Ba core-level shift in x-ray photoemission spectroscopy on single-phase $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$ compounds

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We have measured x-ray photoemission spectra of single-phase $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8) and of $YBa_2Cu_3O_{7-y}$ ($y = 0.0$, 0.15, 0.40) compounds, in which superconductivity is suppressed by increasing x and y. Ba $3d$ and Ba $4d$ core-level spectra were observed to shift significantly towards higher binding energy as x and y increase, while Y $3d$, Cu $3p$, O $1s$ spectra were not. The shift of Ba core-level spectra is interpreted as resulting from a distinct initial-state Ba $5d$–O $2p$ covalency common to 1:2:3 structures, as opposed to final-state effects. This energy shift may constitute a sensitive fingerprint of the degree of hole localization at Ba sites, which is related to the quenching of superconductivity in these compounds.

INTRODUCTION

Among the $(L)Ba_2Cu_3O_7$ compounds that are isostructural to $YBa_2Cu_3O_7$ (hereafter 1:2:3), where L is a lanthanide element, only $PrBa_2Cu_3O_7$ is nonmetallic and nonsuperconducting. $PrBa_2Cu_3O_7$, like $YBa_2Cu_3O_7$, has features that are thought to be essential for high temperature superconductivity such as CuO_2 planes, Cu-O linear chains, and stoichiometric oxygen content in the unit cell. For this reason, the $PrBa_2Cu_3O_7$ compound has attracted numerous research activities in attempts to illuminate the mechanism of the high-temperature superconductivity.

The solid-solution system $Y_{1-x}Pr_xBa_2Cu_3O_7$ is particularly interesting since it is, if prepared properly, a single-phase 1:2:3 structure and yet superconductivity is gradually suppressed by the increase of Pr concentration x. The mechanism for suppression of superconductivity in this compound is not well understood. Magnetic susceptibility measurements indicate that Pr valence is close to 4+,[1-4] which would reduce the carrier hole density necessary for the superconductivity. However, photoemission,[5] x-ray absorption,[6,7] and structural measurements,[3,8] for example, suggest that Pr is trivalent. A magnetic pair-breaking mechanism[9] was adopted in fitting the T_c versus x curve[1,2] in order to explain the results of magnetic measurements.[1,2,10] The possibility of Pr $4f$–O $2p$/Cu $3d$ hybridization was suggested from the valence-band resonant photoemission,[5] pressure measurements,[11,12] and low-temperature specific-heat measurements.[12] Most explanations are based on the direct disturbance of the Pr ion on CuO_2 planes. In the oxygen-deficient $YBa_2Cu_3O_{7-y}$ case, on the other hand, the disturbance occurs at the Cu-O chains, remote from CuO_2 planes. Namely, oxygen is lost from the Cu-O chains as y increases in $YBa_2Cu_3O_{7-y}$ resulting in the loss of superconductivity at $y \approx 0.5$. It is of interest to compare the two cases and find the common mechanism, if there is any, for the suppression of superconductivity in both cases.

In this paper, we performed x-ray photoemission spectroscopy (XPS) measurements on well-characterized, single-phase $Y_{1-x}Pr_xBa_2Cu_3O_7$ (nominal oxygen content) compounds in order to assess possible effects of Pr substitution for Y on core-level spectra and eventually to look for a clue for the mechanism of suppression of superconductivity. Our results differ from those of previous XPS work[13] on these compounds as will be discussed in the results section. The 1:2:3 oxides are known to be prone to surface contaminations with carbonates, hydroxides, and other nonsuperconducting oxides, making surface sensitive measurements difficult.[14] In addition, it is known that this $Y_{1-x}Pr_xBa_2Cu_3O_7$ compound tends to phase-separate resulting in as much as 30% of the 90-K phase if sample-preparation procedure is not proper.[1,15] Therefore, XPS results would critically depend on surface contamination and spurious phases. In our measurements, Ba $3d$ and $4d$ core-level spectra continuously shift towards higher binding energy up to ≈ 0.4 eV as Pr concentration x increases to 0.8, while other core levels such as Y $3d$, Cu $3p$, and O $1s$ do not shift. From the shift of Ba core-level spectra, we suggest the possibility of hole localization on Ba sites as Pr replaces Y, contributing to the suppression of superconductivity in these compounds. We performed a similar analysis for oxygen-deficient $YBa_2Cu_3O_{7-y}$ compounds, which also exhibit a shift in the Ba core-level spectra.

