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X-ray absorption spectroscopy of detwinned $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ single crystals: Electronic structure and hole distribution

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Substituting Y in orthorhombic $(Y,R)\text{Ba}_2\text{Cu}_3\text{O}_7$ by any rare-earth element $R$ has generally little effect on the superconducting properties. For $R=\text{Pr}$, however, superconductivity is completely suppressed. To understand this effect we have studied the unoccupied electronic structure of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($x=0.0, 0.4, 0.8$) using polarization-dependent O 1s near-edge x-ray absorption spectroscopy of detwinned single crystals. We identify the hole states in the CuO$_2$ planes and the CuO$_3$ chains and give estimates of the relative contributions of the O 2$p_x$, O 2$p_y$, and O 2$p_z$ orbitals to these states. Along with the comparison of oxygen-rich ($y=0.1$) to the oxygen-depleted materials ($y=0.9$), this allows a test of the current theoretical explanations for the Pr-induced suppression of superconductivity. While we can rule out models involving hole filling or charge transfer between the planes and the chains, our data are consistent with approaches based on Pr 4$f$–O 2$p_z$ hybridization. [S0163-1829(97)03313-4]

I. INTRODUCTION

The discovery of high-temperature superconductivity (HTSC) in 1986 (Ref. 1) has triggered a cascade of theoretical and experimental research concerning the underlying mechanism of HTSC, but nevertheless an unambiguous answer to the question of the origin of HTSC remains elusive. Much work has concentrated on direct determinations of the spatial, electronic, and phonon structure of high-temperature superconductors. One complementary approach is to investigate compounds obtained from high-temperature superconductors. By specifically substituting characteristic elements, gate compounds obtained from high-temperature superconductors. One complementary approach is to investigate compounds obtained from high-temperature superconductors. While we can rule out models involving hole filling or charge transfer between the planes and the chains, our data are consistent with approaches based on Pr 4$f$–O 2$p_z$ hybridization. [S0163-1829(97)03313-4]
In order to explain the $T_c$ suppression in the $p$-type system $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$, up to now several models have been suggested while still no general agreement on the Pr valence has been reached. The prevailing proposals can be divided into three main categories: (i) filling of mobile holes, (ii) magnetic interaction and/or localization effects mediated through hybridization of Pr 4f with O 2p states, and (iii) gradual hole transfer between the planes and the chains.

In the hole-filling model the Pr valence is assumed to be greater than +3 to explain the lack of metallic behavior in PrBa$_2$Cu$_3$O$_y$. In the case of the Ca-induced recovery of superconductivity in thin films of Pr$_{0.5}$Sr$_{0.5}$Ba$_2$Cu$_3$O$_7$, since superconductivity in YBa$_2$Cu$_3$O$_{7-y}$, just as in La$_2$-Sr$_x$Cu$_3$O$_{4+y}$, requires holes in the conducting CuO$_2$ planes, delocalized holes in the planes are annihilated due to the substitution of trivalent Y by Pr with a valence greater than 3+. This approach implies that the suppression of superconductivity results from a reduced number of charge carriers in the CuO$_2$ planes. Magnetic susceptibility,$^{6,8,12}$ Hall effect,$^3$ thermopower,$^{7,9,10}$ nuclear magnetic resonance,$^{15}$ muon-spin relaxation,$^{16}$ and neutron diffraction measurements$^{22-24}$ have been interpreted in terms of hole depletion. On closer inspection, however, it has been shown that these results can also be understood as an indication for Pr$^{3+}$. For example, Söderholm et al.$^{25}$ and Hilscher et al.$^{26}$ were able to explain the reduced magnetic moment, taking a crystal field splitting of the $3H_4$ ground state of Pr$^{3+}$ into consideration. On the other hand, most band structure calculations$^{27}$ and high-energy spectroscopy experiments support a trivalent Pr atom. These experiments include resonant photoemission spectroscopy,${}^{28}$ x-ray absorption,$^{29,30}$ and electron energy-loss spectroscopy$^{31}$ on the O 1s, Pr 2p, and Pr 3d edges. Taken together, this evidence effectively rules out hole filling as responsible for the lack of superconductivity.

Alternatively, a magnetic pair-breaking effect by the local moment of the Pr atom has been invoked as an explanation,$^{12,27}$ since the degradation of $T_c$ with increasing Pr concentration seemed to be compatible with Abrikosov-Gorkov theory. However, pair breaking itself does not localize charge carriers and, thus, explains neither the nonmetallic PrBa$_2$Cu$_3$O$_7$ nor the recovery of superconductivity upon doping with Ca. In addition, $T_c$ remains wholly unaffected upon substitution of Y by Gd although the Gd $^{89}S_{7/2}$ ground state exhibits a much stronger magnetic moment than the $3H_4$ ground state of Pr$^{3+}$.

Quite early on, a further approach to this problem was put forward: O 2p$_z$ holes (for nomenclature see Ref. 34) are still present in the CuO$_2$ planes but are assumed to be strongly hybridized with Pr 4f states.$^{31}$ This renders the initially mobile holes localized and in effect leads to the insulating and nonsuperconducting behavior observed. However, this explanation was also refuted as hybridization of Pr 4f with O 2p states vanishes by symmetry and the hybridization with Cu 3d$_{x^2-y^2}$ states is very small. Thus, based on the optical data of Takenaka et al.$^{32}$ and Fehrenbacher and Rice (FR), the absence of superconductivity in PrBa$_2$Cu$_3$O$_7$ by the existence of a local Pr 4f$_{(x^2-y^2)-O}$ 2p$_z$ hybridized state$^{33,34}$ which binds the holes of the planes to Pr sites. They conclude that holes are transferred from primarily planar O 2p$_z$ to O 2p$_z$ orbitals, i.e., from the Zhang-Rice (ZR) state$^{35,36}$ into this FR state. According to Fehrenbacher and Rice, the only possible hole state is a superposition of the eight O(2,3) 2p$_z$ orbitals with $f_{(x^2-y^2)}$ symmetry with respect to the central Pr atom, and they assume that the O 2p$_z$ orbitals point towards the Pr atom. This seems to suggest that the O 2p$_z$ orbitals are "rotated" by about 45° with respect to the CuO$_2$ planes.$^{33,34}$ To facilitate the hybridization between the eight O 2p$_z$ orbitals and the $f_{(x^2-y^2)}$ states of the central Pr atom a fraction $n_F \approx 0.5$ of all Pr atoms has to be in the formal oxidation state IV. Finally, Fehrenbacher and Rice assess the number of holes transferred to the Pr atom to be $n_p \approx 0.15–0.2$. Remarkably, this small number—still compatible with the experimental findings for the Pr valence—suffices to stabilize the FR hybridization, thus localizing the holes in the Pr 4f$_{(x^2-y^2)-O}$ 2p$_z$ orbitals.

