Theoretical possibilities for superconductivity in $PrBa_2Cu_3O_7$

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Recent reports about observations of superconductivity in $PrBa_2Cu_3O_7$ raise a number of questions. (i) Of the various theories striving to explain the T_c suppression in $Pr_xY_{1-x}Ba_2Cu_3O_7$, are there any compatible with possible superconductivity in stoichiometric $PrBa_2Cu_3O_7$? (ii) If this superconductivity is not an experimental artifact, are the superconducting carriers (holes) of the same character as in the other high-T_c cuprates, or do they represent another electronic subsystem? (iii) Is the underlying mechanism the same as in other high-T_c superconductors? I present an answer to the first two questions, leaving the last one open. [S0163-1829(99)13925-0]

One of the most exciting cases of superconductivity suppression in high-T_c cuprates is that of $RE_{1-x}Pr_xBa_2Cu_3O_7$, where RE stands for a rare earth (see Refs. 1,2 for reviews). Even more exciting are recent indications that conductivity and superconductivity can be restored in pure stoichiometric $PrBa_2Cu_3O_7$.[3,4] This is such an unexpected result[5] that it is still not generally accepted and further experimental confirmation is required. Nevertheless, this fact was reported by two independent groups, and it is time now to understand the theoretical consequences of this finding. The most important message, if this finding is true, is that at $x=1$, and, presumably, at intermediate x's, there are free carriers in $RE_{1-x}Pr_xBa_2Cu_3O_7$, and the suppression of metallic conductivity at sufficiently large x must be due to localization of those carriers. This statement effectively eliminates the possibility of hole depletion due to hole transfer into occupied states ("four-valent Pr model"). It furthermore becomes highly unlikely that any kind of magnetic pair breaking is in effect, because (1) the normal state conductivity drops sharply with doping, indicating the change of character, if not the number, of carriers, and (2) the superconductivity is, supposedly, restored at $x=1$. It seems that we can then consider only the models which associate the (super)conductivity suppression with a transfer of holes to an itinerant, but different from the undoped YBCO, state, which should furthermore be prone to localization. At first glance the only theoretical model that satisfies this criterion is the itinerant model of Liechtenstein and Mazin.[6,7] I will show below that contrary to the common belief, the Fehrenbacher and Rice model[8] (FR) is *also* compatible with metallic and possibly superconducting behavior in $PrBa_2Cu_3O_7$.[9] In fact, it turns out that the difference between the "local" FR model and the "itinerant" LM model is much smaller than it was thought to be; if handled correctly, the FR model also renders a metallic state in clean limit. This new understanding means that the physics of superconductivity suppression and its possible recovery is essentially the same in both models. There is still a quantitative difference between the two, which is hard to access experimentally, but which is now of limited importance. A generic model based on a strong $df\sigma$ hybridization explains the *entire body* of existing experimental results and does not seem to have any sensible alternative. An exciting fact is that this generic model not only provides

a possibility for metallic and superconducting behavior of $PrBa_2Cu_3O_7$, but that it also predicts the superconducting holes in it to be of entirely different physical nature than the carrier in familiar high-T_c superconductors.

Let me start with a brief reminder of the essence of the FR model. The crystal structure of the YBCO family cuprates is such that a rare earth ion and eight nearest oxygens form a nearly perfect cube. Moreover, among seven orbitals of f symmetry there is one, xyz, which has eight equivalent lobes directed along eight directions $[\pm 1, \pm 1, \pm 1]$. In the standard coordinate system where x, y correspond to the CuO bond directions the same orbital is $(x^2-y^2)z$. Since this f orbital extends directly towards neighboring oxygens, one expects a noticeable $pf\sigma$ hopping between RE and O. Thus the electronic structure of a $RECu_2O_4$ bilayer breaks into two weakly interacting subsystems: usual Cu-O $pd\sigma$ bands, of which two antibonding ones cross the Fermi level in YBCO, and RE-O $fd\sigma$ states. Oxygen p states directed along the Cu-O bonds ("$p\sigma$" orbitals) participate in the former and those perpendicular to the bonds ("$p\pi$" orbitals) in the latter. If one starts with a cluster of one Pr and eight surrounding oxygens and consider formation of an antibonding state of the $f_{(x^2-y^2)z}$ Pr orbital and eight oxygen p orbitals pointing directly towards Pr, we find one bonding, one antibonding, and seven nonbonding states. If the energy difference between the bare O p level and bare Pr f level is not too large, the energy of this antibonding state, $pf\sigma^*$, may become higher than that of the $pd\sigma^*$ Cu-O state and will pull some holes out of the latter. Whether or not this will happen depends on the p-f energy separation and the p-f hopping integral.[10] Suppression of superconductivity in $RE_{1-x}Pr_xBa_2Cu_3O_7$ is thus ascribed to the hole transfer from the superconducting $pd\sigma^*$ band into the $pf\sigma^*$ state. An indispensable component of this model is localization of carriers promoted into the $pf\sigma^*$ state. FR (Ref. 8) argued that the oxygen orbitals forming this state form the 45° angle with the CuO planes and thus the orbitals of the same oxygen pointing towards neighboring Pr ions are orthogonal to each other. They also neglected the bare dispersion of the $p\pi$ bands originated from the hopping between the oxygen $p\pi$ orbitals. In such an approximation the effective bandwidth of the $pf\sigma^*$ band is zero, and the holes there are localized by