EXPERIMENT

Samples of $Y_{1-x}Pr_xBa_2Cu_3O_7$ where $x = 0.0$, 0.2, 0.4, 0.6, and 0.8, were prepared as follows. High purity Y_2O_3, CuO, and Pr_6O_{11} powders were fired separately in flowing oxygen gas at 700 °C for 2 h. The resulting powders were mixed with 99.9% pure BaO powder in stoichiometric ratio and ground thoroughly. The mixed powders were pressed into pellets under 28 MPa pressure and heated to 950 °C for 42 h in air, then cooled to 750 °C in the furnace, and annealed 24 h in flowing oxygen. The samples were then cooled in the furnace to room temperature in

about 7 h. The resultant pellets were reground thorough-ly and the forementioned procedure was repeated. Long reaction time at high temperature and thorough grinding appears to be essential in achieving single-phase sam-ples.[15] All the samples were prepared at the same time in the same furnace to ensure the same sample history. The cross contamination of Pr and Y atoms between $YBa_2Cu_3O_{7-y}$ and $PrBa_2Cu_3O_{7-y}$ samples determined by atomic emission method was less than 0.02 Wt %. Powder x-ray-diffraction patterns showed that all the samples were single phase with orthorhombic structure. The measured lattice parameters were in agreement with previous results.[16] Impurity phases detected were less than 3 mol % in total. Electric resistivity measurements and field-cooled magnetization measurements showed sin-gle transition temperatures with rather narrow transition widths for the superconducting samples supporting the view that all the superconducting samples were single phase. The transition temperatures T_c determined by the midpoints of the resistivity data and the 10–90% resis-tivity transition widths ΔT_c were $T_c = 91.5$ K, $\Delta T_c = 1.5$ K for $x = 0.0$; $T_c = 71.4$ K, $\Delta T_c = 3.2$ K for $x = 0.2$; and $T_c = 41.3$ K, $\Delta T_c = 6.2$ K for $x = 0.4$. The exact values for oxygen contents of $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds were measured, after XPS measurements, by iodometric titration technique and determined to be 6.90 ± 0.03 for $x = 0.0$ and 6.87 ± 0.03 for $x = 0.8$. This is in agreement with the previous studies[1,11] which show that substitution of Y by Pr in $YBa_2Cu_3O_{7-y}$ does not affect oxygen con-tent significantly. The oxygen-deficient $YBa_2Cu_3O_{7-y}$ ($y = 0.15, 0.40$) samples were prepared by annealing our best $YBa_2Cu_3O_{7-y}$ samples (nominally $y = 0$) at 500 °C in a flowing He atmosphere for 1–6 h and cooling in He to 100 °C in about 5 h. The value of y was determined by weight loss.

Photoemission measurements on Pr-doped samples were done in a VG ESCALAB MK II system with a monochromatic Al-$K\alpha$ source, at room temperature with a pass energy of 20 eV. The background pressure of the spectrometer was 7×10^{-10} torr. All the Pr-doped sam-ples were scraped in situ at room temperature using a tungsten knife immediately before the photoemission measurements. Scraping was repeated until no further change was observed in C 1s intensity at the carbonate binding energy (≈ 289 eV). The oxygen-deficient samples were measured in a similar system with a liquid nitrogen cooling capability. These samples were scraped and mea-sured at $T \approx 130$ K in a background pressure of 5×10^{-11} torr. In this case, we used a nonmonochromatic Al source.

