Location of holes in $Y_{1-x}Pr_xBa_2Cu_3O_7$

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(Received 25 June 1997)

Recent experiments by Merz *et al.* [Phys. Rev. B **55**, 9160 (1997)] demonstrated that the loss of superconductivity upon Pr doping is associated with the change of the character of the oxygen holes from p_σ to p_π. This experiment sheds light onto the long-standing problem of T_c suppression by Pr, and helps to rule out a number of theoretical models, leaving only those which predict such a transfer of the O holes. To distinguish between the two models that do predict such an effect, one has to access the ratio of the planar and axial character of the holes. We do so in this paper.
[S0163-1829(98)03202-0]

One of the most exciting cases of superconductivity suppression in high-T_c cuprates is that of $R_{1-x}Pr_xBa_2Cu_3O_7$, where R stands for a rare earth. A number of explanations, including magnetic pair breaking,[1,2] disorder on Ba site,[3] and hole transfer from planes to chains,[4] have been suggested. All these models have problems of various degrees explaining the available experimental data. Most notably, recent polarization-dependent O $1s$ near-edge x-ray-absorption measurements on single-domain Pr-doped single crystals[5] succeeded in measuring not only the total amount of O holes in CuO_2 planes, but also the relative weight of their planar (p_x, p_y) and axial (p_z) components. It is hard to overestimate the importance of this experiment, which essentially rules out the models that assume the total hole concentration in planes to be dependent on the Pr doping.

To the contrary, this result strongly favors models that assume that hole depletion of the superconducting $pd\sigma$ states occurs because of the hole transfer into the $pd\pi$ states. The first model of this sort is that of Fehrenbacher and Rice.[6] They assumed that p_π orbitals of the planar oxygens neighboring a Pr ion form a hybride state with the Pr $f_{z(x^2-y^2)}$ orbital. They noticed that oxygens around a rare-earth site form a nearly perfect (better that 10%) cube, and so the lobes of the $f_{z(x^2-y^2)}$ at a rare-earth site point nearly exactly towards the oxygens. They assumed further that such a hybride orbital is strongly localized. This assumption followed from the implicitly implied statement in Ref. 6 that the corresponding combination of the oxygen orbitals forms *only* when the rare-earth site is occupied by Pr, but not by Y (where the $f_{z(x^2-y^2)}$ state is unoccupied and lies much higher the O p states), in other words, that direct hopping between involved O orbitals, without assistance of the Pr $f_{z(x^2-y^2)}$ orbital, is negligible. This seemed to be a plausible idea, because in the considered O_8 cube the O-O distance is relatively large, $d_{\text{O-O}} \approx a/\sqrt{2} \approx 3$ Å. Besides, the hopping matrix elements between two orbitals pointing to the center of the cube is $t_{\text{O-O}} = \frac{1}{3}t_{pp\sigma} + \frac{2}{3}t_{pp\pi}$, more $pp\pi$ than $pp\sigma$.

On the other hand, a closer look at the band structure shows that the O-O hopping may be not small even in the absence of Pr. For instance, Andersen *et al.*[7] found substantial $pp\sigma$ hopping perpendicular to the planes (that is, between p_z orbitals), of the order of 0.35 eV. O-O hopping inside the planes is even larger, because it is assisted by the diffuse Cu s orbital (see Ref. 7 for the details). Thus, it is *a priori* unclear whether the p_π orbitals should form a localized state or rather a band comparable in width with the superconducting $pp\sigma$ band. To answer this question, Liechtenstein and Mazin[8] identified among the manifold of occupied O-derived bands the oxygen band that has the $z(x^2-y^2)$ symmetry, and found it to be rather dispersive (bandwidth ≈ 1.5 eV). Based on this finding, they suggested a modification of the original Fehrenbacher-Rice model, in which holes are transferred from the $pd\sigma$ band not to a localized state, but to the band derived from the Fehrenbacher-Rice states with substantial overlap between them. Parameters of the model were found from local density approximation (LDA)+U_{Pr} calculations, which should be valid at small and moderate Pr doping (at large doping, that is, close to the metal-insulator transition, one has to take into account Hubbard U at the Cu site, which was not done in Ref. 8). This modified Fehrenbacher-Rice model was very successful in describing T_c suppression rates in $R_{1-x}Pr_xBa_2Cu_3O_7$, including the dependence of the suppression rate on the rare earth. The latter constitutes a serious problem in the original model,[6] because the only effect of substituting on R by another in that model is ''chemical pressure,'' that is, contraction of the Cu-O and R-O bonds. The two contractions shift the energy balance in favor of the $pd\sigma$ band and the $pp\pi - f_{z(x^2-y^2)}$ state, respectively.[9] However, the latter effect is stronger (cf. canonical scaling of Harrison, which implies the d^{-4} and d^{-5} scaling for pd and pf hopping amplitudes, respectively). Correspondingly, external pressure enhances T_c suppression, the most striking manifestation being the recently observed suppression of superconductivity by external pressure in pure $NdBa_2Cu_3O_{6.7}$.[10] To the contrary, bond contractions due to host R substitutions *decrease* the T_c suppression rate, opposite to what one would

expect in the localized model of Ref. 6. On the other hand, in the modified model of Ref. 8 this effect appears naturally as a result of hopping between the host R and the Pr f orbitals.

