

## High-temperature superconductivity in the presence of O 2*p*-Cu 3*d* holes: A spectroscopic study

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We report core-level spectroscopic measurements of several cuprate perovskites comparing those which exhibit superconductivity above 90 K to others which do not. Both x-ray photoemission and x-ray absorption results show that in the former Cu is more oxidized, as in CuO (nominally Cu<sup>2+</sup>), than in the latter. Trivalent Cu is clearly excluded. The O 1*s* core level is at higher binding energy in the superconductors, implying the presence of O 2*p* holes. The rare-earth valence in Ce- and Pr-based perovskites is more than 3+, apparently related to their failure to superconduct.

Superconductivity has been observed at increasingly high temperatures in a number of cuprate perovskites, most recently with the generic formula  $R\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ , in which  $R$  may be Y or most rare earths.<sup>1</sup> In spite of intense investigations of these materials, the basic origin of the superconductivity remains controversial. We describe new core-level measurements using x-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) which show there are clear differences between the electronic properties of perovskites which superconduct and others which do not. In the former, the Cu is nominally divalent Cu<sup>2+</sup> as in CuO, and the oxygen is incompletely reduced; O 2*p* holes are present. Moreover, in the only two rare-earth-based cuprate perovskites, Ce and Pr, which do not exhibit superconductivity, the valence of the rare-earth ion is higher than three. These results imply an overall electronic charge shortage in the perovskite superconductors, consistent with theories based on hole conductivity; see, e.g., Ref. 2.

In this work, we used samples prepared at three different laboratories (New York University, Rutgers, and Los Alamos National Laboratory) using techniques by now well documented in the literature.<sup>3</sup> Stoichiometric ratios of oxide powders of the desired materials were ground, pressed into pellets, and heated at about 900°C in flowing oxygen gas for three to five periods of several hours each, between which they were repowdered. Two different samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  were prepared. Sample *A* was cooled slowly from 900°C and exhibited superconductivity (bulk Meissner effect) at 93 K, while sample *B* was rapidly quenched from the same temperature, a procedure known to cause a larger oxygen deficiency and suppress superconductivity.<sup>4</sup> Samples using slow cooling were made with Yb, Ce, and Pr substituted for the Y. The Yb-based samples superconducted (bulk Meissner effect<sup>5</sup>) at about 88 K, while the Ce- and Pr-based samples did not, in agreement with other work.<sup>6</sup>

X-ray diffraction patterns showed all samples were single phase with the superconductors in the well-known orthorhombic unit cell, while the Pr was tetragonal within the resolution of our diffractometer (Philips PW 1840). All spectroscopic measurements reported here were at room temperature.

Photoemission measurements were made in a standard ultrahigh vacuum system with a base pressure below  $10^{-10}$  Torr after baking to 150°C. Spectra were taken with a typical overall energy resolution of 1.5 eV using Mg and Al  $K\alpha$  radiation and a VSW 100-mm hemispherical analyzer. Sample pellets were measured before and after scraping with an Al<sub>2</sub>O<sub>3</sub> file. No charging effects or spectral changes were observed in exposures to the x-ray beam of up to several hours. In our spectra, an integral background has been removed but the  $\alpha_{3,4}$  satellites have not. For XAS, under N<sub>2</sub> gas the samples were powdered and sealed in Kapton tape before exposure to the x-ray beam. XAS measurements were made in transmission on beam line C1 of the Cornell High Energy Synchrotron Source (CHESS) using a dual Si(111) crystal monochromator calibrated on the Cu  $K$  edge and with a typical energy resolution of about 3 eV. XAS absorption coefficients are normalized to the edge jump and plotted relative to the relevant energy zero,<sup>7</sup> i.e., the Cu 1*s* (8979 eV) and the 2*p*<sub>3/2</sub> of Ce (5723 eV), Pr (5964 eV), and Yb (8944 eV).