RESULTS

The XPS spectra from our samples did not exhibit significant differences with respect to one another, with the exception of the Ba lines, which experienced an ener-gy shift towards higher binding energies correlated with increasing Pr concentration. Changes in the Cu $2p$ spec-tra were also observed, but they could be interpreted as arising from superposition with the Pr $3d$ lines. This is in contrast with previous work.[13] The discrepancy can be
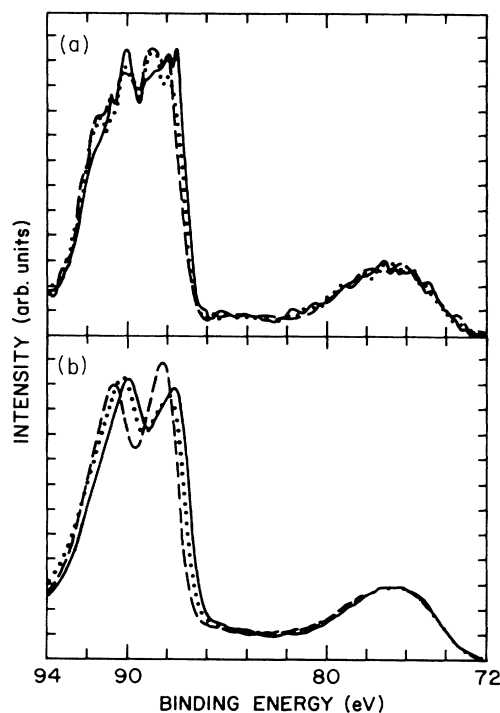

FIG. 1. XPS spectra of Ba $4d$ including the Cu $3p$ line (≈ 77 eV). The spectra are normalized to the intensity of the Cu $3p$ line. (a) The solid, dotted, and dashed curves are for $x = 0.0, 0.2$, and 0.8 in $Y_{1-x}Pr_xBa_2Cu_3O_7$, respectively. (b) The solid, dot-ted, and dashed curves are for $y = 0.0, 0.15$, and 0.40 in $YBa_2Cu_3O_{7-y}$, respectively. Note the shift of the low binding-energy feature of Ba $4d$ spectra and no shift in Cu $3p$ spectra.

related to the presence of extra phases and will be dis-cussed later. Figure 1(a) shows the Ba $4d$ and Cu $3p$ XPS peaks for various Pr concentrations. The spectrum of the solid curve, for $x = 0$, is similar to those typically ob-tained from scraped 1:2:3 surfaces.[17,18] The low binding-energy excursion of the Ba $4d$ line shape is gen-erally attributed to the $4d_{5/2}$ component intrinsic to 1:2:3. The higher binding-energy peak at ≈ 90 eV arises from both the $4d_{3/2}$ component of the signal from 1:2:3 and the $4d_{5/2}$ component from Ba in $BaCO_3$.[17] These spectra exhibit more than two peaks. The extra features were observed to change after each scraping procedure and they probably arise from damage induced by scrap-ing at room temperature.[18] The dotted curve in Fig. 1(a) corresponds to a Pr concentration of $x = 0.2$ with $T_c = 71.4$ K. In this curve, the Ba $4d$ lines appear at higher binding energies than those of the solid curve, whereas the Cu $3p$ line remains unchanged. This energy shift increases gradually with increasing Pr concentration up to $x = 0.8$ [dashed curve in Fig. 1(a)]. Although it is not shown in any of the figures, a similar effect is also ob-served in the Ba $3d$ lines. Figure 1(b) shows equivalent spectra corresponding to oxygen-deficient samples. The solid curve corresponds to a nominal oxygen concentra-tion of 7. Notice that the position of the Ba leading edge is the same as in the solid curve of Fig. 1(a). The dotted and dashed curves in Fig. 1(b) correspond to nominal ox-