However, closer to the metal-insulator transition the model of Ref. 8 becomes less and less realistic and it was pointed out[9] that uncritical extention of this model to pure $PrBa_2Cu_3O_7$ leads to serious problems with explaining away possible metallic conductivity in the $pp\pi$ band. Thus, it is highly desirable to address the differences between models of Refs. 8 and 6, by an independent experiment. This was one of the goals of Merz *et al.*[5] Essentially, they noticed that the p_π holes have different character in the two models: According to Ref. 8, they are predominantly planar ($p_{x,y}$), while according to Ref. 6, the p_π orbitals in question point towards neighboring Pr, and correspondingly have comparable amount of the $p_{x,y}$ and of p_z character.

As mentioned above, around each Pr eight nearest-neighbor O ions form nearly perfect cube; correspondingly, p orbitals pointing to the Pr according to the model of Ref. 6 form an angle $\alpha=\arctan(1/\sqrt{2})\approx 35°$ with the xy plane [in reality, the interplanar O-O distance is slightly larger than intraplanar one, and so the angle is $\approx 36°$ for O(2) and $\approx 37°$ for O(3)]. Incidentally, in the original paper[6] this angle was mistakenly identified as 45°, which did not influence the calculations of Fehrenbacher and Rice,[6] but misled the authors of Ref. 5 and affected their comparison of the experimental results with the Fehrenbacher-Rice model. Furthermore, as was mentioned in Ref. 8, in the band model the $pp\pi$ hole states are strictly planar only in the limit when the number of $pp\pi$ holes tends to zero, i.e., when the $pp\pi$ band touches the Fermi level. The experimental results of Merz *et al.*[5] correspond to substantial Pr doping ($x=0.8$) and a considerable number of the $pp\pi$ holes (0.25 holes/cell). In an elegant analysis of their experimental data, Merz *et al.* deduce that the angle that unoccupied p_π orbitals form with the xy plane is 20°–25°, and conclude that this is equally far from the Fehrenbacher-Rice prediction of 45° and of the Liechtenstein-Mazin prediction of 0°. However, as we mentioned above, the former model predicts 35°–37° instead, and the latter predicts an angle which has yet to be calculated. Below we present such a calculation.

The original paper[8] was aimed at calculating the T_c suppression rate at small Pr concentrations, and utilized a tight-binding model where p_z orbitals were not included. In order to analyze the hole character at finite dopings, we have to include both $p_{x,y}$ and p_z states. We will, however, neglect the $pf\pi$ hopping and leave only the $pf\sigma$ one. The hopping amplitude between the $f_{z(x^2-y^2)}$ and the $p_{x,y}$ orbitals is $\sqrt{5}/3\sqrt{2/3}t_{pf\sigma}=\sqrt{2/3}t$, and between the $f_{z(x^2-y^2)}$ and the p_z it is $\sqrt{5}/3\sqrt{1/3}t_{pf\sigma}=\sqrt{1/3}t$ (Ref. 11). Correspondingly, instead of the tight-binding Hamiltonian given in Ref. 8, Eq. (1), we have

$$H=\begin{pmatrix} \epsilon_p & 0 & 0 & 0 & t\sqrt{1/3}C_x \\ 0 & \epsilon_p & 0 & 0 & -t\sqrt{1/3}C_y \\ 0 & 0 & \epsilon_p & -\tau S_xS_y & t\sqrt{2/3}S_x \\ 0 & 0 & -\tau S_xS_y & \epsilon_p & -t\sqrt{2/3}S_y \\ t\sqrt{1/3}C_x & -t\sqrt{1/3}C_y & t\sqrt{2/3}S_x & -t\sqrt{2/3}S_y & \epsilon_f \end{pmatrix}, \tag{1}$$

where the first two orbitals are p_z and the remaining part is the p_x-p_y-f Hamiltonian used in Ref. 8. The same notations as there are used, namely, $S_{x,y}=2\sin(ak_{x,y}/2)$, $C_{x,y}=2\cos(ak_{x,y}/2)$.

