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TITLE **Electron Spectroscopy Studies of High Temperature Superconductors: $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$**

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Electron Spectroscopy Studies of High Temperature Superconductors: $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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ABSTRACT

We itemize our previous work on high T_c-superconductors, and describe more fully the results of an electron spectroscopy study and impurity Anderson Hamiltonian analysis of the Pr 4f spectrum of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, a system in which superconductivity is quenched as x increases. It has been speculated that Pr has valence 4+, resulting in extra charge in the Cu-O planes, and causing T_c-suppression. We find that the Pr valence is close to 3+ for all x but that there is extensive Pr 4f hybridization with other valence band states. The Cu valence is essentially unchanged with x. From these findings, we speculate that Pr 4f hybridization with other valence band states has enabled Pr spin fluctuations to cause the T_c-suppression.

KEYWORDS

$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$; photoemission; BIS; 4f spectrum; quenched superconductivity; spin fluctuations; Anderson Hamiltonian.

INTRODUCTION

Previous Work

Previously (Shen *et al.*, 1987) we have studied the electronic structure of $La_{2-x}Sr_xCuO_4$ for x=0 and 0.2, and $YBa_2Cu_3O_{7-\delta}$ using resonant photoemission spectroscopy (RESPES) and x-ray photoemission spectroscopy (XPS). We analyzed these data in the impurity cluster approximation to the Anderson Hamiltonian to derive approximate values of Hamiltonian parameters and to discuss superexchange interactions. We pointed out that for these parameters Cu^{3+} is largely excluded from the ground state and that the non-metallic materials are charge

holes are created by doping. An overview of this and related work has recently been given. (Shen *et al.*, 1988a) We have also studied the dispersion of hole excitations in the archetype material NiO and found that a rigid-shift correction to band structure calculations is not valid. (Shih *et al.*, 1988) Here we will concentrate on new results for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

The superconductivity of the isostructural alloy system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is quenched with increasing x. (Dalichaouch *et al.*, 1987; Soderholm *et al.*, 1987; Liang *et al.*, 1987) The other $RBa_2Cu_3O_{7-\delta}$ compounds, where R is a rare earth or La, are superconductors with T_c near 90K except for Ce and Tb, for which the compounds do not form. (Yang *et al.*, 1988) For $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ it is found that the normal state electrical resistivity shows a transition from metallic to semiconducting behavior, with the monotonic suppression of T_c from ~90K to ~60K and ~35K for x=0, 0.2 and 0.4, respectively, with the samples for x>0.6 being non-superconducting. The pressure dependence of these electrical properties is complex and interesting. (Neumeier *et al.*, 1988) From magnetic susceptibility measurements an effective magnetic moment of 2.7 μ_B/*Pr-ion* was extracted, independent of x. (Dalichaouch *et al.*, 1987) A possible intepretation of the magnetic moment is that the Pr valence has a fixed value of about 3.8, and that extra charge is then contributed to the Cu-O planes, filling the holes that are widely believed to be the superconducting carriers. This picture is supported by electron energy loss spectroscopy (EELS) measurements of the oxygen 1s→2p transition, which showed that a small pre-threshhold peak thought to indicate valence band holes is reduced, although not eliminated, for x=1 relative to x=0. (Nücker *et al.*, 1988) In contrast, the lattice constants of the $RBa_2Cu_3O_{7-\delta}$ series strongly suggest that Pr is trivalent. (Yang *et al.*, 1987) In fact, the Pr valence was concluded to be close to 3+ from X-ray absorption spectroscopy (XAS) measurements of the Pr L-edge (Horn *et al.*, 1987; Alp *et al.*, 1987; Lytle *et al.*, 1988), although it was proposed that the T_c-quenching is due to charge transfer arising from a modest deviation of the valence from 3+ toward 4+. Other workers have subsequently come to the same conclusion from Pr M-edge studies. (Neukirch *et al.*, 1988)

We have made an electron spectroscopy study of this system for x=0, 0.2, 0.4, 0.8 and 1.0, including XPS for various core levels, bremsstrahlung isochromat spectroscopy (BIS) for the conduction band, and synchrotron-excited RESPES for the Pr 4f and Cu 3d states of the valence band. Our Pr RESPES data were reported in a separate paper. (Kang *et al.*, 1988) In agreement with the XAS results we concluded that the Pr valence is near 3+ for all x. However, the Pr 4f photoemission spectrum, which was found to be largely unchanged with x, shows strong hybridization with other valence band states. In this paper we summarize our BIS and XPS data and the results of efforts to quantify the hybridization by fitting the Pr 4f RESPES and BIS spectra using the impurity Anderson model.

