Quantitative Model for the Superconductivity Suppression in $R_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O_7}$ with Different Rare Earths

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We report local density approximation plus Hubbard parameter U calculations of the electronic structure of $A\mathrm{Ba_2Cu_3O_7}$ (A = Y, Pr, Nd) including Coulomb correlations in the f shell. For A = Pr (but not for A = Nd) an additional band crosses the Fermi level, grabbing holes from the (super)conducting $pd\sigma$ band. On doping Y or Nd with Pr the position of the hole-depleting band depends on the atomic number of the host rare earth, through the position of its f level. This makes T_c suppression in doped compounds different for different hosts the stronger the smaller the atomic number of the host is, and also explains why an external pressure reduces T_c in doped compounds, opposite to the effect of the "chemical pressure" (substituting one rare earth by another with a smaller size).

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Among all rare earths (RE) that form the $R\mathrm{Ba_2Cu_3O_7}$ structure only $\mathrm{PrBa_2Cu_3O_7}$ is nonmetallic and nonsuperconducting. This fact remains one of the remarkable puzzles of high-temperature superconductivity in cuprates and a large number of explanations have been suggested (for a list, see Ref. [1]). Early explanations involved either hole depletion, assuming oxidation state Pr IV, or the influence of Pr^{3+} spins on the $\mathrm{CuO_2}$ planes, assuming oxidation state Pr III. In the latter case, the difference between Pr and other RE's is supposed to be due to the different ionic radii. Both ideas, however, fail to explain many experiments (cf. discussions in Refs. [1,2]) and the only satisfactory model is that of Fehrenbacher and Rice (FR) [2]. The FR model assumes hole depletion in the $\mathrm{CuO_2}$ planes, not because of higher Pr valence, but because of transfer of the holes from the Cu-O $pd\sigma$ band into the FR state which is a mixture of $4f^1$ and $4f^2\underline{L}$ configurations. Here, $\underline{L}$ is a ligand hole in the O $2p$ orbital with $z(x^2-y^2)$ symmetry around the Pr site and distributed over the eight nearest oxygen sites. The chains are assumed metallic in this model, and the absence of metallic conductivity is ascribed to localization due to oxygen disorder.

As discussed in Ref. [1], the FR model still fails to explain some qualitative observations. The most important is that the suppression of superconductivity in the mixed rare-earth compounds $R_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O_7}$ with increasing x depends on the RE component. In case of R = Y, for instance, the superconductivity disappears for $x > 0.6$, while for Nd the critical concentration is as low as $x \approx 0.3$ [3,4]. In the FR model, where the Pr-O hybridization is a purely local phenomenon, this RE dependence of the superconductivity suppression is of geometrical origin; the R-O bond is shorter for the smaller RE's, and so is presumably the impurity Pr-O bond. Since the crucial parameter in the model is the hopping between Pr $4f_{z(x^2-y^2)}$ and the L orbital, one would, however, expect the opposite trend, that is, for larger RE's, like Nd, the superconductivity should be more robust against Pr doping. This observation becomes even more puzzling when one realizes that the above reasoning works perfectly well for the physical pressure [5], which does suppress T_c. This fact indicates that the difference of the ionic radii of the various rare earths is not the only, maybe not even the main reason, for the different behavior upon Pr doping.

Another important fact is that there are only two stable solutions in the FR model: $n_p = 0$ or $n_p = (1-n_c)/2$, where n_p is the number of holes per plane and n_c is the number of holes per chain. In order to explain why of all rare earths only Pr suppresses superconductivity, FR were "left with little option but to conclude that the essential difference between Pr and the other rare earths is the crossing of these two solutions" [2]. However, this conclusion does not fit with the fact that T_c depends smoothly on the Pr concentration x and on pressure.

