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Suppression of superconductivity in $PrBa_2Cu_3O_7$: $4f$ and conduction-band hybridization effect

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In order to understand the suppression of superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_7$ $(0.6 \leq x \leq 1.0)$ and also the electronic properties of the high-T_c superconductors $RBa_2Cu_3O_7$ (R denoting the rare earths except Ce, Pr, Pm, and Tb), we have performed self-consistent, spin-polarized electronic structure and all-electron total-energy calculations for three representative materials: $RBa_2Cu_3O_7$ (R = Y, Pr, and Gd). The salient results are that the band structures of the $RBa_2Cu_3O_7$ compounds are nearly the same as that of $YBa_2Cu_3O_7$ when R ions assume trivalency, and extra electrons donated by the hypothetical tetravalent Pr ions would mainly fill the conduction bands in a rigid-band manner, thereby substantially reducing the important "hole" account. However, the tetravalent Pr compound is shown to be energetically less favorable than the trivalent Pr compound; finally, large spin splittings (up to 75 meV) are found in the conduction bands around the Fermi level in $PrBa_2Cu_3O_7$ when the $4f$ and conduction-band hybridization effects are taken into account. In contrast, such spin splittings are ten to five times smaller in $GdBa_2Cu_3O_7$. This result corroborates that the magnetic pair breaking is responsible for the suppression of superconductivity in the Pr compound.

I. INTRODUCTION

It has been found that substitution of the rare earths La-Lu for Y in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$, with the exception of Ce, Pr, Pm, and Tb, has no significant effect on the superconductivity.[1] For example, $RBa_2Cu_3O_7$ (R denoting Nd, Sm, Gd, Dy, etc.) compounds are also high-temperature superconductors with T_c near 90 K.[1] This was at first surprising as the presence of the magnetic ions would suppress the superconductivity in the ordinary superconductors. However, it now appears from numerous experiments[2] that the essential structural ingredient for the high-T_c superconductivity is the two-dimensional Cu-O_2 planes found in these copper oxides. Band structure calculations[3,4] show that the relevant bands are the highly dispersive planar Cu-O $dp\sigma$ antibonding bands straddling the Fermi level. The electronic properties of these systems, such as electronic transport and superconductivity, seem to be dominated by the carrier concentrations (or electronic hole counts) residing on these Cu-O_2 planes, which are controlled by, e.g., the oxygen vacancy concentration δ.[5] Rare-earth ions in these superconductor oxides show a valence of 3+, i.e., like Y, each contributes three conduction electrons. One thus expects that the electronic band structures of the superconducting compounds $RBa_2Cu_3O_7$ would be similar to that of $YBa_2Cu_3O_7$. The remaining f electrons are presumably localized on the rare-earth ion sites, giving rise to localized magnetic moment behavior.[6] Since the conduction electrons in the Cu-O_2 planes have almost zero density of states at the rare-earth ions sites,[7] the presence of the magnetic moments should have negligible effect on the superconducting property.

$PrBa_2Cu_3O_7$ is isostructural to $YBa_2Cu_3O_7$, while $CeBa_2Cu_3O_7$ and $TbBa_2Cu_3O_7$ could not be synthezied.[8] No investigations on the Pm compound have been reported, presumably because the Pm nucleus is radioactively unstable. However, superconductivity is not detected in $PrBa_2Cu_3O_7$.[9] In the $Pr_xY_{1-x}Ba_2Cu_3O_7$ system, T_c decreases gradually to zero as x is increased up to 0.6 where the system becomes nonsuperconducting[9] and exhibits nonmetallic behavior. Nonsuperconductivity of $PrBa_2Cu_3Cu_7$ has been a puzzle ever since the material was made. Several mechanisms have been proposed to explain the suppression of T_c in $PrBa_2Cu_3O_7$ and $Pr_xY_{1-x}Ba_2Cu_3O_7$ $(0.6 \leq x \leq 1.0)$.

