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X-ray absorption spectroscopy of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ single crystals

M. Merz, N. Nücker, E. Pellegrin, S. Schuppler, M. Kielwein,*
M. Knupfer,* M. S. Golden,* J. Fink,* C. T. Chen,[†]
V. Chakarian,[‡] Y. U. Idzerda,[‡] and A. Erb[§]

Forschungszentrum Karlsruhe, INFP, P.O.B. 3640, D-76021 Karlsruhe

*IFW Dresden e.V., P.O.B. 270016, D-01171 Dresden

[†]SRRC, Hsinchu Science-based Industrial Park, Hsinchu 300, Taiwan

[‡]Naval Research Laboratory, Code 6345, Washington, DC 20375

[§]DPMC, 24, quai Ernest-Ansermet, Univ. de Genève, CH-1211 Genève

Substituting Y in orthorhombic $(Y,RE)\text{Ba}_2\text{Cu}_3\text{O}_7$ by any rare-earth element RE has generally little effect on the superconducting properties. For $RE = \text{Pr}$, however, superconductivity is completely suppressed. To elucidate this effect we have studied the unoccupied electronic structure of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($x = 0.0, 0.4, 0.8$) by polarization-dependent O1s x-ray absorption spectroscopy on detwinned single crystals. Along with the comparison of undoped ($y \approx 0.9$) to the doped materials ($y \approx 0.1$), this allows a test of the current theoretical explanations for the suppression of superconductivity. While we can rule out models involving hole filling or charge transfer from planes to chains our data is consistent with approaches based on $\text{Pr}4f\text{-O}2p_\pi$ hybridization.

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1. INTRODUCTION

Among the rare-earth-based cuprates that are isostructural to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound is an intriguing exception since it shows neither metallic nor superconducting behavior.^{1,2} Upon substituting Pr in the $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system, the superconducting transition temperature T_c decreases^{3,4} and finally vanishes for Pr fractions x

beyond 0.55. This transition seems to be accompanied by a change from metallic to semiconducting characteristics.⁴

Since $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has all the features that are considered essential for high-temperature superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, such as CuO_2 planes, CuO_3 chains, and apical oxygen atoms, differences in the electronic structure and in the distribution of holes between these structural units may reveal key parameters for high temperature superconductivity in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and, therefore, might help to close in on the mechanism that underlies superconductivity. In order to explain the T_c suppression in the p -type system $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, up to now several models have been competing 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 initially delocalized holes in the CuO_2 planes, (ii) magnetic interaction and/or localization effects mediated through hybridization of $\text{Pr}4f$ with $\text{O}2p$ states in the planes, and (iii) gradual hole transfer from the planes to the chains.

The aim of our investigation is to distinguish between the various models by carefully examining the electronic structure of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ close to the Fermi level. For this, we have conducted $\text{O}1s$ near-edge x-ray absorption fine structure (NEXAFS) studies of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$.

2. EXPERIMENTAL

We have grown $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals using standard methods.⁵ For $x = 0.0$ and 0.8 , the samples were grown in an Y_2O_3 -stabilized ZrO_2 crucible while the $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals were grown in a BaZrO_3 crucible.⁵ Crystals with $x = 0.0$ and 0.8 from the same batches were characterized by EDX and neutron diffraction for impurities, stoichiometry, and structural parameters. The oxygen content of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($x = 0.8, 0.0$) was determined to 6.91 ± 0.01 . 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.