In Fig. 1(a) we show XPS Cu 2*p* core levels. The spectrum of unscraped sample *A* exhibits two peaks, corresponding to the Cu 2*p*<sub>3/2</sub> and 2*p*<sub>1/2</sub> levels. The peaks are sharp and essentially resolution limited. All samples measured before scraping are virtually identical to this. The spectrum closely resembles cuprous oxide (Cu<sub>2</sub>O) in both binding energy and peak width.<sup>8</sup> Previous work<sup>9</sup> has shown that higher copper oxides such as CuO heated above 250°C decompose to Cu<sub>2</sub>O under vacuum. After scraping off the surface layer the Cu 2*p* peaks in sample *B*

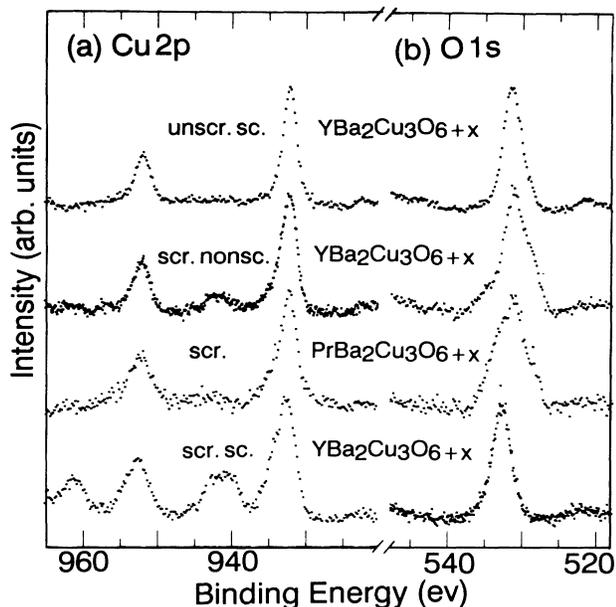


FIG. 1. X-ray photoemission spectra vs binding energy showing (top to bottom) the unscraped surface of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  and scraped nonsuperconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ,  $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ , and superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . (a) Cu  $2p$  core levels. (b) O  $1s$  core levels.

and the Pr perovskite [Fig. 1(a)] remain at essentially the same energy, with the same intensity and width, although there are now weak satellites at higher binding energy. The small high binding energy shoulders visible for the Pr-based sample are the Pr  $3d$ 's. Sample *A* after scraping differs dramatically from all the others, having large shake-up satellites some 10 eV above the two main peaks which are broadened and shifted. This spectrum is similar to that obtained in Ref. 10 and resembles cupric oxide ( $\text{CuO}$ ); differences between it and the others are similar to, but less than, differences between  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , namely, (i) a chemical shift to higher binding energy of 0.7 eV, compared to 1.0–1.2 eV between the two oxides; (ii) a broadening of about 3.5 eV, compared to the 4.0 eV of  $\text{CuO}$ , attributed to multiplet splitting;<sup>11</sup> and (iii) a satellite ascribed to charge transfer from neighboring oxygen ligands to the unfilled Cu  $3d$  shell.<sup>12</sup> The multiplet splitting and charge transfer can occur in  $\text{CuO}$ , in which the nominally divalent Cu is in a  $d^9$  configuration, but not in  $\text{Cu}_2\text{O}$ , where Cu (1+) has a filled ( $d^{10}$ ) shell. Points (i) through (iii) imply that in the superconductor the Cu valence is close to, although slightly less than, the nominally 2+ value of  $\text{CuO}$  while in the nonsuperconductors it is less, more like  $\text{Cu}_2\text{O}$ . The fact that observed differences (i) and (ii) are less than for  $\text{CuO}$  vs  $\text{Cu}_2\text{O}$  excludes the possibility of  $\text{Cu}^{3+}$ , and suggests the spectra may be a superposition of Cu in two valence states at the two dissimilar sites in the perovskite.

The O  $1s$  spectra of the same materials, plotted in Fig. 1(b), also show clear distinctions. Before scraping, all samples have identical spectra, with a single sharp resolution-limited O  $1s$  peak. In the scraped nonsuper-

conducting samples *A* and the Pr-based perovskite, the O  $1s$  peak broadens and can be decomposed into a triplet. In contrast, the superconducting sample shows a single peak at 2 to 3-eV higher binding energy, essentially at the highest binding energy member of this triplet, which is only a weak shoulder in sample *A* and larger in the Pr-based sample. Therefore, in the nonsuperconductors, oxygen is present in at least three configurations with differing charge, while in the superconductor only the state with the smallest valence charge is present. Thus the photoemission results imply the superconducting material has a higher concentration of holes in the hybridized Cu  $3d$  and O  $2p$  bands.

