Valence states of praseodymium in Y-Ba-Cu oxides studied by x-ray-photoelectron spectroscopy

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Pr $3d$ and $4d$ core levels have been studied for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and $PrBa_2Cu_3O_7$ using x-ray-photoelectron spectroscopy to elucidate the valence states. The features of Pr $3d$ and $4d$ are close to those for Pr_2O_3 for both compounds, while they are different from those for Pr_6O_{11}. It is concluded that praseodymium is almost trivalent with a $4f^2$ configuration.

The superconducting transition temperature (T_c) for $Y_{1-x}Pr_xBa_2Cu_4O_7$ (Refs. 1–5) and $Y_{1-x}Pr_xBa_2Cu_4O_8$ (Ref. 6) decreases with x, which is potentially a very interesting phenomenon in relation to understanding the mechanisms of high-T_c superconductivity. It was suggested that, as x increased, holes in the Cu-O_2 planes would be filled by the substitution of tetravalent Pr for the trivalent Y. Most of the works to date on this problem have centered around the examination of the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system,[1–5,7–11] although magnetic-susceptibility data have been obtained for the $Y_{1-x}Pr_xBa_2Cu_4O_8$ system.[6] In general, magnetic-susceptibility[2–6] and Hall-coefficient measurements[2] have suggested Pr valences greater than +3: The effective magnetic moment derived from the analysis of the magnetic susceptibility is intermediate between the free-ion effective moment of Pr^{3+} and Pr^{4+} for the former data and the hole concentration decreases with x for the latter. On the other hand, high-energy spectroscopy measurements have led to a contradictory result: both x-ray-absorption spectroscopy[7] (XAS) and resonant photoemission[8] studies have indicated a praseodymium valence close to +3. Electron-energy-loss spectroscopy[9] (EELS) and XAS (Ref. 10) results on the O $1s$ absorption edge have also showed that the hole states are not filled by the Pr doping. Lattice constant measurements[6,11] also suggested trivalent Pr. These results preclude any possibility of a simple hole-filling model due to a valence of +4 or any value between +3 and +4 for Pr. Hybridization between the Pr $4f$ and the Cu-O_2 valence band as associated with the localization of mobile holes has also, however, been suggested[7–10] to explain the data such as we described above.

Although x-ray-photoelectron spectroscopy (XPS) is a powerful tool for the determination of the valence of ions, extensive overlap between the Pr $3d$ (a major line of the Pr core level) and the Cu $2p$ levels has made us hesitate in applying the technique for studying the Pr valence in

these materials. Here we present the Pr $3d$ and $4d$ core-level photoelectron spectra for the Pr-doped Y-Ba-Cu oxides $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and $PrBa_2Cu_3O_7$. From the results, the valence states of Pr in these materials will be discussed.

$Y_{1-x}Pr_xBa_2Cu_4O_8$ ($x=0$ and 0.6) was sintered in an oxygen atmosphere at 33 atm by heating the ground materials to 930 °C for 24 h and then repeating the process.[6] $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x=0$ and 1) was prepared by solid-state reaction in an O_2 stream (at 1 atm) at 950 °C after four repetitions of heating at 920–950 °C in air and grinding. $YBa_2Cu_4O_8$, $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$, and $YBa_2Cu_3O_7$ are superconductors with T_c of 80, 44, and 91 K, respectively, while $PrBa_2Cu_3O_7$ has a semiconducting-like temperature dependence of the resistivity. X-ray powder diffraction patterns obtained for the different specimens showed that they were single phase except for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$, which contained a small amount of $BaCuO_2$. This would not affect the Pr core-level spectra for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ since Pr is not present in the secondary phase, and the Pr content of the material is only likely to be marginally bigger than the value assumed.

XPS spectra were taken using a SSX-100 electron analyzer (Surface Science Instrument) with a monochromatized Al $K\alpha$ source with a diameter of 300 μm under a vacuum condition better than 1.0×10^{-9} Torr. The energy resolution of the apparatus is about 0.45 eV as estimated from the form of the Fermi edge seen for pure Ni. The sample surfaces were cleaned by scraping them with a diamond file under UHV conditions ($<2.0 \times 10^{-9}$ Torr).

Figures 1(a) and 1(b) show XPS spectra in the range from 920 to 970 eV in binding energy for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and for $YBa_2Cu_4O_8$, respectively. Both spectra exhibit the Cu $2p$ lines, but it is in Fig. 1(a) that we can also see the Pr $3d$ lines, though they are only clear at the low-binding-energy side (marked by an ar-

