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Site-specific electronic structure of the $RBa_2Cu_3O_{7-y}$ family

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With polarization-dependent O 1s near-edge x-ray-absorption spectroscopy on detwinned $RBa_2Cu_3O_{7-y}$ ($R = Y, La, Pr, Nd$) and twinned $Pr_{1-z}Ba_{2+z}Cu_3O_{7-y}$ single crystals, the unoccupied electronic structure of the CuO_2 planes and CuO_3 chains has been investigated. The data underline the exceptional role of Pr among the rare-earth atoms, which leads to the stabilization of the Pr 4f-O 2p $_{\pi}$ states, and therefore to the suppression of superconductivity. Estimates of the out-of-plane fraction for these hybrids are discussed. Moreover, upon substitution of Pr by Ba in $Pr_{1-z}Ba_{2+z}Cu_3O_{7-y}$, a shift of the Pr 4f-O 2p $_{\pi}$ band to below the Fermi level is indicated, concurrent with a transfer of doped holes back to the Zhang-Rice singlets. [S0163-1829(99)03229-4]

One of the most controversial findings in the field of high-temperature superconductivity (HTSC) is the lack of superconductivity when replacing Y by Pr in $YBa_2Cu_3O_{7-y}$. While it was established quickly that the transition temperature T_c strongly depends on the Pr content,¹ there was a long-standing debate on the valency of Pr in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system: Since along with the T_c decrease the number of mobile holes in the CuO_2 planes is also reduced, the depletion of mobile holes in the planes was initially interpreted in terms of hole filling due to an enhanced valency of the Pr ion.² Alternatively, the T_c suppression was attributed to magnetic pair breaking in the CuO_3 chains invoked by Pr/Ba disorder,³ hole localization by a Pr 4f-O 2p $_{\sigma}$ hybridization,⁴ or charge transfer from the planes to the chains.⁵ However, recent near-edge x-ray-absorption fine-structure (NEXAFS) measurements have shown clear signatures for the existence of a hybridization between the Pr 4f states with the 2p $_{\pi}$ orbitals of the surrounding O atoms, thereby ruling out the approaches mentioned above.⁶ It was shown that the substitution of Y by Pr triggers a transfer of the initially mobile holes from the planar O 2p $_{\sigma}$ orbitals hybridized with the in-plane Cu 3d $_{x^2-y^2}$ states, i.e., the Zhang-Rice (ZR) states,⁷ to energetically favored Pr 4f-O 2p $_{\pi}$ hybrids. These hybrids were predicted in Refs. 8 and 9 and are now known as *Fehrenbacher-Rice* (FR) states. A prerequisite for the stabilization of the FR state is a favorable combination of the hopping integral t_{pf} between the relevant R (R denotes rare-earth elements) and O orbitals, the energy ϵ_f as well as the on-site Coulomb energy U_f of a hole in the R 4f shell.^{8,9} Following the arguments given there, an appropriate combination of these parameters is realized only for $PrBa_2Cu_3O_{7-y}$ and hence the transfer of holes from the ZR to the FR state is limited to the case $R=Pr$. In other words, for $R \neq Pr$ an FR state will not be stabilized and the

doped holes remain in the ZR state, thereby retaining superconductivity. Consequently, the occurrence of an FR state in $RBa_2Cu_3O_{7-y}$, and the simultaneous decrease of the ZR spectral weight observed in previous work,⁶ should be restricted to $R=Pr$, too.

This general view has gained renewed interest since Zou *et al.* found recently that $PrBa_2Cu_3O_{7-y}$ single crystals grown by the traveling solvent floating zone method (TSFZ) lead to a $PrBa_2Cu_3O_{7-y}$ modification which exhibits bulk superconductivity up to 80 K and a Meissner fraction of $\approx 15\%$.¹⁰ A conspicuous structural difference to the “standard,” flux-grown crystals is the anomalous expansion of the Cu(2)-Cu(2) distance from 3.484 to 3.505 Å, i.e., a considerable enhancement of the distance between the two CuO_2 planes. One possible but still speculative explanation for this enhancement is the partial replacement of Pr^{3+} atoms by Ba^{2+} with a much larger ionic radius.

