

ELECTRONIC STRUCTURE OF THE QUENCHED SUPER- CONDUCTIVITY MATERIALS $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ *

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Summary

The superconductivity of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is quenched as x increases. It has been speculated that praseodymium has a valence of $4+$, which results in extra charge in the Cu-O planes, and causes quenching of T_c . To study the electronic state of praseodymium, the valence band resonant photoemission of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system was measured for $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 . It was found that the praseodymium valence is close to $3+$ for all x values and that the extracted Pr 4f spectral weight has a complex line shape. This line shape implies extensive Pr 4f-O 2p/Cu 3d hybridization which probably causes the quenching of T_c by disrupting the electronic or magnetic structure of the $x = 0$ material, perhaps via Pr-Cu and Pr-O superexchange interactions.

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1. Introduction

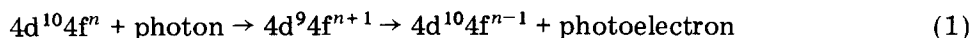
A clue to the origin of the high temperature superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ may lie in the interesting finding that the superconductivity of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ is quenched with increasing x [1 - 3]. Except for lanthanum, with a transition temperature T_c of approximately 70 - 80 K, and terbium and cerium for which the compounds do not exist [4], superconductivity with a T_c value close to 90 K has been found in $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [5 - 9]. From the magnetic susceptibility measurements an effective magnetic moment of $2.7 \mu\text{B}$ per praseodymium ion was extracted, independent of x [1], which suggests that the valence of praseodymium has a fixed value of about 3.8. It can be speculated that if praseodymium has a valence of 4+, there will be extra charge in the Cu-O planes, which may cause the quenching of T_c by filling the holes in the Cu-O planes. In contrast, the lattice constants [9] of the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ series strongly suggest that praseodymium is trivalent. In fact, the valence of praseodymium was concluded to be close to 3+ from X-ray absorption (XAS) measurements [10, 11], although it was proposed that the quenching of T_c was due to charge transfer, arising from a modest deviation of valence from 3+ towards 4+.

Thus it is important to discover whether the praseodymium ion in the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ alloy system is mixed valent or not. The discrepancy in the praseodymium valence obtained from different experiments stimulated us to investigate if there are systematic changes in the Pr 4f electronic states and in the O 2p and Cu 3d states as a function of x . Electron spectroscopy was used, which is one of the most powerful and direct measurements of the electronic structure of materials.

In this paper we focus on the praseodymium electronic state. This was studied by measuring the valence band resonant photoemission (RESPES) or $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ near the Pr 4d absorption edge (for $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0). Photoelectron energy distribution curves and two yield spectra (the constant-initial-state (CIS) spectrum and the constant-final-state (CFS) spectrum, described below) were measured. In agreement with XAS, the praseodymium valence is close to 3+ for all x values. In addition, the extracted Pr 4f spectral weight is very broad and asymmetric, implying extensive hybridization between Pr 4f and other valence band states. The hybridization probably causes the quenching of T_c by disrupting the electronic or magnetic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This mechanism would apply particularly to the rare earths praseodymium, cerium and terbium, which have small 3+ ionization energies degenerate with the other valence band states.

The RESPES technique was used for this material to enhance the 4f emission [12] relative to that from filled copper and oxygen states, which would otherwise dominate the valence band spectrum because of differences in cross-section [13] and because many more electrons contribute. The resonance in the total 4f cross-section arises from the transition of a 4d

electron into the 4f shell, which produces intermediate excited states, followed by an Auger decay such as



The quantum interference between this and the direct photo-ionization channels gives rise to a Fano-type lineshape [14] in the total 4f cross-section with a minimum near the 4d absorption edge followed by a subsequent maximum. These resonance line shapes can be observed in CIS and CFS yield spectra. CIS spectra are taken by sweeping the photon energy $h\nu$ and the kinetic energy E_k of the electron analyzer simultaneously, so as to maintain a fixed $E_i = E_k + \phi - h\nu$, where ϕ is the work function of the analyzer. This technique therefore measures the $h\nu$ dependence of the cross-section of a fixed binding-energy photoelectron peak. CFS spectra are obtained by fixing E_k at a small value (which was set at $E_k = 5$ eV) and varying the photon energy $h\nu$. The CFS spectrum collects primarily inelastically scattered electrons coming from deep within the bulk ($E_k = h\nu + E_i - E_{\text{loss}} - \phi$, where E_{loss} is the energy lost due to inelastic scattering) and hence is generally thought to be proportional to the bulk photoabsorption spectrum.