ygen concentrations of 6.85 and 6.60, respectively. A shift in the Ba lines is also observed in this case as oxygen becomes more deficient. In this regime, the samples are still superconducting. The change in the relative intensity of the two Ba $4d$ peaks in Fig. 1(b) arises from decomposition of the interfacial carbonate during annealing in He atmosphere.[19] These spectra do not exhibit significant effect due to scrape damage since, in this case, scraping was done at low temperature. For oxygen concentrations less than 6.5, all XPS lines shift to higher binding energy, in coincidence with the transition into the tetragonal phase and the semiconducting character.[20] The latter is beyond the scope of this paper and will not be discussed further. This shift of the Ba lines with oxygen deficiency has been discussed before, and has been attributed to final-state effects, namely a decrease in screening resulting from a lower oxygen coordination.[21] In contrast, we believe that the similarities between the evolution of the XPS spectra in both cases; increasing Pr, and decreasing O concentration, reflect a change of the Ba-O overlap in the initial state to be discussed in the next section.

In the remaining part of this section we will consider effects that arise from contamination and compare our results with that of previous work.[13] No rigid shift of various spectra was observed within the period of the measurements even for the $Y_{1-x}Pr_xBa_2Cu_3O_7$, $x=0.8$ samples, indicating no charge effects. The Y $3d$ and O $1s$ spectra (Fig. 2) do not change as x varies and they are

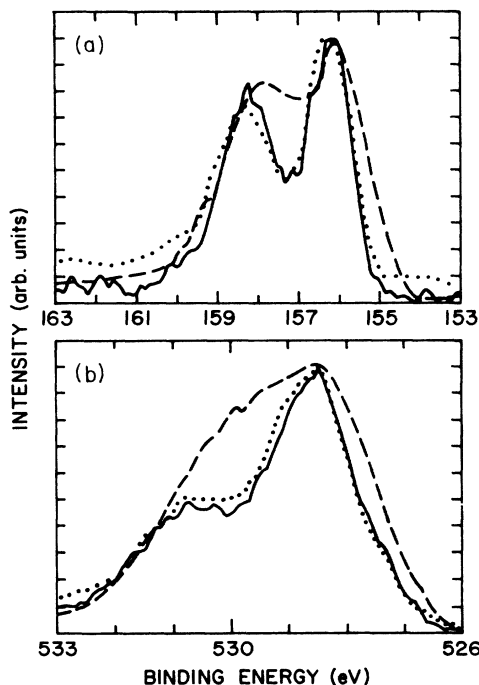FIG. 2. XPS spectra of Y $3d$ (a) and O $1s$ (b) regions. The solid curves are for $x=0.0$, and dotted curves are for $x=0.8$ in $Y_{1-x}Pr_xBa_2Cu_3O_7$. No change was discernible in Y $3d$ and O $1s$ spectra for all Pr concentrations. The dashed curves, shown for comparison, are obtained from our contaminated samples ($x=0.0$). These samples were prepared in a furnace contaminated with Nd, Eu, and other rare-earth elements.

similar to those obtained earlier.[22] The Y $3d_{5/2}$ and Y $3d_{3/2}$ peaks are relatively well resolved for our samples. It is interesting to note that the Y $3d$ peaks which we obtained from samples contaminated with Nd, Eu, and other rare-earth elements are not well resolved and they look similar to Y $3d$ peaks reported in Ref. 13. The O $1s$ core-level spectra are composed of a dominant peak at 528.5 eV and a weak peak at 530.9 eV. It is well accepted that the low binding-energy feature is intrinsic to the 1:2:3 structure and the high binding-energy feature is mainly due to the presence of carbonates and hydroxides. The O $1s$ spectra obtained from the contaminated samples show a relatively strong intensity at ≈ 530 eV.