In Ref. 8 we were interested in calculating the doping dependence of the number of unoccupied states; that is why we had to keep the f orbitals explicitly in the tight-binding Hamiltonian. Now we want to estimate the average weight of the p_z orbital compared to that of the $p_{x,y}$ orbitals for a given number of holes. Thus, we fold down the f state in Eq. (1), using Löwdin perturbation theory. This gives

$$H\approx\begin{pmatrix} C_x^2\tilde{t} & -C_xC_y\tilde{t} & \sqrt{2}C_xS_x\tilde{t} & -\sqrt{2}C_xS_y\tilde{t} \\ -C_xC_y\tilde{t} & C_y^2\tilde{t} & -\sqrt{2}C_yS_x\tilde{t} & 2S_x^2\tilde{t} \\ \sqrt{2}C_xS_x\tilde{t} & -\sqrt{2}C_yS_x\tilde{t} & 2S_x^2\tilde{t} & -\tau S_xS_y-2S_xS_y\tilde{t} \\ -\sqrt{2}C_xS_y\tilde{t} & \sqrt{2}C_yS_y\tilde{t} & -\tau S_xS_y-2S_xS_y\tilde{t} & 2S_y^2\tilde{t} \end{pmatrix}, \tag{2}$$

where we put ϵ_p to zero and denote $\tilde{t}=t^2/3(E_F-\epsilon_f)$. We diagonalized this Hamiltonian numerically and calculated the average angle for unoccupied (hole) states in the upper p_π band as a function of filling (Fig. 1) [$\alpha=\arctan(\langle n_x+n_y\rangle/\langle n_z\rangle)$, where n_x+n_y and n_z are calculated by adding squares of the first two and the last two components of the eigenvectors]. For the hole count 0.25, corresponding to the experiment of Ref. 5, we find $\alpha=18°$. Figure 1 was calculated with $\tau=0$; for a fixed hole count, the angle α depends on τ very little. For instance, for $\tau=\tilde{t}$ we find α to be reduced by about 20%, that is, to 15°. The latter number can be taken as the lower bound for the band model prediction.

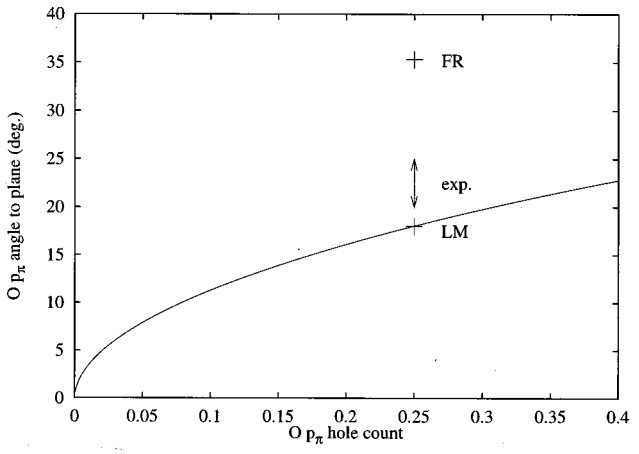

FIG. 1. Average rotation angle of the depleted O(2,3) p_π orbitals as a function of the number of holes, n, in the $pp\pi$ (''Fehrenbacher-Rice'') band, from the band model of Liechtenstein and Mazin (LM). Experimental estimate at $n=0.25$ is shown by the double-headed arrow, as well as the (independent of the hole count) rotation angle in the localized Fehrenbacher-Rice model (FR). The LM curve corresponds to $\tau=0$ in Eq. (2).

In fact, the reason that the band model yields an unexpectingly large rotation angle is that although this angle tends to zero for infinitesimally small doping, it increases very rapidly, as the square root of hole number and, consequently, as the square root of the Pr concentration, a fact that was not appreciated in Ref. 8.

To conclude, we have calculated the relative character of the planar, $p_{x,y}$, and of the axial, p_z, hole states in the $pp\pi$ band in $Y_{1-x}Pr_xBa_2Cu_3O_7$ as a function of hole count in this band, using the localized model of Fehrenbacher and Rice[6] and the band model of Liechtenstein and Mazin.[8] Comparing our results with the x-ray-absorption experiment of Merz *et al.*,[5] we observe that, in agreement with the conclusion of the authors of Ref. 5, their result falls *between* the two theoretical predictions. However, the two predictions are closer to each other than what was supposed in Ref. 5, and correspondingly closer to the experiment. Especially close to the experiment (10–30 %) are predictions of the band model of Ref. 8.

The last remark we would like to make is that, although the *quantitative* difference between the two model appears to be not that large in this case, there is a *qualitative* difference, which can be used in the future experimental studies to distinguish between them. Namely, the band model predicts that the rotation angle increases with Pr doping, especially at low doping levels, while according to the localized model it should stay essentially constant.

We wish to thank M.S. Golden for useful discussions and D.J. Singh for a critical reading of the manuscript. Work at NRL is supported by the Office of Naval Research.

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