row) of the Cu $2p_{3/2}$ main line $(M, 3d^{10}\underline{L}$ final state, where $\underline{L}$ denotes a ligand hole) at about 934 eV. In order to clarify the shape of the Pr $3d$ line, the Cu $2p$ spectra for $x=0$ [as in spectrum in Fig. 1(b)] were subtracted from those for the Pr-doped materials. This was done in such a way that the intensity of the Cu $2p_{1/2}$ satellite line ($\sim$962 eV) was satisfactorily canceled, because the region does not include the Pr $3d$ lines. The spectra thus obtained for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and for $PrBa_2Cu_3O_7$ are shown in the digitized form in Figs. 1(c) and 1(d), respectively. The superposed line spectra represent Pr $3d$, which were obtained for Pr_2O_3. The line shapes of the extracted Pr $3d$ spectra are very close to that for Pr_2O_3 and show marked difference from the spectra obtained for Pr_6O_{11} [Fig. 1(e)]. Furthermore, there is no clear peak corresponding to a $4f^1$ final state ($\sim$967 eV for Pr $3d_{3/2}$) in either spectrum shown in Fig. 1(c) or 1(d) as would be apparent if the bonding in $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and $PrBa_2Cu_3O_7$ for Pr had Pr^{4+} characteristics.[12] This and other characteristics of the extracted spectra, when compared with those for the Pr^{4+} state [Fig. 1(e)] and the
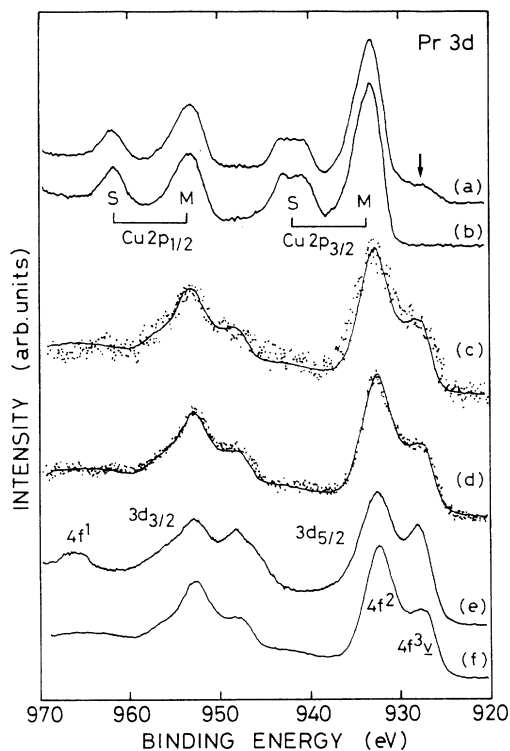

FIG. 1. (a) Pr $3d$ spectrum for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ in which Cu $2p$ and Pr $3d$ lines are superposed. A visible Pr $3d_{5/2}$ feature is shown by an arrow. (b) Cu $2p$ spectra for $YBa_2Cu_4O_8$. M and S mark the main ($3d^{10}\underline{L}$ final state) and satellite lines ($3d^9$ final state), respectively. (c) Pr $3d$ spectrum in the digitized form for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ as extracted after subtraction of (b) from (a). (d) Pr $3d$ spectrum in the digitized form for $PrBa_2Cu_3O_7$ as extracted [as the same way as for (c)]. The superposed line in (c) and (d) shows the Pr $3d$ spectrum for Pr_2O_3. (e) Pr $3d$ spectrum for Pr_6O_{11}. (f) Pr $3d$ spectrum for Pr_2O_3. $4f^1$, $4f^2$, and $4f^3\underline{v}$ denote final-state configurations as discussed in the text.

Pr^{3+} state [Fig. 1(f)], indicate unequivocally that the Pr is in the $3+$ state in the compounds of interest.

The Pr $4d$ spectra for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and for $PrBa_2Cu_3O_7$ are shown in the digitized form along with Pr_6O_{11} [Fig. 1(c)] and Pr_2O_3 [Fig. 1(d)], where the spectra shown in Figs. 1(a) and 1(b) can be compared with the line spectra of Pr $4d$ obtained for Pr_2O_3. Although the Cu $3s$ line at about 123 eV is superimposed on the high-binding-energy side of Pr $4d$, the shape of the low-binding-energy side of the Pr $4d$ lines for the spectra shown in Figs. 1(a) and 1(b) is very similar to that for Pr_2O_3, and very different from that for Pr_6O_{11}. The match for both materials is again indicative of the $3+$ state for Pr. No peaks corresponding to the $4f^1$ final state at about 127 eV are found, which further confirms the lack of any $4+$ tendency.

The Pr $3d$ core-level spectra have been calculated both for Pr_2O_3 ($3+$) (Ref. 13) and for PrO_2 ($4+$) (Ref. 12) using the Anderson impurity model and the results are in good agreement with experimental data. The theory suggests[12,13] that for Pr^{3+} the ground state has almost a single $4f^2$ configuration, whereas for Pr^{4+} the ground state exhibits mixing between $4f^1$ and $4f^2\underline{v}$, where $\underline{v}$ denotes a hole at the valence band. Bearing this in mind, it will be remembered that our results demonstrate that the Pr $3d$ and $4d$ spectra obtained for the Pr-doped cuprates and for Pr_2O_3 are indistinguishable. Accordingly, it would appear that the ground state of Pr in these cuprates has an essentially $4f^2$ configuration. We can be clear that a Pr valence greater than $3+$ is precluded for these materials, which thus in turn indicates that there is no charge transfer from Pr to the Cu-O_2 planes. The result is in good agreement with other high-energy spectroscopic studies.[7-10]