The $\text{O}1s$ absorption spectra were obtained using polarized synchrotron radiation from beamline U4B at the National Synchrotron Light Source, Brookhaven. Applying dipole selection rules, the unoccupied part of the $\text{O}2p$ final states can be reached from the initial $\text{O}1s$ core level. Therefore, polarization-dependent NEXAFS measurements on detwinned single crystals are a powerful method to distinguish whether the hole states have in-plane or out-of-plane orbital character in the CuO_2 planes or if they are situated in the CuO_3 chains. We have recorded our spectra in the fluorescence yield detection mode, using a multi-element Ge detector, to avoid surface sensi-

tivity. Our data are corrected for azimuthal and polar alignment errors as well as for self-absorption and saturation effects.⁶

3. RESULTS AND DISCUSSION

In Fig. 1 the O1s absorption edges with polarization $\mathbf{E}||\mathbf{a}$ are shown for the antiferromagnetic insulator $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$, the *p*-type doped superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ ($T_c \approx 93$ K), and the $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ sample ($T_c < 15$ K).

Fig. 1. Comparison of the O1s absorption cross sections of $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for $\mathbf{E}||\mathbf{a}$. Upon Pr substitution, the upper Hubbard band (UHB) is strongly increased at the expense of the Zhang-Rice (ZR) state.

Below 534 eV, the $\mathbf{E}||\mathbf{a}$ spectra of the three crystals are mainly composed of three peaks (marked by arrows). The first peak at 528.5 eV shows an intensity reduction with increasing Pr concentration whereas the second and third feature at 529.5 eV and 532.2 eV are increased. A further small peak, independent of the Pr substitution, is seen at 530.7 eV. The feature at 528.5 eV which is most pronounced for $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ has a much steeper onset than the following ones. In accordance with previous work, it is attributed to the ZR state.⁷ The steep onset for $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ strongly indicates that the Fermi level is located right below the top of the ZR band. Observing a downward shift of the UHB peak and taking XPS measurements⁸ into account, we conclude that with increasing Pr content the Fermi level E_F

together with the O1s core level is shifted to higher energies. Finally, for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ E_F is located slightly above the top of the ZR band. In this case no doped holes are left in $\text{O}(2,3)2p_{x,y}$ σ -orbitals hybridized with $\text{Cu}(2)3d_{x^2-y^2}$ orbitals and hence the ZR state is not stabilized.

It is well established that if holes are residing in the ZR state, transitions from the O1s core level into the UHB exhibit only little spectral weight due to the transfer of spectral weight from the UHB to the ZR state. In contrast to this, the spectral weight of the UHB should be observed with the same strength as for oxygen-poor $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ or $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ if the holes are moved from the ZR state into states which have no hybridization with Cu atoms.

Since for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ an UHB is observed which is as intense as it is for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ (see Fig. 2), we can draw the conclusion that with increasing Pr concentration holes are pushed out of the ZR state and moved into energetically favored states on the low energy side of the UHB (compare spectra in Fig.'s 1, 2) which have obviously no copper character. Therefore, for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ we regard the feature extending from 527.0 eV to 530.2 eV (Fig.'s 1, 2) as a composition of the UHB plus additional states on the low energy side of the UHB.

Fig. 2. Comparison of the O1s absorption spectra of $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ for polarization $\mathbf{E}||\mathbf{a}$. For both oxygen concentrations the peak position of the UHB is at the same energy.

From the contribution of the O(1) site, obtained by the difference spectra $\mathbf{E}||\mathbf{b} - \mathbf{E}||\mathbf{a}$ (not shown), a gradual redistribution of the doped holes from

the planes to the chains, as suggested in Ref.'s 9 and 10, can be ruled out. Instead of a hole *increase* on the oxygen sites of the CuO_3 chain we do in fact observe a *decrease* by about 14%.

In the following we will discuss aspects of the Fehrenbacher-Rice (FR) model.¹¹ According to this approach, the substitution of Y by Pr causes the initially delocalized holes to be moved from in-plane $\text{O}(2,3)2p_\sigma$ orbitals to the 45° -rotated $\text{O}(2,3)2p_\pi$ orbitals hybridized with the central Pr. The UHB band will then be visible as a consequence of the transfer of spectral weight. As already pointed out, this transfer of spectral weight is indeed observed in our spectra (Fig. 1). Therefore, we assume that the feature at 529.5 eV in the $\text{E}||\text{a}$ spectrum of $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ is composed of the UHB of $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ plus possible FR states (Fig. 2). For the isotropic FR states we have to take into account that for $\text{E}||\text{c}$ all orbitals are involved in the absorption process but for $\text{E}||\text{a}$ half of the orbitals are oriented perpendicular to the polarization vector of the synchrotron radiation. Hence, the difference spectrum in Fig. 2 has to be scaled by a factor of 2 in order to take all planar contributions into account. The scaled difference spectrum is shown in Fig. 3 together with the $\text{E}||\text{c}$ spectrum of $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$.