The main objective of the present paper therefore is, first, to discuss the site-specific unoccupied electronic structure at the Fermi level E_F of $RBa_2Cu_3O_{7-y}$ within a rare-earth series as measured by O 1s NEXAFS. In this context, a comparison between the results for $R=Pr$ and Ce or Nd, i.e., the elements bracketing Pr in the periodic table, is of special interest. Unfortunately, it has not been possible so far to synthesize single crystals of $CeBa_2Cu_3O_{7-y}$, and we have to resort to the next-nearest neighbor La. The second goal of the paper is to investigate how the electronic structure is changed when in $Pr_{1-z}Ba_{2+z}Cu_3O_{7-y}$, (i) Pr is replaced by Ba, or (ii) Ba by Pr. For that purpose, Ba-rich samples ($z > 0$) are compared to Ba-deficient ones ($z < 0$).

The x-ray-absorption measurements were performed at the National Synchrotron Light Source (NSLS) using polarized synchrotron radiation from the NRL/NSLS beamline U4B. Data were taken in the non-surface-sensitive fluores-

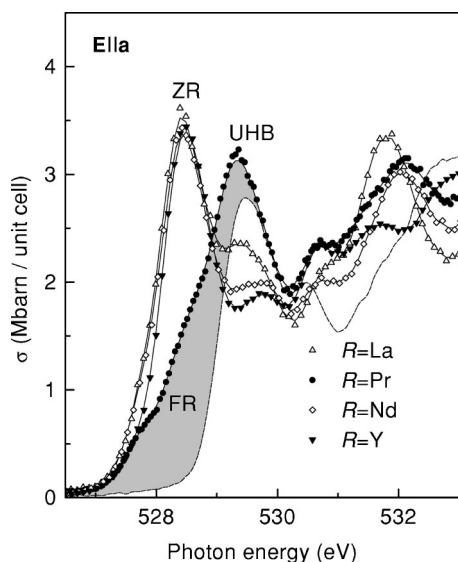


FIG. 1. O 1s $E||a$ absorption spectra of $RBa_2Cu_3O_{6.91}$ for $R = La, Pr, Nd$, and Y . While for $R \neq Pr$ a ZR state is observed, this feature is absent in the case of Pr and a distinct UHB is seen instead. For comparison the data of undoped $PrBa_2Cu_3O_{6.0}$ is included as a dashed curve, the spectral weight of the FR state as a gray shaded area.

cence yield mode with an energy resolution of 220 meV at 530 eV. The spectra were corrected for the energy-dependent incident photon flux as well as for self-absorption effects and were normalized to tabulated cross sections¹¹ in an energy range ≈ 70 eV above the threshold energy. The procedures used and details on the assignment of the various polarization dependent features observed are given in Ref. 6. Details on the crystal growth, the detwinning, and annealing procedures are described in Refs. 12. With the aid of energy-dispersive x-ray emission (EDX) analysis, the additional Ba or Pr content of the $Pr_{1-z}Ba_{2+z}Cu_3O_{7-y}$ single crystals was determined to be $z = \pm 0.05$. The structure and oxygen content of the $RBa_2Cu_3O_{7-y}$ crystals was checked by neutron-diffraction measurements performed at the four-circle diffractometer 5C2 at the Orphée reactor, Laboratoire Léon Brillouin, CE Saclay.¹³

In Fig. 1 the spectra of $RBa_2Cu_3O_{6.91}$ ($R = La, Pr, Nd$, and Y) with the light polarization E oriented parallel to the crystallographic a axis are depicted. The absorption features observed around 527–530 eV for $E||a$ are assigned as usual to the contribution of the O(2) atoms of the CuO_2 planes, while the $E||c$ data and the $E||b - E||a$ difference spectrum correspond to unoccupied states at the apical O(4) and the chain O(1) site of the CuO_3 chain, respectively.⁶ As can be seen from the comparison of the $E||a$ data, the first structure in each of the spectra for $R = La, Nd$, and Y , centered at about 528.4 eV, is very similar and just differs in a slight shift of its threshold toward higher energies when going from larger to smaller ionic radius ($r_{La} > r_{Nd} > r_Y$). In correspondence to previous work,¹⁴ this feature is ascribed to the ZR states mentioned above. The deviation in their threshold energies most probably reflects small changes of the Madelung potentials on the O(2,3) $2p_\sigma$ states when replacing the R atom in the center of the unit cell. Corroborating the results of Refs. 8 and 9 for $R = La, Nd$, and Y the planar holes remain in the