In this Letter we present a quantitative model which exploits the basic idea of Fehrenbacher and Rice [2], namely that the holes from the $\mathrm{CuO_2}$ $pd\sigma$ band can be transferred into FR states. Our model is different from that of the Ref. [2] in that the L orbitals form a dispersive band, which is crucial for resolving the abovementioned difficulties. First, for *pure* $\mathrm{PrBa_2Cu_3O_7}$ and $\mathrm{NdBa_2Cu_3O_7}$ we shall report *ab initio* local density approximation plus Hubbard parameter U (LDA + U) calculations which take the Coulomb correlations on the RE site [6] into account via a self-consistent, spin- and orbital dependent mean field [7]. For $\mathrm{YBa_2Cu_3O_7}$ where there are no electrons in the f bands, the usual LDA result [8] with a full L band ($\equiv$ empty $\underline{L}$ band) whose top is ~1 eV below the Fermi level is valid. For $\mathrm{PrBa_2Cu_3O_7}$, the LDA + U calculations yield occupied $f^{\uparrow}_{z(5z^2-3)}$ and $\sqrt{1-\alpha^2_{\mathrm{Pr}}}\, f^{\uparrow}_{z(x^2-y^2)} + \alpha_{\mathrm{Pr}} L^{\uparrow}$ bands ($\alpha \sim 0.2$), and a partly occupied antibonding $\alpha_{\mathrm{Pr}} f^{\uparrow}_{z(x^2-y^2)} - \sqrt{1-\alpha^2_{\mathrm{Pr}}}\, L^{\uparrow}$ band with a cylindrical hole pocket around the SR line $(\pi/a, \pi/b, k_z)$. In $\mathrm{NdBa_2Cu_3O_7}$, the on-site $f^{\uparrow}_{z(x^2-y^2)}$ electron energy is so low that the top of the antibonding $\alpha_{\mathrm{Nd}} f^{\uparrow}_{z(x^2-y^2)} - \sqrt{1-\alpha_{\mathrm{Nd}}}\, L^{\uparrow}$ band ($\alpha_{\mathrm{Nd}} < \alpha_{\mathrm{Pr}}$) has fallen to ~0.3 eV below the Fermi energy. A rela-

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tively small doping with Pr could, however, push the top of this band partially above ϵ_F.

Furthermore we shall present a simple tight-binding model which gives a good semiquantitative description of the relevant electronic states, namely the FR band, its dispersion, Pr and Nd $f_{z(x^2-y^2)}$ states, and their hybridization. With this model, we have made cluster calculations simulating disordered $\mathrm{Pr}_x R_{1-x}\mathrm{Ba_2Cu_3O_7}$ (R = Nd, Y) systems with various x. In the model, the only difference between Pr, Y, and Nd is the position of the $f_{z(x^2-y^2)}$ level, while the hopping amplitudes are assumed the same. The calculated hole-count reduction depends smoothly on x, and for a given x is considerably larger for Nd based system than for the Y based, in complete agreement with the experiment.

For the calculations we have used the full-potential linear muffin tin orbital program, described in Ref. [9]. The newly developed rotationally invariant (RI) [10] LDA + U has been used to account for the Coulomb correlations on the RE site (ordinary LDA fails to describe correctly the f bands and their hybridization with the Cu-O bands, see Ref. [11]). The most important difference from the original LDA + U [7] formalism is that RI LDA + U automatically selects those linear combinations of the orbitals which are occupied and give the minimum of total energy. The correlation part of RI LDA + U functional is expressed in terms of the occupation matrix $n^{\sigma}_{mm'}$ for the different f orbitals of RE atom ($m, m' = 1, \ldots, 7$ and $\sigma = \uparrow, \downarrow$ is the spin index). Effective Coulomb and exchange matrix for f shell were determined from the screened U and J parameters for the RE metals [12], as described in Ref. [13]. The starting configuration in our self-consistent RI LDA + U calculations was such that the occupied states corresponded to complex f harmonics with $m = \pm 2$. In course of the self-consistent procedure, due to the large hybridization with the FR oxygen band, the program converges to the solution where the real $f_{z(x^2-y^2)}$ harmonic is occupied.

We have applied this formalism to $\mathrm{PrBa_2Cu_3O_7}$ and have found, in agreement with the FR assumption, that there are two occupied f states (i.e., Pr has valence +3), one of which is of the $z(x^2 - y^2)$ symmetry. The calculated band structure is shown on Fig. 1 (for the spin-majority channel). By analyzing the character of the states one can locate the FR band, hybridized with the $f_{z(x^2-y^2)}$ band, and partially empty, as shown by the fat line on Fig. 1. Correspondingly, in the spin-minority channel (not shown) there are no occupied f bands, and the FR band lies deep below the Fermi level, just as in $\mathrm{YBa_2Cu_3O_7}$. In Fig. 1 we indicate the position of the spin-minority FR band by the hatched strip. One should keep in mind that the calculated band structure is conventional LDA with respect to the Cu-O bands, so one should not be confused by the fact that it is formally metallic. This is similar to the metallic LDA band structure of $\mathrm{YBa_2Cu_3O_6}$. What is important, is that, similar to $\mathrm{YBa_2Cu_3O_6}$, the LDA hole count in the $pd\sigma$ band is reduced compared to that of $\mathrm{YBa_2Cu_3O_7}$, which indicates the tendency towards a metal-insulator transition.