Mixed valence generally results in valence band emissions associated with more than one valence state. As discussed elsewhere [12, 15], the resulting spectrum depends greatly on the strength of the 4f-band hybridization and the shape of the band density of states (DOS), especially whether the DOS is metallic or has a gap around the Fermi level E_F . For the compounds discussed here, it is not yet clear how to model the DOS. In any case RESPES can provide a method to separate emissions from different valence states [16, 17], because the intermediate state of the resonance is different for the different valence states, and so their photon-energy dependences, *i.e.* the CIS spectra, are not the same. CFS spectra for the mixed valent material typically show absorption features due to two different valence states. However, it is important to note that with strong hybridization, the relative weights of spectral features from different valence states, in the valence band CIS or CFS spectra, may not accurately reflect the valence. Therefore quantitative conclusions require detailed theoretical analysis.

2. Experimental details

The samples were prepared as described in ref. 1 by mixing stoichiometric amounts of the oxide powders Pr_6O_{11} , Y_2O_3 , BaCO_3 and CuO . The powders were sintered three times at 900 °C for several hours in air. The samples were then annealed at 950 °C in flowing oxygen for about 40 h and were then slowly cooled to room temperature in about 30 h. X-ray diffraction shows that the alloys $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ form in a single phase with the same orthorhombic perovskite crystal structure as for $x = 0$, but that the degree of the orthorhombic distortion relative to the corresponding tetra-

gonal structure is noticeably diminished [1] on substitution of praseodymium. With increasing x from $x = 0$, the normal state electrical resistivity shows a transition from metallic to semiconducting behavior, and a monotonic suppression of T_c which reaches zero at $x \approx 0.6$. BaCuO_2 in amounts of less than 8 mol.% is observed in the X-ray data for $x = 0, 0.2$ and 0.4 . Since it does not involve praseodymium, this impurity does not affect the results reported here.

Room temperature resonant photoemission measurements were performed at the Stanford Synchrotron Radiation Laboratory using photons obtained from the grasshopper monochromator on beam line III-1 and a commercial double-pass cylindrical mirror analyzer (CMA) to analyze the kinetic energies of the emitted electrons. The measured surfaces were obtained by cleaving the samples *in situ* in a vacuum chamber having a base pressure of 7×10^{-11} Torr. The experimental resolution, determined mostly by the CMA, is 0.5 eV unless otherwise indicated. The Fermi level of the system was determined from the valence band spectrum of a gold sample evaporated onto a stainless steel substrate *in situ*. The photon flux was monitored by the yield from a stainless steel target and the spectra reported below are all normalized to this yield.

3. Results

Figure 1 shows normalized valence band spectra for $x = 1.0$ at several photon energies near the Pr $4d \rightarrow 4f$ absorption edge. Inelastic backgrounds were removed from the spectra by a standard method [12]. Although the overall shape for $x = 1.0$ is very similar to that for $x = 0$ in the literature [18 - 23], there are new features due to the resonating behavior of the Pr $4f$ states. The Pr $4f$ emission between E_F and -6 eV shows a Fano minimum at $h\nu = 115$ eV and a Fano maximum at $h\nu = 124$ eV. The resonating Pr $5p$ emission can also be seen at around -20 eV, under which lies a rather broad bump with the character of Y $4p$ and O $2s$ states. The main band with a peak at about -5 eV is due to emission from the Cu $3d$ /O $2p$ states and the -9 eV feature present in all the spectra is not well understood as yet, but may not be intrinsic. The -2.5 eV shoulder, which is also not understood in detail but certainly involves oxygen states, can be seen clearly in the off-resonance spectrum with $h\nu = 115$ eV. This shoulder increases with x relative to the main peak. The -12 eV Cu d^8 satellite peak [22] is hard to distinguish for these photon energies because of the large emissions from the Ba $5p$ states at -13 eV and -16 eV. The emissions from the Ba $5p$ states decrease as the photon energy increases from 115 eV because the cross-section has a Fano resonance at $h\nu = 108$ eV due to Ba $4d \rightarrow 4f$ absorption. Similarly, the emission at around -29 eV from the Ba $5s$ state also decreases.