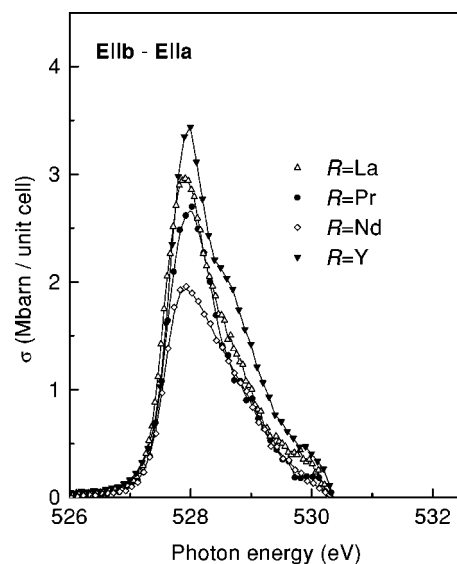


FIG. 2. O 1s chain contribution of $RBa_2Cu_3O_{6.91}$ for $R = La, Pr, Nd$, and Y . Compared to the case $R = Y$ the integral intensity of the rare-earth compounds is somewhat reduced. However, the data for $R = Pr$ fit very well in between those for La and Nd .

ZR state and the samples show T_c values of 88, 92.5, and 93 K, respectively. For $PrBa_2Cu_3O_{6.91}$, however, the spectral weight in the energy range of this feature is strongly reduced, and, contrary to all the other $RBa_2Cu_3O_{6.91}$ compounds, the feature centered at about 529.5 eV, the upper Hubbard band (UHB), is much more pronounced. For the purpose of comparison, the data of oxygen depleted $PrBa_2Cu_3O_{6.0}$ is included in Fig. 1 as a dashed line. From this figure and from previous work on a $Y_{1-x}Pr_xBa_2Cu_3O_{6.91}$ series,⁶ it can be concluded that the increase of the intensity of the UHB at the expense of the ZR intensity observed for $PrBa_2Cu_3O_{6.91}$ is due to the transfer of spectral weight from the ZR state to the UHB. This implies that the holes introduced to the planes of $PrBa_2Cu_3O_{6.91}$ are transferred from the $Cu 3d_{x^2-y^2} - O 2p_\sigma$ to the $Pr 4f_{z(x^2-y^2)} - O 2p_\pi$ hybrids, i.e., from the ZR to the FR states (for a detailed discussion on the transfer of spectral weight and on the identification of the FR state see Ref. 6). In short, since the O $2p_\pi$ orbitals are not hybridized with the $Cu 3d$ states, the crucial point for the identification of an FR state in $PrBa_2Cu_3O_{7-y}$ is the simultaneous occurrence of a fully developed UHB, i.e., with a strength comparable to that for $PrBa_2Cu_3O_{6.0}$, and additional spectral weight on the low-energy side of the UHB due to the doped holes in the O $2p_\pi$ orbitals. In accordance with the predictions of Refs. 8 and 9, this observation clearly shows that Pr is exceptional among the rare-earth elements in developing $R 4f_{z(x^2-y^2)} - O 2p_\pi$ hybrids at E_F . The in-plane contribution of these states can be quantified utilizing the spectral weight of the difference between the $E||a$ spectrum of $PrBa_2Cu_3O_{6.91}$ and $PrBa_2Cu_3O_{6.0}$ (gray shaded area in Fig. 1). By and large, the hole counts derived in this way reproduce the results for $Y_{0.2}Pr_{0.8}Ba_2Cu_3O_{7-y}$ in Ref. 6 very well within the error bar of ± 0.03 holes.