EXPERIMENTAL DETAILS

The samples of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with x=0, 0.2, 0.4, 0.6, 0.8, 1.0 were prepared as described by Dalichaouch *et al.* (1987). The samples with x = 0, 0.2, 0.4, 0.6 and 0.8

were prepared in the same batch, while the sample with x=1.0 was prepared at a different time with a slightly different oxygen treatment. An impurity phase of $BaCuO_2$ in amounts less than 8 mol% is observed in the x-ray diffraction data, the amount of which decreases with increasing x until it is not observed for $x > 0.4$.

The synchrotron-excited photoemission spectroscopy (PES) was performed at the Stanford Synchrotron Radiation Laboratory (SSRL), using equipment and procedures described fully by Shen *et al.* (1987) and Kang *et al.* (1988). For all synchrotron-excited spectra presented below, normalization has been performed by recording the photoelectron yield from a beam flux monitor for each photoemission spectrum. 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*. Room temperature XPS and BIS spectra were obtained at the Xerox Palo Alto Research Center (PARC) using a Vacuum Generators (VG) ESCALAB spectrometer. The equipment and procedures are generally as described by Allen *et al.* (1987). XPS satellites due to the non-monochromatized Mg $K\alpha$ source were subtracted numerically. The base pressure during the BIS measurements rose to about 3×10^{-10} Torr, mostly due to the outgassing of the samples. The Cu 2p XPS spectrum was the same before and after BIS.

PHOTOEMISSION SPECTRA

Valence Band Cu RESPES and O 1s XPS

Panels (a) and (b) of Fig. 1 display the valence band spectra for x=0, 0.2, 0.4, 0.6, 0.8, and 1.0 at photon energies $h\nu$ = 70 eV and 75 eV, respectively, which are below and at the Cu 3d cross-section resonance at the Cu 3p edge. The two sets of spectra are scaled to have the same valence band maximum intensity in each set. As explained by Shen *et al.* (1987), interference from the Ba 4d core level excited by second order light has been removed. The Cu RESPES results of Fig. 3 are like our previous results for x=0. The emission of the d^8-like satellite located at −12.4 eV is clearly enhanced at $h\nu$ = 75 eV. An antiresonance of the states between −7 eV and E_F, which involves hybridized Cu 3d and O 2p states, is concealed by the scaling in the figure. We do not observe any correlation between x and the intensity of the d^8-like satellite relative to the −4.7 eV peak, which implies that there is no systematic change in the Cu 3d state due to the substitution of Pr.

Panel (c) of Fig. 1 shows the O 1s core level XPS spectra for x=0, 0.2, 0.4, 0.6, 0.8 and 1.0. For all x there are multiple peaks, with changing relative intensities. Multiple peaks are often found in ceramic samples, and the developing concensus (Kohiki *et al.*, 1987; Takahashi *et al.*, 1988; Shen *et al.*, 1988b) is that only the 528 eV line is intrinsic. The decrease with increasing x in the intensity of the 531 eV line relative to the 528 eV line correlates with changes in the valence band spectra which show that with increasing x there is a decrease in the −4.7 eV maximum relative to the −2.4 eV shoulder. Since this change is essentially the same in both panels (a) and (b) of the figure, it does not involve primarily the Cu 3d states. We conclude that there is valence band emission in the −4.7 eV range from extrinsic oxygen, possibly water or gases such as CO_2 adsorbed in the grain boundaries, or the $BaCuO_2$ impurity phase. The higher binding energy O 1s peak decreases during BIS measurements.