DISCUSSION

As noted in the previous section, low binding-energy edges of Ba $3d$ and $4d$ core-level spectra shift to higher binding energies as x increases in $Y_{1-x}Pr_xBa_2Cu_3O_7$, and as y increases in $YBa_2Cu_3O_{7-y}$ ($0 \leq y \leq 0.4$) samples. Ba is known to exhibit anomalous binding-energy shifts in the XPS spectra when comparing the metallic with the oxidized state.[23] Namely, the binding energy of the Ba lines is lower in the oxides, contrary to what it is expected from charge transfer. Since metallic screening is more efficient than that due to polarization,[24] this anomaly probably has initial-state character. Wertheim[23] has suggested that while the $5d$ band in metallic Ba is almost empty, Ba $5d$ states play a significant role in the bonding of Ba compounds. A partial occupation of $5d$ orbitals, with smaller radial extent than the $6s$ ones, may have a strong effect in decreasing the observed binding energies. Thus the anomalous core-electron shifts are consistent with a significant initial-state Ba $5d$-O $2p$ electron covalency, which transfers charge from extended to localized orbitals in the formation of the compound. The binding energy of the Ba core lines in stoichiometric 1:2:3 superconducting oxides are lower than those observed in other Ba oxides, and it probably reflects the distinct oxygen coordination at the Ba sites in the 1:2:3 lattice. In particular, the Ba-O(4), the nearest-neighbor oxygen (Fig. 3), distance in the 1:2:3 lattice is shorter than that of BaO. We notice that in the Pr doped 1:2:3 samples,[1,10,16] as well as in the oxygen-deficient ones,[20] a lattice distortion occurs as the Pr (O) content increases (decreases), resulting in an increase in the Ba-O(4) bond length, and bond symmetry. This change is very likely to affect the Ba $5d$-O $2p$ overlap discussed above, and may shift charge from the localized $5d$ orbitals into extended ones, resulting in an effective hole localization at the Ba site. According to Wertheim this certainly would have a significant effect in increasing the binding energies of the Ba core lines. Figures 4(a) and 4(b) show the magnitude of Ba $3d_{5/2}$ and Ba $4d_{5/2}$ peak shift versus Pr (O) concentration (deficiency), respectively. Thus, we believe that the observed energy shifts result from changes in the initial-state Ba $5d$-O $2p$ covalency arising from lattice distortions occurring as a consequence of Pr (O) doping (deficiency). In principle, this binding-energy shift only constitutes a sensitive fingerprint of the Ba-O overlap, mainly that associated with the Ba–NN-O, namely the
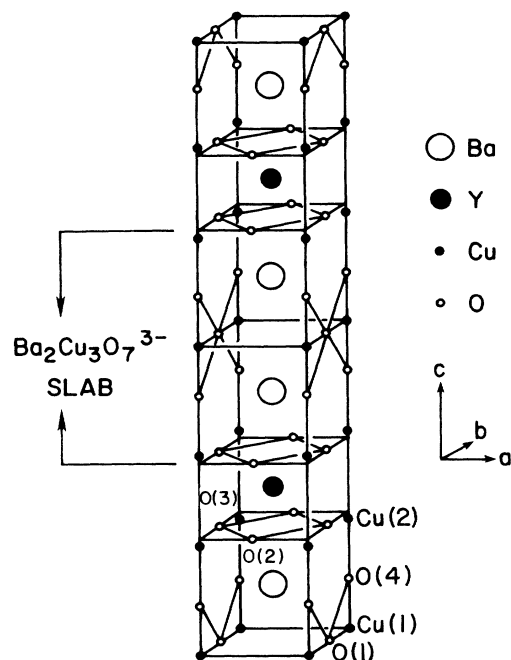
FIG. 3. 1:2:3 structure reproduced from Ref. 27. Pr replaces Y in Pr-doped 1:2:3 samples.

apical oxygen O(4) in 1:2:3. However, due to the nature of the charge transfer, it might also shed light on the mechanisms of high T_c superconductivity, in particular, the importance of the apical oxygen in the coherence length perpendicular to the CuO_2 planes.