infinitesimally small disorder. This was the original explanation of the lack of (super)conductivity in $PrBa_2Cu_3O_7$. Furthermore, since this model renders noticeable presence of Pr states at the Fermi energy, one expects the Curie temperature for ordering of the Pr moments to be much higher than for other $REBa_2Cu_3O_7$, which is indeed the case. A drawback is that total localization in the FR model does not let the given PrO_8 cluster be influenced in any direct way by the rare earths filling other cells, in contradiction with the experiment: the T_c suppression rate even at low doping depends strongly on the host rare earth.

The LM model[6] differs from the FR model in essentially only one aspect: direct hopping between oxygen orbitals[11] is taken into account. LM calculated this hopping as well as other relevant parameters of the electronic structure numerically, using LDA+U method including Coulomb correlation in the rare earth f shell. They found that effective O-O hopping (direct and *via* Cu t_{2g} orbitals) leads, independent of the value of the $pf\sigma$ hopping (and even the very presence of the f orbital) to a dispersive band (FR band). It was originally thought[6] that an advantage of the LM model over the FR model was that a dispersive band would hybridize with all rare earth ions in the crystal, and its position *before* doping with Pr would depend on the position of the f level in the host rare earth. This naturally, and with reasonable quantitative agreement, explains the different rates of suppression with different host RE.[6] Another prediction which was seemingly different from that of the FR model was that the holes transferred to the $pf\sigma^*$ band concentrate near the corner of the Brillouin zone; that is, near $\mathbf{k}=(\pi/a,\pi/b)$. This prediction could be indirectly checked by measuring the ratio of the out-of-plane (p_z) and in-plane ($p_{x,y}$) oxygen characters. At least qualitatively, this prediction was confirmed by experiment.[14]

The main problem with the LM ''band'' model was that, taken literally, it predicted the carrier transfer from one metallic system into another. This could easily explain the superconductivity suppression, but not the loss of metallicity. The explanation suggested in Ref. 6 was that due to the high (compared to the $pd\sigma$ band) effective mass in the new band the carriers are easily localized (note that many-body renormalization, first of all due to spin fluctuations, is expected to increase the effective mass even more[8]). It was pointed out,[12] however, that in such a case one expects stoichiometric $PrBa_2Cu_3O_7$ to be metallic. We argued then[13] that the model is designed for the low x limit, where LDA+U_f description of the Cu-O band is qualitatively correct, but cannot be directly extrapolated onto the large x compositions.

Interestingly, it was not noticed until very recently[7] that the geometric argument of FR (Ref. 8) was incorrect: in fact, the angle that an O-Pr bond forms with the CuO_2 planes is not 45°, but $\tan^{-1}(1/\sqrt{2})\approx 35°16'$, which means that even in the FR limit of no direct O-O dispersion, the $pf\sigma^*$ states form a band whose dispersion is defined by the Pr-O hopping amplitude $t_{pf\sigma}$. Below I show how this band forms, using the nearest-neighbor tight-binding Hamiltonian.

