into O $2p$ holes located in the CuO_3 ribbons and the CuO_2 planes, respectively. The absorption peak at ~ 529.3 eV is assigned to a $3d^{10}L \rightarrow O 1s^{-1}3d^{10}$ transition, i.e., a transition into O $2p$ states hybridized with the UHB with predominantly Cu $3d$ character. Because the substitution of Pr^{3+} for Ba^{2+} will donate the electrons, this results in canceling a hole within the CuO_2 planes. As shown in the inset of Fig. 3, the prepeak at ~ 528.3 eV originating from the O $2p$ hole states in the

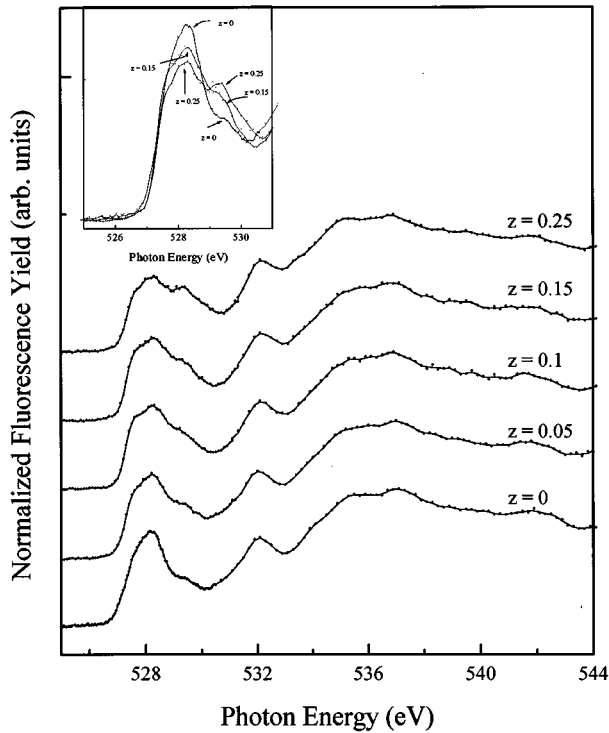


FIG. 3. O K -edge x-ray-absorption spectra of $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ with a Pr content of $z=0.0, 0.05, 0.1, 0.15,$ and 0.2 . The O K -edge x-ray-absorption spectra of various compounds for different Pr dopings were normalized to the integrated area between 535 and 555 eV with respect to the number of O atoms per unit cell.

CuO_2 layers shows a decrease in intensity with an increasing dopant concentration of Pr. This gives evidence in support of the filling of holes in the CuO_2 planes by increasing the Pr content in the $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 system.⁵³

For comparison, the O $1s$ x-ray-absorption spectra of $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 for $z=0.15$ and $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0.3$ are displayed in Fig. 4. The O K -edge absorption spectra in Fig. 4 have been normalized to the integrated area between 535 and 555 eV with respect to the number of O atoms per unit cell, providing the absolute intensities of the prepeaks for the $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 and $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 compounds. This is due to the fact that the spectra above 535 eV for both series of compounds are quite similar. As shown in Fig. 4, the spectral weights of the low-energy prepeaks are nearly identical for both compounds. This indicates that the total number of holes within the in-plane oxygen sites is approximately the same for both compounds. However, it should be pointed out that $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 for $z=0.15$ is not superconducting, while $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0.3$ exhibits a T_c midpoint of ~ 15 K.¹⁵ Based on the results from x-ray-absorption spectra in Fig. 4, it is concluded that the partial hole states in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 may be localized.

Many experiments suggest a close relationship between superconducting transition temperature and carrier concentration in high- T_c cuprate superconductors.^{7,51} Furthermore, it has long been recognized that T_c is strongly influenced by the degree of oxygen vacancy order in the chain sites of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure when the material is oxygen deficient.⁸⁻¹⁰