The Pr ion shows either a valence of four, as in praseodymium dioxides, or a valence of three, as in Pr_2F_3.[10] Therefore, it was first proposed that the superconductivity is destroyed by the presence of the tetravalent Pr ions.[9] When Y is replaced by Pr, some of the electronic holes are neutralized by the extra conduction electrons donated by the tetravalent Pr ions, thereby reducing the electronic hole count believed to be crucial for the high-T_c superconductivity.[11] The effective magnetic moment of the Pr ion in $Pr_xY_{1-x}Ba_2Cu_3O_7$ derived from magnetic susceptibility measurements[9] varies between $3.6\mu_B$ for Pr^{3+} and $2.5\mu_B$ for Pr^{4+}. This presumably suggested that some Pr ions are tetravalent or the Pr ion in $Pr_xY_{1-x}Ba_2Cu_3O_7$ has a mixed valence.[9] Evidence for the presence of the tetravalent Pr ions from electronic transport experiments was also reported.[12] However, several x-ray adsorption spectroscopy measurements[13] show that Pr is essentially trivalent in the $Pr_xY_{1-x}Ba_2Cu_3O_7$ compounds, thereby disputing the plausible "tetravalency" mechanism for the depression of T_c. Therefore, Neukirch *et al.* instead[13] speculated that T_c is suppressed through changes in the band structure when Y is substituted by Pr in $RBa_2Cu_3O_7$. That the Pr ion is trivalent in

$Pr_xY_{1-x}Ba_2Cu_3O_7$ was also concluded from recent photoelectron spectroscopy measurements.[14]

Apart from the "tetravalency" and the band-structure change mechanisms already mentioned, a few other possible mechanisms have also been suggested on the basis of the different properties observed between $Pr_xY_{1-x}Ba_2Cu_3O_7$ and $YBa_2Cu_3O_7$.[13,15] These include the suggestion that a stronger hybridization between Pr $4f$ states and conduction bands is responsible for the destruction of the superconductivity in $Pr_xY_{1-x}Ba_2Cu_3O_7$ ($x > 0.6$).[15] For more information about experimental works on these compounds, see Maple *et al.*[16] and references therein.

In this work, we performed self-consistent electronic band-structure calculations for three representative rare-earth compounds $RBa_2Cu_3O_7$. We want to see how the electronic band-structure changes as Y is replaced by the rare-earth elements and what effects the $4f$ electron spin moments have on the conduction bands. We also want to compare the electronic band structure of the $Pr^{4+}Ba_2Cu_3O_7$ with that of the $Pr^{3+}Ba_2Cu_3O_7$ and other trivalent compounds. Furthermore, we studied the energetics of the tetravalent Pr ion system versus the trivalent Pr ion system by performing all-electron total-energy calculations. Finally, we consider the effects of $4f$ and conduction-band hybridization.

II. METHOD

The crystalline structure of $YBa_2Cu_3O_7$ is shown in Fig. 1. The structure is orthorhombic and its symmetry is described by space group *Pmmm* (or D_{2h}^1).[17] It may be regarded as derived from the ideal perovskite $YBa_2Cu_3O_9$ by the presence of ordered vacancies in two oxygen sublattices, as indicated by $V(1)$ and $V(2)$ in Fig. 1. The important features include two corner-linking Cu-O pyramids planes and one Cu-O ribbon (or chain) running about the y axis. If the chain O randomly occupies either the chain O(1) sublattice or the V(1) sublattice, the system becomes tetragonal.

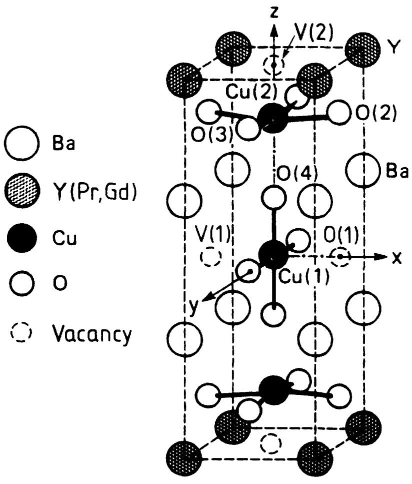

FIG. 1. Crystal structure of $YBa_2Cu_3O_7$.

Self-consistent band structures were calculated using the linear muffin-tin orbitals method (LMTO) with the atomic sphere approximation (ASA).[18] The calculations are based on the density functional theory with the usual local-density approximation (DFT-LDA).[19] The LMTO-ASA method has been used to study several high-T_c superconductors and related oxides and is found to give similar band structures to those obtained using more elaborate methods such as the full-potential linear augmented plane-wave method (LAPW).[3,4] We will avoid a lengthy description of the method, since the details may be found in previous publications.[18,4]

In these calculations, all electrons are separated into either "core" electrons or "band" electrons. The core-electron charge densities were calculated by solving the relativistic one electron Dirac equation in every self-consistent iteration while the band electrons were treated semirelativistically (i.e., all relativistic effects except spin-orbit coupling). The trivalent Pr (Gd) ions were considered as each having two (seven) localized $4f$ electrons that were then treated as core electrons, and three band electrons. Similarly, the tetravalent Pr (Gd) ions have only one (six) localized $4f$ electron and four band electrons.