Figure 2 compares the Pr $4f$ spectra extracted from RESPES for $x = 0.2, 0.4, 0.6, 0.8$ and 1.0 . The spectra are scaled to have the same magnitude

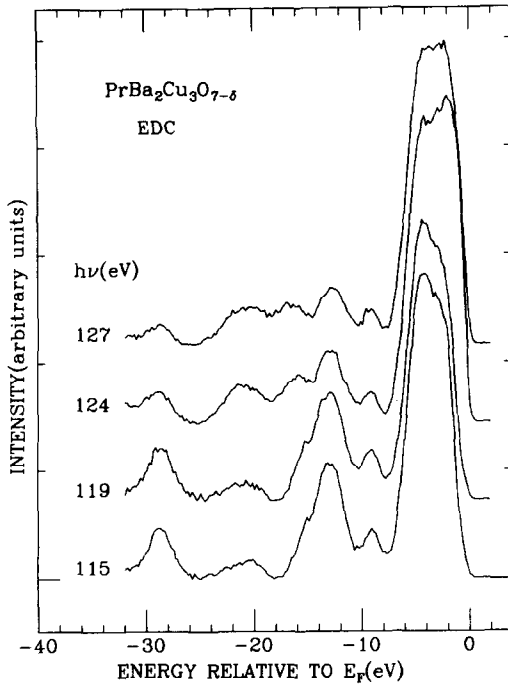


Fig. 1. Normalized valence band spectrum for $x = 1.0$ near the Pr $4d \rightarrow 4f$ absorption edge. The Pr $4f$ emission shows a resonant behavior between E_F and -6 eV.

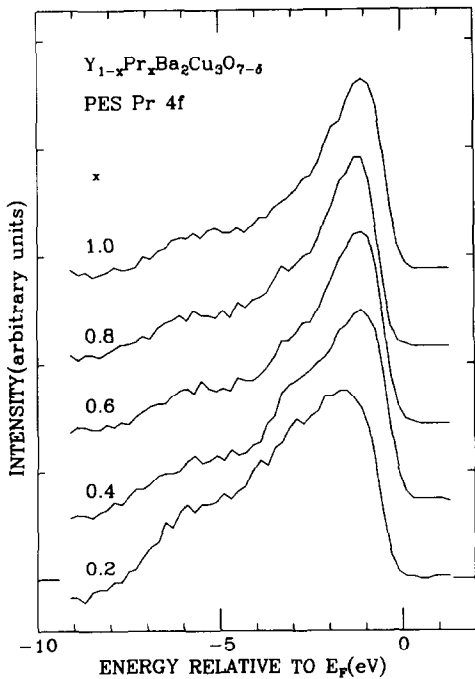
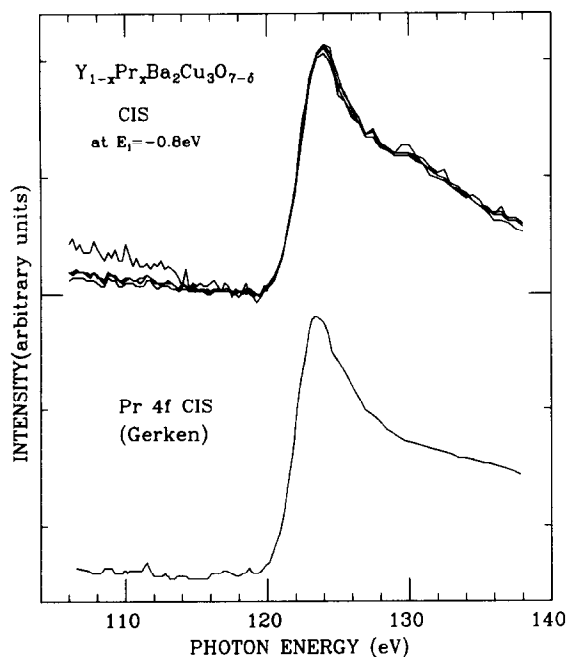


Fig. 2. Extracted Pr $4f$ spectra for $x = 0.2, 0.4, 0.6, 0.8$ and 1.0 (note the broad, asymmetric line shape).