Taking correlation effects on the rare-earth site into account, Liechtenstein and Mazin presented local density approximation (LDA) + $U_{\text{Pr}}$ calculations based on the idea of FR states.$^{37}$ In contrast to Fehrenbacher and Rice,$^{33}$ they find a dispersive ligand band in place of local $p_\pi$ orbitals with $f_{(x^2-y^2)}$ symmetry around the central R atom. Due to the interaction with the Pr 4f state, the top of this ligand band is partially pushed above the Fermi level, thereby grabbing the mobile holes from the ZR state. Liechtenstein and Mazin emphasize that this band has mainly planar character at the zone corner, where the band is above the Fermi level ($E_F$), and $p_\pi$ character only at the zone center, where the FR band lies $\approx 2$ eV below $E_F$. In order to account for the insulating behavior of PrBa$_2$Cu$_3$O$_7$ they assume substantial disorder on the Pr site.

A further model based on the Hamiltonian of Fehrenbacher and Rice was proposed by Wang et al.$^{38}$ In their approach, three states are competing close to the Fermi level: the ZR state, the FR state, and the hole states of the CuO$_3$ chains. Upon increasing the Pr concentration to $x = 0.5$ all of the holes residing on the ZR state are transferred to the FR state. On further Pr doping, chain holes, too, are transferred...
to the FR state and, finally, for PrBa$_2$Cu$_3$O$_{7-\delta}$ all holes reside on the FR state and none are left in the chains.

A qualitative discussion of the electronic structure of Pr$_{0.4}$Y$_{0.6}$Ba$_2$Cu$_3$O$_{7-\delta}$ was given by Khomskii.\textsuperscript{39} He proposed a gradual charge redistribution between planes and chains upon increasing Pr content. Therefore, beyond a critical Pr concentration all the remaining holes should reside on the chains—predominantly on the O(1) 2$p_x$ orbitals—and no holes should be left in the planes.

Lately, Blackstead and Dow suggested a model which is based on disorder effects on the Ba site.\textsuperscript{40} They argue that, while superconductivity is still present in the chains of ideal PrBa$_2$Cu$_3$O$_7$, it is quenched in real crystals by magnetic pair breaking due to Pr impurities on the Ba sites.

The aim of this paper is to distinguish between the various models by carefully examining the electronic structure of PrBa$_2$Cu$_3$O$_{7-\delta}$ close to the Fermi level. For this, we have conducted O 1s near-edge x-ray absorption fine structure (NEXAFS) studies of Pr$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$. Utilizing the linearly polarized character of synchrotron radiation we took a critical look at the various models mentioned above. In particular, if FR states do exist, NEXAFS should be well suited for determining a rotation angle\textsuperscript{34} of the O(2,3) 2$p_x$ orbitals.

The paper is organized as follows: Section II covers sample preparation and data collection. In Sec. III, we will expound the features of the NEXAFS data after briefly reviewing the results of our neutron diffraction measurements. Section IV discusses the implications of the NEXAFS results and, finally, the conclusions are drawn in Sec. V.

II. EXPERIMENT

Pr$_{1-x}$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ single crystals were grown using standard methods. Full details of the growth process can be found in Refs. 41 and 42. The use of Al$_2$O$_3$ crucibles was avoided since they introduce Al impurities of up to 50% on the Cu site.\textsuperscript{42} For $x = 0.0$ and 0.8, the samples were grown in an Y$_2$O$_3$-stabilized ZrO$_2$ crucible, which resulted in crystals with no detectable Zr content. The Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{7-\delta}$ crystals were grown in a novel inert BaZrO$_3$ crucible.\textsuperscript{42} Crystals with $x = 0.0$ and 0.8 from the same batches were characterized by energy-dispersive x-ray emission (EDX) and neutron diffraction (see below) for impurities, stoichiometry, and structural parameters. The oxygen content 7$-\delta$ of Pr$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ ($x = 0.8$, 0.0) was determined to be 6.91$\pm$0.01. Since the Pr$_{0.5}$Y$_{0.5}$Ba$_2$Cu$_3$O$_{7-\gamma}$ crystals were oxygenated by the same method as the $x = 0.8$ and 0.0 crystals, we expect the oxygen content of the former to also be 6.91. Whereas for $x = 0.0$ we find no oxygen on the O(5) site, for $x = 0.8$ an occupancy of up to 5% cannot be excluded from the refinements of the neutron diffraction data.

Oxygen-deficient samples were obtained by annealing as-grown crystals of the same batch at 650 °C in a vacuum of about 10$^{-9}$ mbar for several days. Subsequently, the oxygen content 7$-\gamma$ was checked with optical reflectivity measurements and was estimated to be 6.05 for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{7-\gamma}$, and 6.15 for YBa$_2$Cu$_3$O$_{7-\gamma}$.\textsuperscript{43} The oxygen-loaded Pr$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ crystals were detwinned in a process similar to the one for YBa$_2$Cu$_3$O$_{7-\delta}$, which is discussed in detail elsewhere.\textsuperscript{41,42,44} Well-reflecting flat (001) surfaces of the samples were obtained by cutting off the crystals’ top layers using the diamond knife of an ultramicrotome.

The neutron diffraction experiments were performed on larger, twinned crystals from the same batches at the four-circle diffractometer 5C2 at the Orphée reactor, Laboratoire Léon Brillouin, CE Saclay.\textsuperscript{45} Experimental details, like scan range adjustment in order to achieve a complete integration over the typical multipack structure of the twinned crystals, background, absorption, and extinction treatments, are discussed in Ref. 46. For the structure refinement we used the PROMETHEUS program package in a version for data sets obtained for twinned crystals.\textsuperscript{47} The twinning leads to correlations between some $u_{11}$ and $u_{22}$ mean-square displacements, which were taken into consideration by introducing constraints.