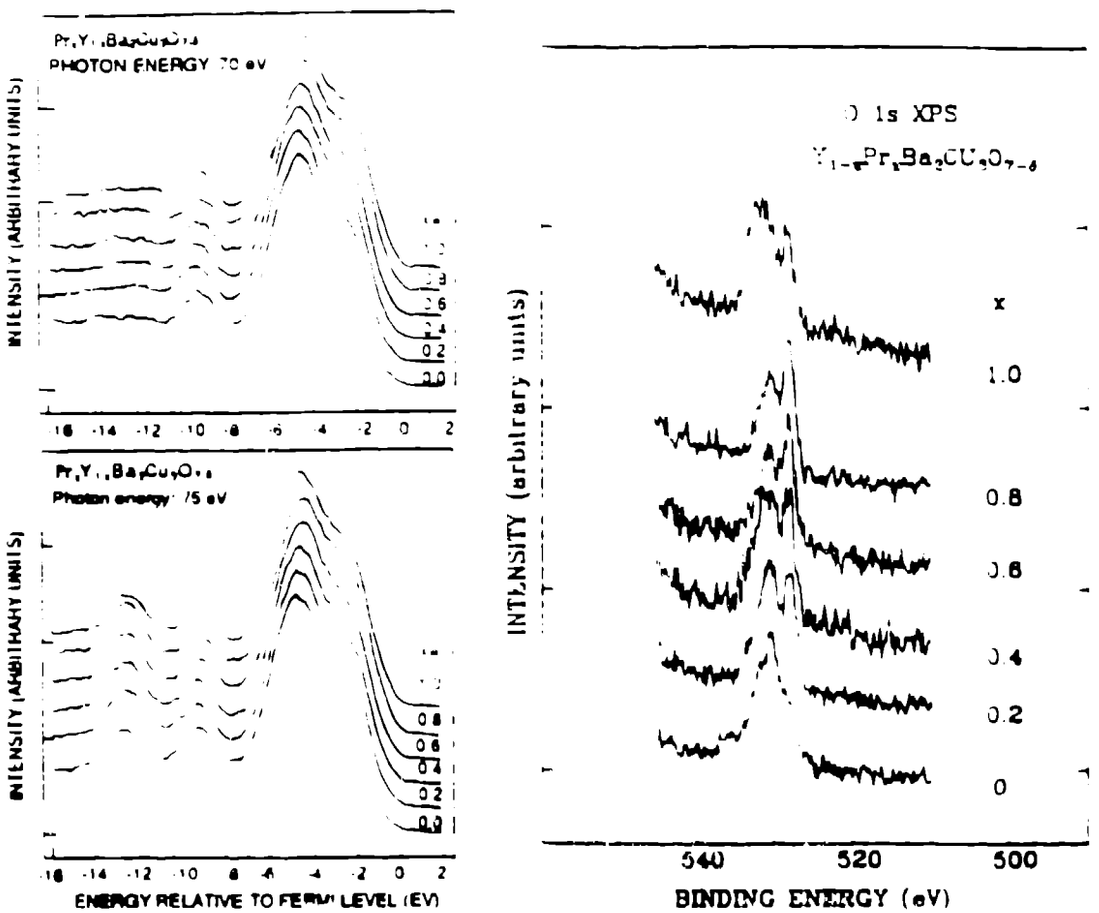

Fig. 1. The valence band spectra of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ at (a) $h\nu$=70 eV, below the resonance, and at (b) $h\nu$=75 eV, above the resonance. The interference from the Ba 4d core level excited by the second order light is removed, as described by Shen *et al* (1987).
(c) The O 1s core level XPS spectra of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

Pr 4f RESPES

The Pr 4f emission is spread throughout the first 7 eV of the valence band and is not explicitly visible in Figs 1 (a,b). It has been determined by RESPES studies described in detail by Kang *et al.* (1988). It is important that the shapes of the extracted Pr 4f spectra for all x are essentially like that shown in Fig. 3 for x=1. We infer that Pr does not occur in combination with the extrinsic oxygen described above.

Pr 3d and Cu 2p XPS

The Pr 3d and Cu 2p core levels consist of spin-orbit split peaks which overlap. The Pr $3d_{5/2}$ states occur between 933 eV and 935 eV for several Pr materials, and the Cu $2p_{3/2}$ peak is observed at 933.7 eV in $YBa_2Cu_3O_{7-\delta}$. Since the two core levels have nearly identical

et al. (1987), each spin-orbit component of the Cu spectrum has a main line and a satellite assigned to $2p^5d^{10}L$ and $2p^5d^9$ final state configurations, respectively, where L denotes a hole of appropriate symmetry relative to filled ligand O 2p states. Taking into account the increase with x of the Pr 3d intensity under the Cu main line, we find that the ratio of the Cu satellite to main line intensity is essentially unchanged with x. This implies that the Cu valence averaged over chain and plane sites does not change much with x.