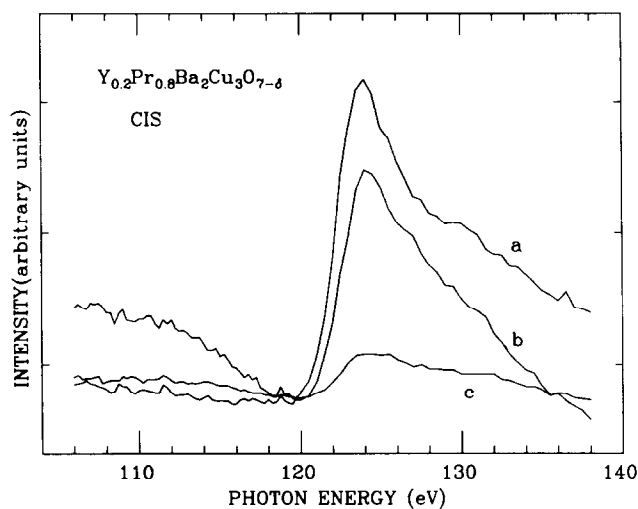
at the main peak. Each was obtained by subtracting the spectrum at the Fano minimum ($h\nu = 115$ eV) from that at the Fano maximum ($h\nu = 124$ eV), both taken with a resolution of 0.35 eV. Before subtraction, the 115 eV spectra were scaled by $\alpha = 0.9$ to account for the $h\nu$ dependence of the non-4f emission, where α was determined from the CIS spectrum of the Cu 3d/O 2p main band for $x = 0$. The shapes of the off-resonance spectra ($h\nu = 115$ eV) are almost identical for all x values. The areas under the Pr 4f spectral weights, calibrated by scaling the off-resonant spectra to be identical, are roughly proportional to the praseodymium concentration as expected, with relative ratios of $A(x = 0.2):A(0.4):A(0.6):A(0.8):A(1.0) = 0.34:0.44:0.58:0.80:1.18$.

The main feature of Fig. 2 is that the shapes of the extracted Pr 4f spectra are essentially the same for all x values. The Pr 4f spectral weight is essentially zero at E_F , rises to a large peak just below E_F , and then spreads out asymmetrically through the Cu 3d/O 2p states, extending to -8 eV. The absence of weight at E_F is contrary to that which usually occurs for strong mixed valence, while the spectral shape for the 4f state reflects extensive hybridization between Pr 4f and other valence band states. Broad, asymmetric 4f line shapes have also been observed in several praseodymium intermetallic compounds [24, 25] with a valence close to $3+$. They have been analyzed using the impurity Anderson Hamiltonian [26]. In this treatment, hybridization effects and the large 4f Coulomb interaction play an important role [12, 26]. Even in praseodymium metal, a weak 4f feature [27] near -1 eV has been described [26] as being due to hybridization effects using the impurity Anderson Hamiltonian.

The top part of Fig. 3(a) shows the CIS spectra taken at the binding energy $E_i = -0.8$ eV for $x = 0.2, 0.4, 0.6$ and 0.8 , scaled to one another to compare their line shapes. They are essentially identical for all x values, suggesting no valence change as a function of x , which is consistent with the magnetic moment results [1]. The Pr 4f CIS spectrum of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is very similar to the 4f CIS spectrum of praseodymium metal [28], for which the praseodymium valence is close to $3+$. The Fano line shape has a maximum at $h\nu = 124$ eV, which suggests that the valence of the praseodymium states at $E_i = -0.8$ eV is also close to $3+$. The praseodymium metal CIS spectrum is shown at the bottom of Fig. 3(a). The only difference is that the Pr 4f CIS spectrum of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ has a more pronounced shoulder near 131 eV than the Pr 4f CIS spectrum of praseodymium metal. This extra shoulder occurs in the CIS spectrum for states near E_F in praseodymium metal [28]. In Fig. 3(b), three CIS spectra taken at E_i values of $-0.8, -3.1$ and -6 eV are compared on the same intensity scale for $x = 0.8$. For other values of x (not shown here), the spectra are very similar to those of Fig. 3(b). The larger intensity at $E_i = -0.8$ eV reflects the peak in the Pr 4f spectral weight at this E_i value. This figure shows that the line shape of the CIS spectrum is invariant for different values of E_i over the range of the Pr 4f spectral weight distribution, which indicates that the emission



(a)



(b)

Fig. 3. (a) Top: CIS spectra at $E_i = -0.8$ eV for $x = 0.2, 0.4, 0.6$ and 0.8 (note that the spectra are essentially identical). Bottom: Pr 4f CIS spectrum of praseodymium metal (Gerken [28]). (b) CIS spectra for Y_{0.2}Pr_{0.8}Ba₂Cu₃O_{7-δ} at different E_i values in the Pr 4f spectrum: curve a, $E_i = -0.8$ eV; curve b, $E_i = -3.1$ eV; curve c, $E_i = -6$ eV.

does not have separate, non-overlapping contributions from two valence states. Thus the CIS spectra of the Pr 4f states provide evidence that the valence of praseodymium is close to 3+ for all x values.