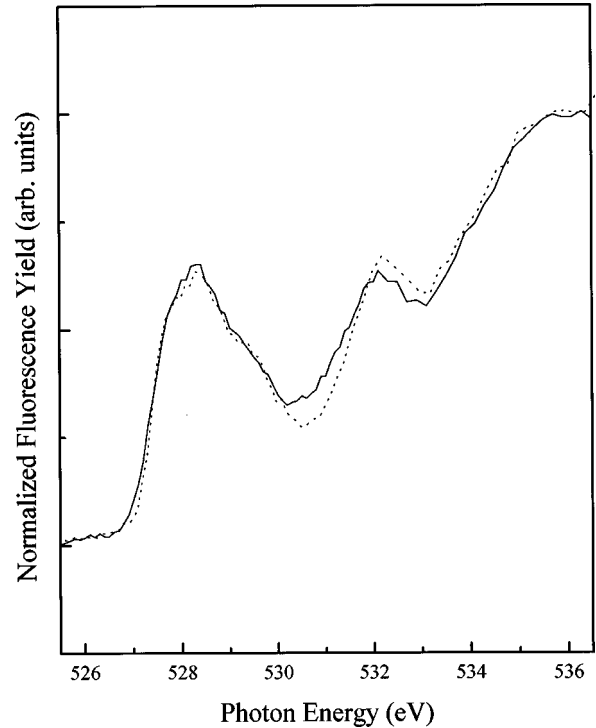


FIG. 4. O $1s$ x-ray-absorption spectra of $\text{Nd}_{1.05}(\text{Ba}_{1-z}\text{Pr}_z)_{1.95}\text{Cu}_3\text{O}_{7+\delta}$ for $z=0.15$ (dashed line) and $(\text{Nd}_{1-x}\text{Pr}_x)_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_7$ for $x=0.3$ (solid line).

Neutron-diffraction data on the $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 system ($z=0-0.3$), refined by the Rietveld method, show that while mixing of the R ions occurs, Pr “favors” the Ba site over Nd nearly 2 to 1.¹⁵ It is also found that the total O content increases to balance the charge of the R ion on the Ba site. In addition, the number of O(1) atoms at $(0, \frac{1}{2}, 0)$ positions on the chain sites decreases by approximately $0.5z$ while the antichain O(5) site at $(\frac{1}{2}, 0, 0)$ positions occupancy increases approximately as z . This indicates that the R ion on the Ba site always causes an O to occupy an adjacent O(5) site. In order to maintain charge balance, half of these O’s are additional atoms incorporated into the structure, while the other half are relocated from O(1) sites. Therefore, chemical substitution of R for Ba sites creates non-fourfold planar coordinated coppers on the chain sites either by introducing an extra O into the structure corresponding to adding a hole to the chains, or robbing a chain O from elsewhere in the structure. Disruption of fourfold Cu chains upon substitution of Ba with R then becomes analogous to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for increasing δ .⁵⁴ According to the calculations of Gupta and Gupta, these sites do not result in hole transfer from the chains to the conducting CuO_2 planes.⁵⁵ The charge transferred to the CuO_2 plane is therefore much lower than that introduced into the chain upon Pr doping.

In addition to disruption of fourfold Cu chains, the fivefold Cu chain sites are created due to occupancy of the O(5) sites. These fivefold Cu chain sites are similar to the fivefold sites on the CuO_2 plane. It is therefore reasonably expected that this state arising from the hybridization of the O $2p$ and Cu states may be competitive in energy to the hole states in the CuO_2 planes. This leads to transfer of the holes from the CuO_2 planes into the antichain oxygen site. As this state is more localized than the plane sites and thus makes a greatly

reduced contribution to the superconductivity of the materials.¹⁴ Although the hole concentrations between $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 for $z=0.15$ and $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0.3$ are approximately the same, as observed in Fig. 4, the significant difference in superconducting properties for both compounds gives an evidence in support of this interpretation. Therefore, the effect of Pr on the Ba site in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 is to reduce the hole concentration in the CuO_2 planes and to create the localized fivefold Cu chain sites. Thus the hole loss and hole localization lead to the decrease in T_c with increasing the Pr content z in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123. A similar chemical model is presented to explain the variation of T_c with oxygen stoichiometry in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the dependence of T_c on oxygen vacancy order.⁵⁴ Accordingly, compared to $(\text{Nd}_{1-x}\text{Pr}_x)$ -123, the enhanced suppression of T_c in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 is primarily due to the hole localization.

IV. CONCLUSION

In this study, we report high-resolution O *K*-edge x-ray-absorption spectra of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 for $x=0-0.5$ and $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 for $z=0-0.25$ to investigate the role of nominally substituting Pr onto Ba sites, and R sites onto the superconductivity. Near the O 1s edge, the multiple prepeak is related to the different O 1s binding energies of the non-

equivalent oxygen sites in the crystal structure. The distribution of holes on the different oxygen sites has been derived for $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 in the doping range $0 \leq x \leq 0.5$. As deduced from O *K*-edge x-ray-absorption spectra of $(\text{Nd}_{1-x}\text{Pr}_x)$ -123, the hole concentrations in the CuO_2 planes and the CuO_3 ribbons decrease monotonically with increasing the Pr doping, consistent with the predictions by the LM model. The present XANES results clearly reveal that the quenching of superconductivity with the Pr substitution in $(\text{Nd}_{1-x}\text{Pr}_x)$ -123 arises predominantly from the hole depletion effect. The effect of Pr on the Ba site in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 is to reduce the hole concentration in the CuO_2 planes and to create the localized fivefold Cu chain site. The T_c of $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 is depressed upon Pr doping primarily due to hole filling and hole localization. Compared to $(\text{Nd}_{1-x}\text{Pr}_x)$ -123, the enhanced suppression of T_c in $\text{Nd}(\text{Ba}_{1-z}\text{Pr}_z)$ -123 is primarily due to the hole localization.

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