BIS SPECTRA

Fig. 2 compares BIS spectra for x=0, 0.2, 0.4, 0.6, 0.8, and 1.0. All the spectra are scaled to have the same magnitudes at the narrow peak at 15 eV. The spectrum for x=0 is very similar to those in the literature (van der Marel *et al.*, 1987) in having a peak at ~ 2 eV, which we assign to the Cu d^{10} final state, a wide band starting at ~ 7 eV above E_F arising from a mixture of O 3s, Cu 4s, Ba 5d and Y 4d states, and a narrow peak at 15 eV due to the Ba $4f^0 \rightarrow 4f^1$ transitions. From this figure, it is clear that the spectral weight near E_F is essentially zero for all x, and that features near 2 eV and 7 eV increase as x increases. We have extracted the Pr spectra by subtracting the spectrum for x=0 from that for each x, after matching the magnitudes of the peaks corresponding to the Ba $4f^0 \rightarrow 4f^1$ transitions, assuming that highly atomic-like states are not affected by the Pr substitution. The areas under the Pr 4f spectral weights are roughly proportional to the Pr concentration x, with the exception of x=1.0. The area ratios are $A(x=0.2) : A(0.4) : A(0.6) : A(0.8) : A(1.0) = 0.19 : 0.38 : 0.60 : 0.80 : 0.82$. As with the oxygen 1s XPS spectra, we speculate that the different behavior for

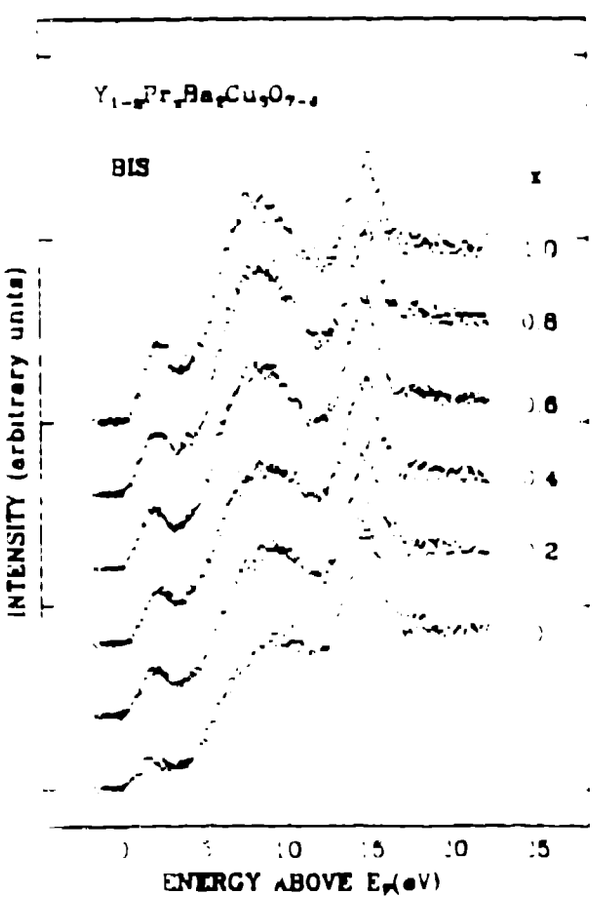

Fig. 2. The BIS spectra of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. The spectra are scaled to have the same magnitudes at the Ba $4f^0 \rightarrow 4f^1$ peak at 15 eV.

x=1.0 reflects the slight difference in its preparation. The extracted Pr spectral weight above E_F is shown in Fig. 3 for x=1. There are two features centered at 2 eV and at 7 eV, with complicated lineshapes and with essentially zero spectral weight at E_F. The spectra for other x are very similar, except that the intensity of the 2 eV feature decreases slightly relative to that of the 7 eV feature as x increases.