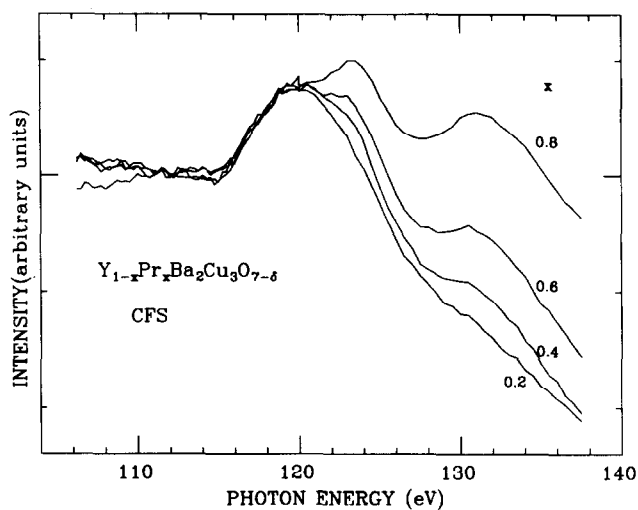
Figure 4(a) shows CFS spectra for $h\nu$ near the Pr 4d absorption edge for $x = 0.2, 0.4, 0.6$ and 0.8 , scaled to one another as in Fig. 3(a). The spectra have two absorption features at 124 eV and 131 eV which are similar to those for praseodymium metal [28], and an extra feature at 119 eV. Since the CFS spectrum for $x = 0$ (not shown here) shows the same feature at about 119 eV, but no features at 124 or 131 eV, this extra feature is identified as originating from Ba 4d \rightarrow 4f absorption. To account for the non-praseodymium absorption for $x > 0$, the CFS spectrum for $x = 0$ was subtracted from each CFS spectrum for $x > 0$, after matching the flat region between $h\nu = 105$ eV and $h\nu = 117$ eV.

The upper part of Fig. 4(b) displays the CFS spectra corrected by removing the non-Pr 4d absorption features as described above. The spectra are scaled to have the same magnitude at 131 eV. The tails to higher photon energy are artifacts of the analysis, reflecting the cut-off of the $x = 0$ spectrum at 131 eV. Apart from this, the corrected spectra are essentially identical for all x values, which provides evidence of no valence change as a function of x . The overall line shapes of these CFS spectra are very similar to that for praseodymium metal [28], shown at the bottom of the figure. Because of insufficient statistics, the weak fine-structure features [29 - 31] which are usually observed between 105 eV and 120 eV just before the giant absorption edge for Pr $^{3+}$, cannot be seen clearly in the CFS spectra of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. This precludes an analysis [32] of these features for hybridization effects. Owing to the dynamic effects of hybridization, XAS spectral weights are typically not in direct proportion to the valence and require detailed theoretical analysis to extract a valence [26]. At present our conclusions are limited to the observation that there is no indication of a separate 4d \rightarrow 4f absorption process corresponding to a different valence state in any of the CFS spectra. This shows, at least, that strong mixed valence does not occur. In addition there is certainly no pure Pr $^{4+}$ state.

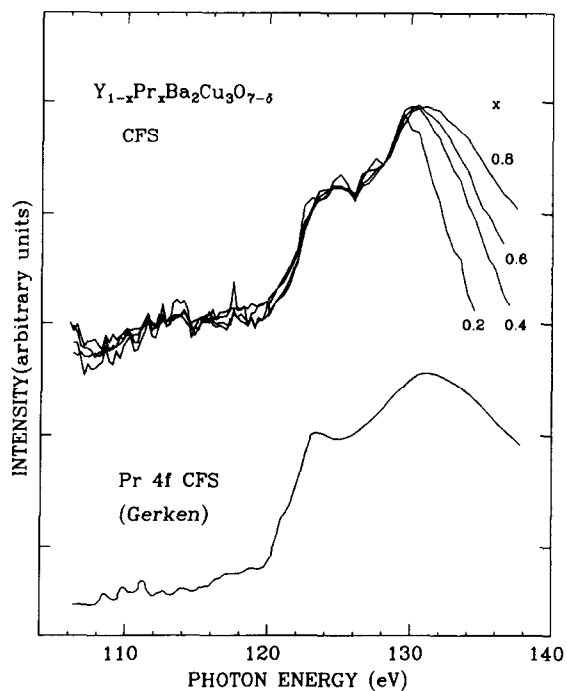
We also measured the RESPES valence band spectra near the Cu 3p \rightarrow 3d and O 2s \rightarrow 2p absorption edges, the conduction band bremsstrahlung isochromat spectrum and the core-level X-ray photoemission spectra of Cu 2p/O 1s Ba 3d states for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system. All of these results will be reported in detail in another paper. Among other things, it was found that the valence of copper is essentially unchanged with x .