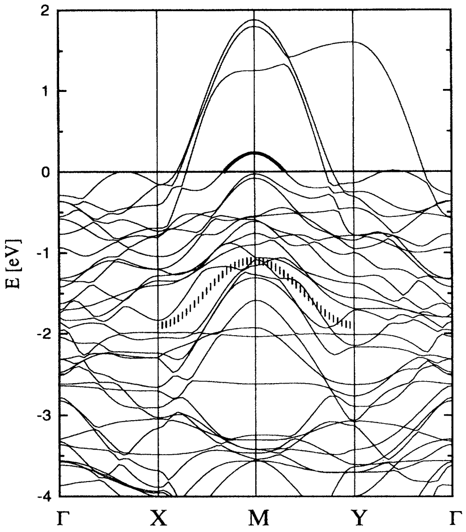

FIG. 1. LDA + U electron band structure of $\mathrm{PrBa_2Cu_3O_7}$ for the majority spin. Fat line shows the depleted part of the FR band. Hatched strip indicates the position of this band in the spin-minority channel (or in $\mathrm{YBa_2Cu_3O_7}$).

Calculated band structure for $\mathrm{NdBa_2Cu_3O_7}$ is very similar to that of $\mathrm{PrBa_2Cu_3O_7}$, but both $f_{z(x^2-y^2)}$ and FR band are shifted down, and the FR band appears fully occupied. Correspondingly, there is no hole depletion and no reason for a metal-insulator transition. It is important to note that the real electronic structure is much richer than the model of Ref. [2]: First, the FR state is very dispersive; it starts (without interaction with the f band) at about -2.7 eV at the Γ point, at the X point it rises to ≈ -1.9 eV, and reaches ≈ -1.1 eV at the S point (in tetragonal notation the M point). Second, this state is *not* the combination of the $p\sigma$ orbitals pointing towards RE (as it would be for an isolated $\mathrm{PrO_8}$ cluster). A simple tight-binding analysis shows that at the zone center the FR state consists of p_z orbitals only, and at the zone corner of $p_{x,y}$ orbitals only.

Now we shall derive a tight-binding model for the bands in question. First, we neglect the, very small, z dispersion. (This means that all orbitals we consider are antisymmetric with respect to $z \rightarrow -z$ reflection.) Then our two-plane problem is equivalent to a one-plane one, as shown below for the five most relevant orbitals:

$$\begin{array}{cccccc} 2\mathrm{O}_b(p_x) & 2\mathrm{O}_a(p_y) & 2\mathrm{O}_b(p_z) & 2\mathrm{O}_a(p_z) & f_{z(x^2-y^2)} & 2\mathrm{Cu}(d_{xy}) \\ p_x & p_y & s_a & s_b & d_{x^2-y^2} & d_{xy}\,. \end{array}$$

Physically, all five orbitals are important. However, we reduce the size of the Hamiltonian by keeping only $p_{x,y}$ and f orbitals. This gives an approximation that is good sufficiently close to the zone corner (where the FR band does not include p_z orbitals by symmetry). We observe from Fig. 1 that this is where the depopulated states are located. On the other hand, this approximation fails to describe the dispersion of the FR band from Γ to $X(Y)$, which is, however, irrelevant for the hole count. Now, we arrive at the standard three-band model for a CuO_2 plane, where the role of the $Cu(d_{x^2-y^2})$ is played by the corresponding f orbital of the RE:

$$H_k = \begin{pmatrix} \epsilon_p & -\tau S_x S_y & t S_x \\ -\tau S_x S_y & \epsilon_p & -t S_y \\ t S_x & -t S_y & \epsilon_f \end{pmatrix}, \qquad (1)$$

where $S_{x,y} = 2\sin(ak_{x,y}/2)$, and the parameters are (Fermi energy is zero): $\epsilon_p = -1.9$ eV, $\epsilon_{\mathrm{Pr}} = -1.9$ eV, $\epsilon_{\mathrm{Nd}} = -4.3$ eV, $\tau = 0.2$ eV, and $t = 0.65$ eV. One should of course remember that these are effective parameters which include, indirectly, other hopping channels. This model agrees well with the LMTO calculations along XM and YM lines.