In these calculations, the lattice constants and atomic position parameters for $YBa_2Cu_3O_7$, $PrBa_2Cu_3O_7$, and $GdBa_2Cu_3O_7$ are taken from Refs. 17, 20, and 21, respectively. In the case of $GdBa_2Cu_3O_7$, atomic position parameters for $NdBa_2Cu_3O_7$ (Ref. 22) are used, since we are not aware of any experimental data for the structural parameter for $GdBa_2Cu_3O_7$. In any case, the structural parameters for $RBa_2Cu_3O_7$ are nearly equal, and therefore these substitutions should not produce any significant changes in the band structure of $GdBa_2Cu_3O_7$. The basis functions for Ba and rare-earth atoms are $s,p,d,5f$, LMTO's, and s,p,d on the Cu, O, and "empty spheres" sites. When Pr (Gd) $4f$ electrons were treated as band states (see Sec. V), the basis function for Pr (Gd) consisted of $s,p,d,4f$ LMTO's. The atomic radii used are, in atomic units, 2.5 for Cu, 2.1 for O and "empty" spheres, 3.85 for Ba, 3.479 for Y, 3.662 for Pr, and 3.638 for Gd. 75 k points within the irreducible wedge ($\frac{1}{8}$) of the Brillouin zone (IWBZ) were included in the self-consistent calculations, while 324 k points inside the IWBZ were used in the final density-of-states calculations.

III. ELECTRONIC BAND STRUCTURE

We first calculated self-consistent band structures for $YBa_2Cu_3O_7$, $PrBa_2Cu_3O_7$, and $GdBa_2Cu_3O_7$. In the case of $PrBa_2Cu_3O_7$, the calculations were carried out for both trivalent and tetravalent Pr ions, as defined in the preceding section. These results are now presented in the following.

A. $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$

In Fig. 2, we compare the energy bands of $GdBa_2Cu_3O_7$ with $YBa_2Cu_3O_7$ along the high-symmetry lines in the orthorhombic Brillouin zone (BZ). Since the

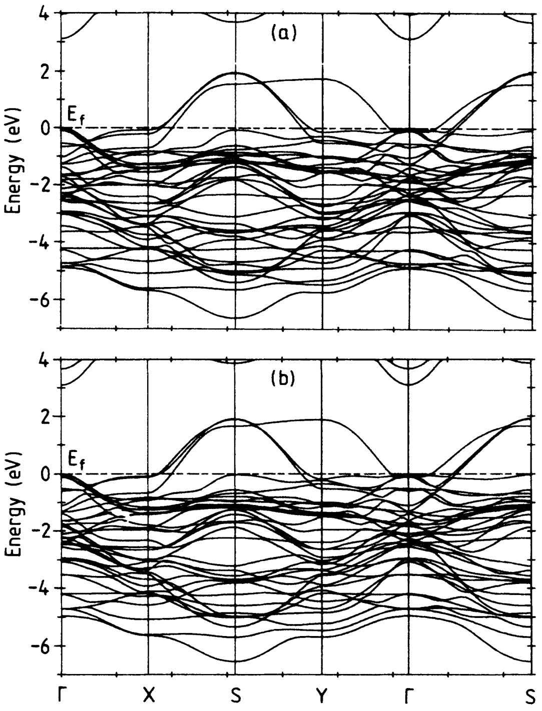

FIG. 2. Band structures (a) $YBa_2Cu_3O_7$ and (b) $GdBa_2Cu_3O_7$.