4. Discussion

The implications of our results for the magnitude of the praseodymium magnetic moment and the mechanism of T_c quenching can now be discussed. The valence of praseodymium is close to 3+ for all x values, which is consistent with XAS results and with lattice parameter measurements [9]. In addition, the extracted Pr 4f spectrum has almost no weight at E_F , while the Pr 4f spectral line shape indicates much hybridization to other valence band



(a)



(b)

Fig. 4. (a) The raw CFS spectra near the Pr 4d absorption for $x = 0.2, 0.4, 0.6$ and 0.8 . (b) Top: CFS spectra corrected from those in Fig. 4(a) as described in the text. The line shapes are the same for all x values and very similar to that for praseodymium metal (Gerken [28]), shown at the bottom.

states. As discussed in the introduction, the measured praseodymium magnetic moment is smaller than one would expect for Pr^{3+} . A reduced moment could arise from quenching of the orbital angular momentum due to the low-symmetry crystal field. Although such effects are usually expected to be larger for transition metal ions than rare earths because the 4f shells of the latter lie deep inside the filled 5s and 5p shells, the observed strong hybridization, which is one microscopic origin of the crystal field, suggests that the crystal field effects could be large in this case. Indeed, crystal field splittings have been observed in specific heat data [33] for $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ materials, although not specifically for $\text{R} \equiv \text{Pr}$. In cerium intermetallic compounds [34] there is strong evidence that hybridization between the 4f and conduction band electrons leads to magnetic moment suppression due to the Kondo effect. For the praseodymium alloys considered here, a Kondo lattice picture would have to be made consistent with the small density of states at the Fermi level, and with the insulating character for $x = 1$. Therefore at present it seems that the magnetic moment reduction must be attributed to the large hybridization, but the exact mechanism has not been identified.

Our findings in this study strongly suggest an alternative to the previous suggestions that superconductivity is quenched by the charge transfer mechanism, *i.e.* that the valence of praseodymium departs from 3+ so that extra electrons from the praseodymium ion are transferred to the Cu-O planes. The fact that praseodymium is close to 3+ makes this mechanism implausible. Our results suggest that extensive hybridization between Pr 4f and other valence band states may disrupt some feature of the electronic or magnetic structure of the $x = 0$ material which is essential for superconductivity. This mechanism would apply particularly to the rare earths praseodymium, cerium and terbium for which the 4f states have small 3+ ionization energies [35] degenerate with the other valence band states, a situation favoring strong hybridization.

The Y/Pr layer is located between two Cu-O planes in the crystal structure [36] and the near neighbors of a Y/Pr site are oxygen atoms and copper atoms in the Cu-O planes. The interatomic distances are comparable with the R-O distances in R_nOm for $\text{R} \equiv \text{Ce}$ and Pr, and to the R-T distances in RT_2 for $\text{R} \equiv \text{Ce}$ and $\text{T} \equiv \text{Ni}$ or Co, for which theoretical analysis of electron spectra shows large hybridization. Comparable magnitudes of hybridization between Pr 4f states and the 2p states of the oxygen atoms or the 3d states of the copper atoms in the Cu-O planes are thus expected. A likely result is superexchange interactions between the moments of the praseodymium atoms and those of the planar copper atoms or planar oxygen holes. For example, rare earth-transition metal exchange interactions are known to occur for the perovskite rare earth orthoferrites and orthochromites [37]. Neutron scattering experiments now being performed [38] for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ may provide direct evidence concerning such exchange interactions in the near future. It can be speculated that such interactions could quench superconductivity by altering magnetic correlations in the Cu-O planes, if indeed these correlations play an important role in the

pairing interaction, as many believe [39 - 42]. Alternatively, the superconductivity may be directly affected through changes in the electronic structure of the oxygen states, since it appears likely that holes in these states provide carriers for pairing.

To summarize, our major findings in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system are that the praseodymium valence is close to 3+ for all x values and that the extracted Pr 4f spectral weight has a broad, asymmetric line shape which implies a large hybridization with other valence band states. From this we infer that Pr 4f-O 2p/Cu 3d hybridization must alter the electronic or magnetic structure of the $x = 0$ material in some essential way to cause the suppression of T_c ; this may possibly involve superexchange with the magnetic moments of planar copper or oxygen holes.

Acknowledgments

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