The O 1s absorption spectra\textsuperscript{48} were obtained using linearly polarized synchrotron radiation from beamline U4B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. For moderate photon energies and a small extension of the core level transitions obeying dipole selection rules dominate, and higher-order transitions can be neglected. Applying dipole selection rules, the unoccupied part of the O 2$p$ final states can be reached from the initial O 1$s$ core level. Therefore, polarization-dependent NEXAFS measurements on detwinned single crystals provide insight into the symmetry of the hole states at $E_F$ and, thus, enable an estimate of the relative hole distribution between the different O sites in the crystal structure. The latter is possible if the binding energies for the various oxygen sites are taken into account. In the setup used, a multielement Ge fluorescence detector was placed at an angle of 55° with respect to the incoming photon beam. The samples were mounted on a manipulator allowing rotation around the horizontal and vertical axes. The in-plane spectra (E||c) and E(b) were obtained in a normal-incidence alignment. To fully explore and separate out the orbital character and symmetry of the hole states in the CuO$_2$ planes, the measurements are best performed for many different azimuthal sample orientations relative to the polarization vector of the incoming light. Such a series of angle-dependent measurements allows the correction of in-plane misalignment. In order to reach out-of-plane orbitals, the samples were rotated to achieve angles of incidence of 15°, 30°, 45°, 65°, and 80° with respect to the surface normal (grazing incidence). Such measurements are indispensable to ensure that the light hits neither parts of the sample holder nor the conducting glue. Furthermore, corrections for polar misalignment are possible if grazing incidence measurements are carried out at many different angles. According to

$$I(\theta) = I_{||c}\cos^2(\theta) + I_{\perp}\sin^2(\theta),$$

the E||c spectra were calculated by correcting for the corresponding angle of incidence. The correction of spectra taken at polar incidence angles of 45°, 65°, and 80° led to nearly identical results.

Since the probing depths for total electron yield and fluorescence yield (FY) in the actual setup were approximately 50 and 600 Å, respectively, we have recorded the NEXAFS
spectra in the FY detection mode to obtain information about the bulk properties and to avoid problems associated with surface sensitivity. However, FY spectra are affected by saturation and self-absorption effects which cannot be ignored. The incoming photon intensity is attenuated not only by the oxygen absorption coefficient $\mu_{\text{oxy}}(E)$, but also by the absorption coefficient $\mu_{\text{bulk}}(E)$ of all the other elements in the sample. The radiative filling of the O 1s core hole after the absorption process results in the emission of fluorescence radiation. The intensity of this emission process is proportional to $\mu_{\text{oxy}}(E)$. On their way to the sample surface the fluorescence x rays are attenuated by the total absorption coefficient $\mu_{\text{tot}}(E_f) = \mu_{\text{oxy}}(E_f) + \mu_{\text{bulk}}(E_f)$ at the energy of the fluorescence radiation, $E_f$. A simple calculation shows that the normalized fluorescence intensity $\mu_{\text{FY}}$ is given by the relation

$$
\mu_{\text{FY}} = \frac{I_f(E)}{I_0(E)} \propto \frac{\mu_{\text{oxy}}(E)}{\mu_{\text{tot}}(E)\cos\alpha + \mu_{\text{tot}}(E_f)/\cos\beta},
$$

where $I_f(E)$ is the intensity of the fluorescence radiation detected, $I_0(E)$ the primary intensity, $\alpha$ the angle between the incoming beam and the sample normal, and $\beta$ the angle between the sample normal and the outgoing beam. In the limit of dilute samples the contribution of $\mu_{\text{oxy}}(E)$ to $\mu_{\text{tot}}(E)$ is very small and, therefore, $\mu_{\text{FY}}(E) \approx \mu_{\text{oxy}}(E)$. For Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ this is not the case, and we have corrected our data for these effects. The spectra were normalized to the tabulated standard absorption cross section$^{51,52}$ in the energy range 590 eV $\leq E \leq$ 600 eV. In this range the spectra are almost structureless and the atomiclike spectral weight is only slightly modified by EXAFS effects as shown for the $\mathbf{E}||\mathbf{b}$ spectra in Fig. 2, which is representative for all polarizations. The energy resolution in our measurements was about 220 meV at an incident photon energy of 530 eV and the degree of linear polarization was estimated to be (97 $\pm$ 1)\% for the experimental configuration used.

### III. RESULTS

Before addressing our NEXAFS results in the main body of this section, we first evaluate the structural information obtained from neutron diffraction: An important result is that there is no indication for any Pr situated on the Ba position and any Ba situated on the Pr position in our Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{7-x}$ single crystals. This follows from two observations: First, the Ba atom is too large to occupy a $R$ site. Second, the Pr concentration revealed by EDX, 0.77, is in excellent agreement with the neutron data if for the refinements Pr on Ba sites is excluded and only Pr at Y sites is taken into account. Therefore, in contrast to the models of Refs. 37 and 40, neither Pr atoms on the Ba site nor Ba atoms on the Pr site are consistent with our results. The structural parameters obtained from neutron diffraction measurements are listed in Table I. The results of the present investigation are in good agreement with previously published neutron diffraction studies on powder samples$^{12,23}$.

![FIG. 2. O 1s absorption spectra of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$, Pr$_{0.4}$Y$_{0.6}$Ba$_2$Cu$_3$O$_{6.91}$, and YBa$_2$Cu$_3$O$_{6.91}$ for polarization $\mathbf{E}||\mathbf{b}$. The data are shown in the entire energy range recorded. Above 540 eV, the cross sections are independent of the Pr concentration.](image-url)
and also the Cu(2)-Cu(2) distances are enlarged due to the substitution of Y by Pr. The Cu(1)-O(4) bond length remains almost unchanged by the substitution whereas the R-O(2,3) distances are strongly enhanced. Compared with other rare-earth substitutions, however, the anisotropy between the R-O(2) and the R-O(3) distances is anomalously reduced. Thus, if Y is substituted by Pr, the CuO2 planes are pushed towards the Ba-O(4) layers due to the larger radius of the rare-earth ion. Since the ionic radius of Pr4+ is smaller than the one of Y3+, this is possible only if most of the Pr atoms are trivalent. Of course, it cannot be excluded that some Pr4+ is present. We will further dwell on this point in Sec. IV where we discuss the hole distribution in PrxY1-xBa2Cu3O7-y.

