

Correlation between electronic states of O, Cu, and Ba in several high- T_c superconductors

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X-ray photoemission measurements of Y-, Sm-, Eu-, and Yb-based high-temperature superconductors show a clear correlation between Cu 2*p* satellite features, which previous work has shown are associated with materials which exhibit superconductivity, and a high-binding-energy peak in the O 1*s* spectrum. In samples with varying oxygen content the intensity of the Cu 2*p* satellites changes, reflecting the Cu valence which varies between 1 + and 2 +. The high-binding-energy O peak appears to track the Cu valence. This high-binding-energy peak may be indicative of the presence of O 2*p* holes, suggested in some models as necessary for superconductivity. The Ba 3*d* peak position also changes systematically with the Cu valence.

A number of core-level x-ray photoelectron spectroscopic studies of high-temperature superconductors of both the 40-K-type (generic formula $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) and 90-K-type (modified perovskites with the generic formula $\text{RBa}_2\text{Cu}_3\text{O}_7$, where R can be Y or most rare earths) have been reported. This work has reached a reasonable consensus on the valence of the Cu; most x-ray photoelectron spectroscopies (XPS's) show that Cu in both types of systems is in a 2 + oxidation state. Fujimori *et al.*¹ observed satellites of the Cu 2*p* peaks, only present in materials which exhibited superconductivity, which resembled those observed in CuO, in which Cu has a formal 2 + valence. Similar observations were made by Horn *et al.*,² who concluded, by comparing superconductors and nonsuperconductors prepared by reducing the oxygen content and by substitution of Pr (valence greater than 3 +) for Y (formal valence 3 +), that Cu in materials which exhibited superconductivity was primarily in a 2 + formal oxidation state as in CuO. The correlation of superconductivity and divalent Cu was also observed by Shen *et al.*³ and Bianconi *et al.*⁴ on the basis of the Cu 2*p* spectra. Within the resolution of the XPS technique, there is no evidence for Cu in other oxidation states. Thus Steiner *et al.*⁵ compared Cu in LaSrCuO_4 with materials in which Cu is formally divalent and trivalent, and concluded that at most 5% of the Cu was trivalent. These studies are directly relevant to determining the mechanism of high-temperature superconductivity, as several models predict charge fluctuations of the Cu ion between 2 + and 3 +. Other models emphasize the importance of both Cu 3*d* holes (hence Cu^{2+}) and O 2*p* holes in order to achieve the superconducting state. Thus a study of the electronic state of oxygen is necessary.

Unfortunately, there has been considerably less agreement on the charge state of the oxygen. Shen *et al.*³ reported that before cleaning, $\text{YBa}_2\text{Cu}_3\text{O}_7$ showed split O 1*s* peaks, and the higher-binding-energy peak became smaller on cleaning, but published no spectra. Steiner *et al.*⁶ also ob-

served a split O 1*s* spectrum in LaSrCuO_4 and concluded by varying the takeoff angle that a peak at a binding energy of 531 eV was due to adsorbed O^- ions while another peak at 529 eV was a feature of the bulk. Kohiki, Hamada, and Wada⁷ measured a similar spectrum in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and found that the 531-eV peak decreased as the temperature decreased from 350 to 180 K. In contrast, Sarma *et al.*⁸ found that the 529-eV peak decreased between 300 and 80 K, while a new peak appeared at 533 eV. They also concluded that the 531-eV peak was due to adsorbed O, as it increased with time after sample cleaning. On the other hand, Horn *et al.*² showed an O 1*s* spectrum with peaks at 529, 531, and 533 eV on an $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample with reduced O content; only the 533-eV peak was present on a sample with higher O content which exhibited superconductivity at 90 K. This seems to support the notion that O 2*p* holes are present. The same conclusion was drawn by Thiry *et al.*,⁹ who observed a resonance in valence-band features related to O at the O 2*s* binding energy. Some of these disagreements may be related to the experimental difficulties involved in measuring oxygen with XPS. Charging may occur in these poorly (normal) conducting materials, particularly before scraping off a surface layer which is produced in air and which we often find is insulating. Besides the sample, oxygen may be present on the sample holder, nearby chamber parts, and adsorbed in the form of CO or CO_2 on the surface or in grain boundaries. In this work, we study oxygen by observing correlations between features in the Cu 2*p* spectra already demonstrated to be related to superconductivity and associated features in the O 1*s* spectra, thus eliminating ambiguities due to spurious oxygen. We show that there is a high-binding-energy oxygen 1*s* peak which is clearly associated with superconductivity. We also find variations in the Ba 3*d* spectrum in these samples.

We have measured the XPS spectra of superconducting Y, Sm, Eu, and Yb perovskites both as initially introduced into the measurement chamber and after successive stages of

cleaning (by scraping with an Al_2O_3 file). Samples were prepared using sintering and oxygen annealing techniques by now well described in the literature. For comparison, an Y-based perovskite with a reduced oxygen content (achieved by rapid quenching from above 900°C) which did not superconduct was also measured. The Y samples were measured soon after preparation, and portions of their XPS spectra have been previously reported;² however, the other samples were stored in air for as much as several weeks before measurement. All spectra were taken at room temperature in a previously described UHV system² equipped with a VSW 100-mm analyzer and a $\text{MgK}\alpha$ x-ray source.