The most interesting question now is the behavior of the system at intermediate dopings. In principle, a good way to study it would be to make coherent potential approximation calculations for the above model, assuming disorder on the RE site (for Y, ϵ_f is to be taken far away from ϵ_p). We have used a simpler "brute-force" approach by making clusters with the periodic boundary conditions and diagonalizing the Hamiltonian in the real space [14]. Typical densities of states are shown on Fig. 2. The number of states above E_F is the number of holes grabbed by the FR oxygen band. The two lower curves in Fig. 3 show the number of the holes grabbed by the FR band as a function of the Pr concentration in $Pr_xNd_{1-x}Ba_2Cu_3O_7$ and $Pr_xY_{1-x}Ba_2Cu_3O_7$, for the above parameter set. We immediately see the correct trend: In $NdBa_2Cu_3O_7$ doping with Pr reduces the number of holes stronger than in $YBa_2Cu_3O_7$.

Of course, in $YBa_2Cu_3O_7$ it is not as easy as, say, in La_2CuO_4, to estimate the critical hole count n_c for superconductivity to disappear, since the number of holes residing in the chains depends on the oxygen content. Furthermore, when hole count is reduced, the LDA calculations for the Cu-O $pd\sigma$ band become less and less reliable. We overcome this difficulty by using the analogy with $YBa_2Cu_3O_{7-x}$. Namely, we assume that T_c suppression in $YBa_2Cu_3O_{7-x}$ and $Y_{1-y}Pr_yBa_2Cu_3O_7$ is about the same, if the LDA hole count for the $pd\sigma$ band and for given x, y is equal in both cases. So, first, we have looked at the area inside the bonding and antibonding plane bands Fermi surfaces in an LDA calculation for $YBa_2Cu_3O_7$ [8] in the $k_z = 0$ plane, and observed the bonding band is nearly exactly half filled, while the antibonding band has an excess of holes over half filling of ~0.39 holes per two planes. Then we made similar calculations for stoichiometric $YBa_2Cu_3O_{6.5}$ compound and found that the bonding band remains half filled, while the antibonding has ≈0.08 holes less. Thus, we conclude that removing ~0.08 holes per two planes reduces T_c from 90 to 60 K. A similar reduction of T_c due to Pr doping occurs at $x_{\mathrm{Pr}} \sim 0.3$ in the Y based, and at $x_{\mathrm{Pr}} \sim 0.15$ in the Nd based compounds [4]; it is possible, however, that this reduction corresponds to a somewhat smaller holes depletion, because of an additional magnetic pair breaking on the FR states.

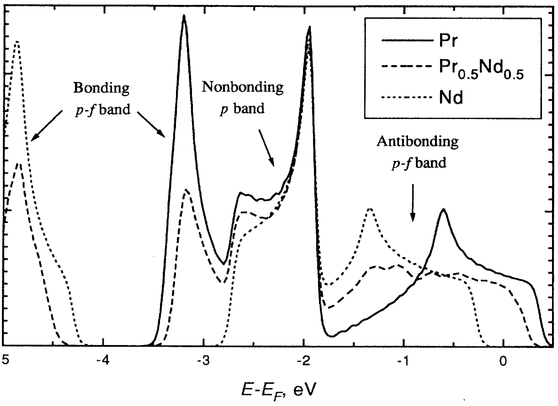

FIG. 2. Density of states in the three-band tight-binding model. Cluster calculations for $Pr_xNd_{1-x}Ba_2Cu_3O_7$ with $x = 0, 0.5, 1$.

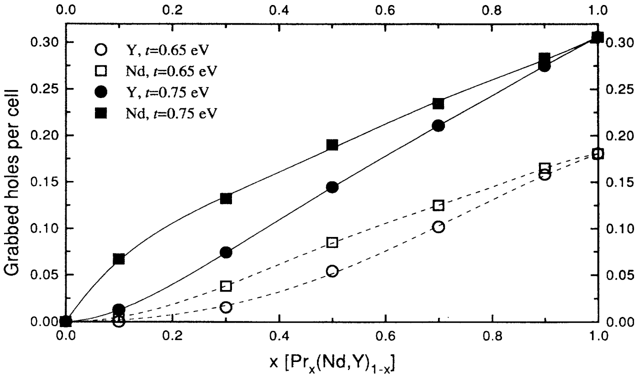

FIG. 3. Number of holes grabbed by the FR $pd\pi$ band in the three-band tight-binding model. Cluster calculations for $Pr_xY_{1-x}Ba_2Cu_3O_7$ and $Pr_xNd_{1-x}Ba_2Cu_3O_7$, for two different values of the R-O hopping amplitude t, and other parameters as in the text. Lines are polynomial fits to guide the eye.