Figure 2 shows the O 1s absorption spectra of PrxY1-xBa2Cu3O6.91 (x = 0.0, 0.4, 0.8) in the entire photon energy range recorded (525 eV ≤ E ≤ 600 eV), with the electric field vector E adjusted parallel to the b axis of the crystals. These E||b spectra are shown as representatives for all polarizations. They were corrected for the intensity variations of the monochromatized synchrotron radiation into as well as for self-absorption and saturation effects, and normalized to the standard absorption cross section as outlined above. Beyond 535 eV, the spectra of the three crystals exhibit only small differences. From 540 eV on, they become virtually indistinguishable within statistics. The hybridized oxygen states situated in the energy range around 535 eV are virtually indistinguishable within statistics. The hybridized oxygen states situated in the energy range around 535 eV are shown for the antiferromagnetic insulator Pr0.8Y0.2Ba2Cu3O6.91, the p-type-doped superconductor YBa2Cu3O6.91 (Tc~93 K), and the Pr0.4Y0.6Ba2Cu3O6.91 sample. The latter compound is still metallic and exhibits a Tc~15 K. Below 534 eV the E||a spectra of the three crystals (see Fig. 3) are composed of three main peaks (marked by arrows). The first peak at 528.5 eV shows a strong intensity reduction with increasing Pr concentration whereas the second and third features at 529.5 eV and 532.2 eV are strongly increased. For the Pr-doped samples the last of these three peaks appears somewhat broader than the other features and extends from about 531.5 eV to 533 eV. A further, smaller peak, independent of the Pr substitution, is seen at 530.7 eV. The feature at 528.5 eV which is most pronounced for YBa2Cu3O6.91 has a width of ΔE~1.2 eV and a steeper onset than the following features. In accordance with previous work, this feature is attributed to ZR states. The steep onset for YBa2Cu3O6.91 indicates that the Fermi level appears to be located below the top of this ZR band. From x-ray photoemission spectroscopy (XPS) measurements on the PrxY1-xBa2Cu3O6.91 system it appears that the binding energies of the O atoms are independent of the Pr concentration. With these XPS results, the downward shift of the second peak observed in Fig. 3 leads to the conclusion that with increasing Pr content the Fermi level together with the O 1s core level is shifted to higher energies. Finally, for Pr0.8Y0.2Ba2Cu3O6.91 Ei is located slightly above the upper edge of the ZR band and no doped holes are left in O(2,3) 2 p_x, y orbitals hybridized with Cu(2) 3d_x, y2 or orbitals. An analogous trend as for E||a is observed in Fig. 4 for the polarization E||b with the main difference that for all samples the peak at 532.5 eV is not as distinct as for E||a but instead a broad shoulder between 531.5 eV and 533 eV is seen.

Neglecting unoccupied π-bonded O orbitals, E||a contribu-
subtraction concentration is observed. Starting at about 530.4 eV, the peak at 530.7 eV for $Pr_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$ may be interpreted as a hybridization between a linear combination of $O_1$ orbitals in the CuO$_2$ chains. Since structural asymmetry between the Cu(2)-O(2) and the Cu(2)-O(3) bond lengths is small (1.4% for $Pr_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$ and 1.7% for YBa$_2$Cu$_3$O$_{6.91}$; see Table I), the symmetry of the Cu(2) $3d_{x^2-y^2}-O(2.3)$ $2p_{x,y}$ hybrids in the CuO$_2$ planes is only slightly distorted. Thus, from the point of view of the CuO$_2$ planes’ electronic structure, equivalence of the $a$ and $b$ directions of the planes is expected to be a good approximation. In this approximation, the difference between the $E\parallel b$ and the $E\parallel a$ spectra can be ascribed to the contributions of the O(1) $2p_\alpha$ orbitals in the CuO$_3$ chains. The contributions $E\parallel b - E\parallel a$ for the three samples are plotted in Fig. 5. A gradual decrease of the spectral intensity with increasing Pr concentration is observed. Starting at about 530.4 eV, the subtraction $E\parallel b - E\parallel a$ leads to negative values, regardless of the Pr concentration. This is due to the fact that the peak observed at 530.7 eV in the $E\parallel a$ spectrum is absent for polarization $E\parallel b$. Since the electronic structure of the planes is assumed to be equivalent along the $a$ and $b$ directions, the peak at 530.7 eV for $E\parallel a$ may be interpreted as a hybridization between a linear combination $\beta_1 [p_\alpha] + \beta_2 [p_\beta]$ of O(1) $2p$ orbitals with Ba states.

For $E\parallel c$, only O(4) $2p_\gamma$ orbitals contribute if holes in $\pi$-bonded O orbitals are neglected. The assumption that $\sigma$-bonded O orbitals are playing the leads is supported by the threshold energies of the pre-edges. Consistent with electronic energy loss spectroscopy (EELS) data, the O 1s threshold energy of YBa$_2$Cu$_3$O$_{6.91}$ is at 528.0 eV for $E\parallel a$ and at 527.3 eV for $E\parallel c$. Most band structure calculations predict that the O 1s level of the O(4) site has the lowest binding energy and that, therefore, the threshold for $E\parallel c$ should occur at the lowest photon energy. The $E\parallel c$ absorption edges are depicted in Fig. 6. The spectra consist in this energy range of two main features: a peak at 528 eV and a broad shoulder extending from 531.5 eV to 533 eV. Both features show an increase of intensity with increasing Pr concentration. While the peak at 528 eV seems to be only slightly affected, a much stronger increase of spectral weight is observed for the broad shoulder. The peak at 528 eV has a constant width [full width at half maximum (FWHM)] of $\Delta E \approx 1.7$ eV for all Pr concentrations, which is broader by about 0.5 eV than the ZR states of the planes (Fig. 3). In previous work, the peak of YBa$_2$Cu$_3$O$_{6.91}$ was wholly ascribed to unoccupied states related to the O(4) apical oxygen atoms.