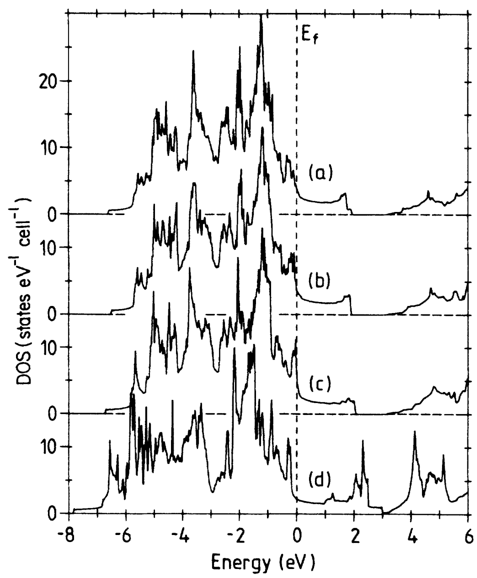

FIG. 3. Total density of states (TDOS) for (a) $YBa_2Cu_3O_7$, (b) $GdBa_2Cu_3O_7$, (c) $Pr^{3+}Ba_2Cu_3O_7$, and (d) $Pr^{4+}Ba_2Cu_3O_7$.

features of the band structure of $YBa_2Cu_3O_7$ have been described in detail elsewhere,[3,4] we shall avoid repetitions. We merely point out that the band structures (Fig. 2) are almost the same. This is expected because, as found in previous band-structure calculations,[3,4] the important valence bands are Cu and O dominant bands that should not be affected by the substitution of Y with the trivalent rare earth. Furthermore, the Fermi level (E_F) remains almost unchanged, since both Y and Gd contribute three conduction electrons. The density-of-states (DOS) functions for these compounds are plotted in Fig. 3. Again, they are nearly identical. These results, confirming the previous speculation that $R^{3+}Ba_2Cu_3O_7$ have a similar band structure, are consistent with the observed similarities in electronic properties, superconductivity in particular, of the superconductor oxides. The total DOS (TDOS) and site-decomposed DOS at E_F for these two compounds are tabulated in Table I for comparison. One sees from Table I that the values for both the TDOS and its decompositions are very close. The TDOS at E_F for $YBa_2Cu_3O_7$ is 3.974 states/eV per cell, larger than our previous result of 3.14 states/eV per cell.[4] This is mainly because these calculations were performed for the real orthorhombic structure instead of the approximate tetragonal one in the previous calculations.[4]

B. $PrBa_2Cu_3O_7$

The band structure for $Pr^{3+}Ba_2Cu_3O_7$ is shown in Fig. 4, together with that of $Pr^{4+}Ba_2Cu_3O_7$. The corresponding TDOS functions are plotted in Fig. 3. We note that the band structure of $Pr^{3+}Ba_2Cu_3O_7$ is very similar to that of $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ (Fig. 2). However, there are discernible differences in band structure between $Pr^{4+}Ba_2Cu_3O_7$ and $YBa_2Cu_3O_7$ (or $Pr^{3+}Ba_2Cu_3O_7$ or $GdBa_2Cu_3O_7$). Firstly, because of one additional conduction electron in the former, the E_F moves up towards the top of two planar Cu-O bands (at the S point in the BZ), in agreement with the rigid-band model. Nevertheless, the E_F shift of 0.51 eV is larger than 0.33 eV predict-

TABLE I. Total and site-decomposed density of states at the Fermi level for (a) $YBa_2Cu_3O_7$, (b) $GdBa_2Cu_3O_7$, (c) $Pr^{3+}Ba_2Cu_3O_7$, and (d) $Pr^{4+}Ba_2Cu_3O_y$ (in units of states/eV per cell). R denotes Y, Gd, or Pr (see Fig. 1 for other symbols).

	Total	Cu(2)	O(2)+O(3)	Cu(1)	O(1)	O(4)	V(1)	Ba	R
(a)	3.974	1.703	0.773	0.438	0.197	0.656	0.013	0.151	0.044
(b)	3.667	1.620	0.719	0.404	0.223	0.532	0.013	0.112	0.043
(c)	6.055	1.486	0.668	0.674	0.939	1.806	0.015	0.422	0.047
(d)	2.208	1.087	0.400	0.209	0.309	0.133	0.206	0.040	0.024