Let us begin with some notations: first, neglect the (very small) z dispersion. (This means that all considered orbitals are antisymmetric with respect to $z\rightarrow -z$ reflection, like the $f_{z(x^2-y^2)}$ orbital.) Then the two plane problem is equivalent to a single plane. If one includes all nearest neighbors, the

following orbitals contribute to the FR band: (1) Pr $z(x^2-y^2)$, (2) O2 z, (3) O3 z, (4) O2 y, (5) O3 x, (6) Cu xy, (7) Cu yz, and (8) Cu zx. Their in-plane 2D symmetries are, respectively, x^2-y^2, s, s, y, x, xy, y, and x, which simplifies the task of the tight-binding description of the band structure. Let us now identify the largest hopping amplitudes between these orbitals. According to FR ideology, this is $pf\sigma$, which I shall denote t_{pf}. It controls the following hoppings: $t_{12}=t_{13}=\sqrt{(5/27)}t_{pf}$, $t_{14}=t_{15}=\sqrt{(10/27)}t_{pf}=\sqrt{2}t_{12}$. This parameter defines the effect of the rare earth substitution on the FR band. Another hopping, which is the strongest according to LDA, is of $pd\pi$ type, denoted t_{pd}. The hopping amplitudes t_{28}, t_{37}, t_{46}, and t_{56} all are equal to t_{pd}. This parameter defines the dispersion of the FR band in the absence of the f states; e.g., in $YBa_2Cu_3O_7$, or in the spin-minority channel of $PrBa_2Cu_3O_7$. (Alternatively, one may integrate out the Cu t_{2g} orbitals and use an effective O-O pp hopping.) Let us first consider these two hoppings separately.

The FR model corresponds to the approximation $t_{pd}=0$. The dispersion of the oxygen $p\pi$ states is completely neglected; an isolated Pr impurity forms a localized antibonding state, shifted up with respect to the bare O p level by

$$\epsilon_{\mathbf{k}}-E_p=\delta\epsilon=\frac{5}{9}\frac{8t_{pf}^2}{E_p-E_f}, \qquad (1)$$

where 8 stands for the eight neighboring oxygens. It is assumed that $t_{pf}\ll E_p-E_f$. In the opposite limit, when all rare earth sites are occupied by Pr, a narrow band is formed with the dispersion

$$\epsilon_{\mathbf{k}}-E_p=\delta\epsilon-\delta\epsilon\cos 2\varphi(\cos ak_x+\cos bk_y)/2, \qquad (2)$$

where $\varphi=\arctan(1/\sqrt{2})$ is the angle that the Pr-O bond forms with the xy plane. Had this angle been 45°, as assumed by FR, the band would be dispersionless and thus fully localized. In reality, it should acquire a finite bandwidth $W=\delta\epsilon\cos 2\varphi=\delta\epsilon/3$, even without Pr. This is an example of dispersion due to nonorthogonality: the Hamiltonian written in terms of the oxygen orbitals pointing towards Pr is diagonal, but such a basis is nonorthogonal and that results in dispersion. Note that the top of the band occurs at the (π,π) point and that is where the holes go from the $pd\sigma$ superconducting band. Figure 1 illustrates that indeed at this point the $pf\sigma$ interaction is antibonding along all bonds.

Now consider the case of finite t_{pd} and no f states. For simplicity, let the energy of the Cu d level be the same as the energy of the O p level. Then four O p orbitals and three Cu d orbitals form three antibonding bands (besides the bonding and nonbonding bands):