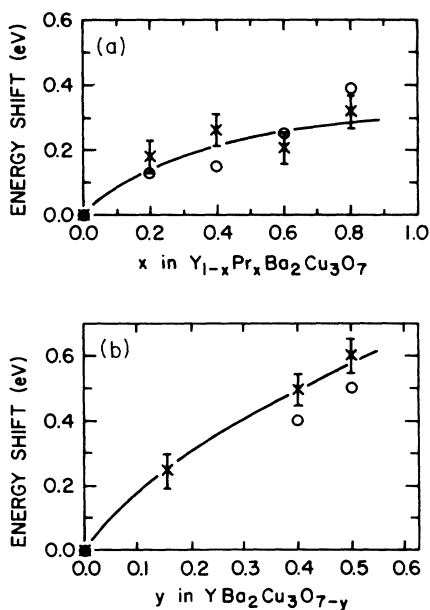FIG. 4. The shift of the low binding-energy feature of Ba $3d_{5/2}$ (O) and Ba $4d_{5/2}$ (X) spectra towards higher binding energy [Figs. 4(a) and 4(b)] as functions of x,y in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$, respectively. The lines are to guide the eye. The shift for $y=0.5$ in (b) is included although, for this value of y, the sample exhibits charging effects.

This interpretation is consistent with the following observations. The lattice parameters increase as x increases in $Y_{1-x}Pr_xBa_2Cu_3O_7$.[1,10,16] Similar behavior was observed for $YBa_2Cu_3O_{7-y}$ as y increases.[20] The Ba core-level spectra of $YBa_2Cu_3O_{7-y}$ compounds shift to higher binding energy as y increases, as they do in $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds as x increases. In contrast, the explanation based on the final-state effects[21] is not consistent with the following; the lost oxygen in the Cu-O chain is not the nearest neighbor to Ba atoms in the 1:2:3 structure, $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples do not lose any oxygen, yet they show a similar Ba-peak shift.

Neumeier et al.[11] observed that T_c of $Y_{1-x}Pr_xBa_2Cu_3O_7$ increases as pressure increases for $0 \leq x \leq 0.2$, and the initial rate of increase of T_c with pressure, $(dT_c/dP)_{P=0}$, increases with x for $0 \leq x \leq 0.3$, reaching 0.32 K/kbar for $x=0.3$. We would like to point out that this pressure effect is remarkably similar to that of oxygen-deficient $EuBa_2Cu_3O_{7-y}$ samples.[25] Namely, T_c increases as pressure is applied at a rate of 0.9 K/kbar in the oxygen-deficient $EuBa_2Cu_3O_{7-y}$. This is much larger than the corresponding rate of 0.1 K/kbar in the fully-oxygenated $EuBa_2Cu_3O_{7-y}$. Essentially the same pressure effect was observed for $YBa_2Cu_3O_{7-y}$ compounds,[26] that is, the pressure coefficient is larger for the oxygen-deficient $YBa_2Cu_3O_{7-y}$ samples than for the fully-oxygenated ($y=0.0$) ones.

We believe that all these similar behaviors between $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds and the oxygen-deficient $YBa_2Cu_3O_{7-y}$ compounds are related to the common mechanism of suppression of superconductivity in these compounds, namely, the Ba-O hybridization dependence on the distance between Ba and its close oxygen neighbors, where the apical oxygen O(4) is the closest neighbor. An increase of lattice constants or an increase of Ba-O distances as well as lattice distortion may affect the Ba-O hybridization in such a way that holes in the conduction bands flow into Ba $5d$ orbitals, which are energetically close to the Fermi energy.[23] This could be reversible for small values of x in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and small values of y in $YBa_2Cu_3O_{7-y}$. That is, as the Ba-O distances become shorter, the holes trapped at Ba sites are delocalized into the conduction bands, resulting in the increase in T_c of these compounds. This, we believe, is seen by the larger values of $dT_c/dP_{P=0}$ for larger values of x in $Y_{1-x}Pr_xBa_2Cu_3O_7$ (Ref. 11) and for larger values of y in $YBa_2Cu_3O_{7-y}$.[26]