In Fig. 7, the $E\parallel a$ spectra for the oxygen-deficient $Pr_{0.8(Y_{0.2}Ba_2Cu_3O_{6.91})}$ ($x = 0.8$, 0.0) samples are plotted. For the oxygen-depleted YBa$_2$Cu$_3$O$_{6.91}$ crystal a small shoulder at 528.5 eV is observed. This shoulder is a consequence of a slight hole doping due to an enhanced oxygen content. In the case of the oxygen-deficient Pr$_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ sample such a shoulder is not observed. Employing optical reflectivity measurements, we estimated the oxygen content of YBa$_2$Cu$_3$O$_{6.91}$ and Pr$_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ to be 6.15 and 6.05, respectively, 43 as mentioned above. The NEXAFS data are corrected for self-absorption and saturation effects and normalized to the cross section of the actual oxygen content. However, our further discussion will not be affected by such a slight difference in the oxygen content of the crystals. Above 535 eV (not shown) the spectra of both samples are identical. Ignoring the small shoulder at 528.5 eV, YBa$_2$Cu$_3$O$_{6.15}$ exhibits its first peak at 530.0 eV. Since YBa$_2$Cu$_3$O$_{6.15}$ is an insulator and this peak belongs to the first unoccupied states above the Fermi level, this feature is ascribed to the oxygen states hybridized with the upper Hubbard band (UHB). For the $Pr_{0.8}Y_{0.2}Ba_2Cu_3O_{6.05}$ sample, the threshold energy of the

![FIG. 5. Difference spectra $E\parallel b - E\parallel a$ for $Pr_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$, $Pr_{0.8}Y_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$, and YBa$_2$Cu$_3$O$_{6.91}$. Assuming only holes in $\sigma$ orbitals, the contribution of the O(1) chain oxygen is derived from the enhanced spectral weight of $E\parallel b$ compared to $E\parallel a$. A reduction of this difference spectrum with increasing Pr concentration is evident.](image1)

![FIG. 6. $E\parallel c$ spectra of $Pr_xY_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$ ($x = 0.8, 0.4, 0.0$). For YBa$_2$Cu$_3$O$_{6.91}$ the complete peak at 528 eV is ascribed to the apical oxygen atoms while for $Pr_{0.8}Y_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.91}$ the peak also contains contributions from the FR state.](image2)
FIG. 7. O 1s absorption spectra of the O atoms in the plane for oxygen-deficient Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ and YBa$_2$Cu$_3$O$_{6.15}$. In both cases a distinct UHB is observed. The onset of the UHB of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ is downshifted by ~0.35 eV.

UHB is shifted down by about 0.35 eV. This result is supported by optical measurements of oxygen-depleted samples which indicate a reduction of the charge transfer gap from $\Delta_{CT} \approx 1.7$ eV to 1.4 eV when the Pr concentration $x$ is raised from 0.0 to 1.0. The 0.35 eV downshift of the UHB, observed not only in the spectra of the oxygen-deficient but also in that of oxygen-rich samples (Fig. 10 and Fig. 3, respectively), confirms the view mentioned above that the O 1s core level together with $E_F$ is shifted to higher energies with increasing $x$. The UHB downward shift can be explained by changes in the Madelung potentials which are caused by the much larger distance between adjacent CuO$_2$ planes in the case of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ (Table I). In contrast to this large increase of the distance between neighboring planes, the in-plane Cu(2)-O(2) and Cu(2)-O(3) bond lengths are only slightly enlarged and, therefore, no significant intensity changes are observed between the UHB of YBa$_2$Cu$_3$O$_{6.15}$ and Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$. As has been the case for the oxygen-rich crystals discussed above, for the oxygen-depleted crystals again additional spectral weight occurs between 531.5 eV and 533.0 eV for the Pr-doped sample.

Figure 8 shows the $E||c$ spectra of the oxygen-deficient samples. Since the UHB has predominantly planar character, these states vanish for $E||c$. The small peak at 528.5 eV for the YBa$_2$Cu$_3$O$_{6.15}$ sample is due to the slightly higher oxygen content, as was discussed above. From preliminary results from PrBa$_2$Cu$_3$O$_{6.1}$ (not shown), we conclude that the feature at 529.7 eV is most likely due to hybridization between oxygen and yttrium atoms. In earlier work we assigned the peak at 531.0 eV in the YBa$_2$Cu$_3$O$_{6.15}$ spectrum to transitions into the O(4)-Cu(1)-O(4) dumbbell of oxygen-depleted samples and regarded the intensity of this peak as a measure of vacant O(1) sites. Studying our spectra, it becomes clear that for the Pr-doped sample no distinct peak is observed around 531.0 eV, but instead a broad shoulder.

This may be due to contributions from higher-energy hybridizations by which this peak is drowned out. In the energy range between 531.5 eV and 533.0 eV the dip which is observed for YBa$_2$Cu$_3$O$_{6.15}$ is filled up with spectral weight for the Pr-doped sample. This additional intensity for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ in the energy range between 531.5 eV and 533 eV is isotropic. It appears both for oxygen-deficient and oxygen-rich samples and grows with increasing Pr concentration. Since these unoccupied isotropic states are located 4–6 eV above the Fermi level, it can be ruled out that they are responsible for the suppression of superconductivity in the Pr$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-y}$ system. In previous NEXAFS measurements these isotropic states 4–6 eV above $E_F$ were ascribed to Pr 4f$_{7/2}$(2$^2_2$)–O 2p$_x$ hybrids.

A more thorough discussion of the features described in this section along with their implications for the electronic structure and the hole distribution on the structural units in Pr$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-y}$ will be given in the following section. We will also examine to what degree the various existing models, mentioned in the first section, agree with our data.

IV. DISCUSSION

A. Electronic structure of Pr$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-y}$ and charge distribution between the structural units