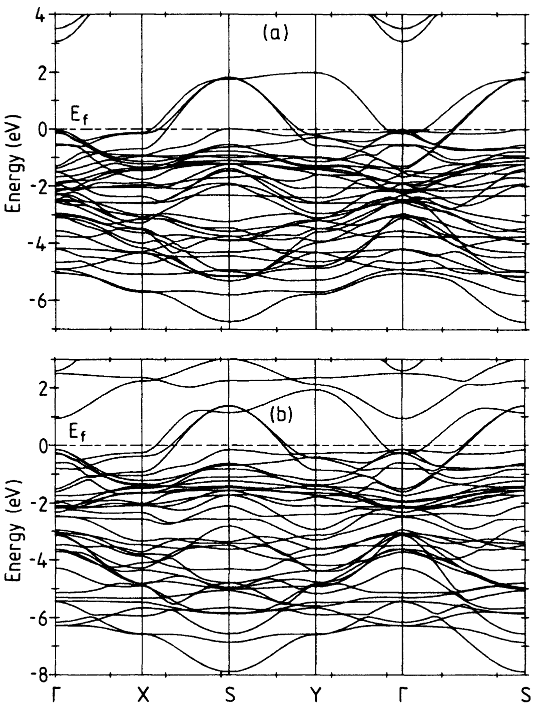

FIG. 4. Comparison of the band structure of (a) $Pr^{3+}Ba_2Cu_3O_7$ with that of (b) $Pr^{4+}Ba_2Cu_3O_7$ (see the text).

ed by the rigid-band model. Secondly, two additional conduction bands of Pr 5*d* character appear just above the Cu-O *dpσ* conduction bands. In $PrBa_2Cu_3O_7$, when one Pr 4*f* electron is promoted to the conduction bands (i.e., Pr transits from Pr^{3+} to Pr^{4+}) the orbital energy levels on the Pr site are significantly lowered. For example, the center of the Pr 5*d* band moves down by about 4.2 eV, and thus we have these two low-lying Pr 5*d* dominant bands. For the Pr core levels, the *s,p,d* states of the first, second, third, and fourth shells move down by about 11.0–13.0 eV. These changes in band structure and in the Pr ion core levels, if they can be monitored by experiments, will help to determine the valence of the Pr ion in $PrBa_2Cu_3O_7$. Thirdly, the shape and position of the chain Cu-O *dp* band also change (Fig. 4). For comparison, the TDOS and site-decomposed DOS at E_F for the Pr compounds are listed in Table I.

One also notes that the TDOS at E_F for $Pr^{3+}Ba_2Cu_3O_7$ is much larger than for $YBa_2Cu_3O_7$ (or $GdBa_2Cu_3O_7$) (Table I). In $Pr^{3+}Ba_2Cu_3O_7$, there are four bands crossing the E_F (Fig. 4) rather than three in $YBa_2Cu_3O_7$ (Fig. 2). The E_F just cuts the flat edge of this fourth band, resulting in a much larger TDOS at E_F. However, raising the E_F by only 2 mRy will reduce the TDOS at E_F to that of $YBa_2Cu_3O_7$. In fact, four bands were also found crossing the E_F in $YBa_2Cu_3O_7$ in the full-potential LAPW calculations.[3] Therefore, this small difference in the TDOS at E_F between $PrBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$ is regarded as insignificant for the electronic properties, in particular, superconductivity.

IV. VALENCY OF THE Pr ION IN $PrBa_2Cu_3O_7$

Given the electronic "hole count" is crucial to the high-T_c superconductivity in $RBa_2Cu_3O_7$, our results for $PrBa_2Cu_3O_7$ presented in the preceding section suggest that the superconductivity would be quenched by substitution of Y with a sufficient amount of Pr^{4+}. Does Pr indeed exist in $PrBa_2Cu_3O_7$ as a tetravalent ion or, just like Gd or Nd, as a trivalent ion? In Sec. III, we found some distinct differences in electronic structure (band structure and core-level binding energy) between $Pr^{3+}Ba_2Cu_3O_7$ and $Pr^{4+}Ba_2Cu_3O_7$. Comparing these results with experiments will help to determine the valence of the Pr ions. Here, however, we want to present the results of our total electronic energy calculations.