Y, Ba, and Pr  $3d$  core levels in unscraped and scraped samples, both superconducting and nonsuperconducting, are less interesting, and we relegate them to a later report.<sup>13</sup> In summary, these spectra indicate that there are no systematic differences between the Ba, Y, and Pr  $3d$  spectra of superconducting and nonsuperconducting samples; all resemble the corresponding oxidized element. This is expected in view of the indifference of the superconducting properties to substitution of these elements.

All measurements were repeated several times after scrapings to check for surface effects. No differences either in spectral shape or relative intensities were observed. In the unscraped samples, the only impurity observed was C, as betrayed by the C  $1s$  line, probably reflecting the presence of adsorbed CO or  $\text{CO}_2$ . Lesser amounts of C were observed on unscraped samples only after at least 20 h in UHV. After such long periods, a shoulder developed on the low binding energy side of the O  $1s$  peak in the scraped superconducting sample *A*, so that it began to resemble the unscraped surface. Simultaneously, the satellites in the Cu  $2p$  peak began to diminish. We interpret these results as reassuring indications that the scraped surface was beginning to revert to its prescraped form, developing a  $\text{Cu}_2\text{O}$  layer.

The Cu  $1s$  ( $K$ ) XAS spectra plotted in Fig. 2 are also sensitive to the Cu valence. The spectrum of the Yb-based material is distorted by an underlying contribution from the Yb  $L_{III}$  edge 40 eV below, which was reduced, but not eliminated, by subtracting an appropriately normalized spectrum of  $\text{Yb}_2\text{O}_3$ . Comparison of Cu metal to  $\text{Cu}_2\text{O}$  shows shape differences and only a small shift in edge energy, as in previous work,<sup>14</sup> which also found that divalent Cu, as for example in  $\text{CuO}$ , is shifted by about 6 eV to higher binding energy. None of the perovskites, also plotted in Fig. 2, resemble  $\text{Cu}_2\text{O}$ . All are shifted by roughly 6 eV, similar to the older La-based superconductors,<sup>14</sup> showing Cu is not far from divalent in all cases. However, relative to the Yb-based perovskite and sample *A*, the Cu  $1s$  edges of the Ce- and to a lesser extent the Pr-based (nonsuperconducting) samples are (i) shifted to lower energy, consistent with our measured  $2p$  shifts, and (ii) exhibit more intensity below the inflection point of the edge. These facts imply that in those nonsuperconductors, the Cu valence is less than in the superconductors. Therefore, reinforcing the photoemission results, the Cu is predominantly divalent in the superconductors and slightly less so in the similar nonsuperconductors. The near absence of satellites in the  $2p$  spectra of the nonsupercon-