Considering a charge-transfer model for the Cu(2)-O(2,3) planes of YBa$_2$Cu$_3$O$_{6.0}$, the spectral weight for electron addition experiments (e.g., NEXAFS) contains an unoccupied UHB with Cu 3d character above the Fermi level, and the spectral weight for electron removal experiments (e.g., photoemission) shows a valence band with O 2p character below the Fermi level. In this picture, with increasing oxygen doping $E_F$ is shifted below the top of the ligand band and holes will be created exclusively on oxygen sites. This
picture changes if hybridization between O and Cu atoms is included. With increasing hybridization, i.e., with larger hopping integral $t_{pd}$ between Cu 3$d_{x^2-y^2}$ and O 2$p_{x,y}$ orbitals, Cu 3$d$ states are mixed into the valence band and O 2$p$ states are admixed to the UHB. Hybridization then causes correlation effects on copper sites to be important for the valence band and the ZR state as well (see also Ref. 36). In effect, it leads to a transfer of spectral weight from the UHB to the ZR state upon oxygen doping. This is demonstrated in Fig. 9 where the $E\|\alpha$ spectra of oxygen-depleted ($y \approx 0.9$) and almost fully oxygenated ($y \approx 0.1$) YBa$_2$Cu$_3$O$_{7-y}$ samples are depicted: At higher O content the UHB is reduced while the ZR band is strongly increased. The ZR state is located at 1.4 eV below the UHB. If we now compare the $E\|\alpha$ spectra of oxygen-deficient and oxygen-rich Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_7$ (Fig. 10), we note that both show a strong UHB peak at 529.5 eV. In the Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ spectrum, however, much more spectral weight on the low-energy side of the UHB is observed, as depicted by the difference spectrum in Fig. 10. From Fig. 3 it is evident that these additional states are located in the energy range between $E_F$ (known from the onset of the YBa$_2$Cu$_3$O$_{6.91}$ spectrum) and the peak position of the UHB of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$. Therefore, these additional states in Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ are located in the same energy range as the ZR state in YBa$_2$Cu$_3$O$_{6.91}$. For oxygen-rich samples, the additional spectral weight in the energy range between $E_F$ and the UHB together with the UHB itself rises at the expense of the ZR state (Fig. 3), as the Pr content increases. Considering Fig. 11, we emphasize that if the holes were residing in the ZR state, transitions from the O 1$s$ core level into the UHB would exhibit little spectral weight due to the transfer of spectral weight from the UHB to the ZR state.\(^{21,58,60,61}\) In contrast to this, the spectral weight of the UHB should be observed with the same strength as for oxygen-depleted YBa$_2$Cu$_3$O$_{6.15}$ or Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ if the holes are moved from the ZR state into states which have no hybridization with Cu atoms and, therefore, are unaffected by correlation effects on Cu sites. Since for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ an UHB is observed which is as intense as for YBa$_2$Cu$_3$O$_{6.15}$ or Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$, we can draw the conclusion that with increasing Pr concentration holes are pushed out of the ZR state and moved into the energetically favored additional states on the low-energy side of the UHB (Fig. 10) which...
have no copper character. Thus, O $2p_{\sigma}$ states are ruled out. The fact that the holes are removed from the ZR state is reflected on the one hand by the strong reduction of the ZR state and on the other hand by the strong increase of the UHB as shown in Figs. 3 and 10. Therefore, we regard the feature extending from 527.0 eV to 530.2 eV for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ (Fig. 10) as a combination of an UHB like that of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.05}$ plus additional states on the low-energy side of the UHB. On the high-energy side additional spectral weight is not only observed for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ but also for YBa$_2$Cu$_3$O$_{6.91}$ compared to their oxygen-depleted counterparts (Figs. 9 and 10) and is, therefore, attributed to a generally higher degree of hybridization in this energy range, independent of the Pr concentration.

Unfortunately, the amount of spectral weight transferred to lower energies upon doping has not been calculated for this system up to now. To nevertheless obtain an estimate of the number of holes residing on the various structural units, we are forced to consider the additional spectral weight on the low-energy side of the UHB to be proportional to the Pr concentration $x$ and to the oxygen content $7-y$, despite the existence of the gradual transfer of spectral weight mentioned above. For YBa$_2$Cu$_3$O$_{7-y}$, the total number of holes per unit cell residing on the O sites was assumed to be 1. The total integrated cross section of the seven O sites in YBa$_2$Cu$_3$O$_{6.91}$ then corresponds to 17.8 Mb eV/unit cell. Using this scaling factor, the site-specific and Pr-concentration-dependent hole numbers were derived from the integrated cross sections of the first absorption peak in the O 1s spectra of the O(1) atom (Fig. 5), of the four O(2,3) atoms (Fig. 3), and of the two O(4) atoms (Fig. 6). We point out that only about 80% of the holes which reside in YBa$_2$Cu$_3$O$_{6.91}$ on oxygen sites are found for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ and also for Pr$_{0.0}$Y$_{0.8}$Ba$_2$Cu$_3$O$_{6.91}$. For all Pr concentrations measured, the holes observed for different light polarizations are listed in Table II. A total of about 0.4 holes is observed for YBa$_2$Cu$_3$O$_{6.91}$ on both the O(2) and O(3) sites of the planes (2E)$_i[a]$. When the Pr concentration is increased, the number of holes in both planes is gradually reduced. In other words, the Fermi level is moved up towards the top of the ZR band. For Pr$_{0.0}$Y$_{0.8}$Ba$_2$Cu$_3$O$_{6.91}$, still about 0.15 holes per plane are residing on planar oxygen orbitals forming the ZR band. Therefore, the sample still exhibits metallicity and superconductivity. This is consistent with previous NEXAFS investigations on a series of YBa$_2$Cu$_3$O$_{7-y}$ single crystals with different O stoichiometries where it was shown that similar amounts of O-doped holes per CuO$_2$ plane lead to similar $T_c$'s. For further Pr doping, the holes in the ZR band are increasingly filled up, and at the same time the amount of holes residing on the additional states which are competitive in energy with the ZR state is growing. Finally, for Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$, no doped holes reside on the ZR state, i.e., on O(2,3) $2p_{\sigma}$ orbitals, but rather are all on these additional states. Unfortunately, it cannot be distinguished by our experiments if there exists a gap between the ZR and FR bands or if these two bands exhibit an overlap (see sketch of electronic structure in Fig. 11). In the former case, the insulating behavior of the sample would be explainable by the existence of the gap. In the latter, $E_F$ is located above the upper edge of the ZR band but also above the bottom of the FR band, implying that the suppression of metallicity must be related to an extrinsic origin.

The contribution of the O(1) site, obtained by the difference spectra (E$_i[a]$ - E$_i[b]$), is also gradually reduced on raising the Pr content. For Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ this contribution has already fallen from 0.24 to 0.18 holes per O(1) site while the slight decrease upon further doping (see Table II) can hardly be regarded as significant. Hence, the contribution from the O(1) atoms seems to be already strongly altered at low doping concentrations due to the presence of Pr atoms and shows saturation at larger Pr content. The number of holes residing on the apical O(4) site is not changed at all by increasing the Pr concentration to 0.4 but the number of holes observed for E$_i[c]$ is slightly enhanced from 0.27 to 0.31 holes if the Pr-doping concentration is increased to 0.8. Thus, in contrast to the O(1) site, the E$_i[c]$ hole count is slightly increased and is mostly affected at higher Pr concentrations. This implies that the total amount of holes residing on the CuO$_3$ chains is slightly reduced. This small decrease of holes on the chain sites is in accordance with recent optical investigations where a reduction by about 14% of the amount of holes residing on the CuO$_3$ chains was reported. Furthermore, NMR and nuclear quadrupole resonance (NQR) data have shown that for a fixed oxygen concentration the electric field gradients at the Cu(1) and at the apical O(4) site remain almost unchanged, regardless of the $R$ substituent in $R$Ba$_2$Cu$_3$O$_{7-y}$. Therefore, a substantial charge transfer in connection with the apical O(4) site can be excluded.