$$\epsilon_{\mathbf{k}}-E_p=2t_{pd}\sin\frac{ak_x}{2}, \qquad (3)$$

$$\epsilon_{\mathbf{k}}-E_p=2t_{pd}\sin\frac{bk_y}{2}, \qquad (4)$$

$$\epsilon_{\mathbf{k}}-E_p=2t_{pd}\sqrt{\sin^2\frac{ak_x}{2}+\sin^2\frac{bk_y}{2}}. \qquad (5)$$
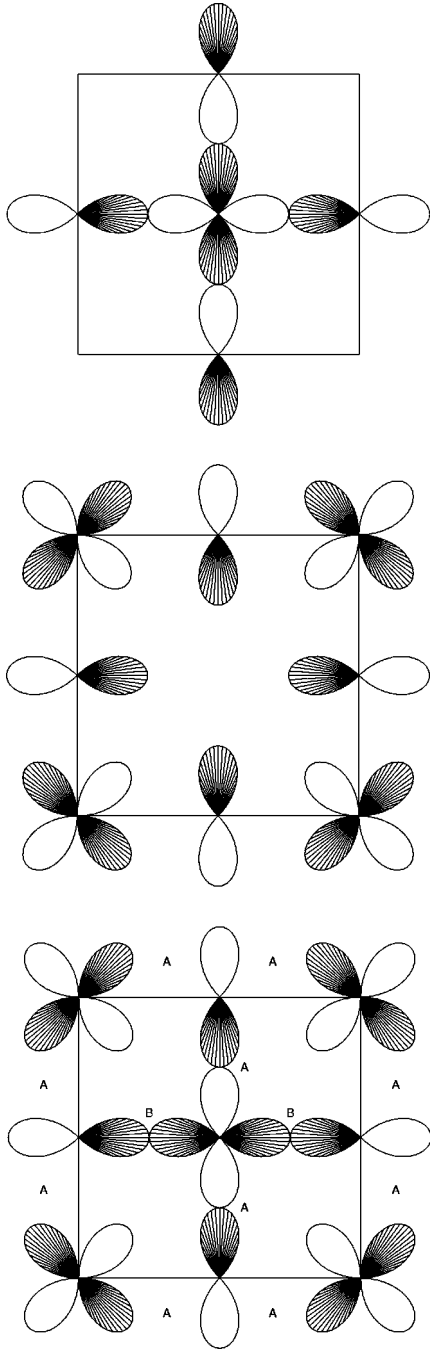
FIG. 1. Tight-binding orbitals at the point $\mathbf{S}=(\pi,\pi)$ projected onto x-y plane. Upper panel: FR model, $t_{pd}=0$. The Pr ion is in the center. Middle panel: LM model for $YBa_2Cu_3O_7$, no Pr $z(x^2-y^2)$ orbital, finite t_{pd}. Cu2 ions are in the corners. Lower panel: Illustration of inability of the O2 y and O3 x orbitals to make an antibonding combination simultaneously with the Cu2 xy orbital (in the corners) and Pr f orbital (in the center).

The top of the highest (third) band is again at (π,π), as illustrated in Fig. 1, showing again the antibonding interactions for all bonds.

The case of $pd\pi$ and $pf\sigma$ interactions taken together cannot be solved analytically. Before reporting the numerical results, I make one additional observation: since both cases separately produce dispersive bands with the maximum at (π,π), one might expect this effect (band dispersion) to be enhanced when both interactions are included. One can eas-

ily see (Fig. 1) that this is not true: the configuration of the O p orbitals, which is antibonding in the first case, is nonbonding in the second case, and vice versa.

The main shortcoming of the original FR model was its inability to describe the different rate of T_c suppression with the different rare earth hosts. The LM model with its dispersive $pf\sigma$ provides a natural explanation. However, comparing Eqs. (2) and (5) one can see that at low doping, that is, near the (π,π) point, the shape of the FR band is very similar to that of the LM band. Note that the scale of the dispersion, i.e., the effective masses, may be different — the FR band should be heavier than the LM band and thus easier to localize. However, for the ideal stoichiometric $PrBa_2Cu_3O_7$ at zero temperature both models give a metal and possibly a superconductor.

Another indirect argument in favor of the LM model over the original FR model was deduced from recent near-edge x-ray absorption experiments.[14] It was found that O p_π orbitals form a relatively small angle with the CuO_2 planes: 20 to 25° at the doping level of 80% Pr. This is closer to the prediction of the LM model[7] (15 to 18°) than to the original FR prediction[8] (45°), and even to the corrected number of 36°. However, the fact that the correct FR model is nonorthogonal not only yields a finite bandwidth in pure $PrBa_2Cu_3O_7$, but also makes the average angle of the O p_π orbitals dependent on doping at small doping — similar, but quantitatively different from the prediction of the LM model.

Indeed, the orbitals around an isolated Pr impurity are tilted by $\varphi=\arctan(1/\sqrt{2})$; on the other hand, if an oxygen atom has Pr ions on *both* sides, a pair of bonding/antibonding states is formed, of which the higher state does not include $O(p_z)$ character of this oxygen at all (and since the bonding-antibonding splitting here is defined by the sizeable energy $t_{pf\sigma}$, the the bonding combination is unlikely to be sufficiently high to carry holes). In the low doping limit, for the Pr concentration x, the probability for an oxygen to have one Pr neighbor is $\nu_1=2x(1-x)$, and to have two neighbors is $\nu_2=x^2$. Thus the average p_z character for the in-plane oxygen holes, seen in an experiment like Ref. 14 is $n_z=\nu_1\sin^2\varphi$, while the total number of the holes in the FR state is $n=\nu_1+\nu_2$. The average tilting angle is thus $\sin^2\alpha=\frac{2}{3}(1-x)/(2-x)$. For $x=0.8$ I find $\alpha\approx19.5°$, in excellent agreement with the experiment. Moreover, this number is the lower bound on α in the FR model, because at large x one cannot neglect dispersion of the FR band, which will force α to deviate from the formula above (at $x=1$ the FR model should give the same number as the LM model, which is[7] about 20°), so that at $x=0.8$ I find $\alpha\gtrsim20°$. Interestingly, while both the FR and LM models predict a dependence of the angle on concentration, and both must give the same value at $x=1$ (α does not depend on the effective mass at this point), they predict the opposite dependences: in the LM model α falls to zero when $x\rightarrow0$, while in the FR model it increases up to $\alpha=\varphi\approx36°$.