Pr 4f SPECTRUM

Qualitative Assignments

The top panel of Fig. 3 shows the complete Pr 4f spectral weight distribution for x=1.0, obtained by combining the spectra extracted from RESPES and BIS. The RESPES spectrum is scaled relative to the BIS spectrum so that the weight distribution has 2/14 of its area below E_F, corresponding to the Pr^{3+} state. For comparison, the bottom panel of the figure shows the analogous Pr 4f spectrum for Pr metal, obtained by combining BIS (Lang *et al.*, 1981) and PES data for $h\nu$=80 eV. (Wieliczka *et al.*, 1984) The spectrum is essentially that expected for a single-valent Pr^{3+} ion. Thus the vertical bars show the weights and positions of the final state multiplets of $4f^1$ and $4f^3$ configurations arising in a calculation of the $4f^2 \rightarrow 4f^1$ and $4f^2 \rightarrow 4f^3$ PES and BIS transitions using the method of coefficients of fractional parentage. (Lang *et al.*, 1981) The large 4f Coulomb interaction U_{ff} is shown by the 5 eV separation of the lowest PES ionization and BIS affinity lines. The PES spectrum also shows a small peak near E_F, which arises from hybridization between the 4f state and the conduction band, and can be

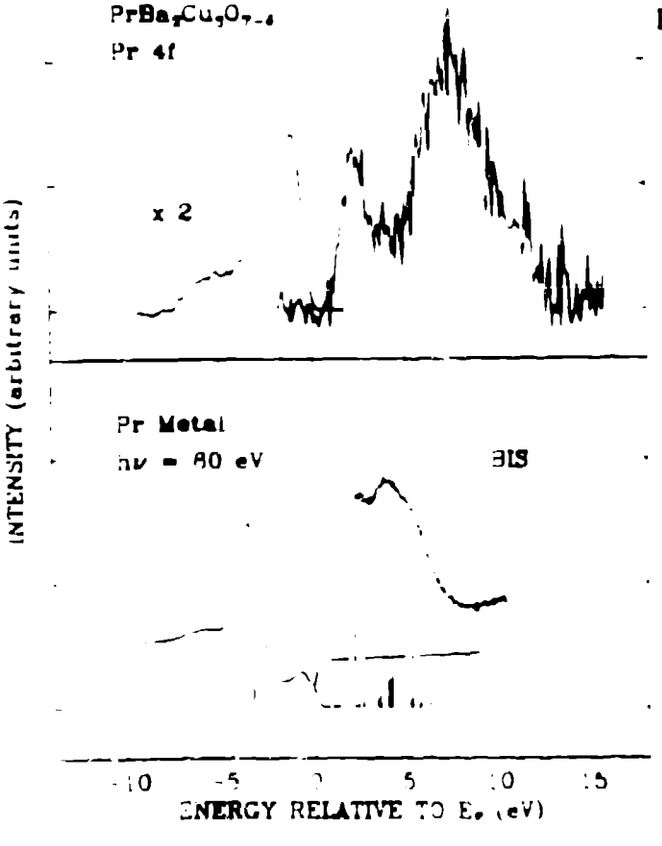

Fig.3. (a) Top: The complete Pr 4f spectrum for $PrBa_2Cu_3O_{7-\delta}$, obtained by combining the spectrum extracted from RESPES (Kang *et al*, 1988) and BIS. The RESPES spectrum is scaled relative to the BIS spectrum so that the ratio of the area below E_F and above E_F is 2:12.
(b) Bottom: The complete Pr 4f spectrum for Pr metal, by combining the PES spectrum for $h\nu$=80 eV (Wieliczka *et al*, 1984) and the BIS spectrum (Lang *et al*, 1981). Vertical lines show final state mulplets.
The difference near E_F signals much larger hybridization effects for $PrBa_2Cu_3O_{7-\delta}$ than for Pr-metal.

fit using the Anderson impurity model. (Gunnarsson and Schönhammer, 1983, 1985, 1987) More complex PES lineshapes in essentially trivalent Pr intermetallic compounds (Parks *et al.*, 1984; Sampathkumaran *et al.*, 1985) arise from hybridization to a structured conduction band and can also be fit with this model. (Gunnarsson and Schönhammer, 1985, 1987)