All-electron total-energy calculations, based on the DFT-LDA,[19] were carried for $PrBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ and for both trivalent and tetravalent Pr (Gd) ions. In the nonmagnetic case, the results are −61 976.3548 Ry (−66 050.0009 Ry) for $Pr^{3+}Ba_2Cu_3O_7$ ($Gd^{3+}Ba_2Cu_3O_7$), and −61 976.1832 Ry (−66 049.5816 Ry) for $Pr^{4+}Ba_2Cu_3O_7$ ($Gd^{4+}Ba_2Cu_3O_7$). The total-energy difference between the trivalent and tetravalent Pr (Gd) compounds is 2.33 eV (5.70 eV), and the trivalent compounds are energetically more favorable. Including the Pr (Gd) 4*f* core spin polarization enhances this total-energy difference and is estimated to increase to 2.66 (7.59) eV for the Pr (Gd) compound (see Sec. V). Including the spin-orbit terms in the band Hamiltonian[18] changes the total-energy difference between $Pr^{3+}Ba_2Cu_3O_7$ and $Pr^{4+}Ba_2Cu_3O_7$ only slightly, increasing it from 2.33 to 2.39 eV. This spin-orbit correction is expected to be rather insensitive to the number of 4*f* electrons, and thus a similar correction should be applicable to the energy difference between $Gd^{3+}Ba_2Cu_3O_7$ and $Gd^{4+}Ba_2Cu_3O_7$. We therefore conclude that the energy barrier for the transition from the Pr^{3+} to Pr^{4+} is large and is unlikely to be overcome by, e.g., heating the samples up to several hundreds of degrees Kelvin. In other words, the Pr exists as Pr^{3+} in $PrBa_2Cu_3O_7$ under the ambient conditions.

In fact, the calculated total-energy differences discussed previously are equal to the excitation energies of the "screened" transition[23] from the localized $R4f^n$ to $R4f^{n-1}E_F$ in $RBa_2Cu_3O_7$. Therefore, the reliability of our calculations can be checked by comparing these results with the 4*f* electron binding energies measured by, e.g., photoemission experiments. The measured Gd 4*f* binding energy in $GdBa_2Cu_3O_7$ is 7.4 eV,[24] in good agreement with the calculated value of 7.59 eV. For $PrBa_2Cu_3O_7$, however, such a comparison is less straightforward because of the strong hybridization between Pr 4*f* states and conduction bands (see Sec. V). The peak position of the extracted Pr 4*f* spectra from the photoemission experiment on $Pr_xY_{1-x}Ba_2Cu_3O_7$ (Ref. 14) is about 1.2 eV below E_F. Thus, there is a large difference of about 1.4 eV between the calculated value of 2.66 eV and the observed Pr 4*f* peak position.

V. 4*f* AND CONDUCTION-BAND HYBRIDIZATION

To continue our search for the key differences between $PrBa_2Cu_3O_7$ and other $RBa_2Cu_3O_7$ compounds that may be responsible for the suppression of the superconductivity in the former, we performed self-consistent, spin-polarized band-structure calculations with 4*f* treated as band states. The aim was to study the effects of the hybridization between 4*f* and conduction electrons.

We find that while the induced spin moments within Cu, O, and Ba spheres in $GdBa_2Cu_3O_7$ are zero (within $0.01\mu_B$/atom), the induced spin moments within the planar Cu and O spheres in $PrBa_2Cu_3O_7$ are significant. For example, the sum of the spin moments in these planar Cu and O spheres is $0.25\mu_B$ in $PrBa_2Cu_3O_7$, but practically zero ($0.02\mu_B$) in $GdBa_2Cu_3O_7$. Furthermore, the spin moments on these planar Cu and O sites are antiparallel to that of the Pr ion, indicating the coupling is antiferromagnetic. The spin moment within the Pr atomic sphere is $1.77\mu_B$ and is substantially less than $2.0\mu_B$ for two localized 4*f* electrons. In contrast, the spin moment within the Gd sphere is 6.97, which is close to $7.0\mu_B$ for seven localized 4*f* electrons.

The interaction between 4*f* and conduction electrons can lift the spin degeneracy, can open up gaps other than spin degeneracy, and can also change the shape and position of the conduction bands. Phenomena associated with the latter two include metal-to-semiconductor transitions and a large enhancement of the conduction-electron effective masses. Because of the strong correlation among 4*f* electrons, quasiparticle energy bands associated with 4*f* electrons are often poorly described by the DFT-LDA eigenvalues; so are the latter two effects. Nevertheless, in this paper, we are mainly interested in the conduction bands and their spin splittings. In order to examine the band effects of Pr (Gd) 4*f* states on the conduction (*s*,*p*,*d*) bands we projected the 4*f* states out of the Hamiltonian. This is easily accomplished in the LMTO-ASA method as follows. First, we performed a self-consistent calculation with the *s*, *p*, *d*, and 4*f* states included in the band Hamiltonian, as has been presented. Second, we used this self-consistent potential to calculate the bands in a basis of the *s*,*p*,*d* radial wave functions augmented by the 5*f* radial wave function. The role of the 5*f* radial wave function is to give the conduction states on a particular site the freedom to be reexpanded into wave functions of *f* character centered on a different site. In a word, we calculated spin-polarized energy bands with 4*f* on the Pr (Gd) site replaced by 5*f*, and using the spin-polarized self-consistent potentials. The resultant band structures should approximately describe the conduction-band spin splittings due to Pr (Gd) 4*f* and conduction-band hybridizations. The results for $PrBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ are shown in Fig. 5.