To estimate the number of holes residing on the additional planar states on the low-energy side of the UHB (Fig. 10), we have subtracted the UHB of the (E$_i[a]$ spectrum of the oxygen-depleted Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ sample from the E$_i[a]$ spectrum of the oxygen-rich Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ crystal. The resulting difference spectrum is depicted in Fig. 10. The integrated spectral weight of the difference spectrum corresponds to 0.25 holes per unit cell. Since we observe for YBa$_2$Cu$_3$O$_{6.91}$ a total of 0.91 holes and in the case of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$ just 0.73 holes, we assume that the missing 0.18 holes reside on Pr. Thus, we can draw the following conclusions: With increasing Pr concentration a total of about 0.2 holes is transferred away from the ZR state and the O(1) site, and is probably moved to Pr. Upon further increasing the Pr concentration 0.25 holes are moved from

<table>
<thead>
<tr>
<th>$x=0.0$</th>
<th>$x=0.4$</th>
<th>$x=0.8$</th>
</tr>
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<td>$2n_o$</td>
<td>0.40</td>
<td>0.29</td>
</tr>
<tr>
<td>$n_{\text{chain}}$</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>$n_c$</td>
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<td>0.27</td>
</tr>
<tr>
<td>$n_{\text{tot}}$</td>
<td>0.91</td>
<td>0.74</td>
</tr>
</tbody>
</table>
the ZR state into the energetically favored states on the low-energy side of the UHB. These additional states are not hybridized with Cu. The apical O(4) site remains essentially unaffected by Pr doping.

B. Comparison with current models

Based on these quantifications we can finally examine the various models mentioned in Sec. I. As we already pointed out in Sec. III, the model of Ref. 40 fails to describe our results since disorder effects at the Ba site are inconsistent with our neutron diffraction and EDX results.

It is also evident from the NEXAFS data that a gradual redistribution of the doped holes from the CuO2 planes to the CuO3 chains as proposed in Ref. 39 can be ruled out, too. Instead of a hole increase on the oxygen sites of the CuO3 chain, as expected in this model, we do in fact observe a decrease by 14% of the total hole count on the chain. Further support for this comes from optical experiments also reporting a decrease of 14%.

The rest of this section will be devoted to discussing aspects of a Pr 4f\((x^2-y^2)\)-O 2p\(_x\) hybridization and their consequences for the electronic structure observed in NEXAFS. According to Fehrenbacher and Rice, the substitution of Y by Pr causes the initially delocalized holes to be moved from in-plane O(2,3) 2p\(_o\) orbitals to the O(2,3) 2p\(_\pi\) orbitals hybridized with the central Pr. The UHB band will then be visible since in this case there is no transfer of spectral weight from the UHB to the ZR state that we see Fig. 11. As already pointed out above this lack of transfer of spectral weight is indeed observed in our spectra. Therefore, we assume that the feature at 529.5 eV in the E||c spectrum of Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.91\) is composed of an UHB like that of Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.05\) plus possible FR states (Fig. 10). We will now examine if the above-mentioned additional low-energy states are in fact consistent with further characteristics of FR states. In the FR model it was assumed that the O(2,3) 2p\(_\pi\) orbitals point towards the central Pr ion, which means a rotation of the O 2p\(_\pi\) orbitals of about 45°. Therefore, an isotropic contribution from in-plane transitions and from transitions perpendicular to the CuO2 planes should be observed if the FR states can be identified with the additional states observed in the spectra. To obtain a numerical estimate of these states, we have to take into consideration, that only O 1s–O 2p\(_x\) transitions are allowed for E||c while, for E \perp c, O 1s–O 2p\(_x\) and O 1s–O 2p\(_\pi\) transitions are possible. This implies that in the former case all orbitals are involved in the absorption process but in the latter half the orbitals are oriented perpendicular to the polarization vector of the synchrotron radiation. Hence, the difference spectrum (Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.91\)–Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.05\)) for polarization E||c has to be scaled by a factor of 2 in order to take into account the contributions into a spectrum. The scaled difference spectrum is shown in Fig. 12 together with the E||c spectrum of Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.91\). The common area below both curves can be regarded as an upper limit for isotropic Fehrenbacher-Rice states. The integrated area common to both curves corresponds to 0.21 holes. This accounts for only half the states since the orbitals are assumed to be rotated by 45°. Therefore, a total of 0.42 holes could reside on the possible FR state. The peak of the E||c absorption spectrum is shown in Fig. 12 together with the E||c spectrum of Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.91\). The area enclosed by both curves constitutes an upper limit for isotropic FR states.

Combining our results with optical data, it is evident that the reduction of holes residing on O sites of the chain takes place predominantly on the O(1) site since the reduction by about 14% of the chain holes is already fulfilled by the O(1) hole decrease as can be inferred from Table II. This conclusion is corroborated by NMR data where no changes for the O(4) site and Cu(1) sites were detected. Thus, it can be concluded that the number of holes on the apical O(4) site remains unaffected by Pr substitution while the decrease of O(1) holes is responsible for the 14% reduction of the chain holes. Even with this reduction, there are still 0.44 holes located on the chain unit of Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_6.91\). This refutes the approach of Wang et al., according to which no holes are left in the CuO3 chains.

In contrast to the isotropic FR state suggested in the FR model, Liechtenstein and Mazin (LM) proposed that the FR state which grabs the holes has exclusively planar character. They have calculated the Pr-concentration-dependent number of holes in this planar FR state. For Pr\(_{0.8}\)Y\(_{0.2}\)Ba\(_2\)Cu\(_3\)O\(_7\) they find 0.25 holes, exactly the value we observe in the additional planar states on the low-energy side of the UHB (see Fig. 10 and Table II). However, they consider a dispersive and conducting pd\(\pi\) band with a hopping integral \(t_{pd}\) = 0.75 eV between the FR state and Pr 4f orbitals. In order to obtain a narrow band and, therefore, insulating behavior, they have to resort to strong scattering
effects due to more than 6% Ba on the Pr site. Although the number of holes in planar FR states is consistent with the NEXAFS data of Pr$_{0.8}$Y$_{0.2}$Ba$_2$Cu$_3$O$_{6.91}$, this scattering due to Ba on the Pr site as invoked by Liechtenstein and Mazin\textsuperscript{37} is inconsistent with the findings of the neutron diffraction measurements, as mentioned above. By and large, it may be said that the LM approach would, in principle, agree with our NEXAFS data if the FR band exhibited greater $p_z$ character above $E_F$ than expected from Fig. 1 in Ref. 37.