In Fig. 2 the difference $E||b - E||a$ is shown, i.e., the contribution which is usually assigned to the O(1) chain oxygen site. This figure seems to suggest that the amount of holes residing on the O(1) site is slightly reduced if Y is replaced

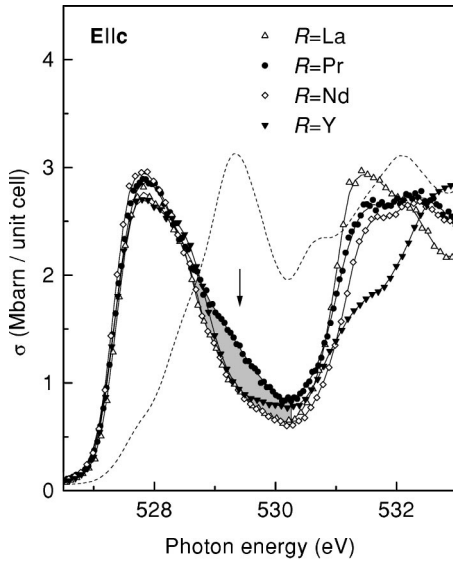


FIG. 3. O $1s$ $\mathbf{E}||c$ absorption spectra of $\text{RBa}_2\text{Cu}_3\text{O}_{6.91}$ for $R = \text{La}, \text{Pr}, \text{Nd}$, and Y . Only in the case of $R = \text{Pr}$ an additional small shoulder is seen at about 529.5 eV. The $\mathbf{E}||a$ spectrum for $R = \text{Pr}$ is included as a dashed curve, and the section in the relevant energy range which constitutes an upper limit for out-of-plane contributions of FR states is depicted as a gray shaded area.

by rare-earth atoms like La, Pr, or Nd. Our neutron-diffraction data, however, show a small occupation ($<5\%$) of the O(5) *antichain* site, which scales with the amount of R atoms situated on the Ba site. Even such a tiny O(5) occupation leads to an appreciable decrease of the difference $\mathbf{E}||b - \mathbf{E}||a$ and hence nicely explains the reduction observed in Fig. 2. The figure therefore strongly suggests that R atoms with radii larger than Y more frequently occupy Ba sites. Such R/Ba disorder effects have been discussed to explain the T_c suppression in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$.³ A significant T_c reduction caused by Pr-Ba exchange, however, can be excluded from Fig. 2 since the spectrum for $R = \text{Pr}$ lies clearly above the data of the superconducting $R = \text{Nd}$ sample.

While all the approaches based on the FR state idea agree that the Pr $4f_{z(x^2-y^2)}\text{-O } 2p_\pi$ hybridization is responsible for the absence of T_c in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$, the proposed models deviate somewhat concerning the rotation angle γ which denotes the out-of-plane contribution of the O $2p_\pi$ orbitals.⁶ To date, suggested values for this angle cover the range between 0° (totally in-plane orbitals) and 45° (out-of-plane orbitals with an angle of 45° toward the planes).^{6,8,9} In order to give an experimental upper limit to the interval of possible out-of-plane contributions of the π orbitals, we compare in Fig. 3 the $\mathbf{E}||c$ data of $\text{RBa}_2\text{Cu}_3\text{O}_{6.91}$ for several R atoms. The first feature observed in the spectra is very similar for all R atoms including Pr and is ascribed to the holes doped on the O(4) apical oxygen site. Thus the doping level of the CuO_2 chains is nearly the same for all of the samples. What is different between Pr and other rare-earth elements is the spectral region around 529–530 eV: while for $R \neq \text{Pr}$ the spectra are almost identical, in the case of Pr an additional small shoulder is seen (gray shaded area in Fig. 3). Intriguingly, this shoulder lies in the same energy range as the additional intensity observed for the $\mathbf{E}||a$ spectrum below the UHB. Therefore it seems reasonable to ascribe the additional

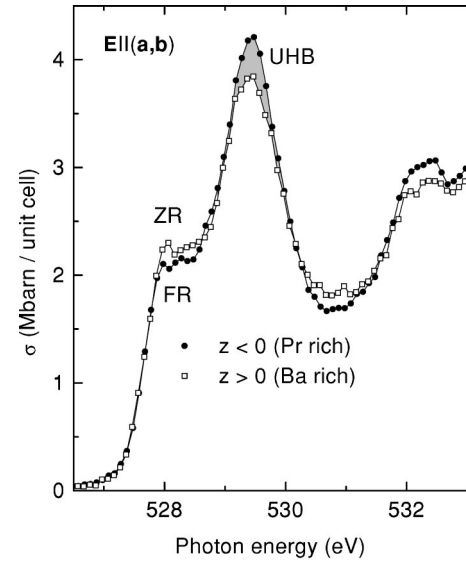


FIG. 4. O $1s$ $\mathbf{E}||a,b$ absorption spectra of twinned Pr- and Ba-rich $\text{Pr}_{1-z}\text{Ba}_{2+z}\text{Cu}_3\text{O}_{7-y}$ single crystals. For the Ba-rich sample the spectral weight at E_F is slightly increased and, along with this, the UHB peak is reduced.