Considering this previous work on hybridization effects in Pr and its compounds, we interpret the $PrBa_2Cu_3O_{7-\delta}$ 4f spectrum as essentially trivalent, but with the BIS/PES peaks near E_F signaling much larger hybridization effects than for Pr metal. We assign the 7eV BIS feature as the $4f^2 \rightarrow 4f^3$ transition. This interpretation implies a shift of the $4f^3$ states by about 3 eV to higher energies, relative to the BIS spectrum of Pr metal, and in addition, a decrease by approximately 20% in the overall multiplet splitting, to about 4 eV at FWHM, from the metal value of about 5 eV. Such changes are known in compounds of the light lanthanides with transition metals (Laubschat *et al.*, 1987), and are most likely due to hybridization effects and to a larger 4f Coulomb interaction, as found in cerium oxides. (Nakano *et al.*, 1987)

Impurity Anderson Hamiltonian Analysis

We have attempted to quantify our interpretation by fitting the Pr 4f spectrum using the impurity Anderson Hamiltonian. This Hamiltonian models the Pr 4f state as a 14-fold degenerate local orbital, characterized by its binding energy ϵ_f relative to E_F, and its Coulomb interaction U_{ff}. The orbital is hybridized to a continuum density of states, with strength characterized by a parameter Δ_{sv}. The Gunnarsson/Schönhammer (1985, 1987) calculation for Ce has been adapted approximately to Pr as described by them, with the 4f spin-orbit and multiplet splittings included only in simulating the BIS final states. Our fitting effort has been only partially successful. If we assume hybridization to a metallic density of states, the weights of the BIS and PES peaks near E_F relative to those far from E_F can be reproduced rather well with only a modest departure from trivalence. However, the theoretical spectra perforce show BIS and PES peaks meeting at E_F, whereas our experimental peaks lie away from E_F somewhat. On the other hand, if we assume hybridization to a continuum with a small gap at E_F, we can produce theoretical 4f spectra which also display a gap, but to obtain a BIS feature near E_F of adequate size, we must use such a large hybridization that the valence is driven nearly 50% away from f^2 (toward f^3, since f^1 is excluded with a filled valence band) and the PES spectrum also develops extra features not seen experimentally. A compromise scenario appears to be impossible within the framework of the impurity Anderson model.

The solid lines of panels (a) through (c) of Fig. 4 show, respectively, the 4f BIS, 4f PES, and 3d XPS spectra of our metallic mixed valence model. The inset of (b) shows the continuum density of states, with the important part below E_F essentially the same as the Pr 4f off-resonance spectrum shown, where the Cu 3d emission dominates, but with an increased intensity between ~2 eV and E_F to account for the contribution from oxygen p-states. We note that interatomic spacings from Pr to both Cu and O permit strong hybridization, and $\Delta_{sv} = 0.16$ eV, intermediate between smaller values for α-like Ce intermetallics (Allen *et al.*, 1987) and larger values for cerium oxides. (Nakano *et al.*, 1987) The other model parameters