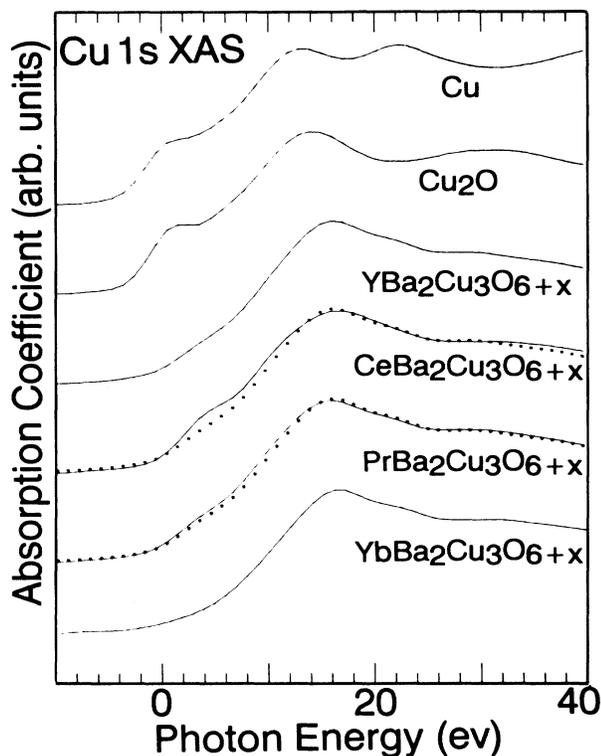


FIG. 2. X-ray absorption spectra at the Cu 1s ( $K$ ) edge in various materials. The Yb spectrum was obtained by subtracting an underlying contribution from  $\text{Yb}_2\text{O}_3$  as described in the text. To highlight differences, the spectrum of the Y-based material is dotted over the spectra of the Ce- and Pr-based materials.

ductors is usually associated with  $\text{Cu}^+$  while the XAS results imply a much smaller valence change between superconductors and nonsuperconductors; this difference may be due to the effects of dissimilar hybridization in the respective samples. It was not possible to reproduce the spectrum of the nonsuperconductors with a superposition of the  $\text{Cu}_2\text{O}$  and Y spectra, indicating that probably the sample does not contain Cu in distinct 1+ and 2+ oxidation states.

In Fig. 3, we show the x-ray absorption coefficient in the vicinity of the  $2p_{3/2}$  ( $L_{III}$ ) core level of the Ce, Pr, and Yb perovskites, as well as a number of reference materials. In metallic form, Yb is in a  $[\text{Xe}]4f^{14}(5d6s)^2$  electronic configuration<sup>15</sup> with a chemical valence of 2+, while in  $\text{Yb}_2\text{O}_3$ , with an electronic configuration of  $[\text{Xe}]4f^{13}(5d6s)^3$  its valence is 3+. The energy difference of the two possible final states  $2p^*4f^{13}s$  and  $2p^*4f^{14}$  is about 7 eV because of the large  $p$ - $f$  Coulomb term, due to the highly localized  $4f$  electron. The localized  $4f$  orbital probes the rare-earth valence. It is immediately apparent that in the perovskite the valence is similar to that in the oxide. Therefore, the Yb ion contributes three electrons per unit cell to the material, as does Y and those rare earths which have a maximum chemical valence of 3+. This result is consistent with Murphy *et al.*<sup>6</sup> who showed that Eu, which may also adopt 2+ and 3+ valence states,