spectral weight in the $\mathbf{E}||c$ data of $\text{PrBa}_2\text{Cu}_3\text{O}_{6.91}$ to the out-of-plane fraction of the O $2p_\pi$ orbitals. Nevertheless, the integral intensity below this additional shoulder is obviously very small, implying that the out-of-plane contribution of the π orbitals has to be small as well. A rough estimate of the rotation angle γ can be obtained from the ratio of the spectral weight below this shoulder and the in-plane contribution of the FR state, i.e., the area below the scaled¹⁵ $\mathbf{E}||a$ difference spectrum $\text{PrBa}_2\text{Cu}_3\text{O}_{6.91} - \text{PrBa}_2\text{Cu}_3\text{O}_{6.0}$. Taking an error bar of ± 0.03 holes for this quantification into account, the rotation angle has to lie in the interval $0^\circ \leq \gamma \leq 28^\circ$. As expected from Refs. 6, 8, and 9, only in the case of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ the holes of the CuO_2 planes are transferred from the ZR to the energetically favored FR states; the interval of possible rotation angles, on the other hand, differs strongly from the 45° suggested in Ref. 8 and the $\approx 35^\circ$ derived by a purely *geometrical* calculation of the angle between the Pr-O(2,3) bond and the Cu(2)-O(2,3) planes as proposed in Ref. 9.

Finally, we want to discuss the replacement of Pr atoms by Ba in terms of a possible mechanism for rendering the TSFZ samples superconducting. On the condition that such a substitution is present in the TSFZ crystals, it produces two consequences on the electronic structure observable with NEXAFS: First, due to the different valencies of Ba and Pr additional holes are introduced into the planes of Ba-rich samples, similar to the situation for Ca doping discussed in Ref. 16. In effect, this leads to a total hole count which exceeds the number of holes introduced by pure O doping. Second, according to the strong differences in the parameters t_{pf} , ϵ_f , and U_f provoked by this replacement, the electronic structure calculated in Refs. 8 and 9 has to be modified, resulting in a (locally hole-depleted) FR state which is pushed below the Fermi level, and hence in a transfer of the doped holes from the FR back to the ZR band.¹⁷ For the twinned, “standard” $\text{Pr}_{1-z}\text{Ba}_{2+z}\text{Cu}_3\text{O}_{7-y}$ single crystals investigated here with their low Pr and Ba excess concentrations z , these effects will certainly be very small. Neverthe-

less, there are signatures for both effects in Fig. 4: The $E||a,b$ spectra of the twinned $\text{Pr}_{1-z}\text{Ba}_{2+z}\text{Cu}_3\text{O}_{7-y}$ ($z = \pm 0.05$) crystals depicted show a small increase of the intensity near E_F for the Ba-rich samples, and thus a slight enhancement of the number of doped holes. Most significantly, a *decrease* of the spectral weight of the UHB occurs at the same time (indicated by the gray shaded area in Fig. 4), confirming that holes are introduced to the ZR, *not* to the FR band. Correspondingly, these holes are again located in the $\text{Cu } 3d_{x^2-y^2}\text{-O } 2p_\sigma$ states, that is, in the same hybrids as for $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($R = \text{Y, La, Nd}$) which may render the sample metallic and also superconducting in the case of crystals which are more Ba rich than the samples investigated here.¹⁸

This observation is consistent with the large inhomogeneity in transport and magnetic properties found by Zou *et al.* for their superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ samples,¹⁰ and the interpretation of the NMR signal of Ba-rich $\text{Pr}_{1-z}\text{Ba}_{2+z}\text{Cu}_3\text{O}_{7-y}$ single crystals given in Ref. 19.

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