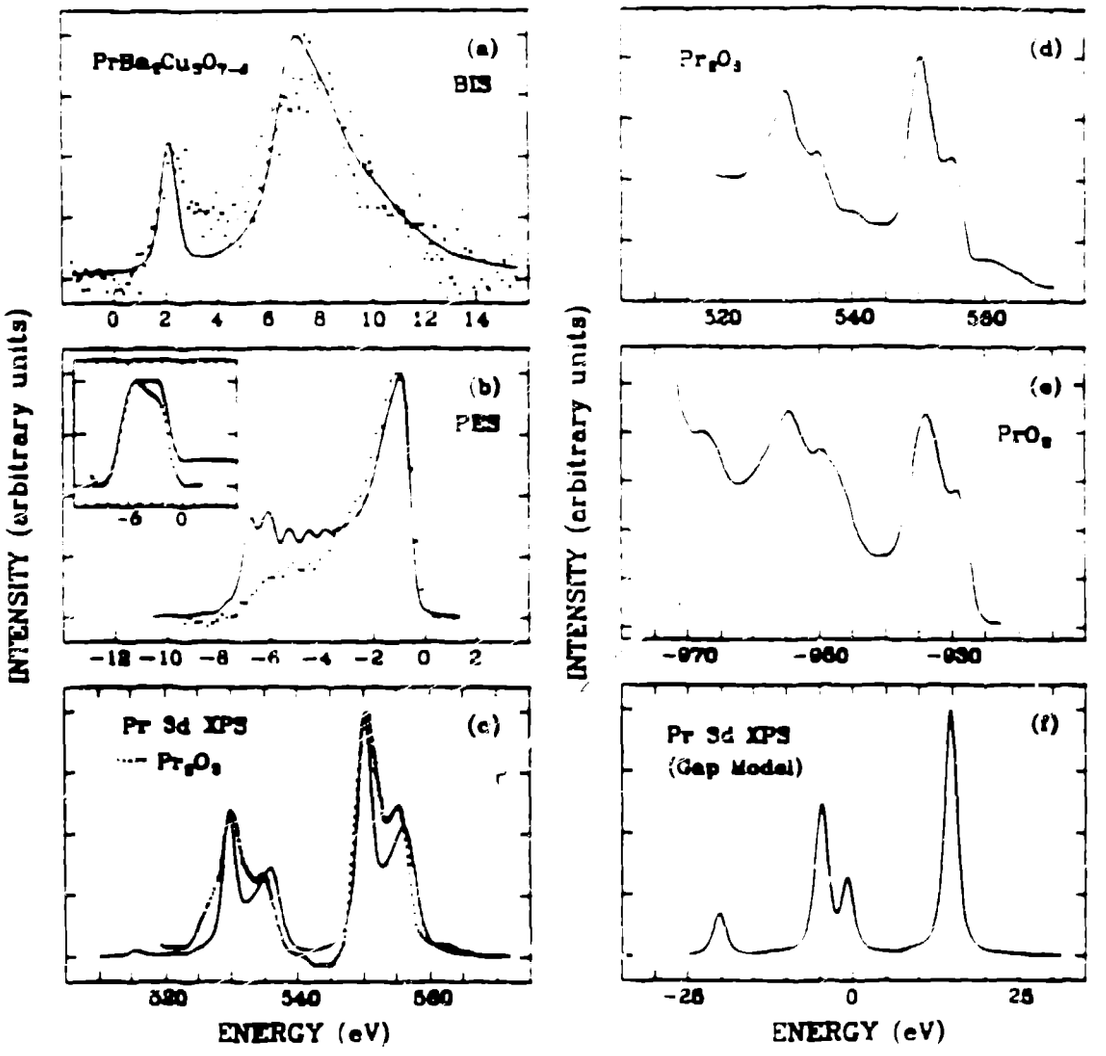

Fig. 4. The solid line and the dots in the inset of the panel (b) show, respectively, the continuum density of states and the Pr 4f off-resonance spectrum of $PrBa_2Cu_3O_{7-\delta}$. The solid lines in the panels (a), (b), and (c) show, respectively, the calculated 4f BIS, 4f PES, and 3d XPS spectra of our metallic mixed valence model. The theoretical PES and BIS spectra have been shifted away from E_F by 0.6 eV and 2 eV, respectively, and superposed on experimental spectra (in dots) of $PrBa_2Cu_3O_{7-\delta}$. The dots in the panel (c) is the 3d XPS spectrum of Pr_2O_3 (Burroughs, *et al.* 1976), with its inelastic background and non-monochromatic-source satellites (incompletely) removed.

Panels (d) and (e) show the 3d XPS spectra of Pr_2O_3 (Burroughs *et al.*, 1976) on a kinetic energy scale, and PrO_2 (Bianconi *et al.*, 1988) on a binding energy scale, respectively. Panel (f) shows the calculated 3d spectrum for our gapped-continuum model.