Comparing that with the two lower curves in Fig. 3, we observe that the number of the grabbed holes is underestimated in the calculations. Even for pure $PrBa_2Cu_3O_7$ it is 0.18 holes per two planes only. This is not surprising: First, LDA + U, although a rather good approximation for f electrons, does not account for all strong-correlation effects in the system. Second, we have used U and J for metalic RE, which may differ from those in a compound. Third, the simplified tight-binding model that we used in the cluster calculations had considerable error margin. In view of that, it is important to know how sensitive the model calculations are to the parameters. To find that out, we have repeated the cluster calculations increasing the FR-RE hopping t by 0.1 eV, well within the inaccuracy of the model. The results are also shown in Fig. 3. This brings the result in rather good agreement with the experiment, namely the hole depletion both for $x \sim 0.3$

in the Y based, and for $x \sim 0.15$ in the Nd based compounds, is about 0.07 per two planes.

In the above, we were able to solve the main problem of the hole-depletion scenario, namely the anomalous dependence of the Pr-induced T_c suppression on RE. Nevertheless, some other problems were brought up [1,2]. Of particular importance is the issue of a nonmetallic conductivity of the CuO_2 planes in $PrBa_2Cu_3O_7$. The problem here is that while the $pd\sigma$ band becomes insulating due to hole depletion, the $pd\pi$ should now be conducting. The authors of Ref. [2] conjectured that the corresponding bandwidth is small, "due to the orthogonality of the involved orbitals on shared O sites of neighboring Pr cubes," which combines with a strong coupling to spin degrees of freedom and with a potential disorder. From our calculations we observe that the bandwidth is not really small. We can give an argument, however, in favor of the last part of the conjecture. It is known that $PrBa_2Cu_3O_7$ has substantial disorder (more than 6%) between Pr and Ba [15]. Normally, the CuO_2 plane transport will be hardly affected by this sort of disorder. However, for the FR state, which is a band state, a substitution on a Pr site is a very strong scatterer.

We can make the above arguments more quantitative: The mobility of the electrons is defined by the squared plasma frequency ω_p^2. We have calculated the FR band in $PrBa_2Cu_3O_7$ to be ≈ 5 times smaller than the total ω_p^2 in $YBa_2Cu_3O_7$, which is by far not enough to explain the nonmetallic conductivity, and reflects the fact the FR band is not really narrow. However, the scattering due to the disorder on the Pr site becomes very strong. A rough estimate of the corresponding scattering rate can be gotten as $\gamma_{\text{imp}} \sim 2\pi n_{\text{imp}} N(E_F) \Delta E_k^2/\hbar$, where $\Delta E_k \approx 1.5$ eV is the shift of the FR band at the zone corner due to Pr substitution. We estimate that $\gamma_{\text{imp}} \sim 7 n_{\text{imp}}$ eV. Such a large scattering rate, combined with the relatively small ω_p^2, can easily render the electron localized.

To conclude, we have presented the first LDA + U calculations for $R\text{Ba}_2\text{Cu}_3\text{O}_7$ ($R = \text{Pr}, \text{Nd}$). The results demonstrate that under Pr doping an additional band crosses the Fermi level, grabbing holes from the superconducting $pd\sigma$ band. In case of Nd this band remains completely filled, thus explaining the absence of T_c suppression. We also provide a simple tight-binding model describing the essential features of this band. Using this tight binding model, we have studied the intermediate doping regime and found that in this case the position of the hole-depleting band depends crucially on the host rare earth (more precisely, on the position of its f level). Because of that, Pr doping suppresses T_c more strongly when the host rare earth has smaller atomic number. This provides a natural explanation of the opposite effect of the "chemical" and "physical" pressure on T_c in $R_x\text{Pr}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$, in the sense that by making Pr-O bond shorter by applying a pressure one lowers T_c, while making it shorter by changing the host RE one increases T_c. Last, we have calculated the plasma frequency and estimated the scattering rate for the electrons in the hole-depleting band to show that the reason for their localization is not the small bandwidth, but the strong scattering.

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