My conclusion is that after being corrected to take into account the right geometry of the Pr-O bonds, the FR model provides slightly better agreement with the experiment than the LM model. I emphasize that after such correction the difference between the two models is not the difference between a band model and a localized model, but the difference

between two band models, one where dispersion originates from the $pf\sigma$ Pr-O hopping, and another where it appears mostly due to the $pd\pi$ Cu-O hopping. The fact that the former appears more successful (however, the final word will be said by an experiment accessing x dependence of the angle α), does not mean that the $pd\pi$ hopping is negligibly small. As illustrated on the lowest part of Fig. 1, it merely means that the dispersion due to this hopping is weaker than that due to $t_{pf\sigma}$. One should also remember that both models are subject to further many-body effect, particularly of magnetic origin, and in either picture the effective bandwidth should be smaller that the one-electron TB bandwidth.

To summarize, the current experimental situation in $Pr_xRE_{1-x}Ba_2Cu_3O_7$ is such that the band version of the Fehrenbacher-Rice model presented here explains all existing experiments addressing superconducting and transport properties of this system, including the recent observation of superconductivity at full substitution. In fact, $PrBa_2Cu_3O_7$ is a more novel superconductor than all other cuprate high-T_c materials known: it is the only one where superconducting carriers are not residing in the $Cu(x^2-y^2)-O(p_\sigma)$ bands, but are of entirely different character. One can ask why are the critical temperatures in the two compounds, YBCO and PBCO, so similar? In the framework of the suggested model it is a sheer coincidence, which should be removed, for instance, by external pressure. Indeed, it was observed recently[15] that the pressure coefficient dT_c/dP in PBCO is an order of magnitude larger than in any other $REBa_2Cu_3O_7$. Interestingly, in the $df\sigma$ hybridization model one expects dT_c/dP to be negative in $RE_{1-x}Pr_xBa_2Cu_3O_7$ at small x, because pressure increases hybridization and thus the charge transfer from the $pd\sigma$ to the $pf\sigma$ states, while the same argument predicts dT_c/dP to be positive in $PrBa_2Cu_3O_7$ (since in this system the superconductivity occurs in the $pf\sigma$ band itself). Both predictions are in agreement with the experiment. Finally, I would like to point out recent measurements[16] that yielded qualitatively different Compton profiles in $YBa_2Cu_3O_7$ and $PrBa_2Cu_3O_7$. This usually indicates different topology of the Fermi surface and is in agreement with the concept of qualitatively different carriers in these two compounds.

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[5] Note however that even in earlier works electrical properties of $RE_{1-x}Pr_xBa_2Cu_3O_7$ were found to depend nonmonotonically on x, $PrBa_2Cu_3O_7$ being more metallic than intermediate compounds; see, e.g., M. Lee, M.L. Stutzman, Y. Suzuki, and T.H. Geballe, Phys. Rev. B **54**, 3776 (1996).

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[9] I concentrate in this Brief Report on these two models (Refs. 6 and 8) because no other model I am aware of has any mechanism for higher conductivity and, eventually, superconductivity in fully substituted $PrBa_2Cu_3O_7$ compared with a partially substituted $Pr_xY_{1-x}Ba_2Cu_3O_7$.

[10] It also depends of course, on the Fermi level position. The higher the Fermi level, the higher should the antibonding $pf\sigma$ state be pushed to start grabbing holes from the $pd\sigma$ band. In some sense it is counterintuitive, because it means that a system with less holes and thus higher E_F (e.g., $YBa_2Cu_3O_{7-\delta}$, $\delta>0$) is less prone to the Pr-induced T_c suppression than a fully oxygenated YBCO with higher T_c. However, this counterintuitive feature has been observed experimentally [K. Koyama *et al.*, Physica C **235-240**, 1469 (1994)].

[11] In this context ''direct hopping'' includes also all assisted hoppings which do not involve the Pr f states, e.g., *via* Cu d_{xz} and d_{yz} orbitals.

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