are $\epsilon_f = E(f^2 \rightarrow f^1) = -3$ eV, $U_{ff} = 8.45$ eV, and the 4f-3d Coulomb interaction $U_{fc} = 12.1$ eV. The theoretical PES and BIS spectra have been shifted away from E_F by 0.6 eV and 2 eV, respectively, and superposed on experimental spectra, producing the appearance of fits as good as typically are obtained for Ce spectra. (Allen *et al.*, 1987) Although the Pr 3d spectrum is obscured in $PrBa_2Cu_3O_{7-\delta}$ by the Cu 2p spectrum, as described above, we can guess that it should resemble that of Pr_2O_3, and be different from that of PrO_2, from the finding that the Pr L-edge XAS spectrum is very much like that of Pr_2O_3 and very much different from that of PrO_2. (Alp *et al.*, 1988) Panels (d) and (e) show the 3d XPS spectra of Pr_2O_3 (Burroughs *et al.*, 1976) and PrO_2 (Bianconi *et al.*, 1988), respectively. The Pr_2O_3 spectrum, with its inelastic background and non-monochromatic-source satellites at 540 eV and 561 eV (incompletely) removed numerically, is also shown in panel (c), and it is indeed much like that of our theory curve. Panel (f) shows the calculated 3d spectrum for our gapped-continuum model and it is obvious that it looks much different from that of Pr_2O_3 due to the strong f^2/f^3 valence mixing. It is not merely coincidence that it resembles the PrO_2 spectrum, which displays the effects of strong f^1/f^2 valence mixing, analogous to the nearly equal f^0/f^1 valence mixing in CeO_2. (Nakano *et al.*, 1987)

The metallic continuum model reproduces the various 3d and 4f spectral signatures generally thought to measure the Pr 4f valence and hybridization strength. The calculated ground state is 4.2% f^1, 89.9% f^2 and 5.9% f^3, giving 2.02 f-electrons. The seriousness or significance of the problem that we cannot reproduce the experimental 4f gap around E_F is not clear. Of great concern is the possibility that the gap is an experimental artifact associated somehow with the use of ceramic samples, or of surface oxygen loss, or a charging effect induced in some unknown way. For example, Arko *et al.*(1988) reported recently that single crystals of $YBa_2Cu_3O_{7-\delta}$ cleaved at 20K, where oxygen diffusion is very slow, show much larger photoemission intensity at E_F than we find in our room temperature measurements of ceramic samples for x=0. Fujimori *et al.* (1988) suggested that oxygen-vacancy disorder in these low carrier density materials can produce a Coulomb gap at E_F, which might be simulated by a shift. Our present inclination is to give credence to our characterization of the Pr valence and hybridization strength, while working to resolve the experimental uncertainties concerning the gap around E_F.

DISCUSSION

A suitable model for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ must account for the magnitude of the Pr magnetic moment and the change from a superconductor to a semiconductor with increasing x. We have found that the Pr valence is close to 3+ for all x, consistent with XAS results and with lattice parameter measurements. In addition, the extracted Pr 4f spectral lineshape indicates much hybridization to other valence band states. We have previously discussed (Kang *et al.*, 1988) various alternatives for explaining the Pr moment and concluded that its reduced value below that expected for Pr^{3+} must be attributed to the large hybridization but that the exact mechanism is not clear. Our findings also cast doubt on the possibility that the transformation from a superconductor to a semiconductor occurs merely by the charge-transfer mechanism. It

is natural to speculate instead that the extensive hybridization between Pr 4f and other valence band states may have disrupted some features 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 Ce, Pr and Tb for which the 4f states have small 3+ ionization energies (Lang *et al.*, 1981) degenerate with the other valence band states, a situation favoring strong hybridization.

Expanding our previous discussion (Kang *et al.*, 1988), we suggest here that it is the Pr magnetic degrees of freedom that are most important. Much of the theoretical thinking within correlated electron models for the electronic structure of the Cu-O planes leads to the conclusion that the electrical behavior of holes in the Cu-O planes is determined in one way (Anderson, P.W. 1987) or another(Birgeneau *et al.*, 1988; Hirsch *et al.*, 1988; Stechel and Jennison, 1988) by Cu-O and/or Cu-Cu magnetic interactions. From an insulator point of view, it is expected that hybridization between Pr 4f states and the 2p states of the O atoms in the adjacent Cu-O planes leads to superexchange interactions between Pr and Cu or O moments which would have the potential to profoundly alter the behavior that would occur in their absence. Alternatively, from the view of the metallic model, there occur Kondo spin fluctuations with an associated energy scale of T_K. Although our model calculation is very unrealistic for T_K in neglecting spin-orbit and multiplet splittings, it is suggestive that the value of T_K obtained is about 125 K, the same order of magnitude as T_c. $T_c \sim T_K$ is the condition for maximum suppression of T_c by a magnetic impurity in a BCS superconductor with singlet pairing (Müller-Hartmann and Zittartz, 1970) and may have generic significance in the present case.

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