Based on the idea that the rotation angle may be situated somewhere between the two suggested extremes of 0° and 45°, we propose a very simple and straightforward extension of the original FR calculations. For this extension, a simple dependence on the rotation angle is introduced while all other results of Ref. 33 are retained unchanged. According to the recent measurements the following picture for the electronic structure of Pr$_{1-\gamma}$Y$_\gamma$Ba$_2$Cu$_3$O$_{7-\gamma}$ single crystals with different Pr and O concentrations. The main result of our investigations is that we can rule out models involving hole filling or charge transfer between the planes and the chains while our data are consistent with approaches based upon Pr 4f–O(2,3) $2p_\pi$ hybridization and indicate a rotation angle of the O(2,3) $2p_\pi$ orbitals that is situated in the middle of the proposed ones.

V. CONCLUSIONS

In summary, we have conducted NEXAFS and neutron diffraction measurements on Pr$_{1-\gamma}$Y$_\gamma$Ba$_2$Cu$_3$O$_{7-\gamma}$ single crystals with different Pr and O concentrations. The main result of our investigations is that we can rule out models involving hole filling or charge transfer between the planes and the chains while our data are consistent with approaches based upon Pr 4f–O(2,3) $2p_\pi$ hybridization. From our measurements the following picture for the electronic structure of Pr$_{1-\gamma}$Y$_\gamma$Ba$_2$Cu$_3$O$_{6.91}$ arises: Due to Pr doping of YBa$_2$Cu$_3$O$_{6.91}$, at first about 0.2 holes are lost from the O...
subsystem and presumably transferred from O(1) and O(2,3) sites to the Pr atom. On further doping the additional states on the low-energy side of the UHB are stabilized and about 0.3 holes are transferred from the energetically competing ZR state to these additional states. If the additional states are interpreted as FR states, they neither have the proposed rotation angle of 45° (FR model) nor do they show exclusively planar character (LM model); rather, the O(2,3) 2p_x orbitals are rotated by an angle of about 20°–25°. Therefore, for Pr_{0.8}Y_{0.2}Ba_2Cu_3O_{6+y}, about n_{apex} + n_{chain} = 0.5 holes still reside on the oxygen chain sites, n_{pr} = 0.2 holes are presumably transferred to the Pr atom, and n_{fr} = 0.3 holes are moved from the ZR state into the energetically favored FR states. Following the arguments of Fehrenbacher and Rice\textsuperscript{33} and those of Liechtenstein and Mazin,\textsuperscript{37} it is likely that an enhanced t_{pf} for Pr as compared to other rare earths or Y combined with favorable values of \epsilon_f and U_f is responsible for the stability of the FR state. The discrepancy in the rotation angle of the p_z orbitals between our NEXAFS data and theory may be due to the fact that in the calculations of Ref. 33 possible effects of the copper potentials on the Pr 4f−O(2,3) 2p_y hybridized states are neglected, and that in Ref. 37 correlation effects on the copper sites are disregarded.

ACKNOWLEDGMENTS

We are grateful to K. Widder and H. P. Geserich for performing the optical reflectivity measurements on oxygen-deficient Pr_{1−x}Ba_{2−x}Cu_3O_{7−y} and for stimulating discussions. We greatly appreciate fruitful discussions with R. Fehrenbacher and I. Mazin. We thank H. Winter, B. Seibel, E. Seibel, and S.-L. Drechsler for clarifying comments about theoretical aspects, B. Scheerer for his excellent technical support, and E. Søjmen and J.-H. Park for their experimental assistance. We are indebted to G. Meigs for his very generous help in sorting out technical difficulties. P. Adelmann provided valuable insight into the chemistry of impurities. The NSLS is part of Brookhaven National Laboratory, which is funded by the U.S. DOE. Part of this work was supported by the EU under Contract No. SCI CT91-0751 and the HCM network under Contract No. ERB CH RXCT 940438. V.C. was supported by the Office of Naval Research. M.S.G. is grateful for support from the HCM program of the EU.
Magnetic interactions have been thought to be responsible for the \textit{ZR state} for the uppermost part of the valence band although our experiments cannot provide any insight into its magnetic character. This can be visualized by a 45° "rotation angle" of the O\(2p_x\) hybrids toward the plane, and it is in this sense that we will be using the expression "rotation angle" throughout this paper. By the same token, the FR state as proposed in Ref. 33, i.e., with a rotation angle of 45°, will be referred to as an "isotropic" FR state.


Magnetic interactions have been thought to be responsible for splitting off the so-called Zhang-Rice singlet from the valence band in the following way: Strong hybridization between Cu 3d\(_{x^2-y^2}\) and O 2p\(_{x,y}\) orbitals leads to interaction of the spin of an intrinsic hole on a Cu(2) site and the spin of a doped hole on the four surrounding O(2,3) sites. For antiparallel spin orientation, the Zhang-Rice singlet is pushed out of the valence band. Since this is a widespread interpretation, we will adopt the notation "ZR state" for the uppermost part of the valence band although our experiments cannot provide any insight into its magnetic interaction.


K. Widder and H. P. Geserich (private communication).


Laboratoire commun CEA-CNRS.


We note that an inspection of the Pr \( M_{IV-V} \) edges cannot add any further information or significance to O K results: (a) The interference of the Pr \( M_{IV} \) and \( M_{V} \) edges with the Cu \( L_{II} \) and \( L_{III} \) edges, respectively, renders a deconvolution of these structures impossible. (b) Even without this interference a cross-examination of the O K results would not be reliable since the Pr \( M \) features correspond to 12 holes in the \( f \) shell of Pr\(^{3+}\), not to just about one as for the O K edge. The amount of, say, 0.2 holes added to or removed from the edge structure constitutes a substantial fraction of the O K edge while it is a mere 2% effect for the Pr \( M \) features.


W. E. Pickett, Rev. Mod. Phys. 61, 433 (1989).