From the empirical atom-atom potential calculations, Whangbo et al.[27] suggest that the interaction between the CuO_2 planes in each $Ba_2Cu_3O_{7-y}{}^{3-}$ slab through Cu(2)-O(4)-Cu(1)-O(4)-Cu(2) linkages (Fig. 3) is essential for the superconductivity in $YBa_2Cu_3O_{7-y}$. They show that slight displacement (~ 0.04 Å) of O(4) atoms crucially affects the calculated valence-band structure and the interaction between the CuO_2 planes.[28] Whether it be the position of O(4) or the charge state of O(4) that matters for the superconductivity, O(4) seems to plan an important role in determining the superconducting states.

Other explanations for the quenching of superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds have been pro-

posed; for example, the magnetic pair-breaking mechanism[1,2,10] because the T_c versus Pr concentration curve fits well with magnetic pair-breaking theory,[9] and because the upper critical field versus temperature curves are bell shaped for Pr concentration $x \geq 0.3$. However, it is not explained why only Pr would suppress superconductivity in $(R)Ba_2Cu_3O_{7-y}$ structure, where R designates rare-earth elements, while other rare-earth elements, some of which have higher magnetic moment, do not. In addition, within the magnetic pair-breaking theory, it is hard to explain the increase of the resistivity, its nonmetallic temperature dependence, and finally, the destruction of the metallic state as Pr concentration increases.

The possibility of the Pr valence being 4+ has been postulated, thus there would be no free carriers to form metallic and superconducting phases. Magnetic susceptibility measurements[1-4] show much reduced values of the effective Bohr magneton compared to that of the free Pr^{3+} ion. In fact, the values are close to that of the free Pr^{4+} ion, indicating that the Pr valence is close to 4+. However, the relatively small effective magnetic moments may result from a strong crystalline electric field which partially lifts the degeneracy of the Pr ion ground state. Photoemission,[5] x-ray absorption measurements,[6,7] Raman studies,[29] and structural measurements[3,8] indicate that the Pr valence is closer to 3+. These seemingly contradicting results can be explained if one assumes a strong hybridization of Pr $4f$ levels with Cu-O valence states.[3,4] Kang et al.[5] inferred a strong hybridization of Pr $4f$ with other valence-band states from the shape of their "extracted" Pr $4f$ spectral weight. Anomalous behavior of the low temperature specific heat of $PrBa_2Cu_3O_{7-y}$ also indicates the possibility of the Pr $4f$ valence-band state hybridization.[12] Neumeier et al.[11]

found that T_c of $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds decreases rapidly with hydrostatic pressure to 20 kbar for $x \geq 0.4$, which they associated with the increase in the degree of hybridization between Pr $4f$ and valence-band states as pressure is applied. Although plausible, this argument does not provide a full explanation for the opposite behavior of $(dT_c/dP)_{P=0}$, the initial rate of increase of T_c with applied pressure, for low and high Pr concentration samples.[11]

Our arguments relate our XPS data and other existing results with the suppression of high-temperature superconductivity in a consistent manner. However, it is possible that the observed Ba-peak shifts are only a consequence of changes in lattice parameters, and not related to the suppression of superconductivity in these compounds. Moreover, as mentioned by several authors,[1,11] more than one mechanism could be responsible for the suppression of superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds. Additional experiments, such as x-ray absorption measurements at the Ba $4p_{3/2}$ edge, which may be sensitive to changes in the Ba $5d$ occupancy, would be informative.

In summary, we measured the XPS of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$ compounds, and observed the intrinsic Ba core-level spectra shift to higher binding energy as x and y increase. We interpret this as that portion of conduction holes are localized at Ba sites, which may lead to the suppression of superconductivity in these compounds.

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