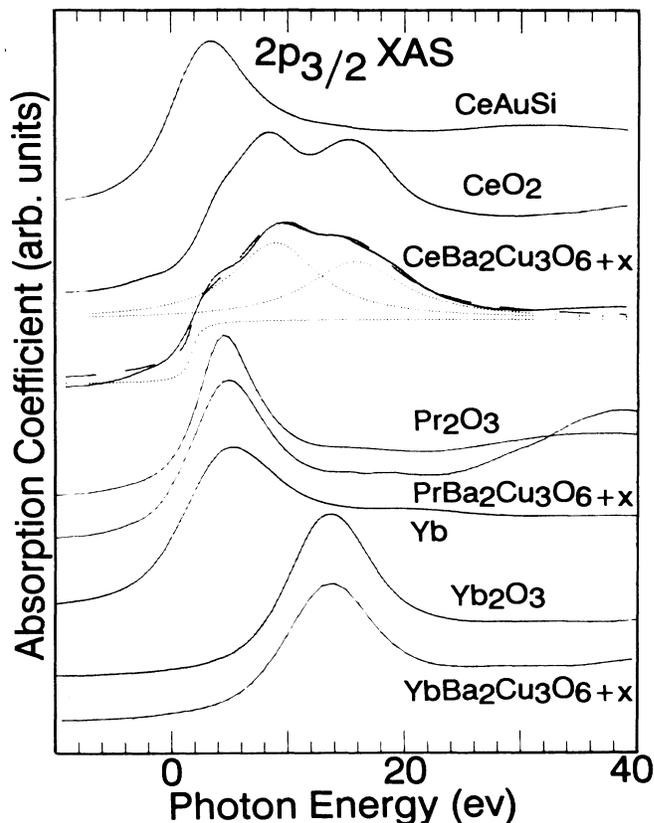


FIG. 3. X-ray absorption spectra at the  $2p_{3/2}$  ( $L_{III}$ ) edge of several materials, as indicated. Two spectra are distorted, the Yb by the Cu  $K$  edge at 45 eV and the Pr by the Ba  $L_I$  edge at 30 eV. The  $\text{CeBa}_2\text{Cu}_3\text{O}_{6+x}$  spectrum shows the fitting procedure used to extract the Ce valence as described in the text. In both  $\text{CeBa}_2\text{Cu}_3\text{O}_{6+x}$  and in  $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$  the rare-earth valence is larger than three, while in  $\text{YbBa}_2\text{Cu}_3\text{O}_{6+x}$  it is three.

was trivalent in a Eu-based perovskite superconductor.

On the other hand, both Ce and Pr may have a valence greater than 3+, and we believe that this is related to the fact that perovskites based on them do not exhibit superconductivity. For Ce, although the case remains controversial, it is generally agreed that in sufficiently electronegative compounds Ce may have a formal (mixed) valence of at least 3.4. In  $\text{CeO}_2$ , shown in Fig. 3, the two prominent peaks correspond to the presence of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  in the mixed-valent ground state.<sup>16</sup> The ground-state configuration may be estimated by fitting this spectrum to an arctangent function to represent the edge jump and two Lorentzians to represent transitions from the  $2p$  level to unoccupied  $5d$  orbitals in the presence and absence of a  $4f$  electron, respectively, as indicated in the inset. Using this procedure, we estimate that the Ce ground-state valence is 3.44; the exact figure is less important than the comparison to other compounds using the same procedure. In  $\text{CeAuSi}$ , in which the other elements are substantially less electronegative than O and less charge transfer from the Ce is expected, the estimated valence is 3.00. For the Ce-based perovskite, the valence

is 3.39, so the Ce has donated more charge to the system than Yb. Although the spectrum of Pr in the perovskite is complicated by the presence of the Ba 2s edge 40 eV above the Pr 2p<sub>3/2</sub> edge, careful inspection indicates that relative to trivalent Pr in Pr<sub>2</sub>O<sub>3</sub>, this spectrum exhibits a broadening on the high-energy side similar to that observed from 1.4% Pr in Pd, in which analysis<sup>17</sup> showed the Pr valence was 3.1. The Pr has therefore also donated more than three electrons per unit cell to the system. This extra charge provided by the Ce and to a lesser extent Pr tends to fill the O 2p and Cu 3d holes, consistent with the observed shifts in the Cu 1s and 2p energy shifts, and may be responsible for the suppression of superconductivity.

These measurements, using two very different electron spectroscopies, present a remarkably coherent microscopic picture of the electronic structure of these cuprate perovskites. In the superconductors, there are Cu 3d<sup>9</sup> satellites indicating that much of the Cu is oxidized to a 2+ configuration as in CuO, while in the nonsuperconductors the Cu is less oxidized. In the superconductors the Cu 1s XAS shows the same shift of 0.7 eV to higher binding energy as the 2p XPS spectra, also reflecting the higher valence of Cu in the superconducting materials. On the other hand, the larger binding energy of the O 1s peak in the superconductor implies the oxygen is reduced; there is less charge present on the oxygen ion than in the nonsuperconductors. The conclusion is that in the superconductors there is a charge shortage produced by extra oxygen with its appetite for electrons. Even an increase in the Cu valence is unable to satisfy all the oxygen ions. The

charge shortage in the superconductor, thus, both oxidizes Cu to produce 3d holes and prevents full reduction of the oxygen, leaving it with holes presumably of 2p character. The XAS valence determinations support this interpretation. In the superconducting samples the rare earth or Y contributes three electrons per unit cell, but in nonsuperconductors they (Ce and Pr) introduce more charge, which eases the charge shortage in the material and diminishes the number of Cu 3d and O 2p holes. Thus, these measurements all indicate superconductivity is eliminated if too much charge is made available to the system, and that much of this excess superconductivity-suppressing charge appears on the oxygen sites. Consistent with theories based on hole conductivity, such as that by Emery,<sup>2</sup> we suggest that substantial numbers of O 2p and/or Cu 3d holes are required for superconductivity in the perovskites.

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