It is well known that the surface of $YBa_2Cu_3O_7$ is degraded at room temperature, even by *in situ* scraping due to oxygen loss.[14] It might be thought that Pr is found in the $3+$ state for $PrBa_2Cu_3O_7$ because of the reduction of Pr from the $4+$ or an intermediate state when oxygens are lost from the surface layer probed by XPS. However, we have shown that the Pr $3d$ and $4d$ spectra for $PrBa_2Cu_3O_7$ are essentially the same as those for the Pr-doped $YBa_2Cu_4O_8$. This shows that the trivalency of Pr, as indicated by our XPS results, is an intrinsic feature of the Pr-doped Y-Ba-Cu oxides because the scraped surface of $YBa_2Cu_4O_8$ is stable even at room temperature and under UHV conditions.[15]

For Pr^{3+} it has been shown[13,16] that the final state of Pr core-level photoemission is a mixture of the $4f^2$ and $4f^3\underline{v}$ states [spectrum (f) in Fig. 1]. This is because the charge-transfer energy between the $4f$ and valence-band states is comparable to their hybridization energy. In our data we see that the energy separation and relative intensities of the $4f^2$ and $4f^3\underline{v}$ states for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and for $PrBa_2Cu_3O_7$ are again indistinguishable from these features for Pr_2O_3 (see Fig. 1). Accordingly, it would seem that the hybridization between the Pr $4f$ and valence-band states in the cuprates is the same as it is for Pr_2O_3. Indeed, our XPS measurements showed that the width of valence band for the Y-Ba-Cu oxides (5.1–5.4
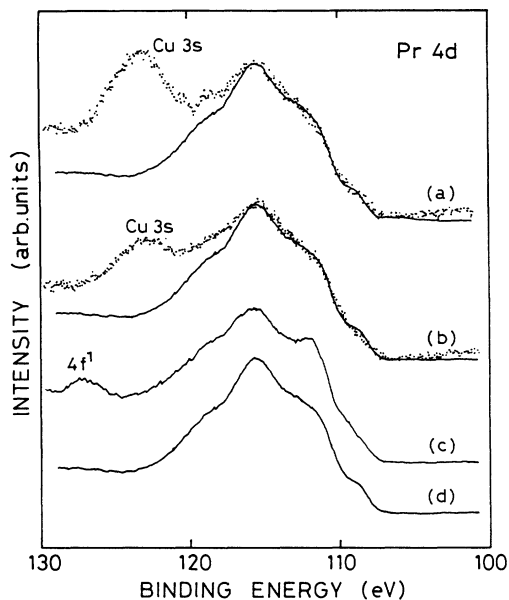
FIG. 2. Pr $4d$ spectra for (a) $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and (b) $PrBa_2Cu_4O_7$ shown digitally. The Cu $3s$ line appears at about 123 eV in both spectra (a) and (b). The lines in (a) and (b) are the Pr $4d$ spectrum for Pr_2O_3. Pr $4d$ spectra for Pr_6O_{11} and Pr_2O_3 are shown in (c) and (d), respectively, and the peak for the $4f^1$ (characteristic of Pr^{4+}) is marked in (c).

eV) is very similar to that for Pr_2O_3 (~ 5.5 eV). Ikeda et al.[16] have carried out a systematic analysis of experimental $3d$ XPS spectra for a number of rare-earth oxides and showed that it is especially for La_2O_3, Ce_2O_3, Pr_2O_3, and Nd_2O_3, the rare-earth trivalent oxides, that the final-state hybridization effects are important. This is because of the decrease in the charge-transfer energy due to the

$3d$ core-hole potential and the relatively strong hybridization between the $4f$ and the valence-band states. It is plausible that the latter hybridization suppresses superconductivity (as has been previously suggested[7-10]), because the hybridization between the $4f$ states and the Cu-O_2 states would be expected since the Y/Pr layers have no oxygen atoms in them and are located between the double Cu-O_2 planes. It might be possible, for example, that trivalent Ce, Pr, and Nd ions could all localize mobile holes in the Cu-O_2 plane due to the $4f$-electron$-2p$-hole coupling through strong hybridization of this type. It might be also possible that this hybridization causes magnetic pair-breaking.

It is interesting in relation to our work that the superconducting properties of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $Y_{1-x}Pr_xBa_2Cu_4O_8$ are different.[6] The critical Pr content (x_c), at which superconductivity disappears, is 0.6 for the former material[1-5] and 0.9 for the latter.[6] Our result indicates that the valence state of praseodymium is essentially the same in these two systems. The origin of the difference in x_c thus remains open to question. Further experimental and theoretical studies will be needed to solve the problem.

In summary, we have presented Pr $3d$ and $4d$ core-level photoelectron spectra for $Y_{0.4}Pr_{0.6}Ba_2Cu_4O_8$ and $PrBa_2Cu_3O_7$. The line shapes of the Pr $3d$ and $4d$ spectra can be interpreted consistently on the basis that praseodymium is trivalent with a $4f^2$ configuration.

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