Fig. 3. Comparison of the difference spectrum ($2 \cdot \text{E}||\text{a}$) and the $\text{E}||\text{c}$ spectrum. The area enclosed by both curves constitutes an upper limit for isotropic FR states.

The integrated area common to both curves corresponds to 0.21 holes. Therefore, a total of 0.42 holes could reside on the possible FR states. The number of holes of the $\text{E}||\text{c}$ absorption spectrum amounting in total to 0.31 holes would then be composed of 0.21 holes in the FR state and 0.10 holes on the apical $\text{O}(4)$ site. However, this indicates a problem with the original FR approach, since such a small number of holes on the apical sites is inconsistent with optical¹² and NMR data¹³ showing that in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ the

apical site remains unaffected by substitution.

This problem can be addressed in the following way: In contrast to the *isotropic* FR states suggested in the FR model,¹¹ Liechtenstein and Mazin¹⁴ propose that the FR states grabbing the holes have exclusively *planar* character in the interesting region around E_F . Based on the idea that the rotation angle may be situated somewhere between these two extremes of 0° and 45° , we propose a very simple and straightforward extension of the original FR calculations.¹⁵ According to this, the peak at 528.7 eV for $\mathbf{E}||\mathbf{a}$ in Fig. 3 is assumed to belong to the FR state plus holes which remain in the ZR state due to the Y fraction in the material, while the $\mathbf{E}||\mathbf{c}$ feature at 527.8 eV is composed of the FR state plus holes on the apical oxygen. All constraints from our experimental results are taken into account, including the number of holes determined for the various sites. The main result of these considerations is that one can have a stable FR state and an unchanged apical hole concentration at the same time if the $\text{O}(2,3)2p_\pi$ orbitals are rotated by about $20^\circ - 25^\circ$. Thus, our results are consistent with a $\text{Pr}4f_{z(x^2-y^2)}-\text{O}2p_\pi$ hybridization, and the rotation angle deduced by our analysis lies in-between the two extremes proposed.

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REFERENCES

1. Y. Dalichaouch *et al.*, *Solid State Commun.* **65**, 1001 (1988).
2. A. Matsuda *et al.*, *Phys. Rev. B* **38**, 2910 (1988).
3. L. Söderholm *et al.*, *Nature* **328**, 604 (1987).
4. A. Kebede *et al.*, *Phys. Rev. B* **40**, 4453 (1989).
5. A. Erb, E. Walker, and R. Flükiger, *Physica C* **258**, 9 (1996).
6. L. Tröger *et al.*, *Phys. Rev. B* **46**, 3283 (1992).
7. F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1987).
8. O. Cohen *et al.*, *Physica C* **201**, 58 (1992).
9. D. Khomskii, *J. Super.* **6**, 69 (1993).
10. Y. Wang, H. Rushan, and Z.-B. Su, *Phys. Rev. B* **50**, 10350 (1994).
11. R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).
12. K. Takenaka *et al.*, *Phys. Rev. B* **46**, 5833 (1992); K. Widder *et al.*, *Physica C* (1996), in press.
13. K. Nehrke and M. W. Pieper, *Phys. Rev. Lett.* **76**, 1936 (1996).
14. A. I. Liechtenstein and I. I. Mazin, *Phys. Rev. Lett.* **74**, 1000 (1995).
15. M. Merz *et al.*, to be published.