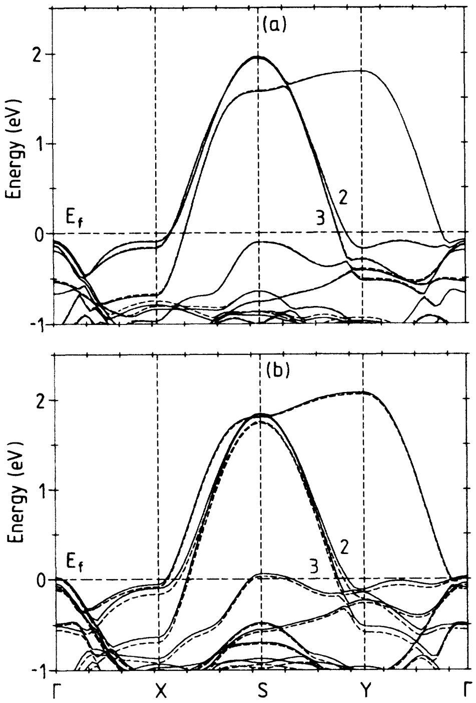

FIG. 5. Spin-split energy bands for (a) $GdBa_2Cu_3O_7$ and (b) $PrBa_2Cu_3O_7$ (see the text). Solid lines are for the majority spin, and the dashed lines are for the minority spin.

One immediately sees that the spin splittings near E_F in $PrBa_2Cu_3O_7$ are far bigger than those in $GdBa_2Cu_3O_7$. In fact the splittings of the former are about ten to five times larger than in the latter. For example, for the planar Cu-O $dp\sigma$ conduction bands, marked as 2 and 3 along the *S*-*Y* symmetry line in Fig. 5, the splittings near E_F are, respectively, 73 and 69 meV for the Pr compound, but only 5 and 13 meV for the Gd compound. Interestingly, the majority spin bands shift upwards while the minority spin bands shift downwards in $PrBa_2Cu_3O_7$ [Fig. 5(b)]. This, as pointed out before, results from the antiferromagnetic coupling between Pr 4*f* and conduction bands.

We now examine whether the large spin splittings of the conduction bands in $PrBa_2Cu_3O_7$ result predominantly from a stronger hybridization between Pr 4*f* and conduction bands. To this end, we have performed all-electron, self-consistent calculations with Pr (Gd) 4*f* electrons treated as "core states" and spin polarized. Two Pr 4*f* (seven Gd 4*f*) electrons were put in the majority spin channel and no 4*f* electrons in the minority spin channel, in accordance with the Hund's rule. The resultant total energies have already been used in the preceding section to estimate the enhancement of the 4*f* binding energy due to Pr (Gd) core spin polarization.

We found the changes in the band structure due to the spin-polarized 4*f* cores are negligible in both $PrBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$. The spin splittings of conductions bands near E_F, for instance, are smaller than 1 m Ry d. Furthermore, the induced spin moments within Cu, O, and Ba spheres for $PrBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ are practically zero. Note that Gd ions have a largest spin moment among the rare earths in $RBa_2Cu_3O_7$. Therefore we expect that in general the effects on the conduction bands due to the localized 4*f* moments of rare-earth ions in $RBa_2Cu_3O_7$ are negligible. It is worthwhile to point out that when Gd $4f$ states were treated band states, the spin splittings of the conduction bands near E_F in $GdBa_2Cu_3O_7$ were equally small. This indicates that in contrast to Pr $4f$, Gd $4f$ does not hybridize with the conduction bands.

Despite their negligible effects on the band structure, $4f$ spin moments substantially split core levels. For example, the splittings for Gd $4s$ and $4p$ are as large as 5.8 eV and for Pr^{3+} $4s$ and $4p$, about 1.5 eV. Such core-level spin splittings for the Pr^{4+} ions are, however, only about half as large as those of the Pr^{3+} ions.

VI. DISCUSSION AND SUMMARY

It is currently of great interest to find out the mechanism of the suppression of superconductivity in $YBa_2Cu_3O_7$ due to substitution of Pr for Y. This will also help to understand the high-T_c superconductivity in $RBa_2Cu_3O_7$ (R denotes the rare earths except Ce, Pr, Pm, and Tb). As mentioned in Sec. I, one possibility first suggested[9] is that the Pr exists as Pr^{4+} or a large proportion of it does. The extra electron (as opposed to Pr^{3+}) then compensates the hole carriers in the planar Cu-O $dp\sigma$ conduction bands. When the hole carrier concentration is reduced, superconductivity is destroyed in a manner analogous to what happens as oxygen is removed from $YBa_2Cu_3O_7$.[11]

However, our calculations predict that the Pr^{3+} system is energetically more favorable than the Pr^{4+} system. This is in good agreement with many recent electron spectroscopy experiments[13,14] which show that the Pr ion is close to Pr^{3+} in $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($0 \leq x \leq 1$). Furthermore, our calculations also predict that if the Pr ion in $Pr_xY_{1-x}Ba_2Cu_3O_7$ had a mixed Pr^{3+} and Pr^{4+} state, as proposed early on based on the magnetic susceptibility measurements, all core levels would be splitted by about 12.0 eV. Such splittings are not evident in, e.g., photoemission and x-ray absorption measurements.[13,14] We therefore argue that the tetravalency mechanism is highly unlikely. As for the apparently contradictory implications of the magnetic susceptibility measurements suggesting a Pr^{4+} or a mixed valence of Pr, and the electron spectroscopy experiments suggesting a Pr^{3+}, Sec. V has already offered a solution, i.e., the magnetic moment is substantially reduced from that of the Pr^{3+} due to the hybridization between Pr $4f$ state and conduction bands.

The second possibility, suggested by Neukirch *et al.*,[13] namely that the superconductivity is quenched due to a different band structure of $PrBa_2Cu_3O_7$, is not likely either, because our results (see Sec. III) show that there are no significant differences in the band structure between $Pr^{3+}Ba_2Cu_3O_7$ and the superconducting $RBa_2Cu_3O_7$ compounds.

The distinct difference between $PrBa_2Cu_3O_7$ and the superconducting $RBa_2Cu_3O_7$ compounds emerging from this work is that the hybridization between $4f$ states and conduction bands is much stronger in $PrBa_2Cu_3O_7$ than in other $RBa_2Cu_3O_7$ compounds. Consequently, the spin splittings of the important Cu-O conduction bands near E_F in the Pr compound are up to ten times larger than, e.g., those in the Gd compound. Many experiments, such as tunneling and infrared spectroscopy, have been carried out to measure the superconducting gap Δ in $RBa_2Cu_3O_7$.[25,26] The energy gap Δ is about 18 meV,[26] although the reported value varies.[25] The calculated sizes of the conduction-band spin splittings in $PrBa_2Cu_3O_7$ are comparable to the Cooper pair binding energy (2Δ). This result therefore indicates that the Cooper pairs, or the supercurrent carriers, in the superconducting $YBa_2Cu_3O_7$ are broken up when Y is replaced by Pr, and consequently the superconductivity is suppressed.

Evidence for a strong hybridization between $4f$ and conduction bands in $Y_{1-x}Pr_xBa_2Cu_3O_7$ has been found in previous experiments including high-pressure transport[15] and photoemission spectroscopy,[14] and critical magnetic field measurements.[27] Thus, the magnetic pair breaking due to the strong coupling between Pr $4f$ and conduction electrons as the origin of the suppression of superconductivity in $PrBa_2Cu_3O_7$ has been proposed.[27] Our calculations corroborate this suggestion.

To summarize, we have performed all-electron, self-consistent and spin-polarized electronic structure calculations for three representative members of the high-T_c superconductor and related oxide family, $RBa_2Cu_3O_7$ (R denoting the rare earths). In light of these calculations, we have examined plausible mechanisms proposed for the suppression of superconductivity in $Pr_xY_{1-x}Ba_2Cu_3O_7$. We conclude that the suppression of superconductivity in the Pr compounds is due to the magnetic pair breaking caused by the hybridization between Pr $4f$ states and conduction bands.

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