At the top of Fig. 1 we show that Cu $2p_{3/2}$ and O 1s spectra of the superconducting Y sample before scraping and corresponding spectra of the nonsuperconducting Y sample after cleaning. The satellite features of the Cu spectrum characteristic of Cu^{2+} , and corresponding to "well" and "poorly" screened final states,¹⁰ are weakly evident in the latter, reinforced by the $\text{MgK}\alpha$ high-energy satellites of the Cu $2p_{1/2}$ peak which have not been removed. On the unscrapped sample, a single sharp O 1s peak at about 531 eV is apparent, while the nonsuperconducting sample exhibits a split O 1s spectrum with peaks at 529 and 531 eV and a weak shoulder at higher binding energy. Both the Eu- and Sm-based samples plotted below in Fig. 1 show almost no sign of the well-screened Cu $2p$ satellite, indicating that Cu in the surface region measured by XPS is not in the formally $2+$ valence state of CuO . Correspondingly, the O 1s spectra show only two peaks at about 529 and 531 eV, with no sign of a high-binding-energy shoulder. In contrast, the Yb-based sample shows a noisy, but significant, Cu $2p$ satellite, and its O 1s spectrum shows, besides the low- and medium-binding-energy peaks at 529 and 531 eV, a high-binding-energy peak at about 533 eV. Finally, the superconducting Y-based sample shows a very prominent Cu $2p$ satellite, indicating in agreement with previous work⁵ that the Cu is nearly divalent. The corresponding O 1s spectrum now consists of a

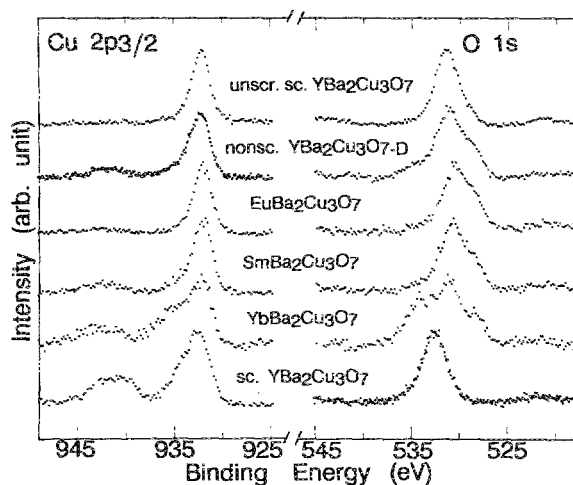


FIG. 1. X-ray photoelectron spectra (XPS) of the Cu $2p_{3/2}$ and O 1s core levels of a number of superconducting and nonsuperconducting oxide perovskites as labelled and discussed in the text. The high binding energy peak observed most prominently in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ is characteristic of Cu^{2+} , and is associated with a high binding energy feature in the O 1s spectrum.

single sharp peak at a high binding energy of 533 eV.

A similar systematic trend is also apparent in the Ba $3d$ spectra plotted in Fig. 2. The unscrapped spectrum shows a single sharp $3d_{5/2}$ peak at a binding energy of 780.2 eV. In the nonsuperconducting Y and the Eu- and Sm-based samples, which have only weak Cu $2p$ satellites, the spectrum broadens and shifts about 0.5 eV to lower binding energy. In the Yb-based sample, in which the Cu satellites become significant, the spectrum shifts an additional 0.5 eV lower. In the superconducting Y-based sample in which the Cu satellites are most prominent, the spectrum has shifted a total of 1.5 eV to lower binding energy than in the unscrapped surface.

In Table I we list the binding energy of the Cu $2p_{3/2}$, O 1s, and Ba $3d_{5/2}$ of the superconducting and nonsuperconducting Y-based samples. We also list the relative concentrations of each element at the surface region, estimated using the following procedure. First, we subtracted the background under a particular peak and integrated to find its total area. This was then corrected for the photoionization cross section of the particular level as tabulated by Ley and Cardona¹¹ and for the analyzer transmission function, which is inversely proportional to the electron kinetic energy. A value of 2 was assigned to the Ba $3d_{5/2}$ level. Previous experience has shown that this procedure is not usually accurate to better than 50%, although relative concentration determinations may be more precise.¹² Table I indicates reassuringly that the amount of each element in the surface region does not differ significantly from that expected from the bulk stoichiometry, with the principal difference between the superconducting and nonsuperconducting samples being the lower oxygen content of the latter.

The O 1s and Cu $2p$ results have important implications for the electronic structure of O in the high-temperature superconductors. Although we are unable to vary the takeoff angle, in agreement with other authors^{6,8} we identify the medium-binding-energy 531-eV peak as an impurity due to species such as CO or OH^- , adsorbed on the surface or in grain boundaries of the sample, or originating from the sample holder. This is suggested both by its prominence on unscrapped surfaces and by the observation that, if the superconducting Y-based sample is allowed to remain in the vacuum system for many hours, a shoulder at about 531 eV begins to form on the 533-eV peak. We identify the low-binding-energy

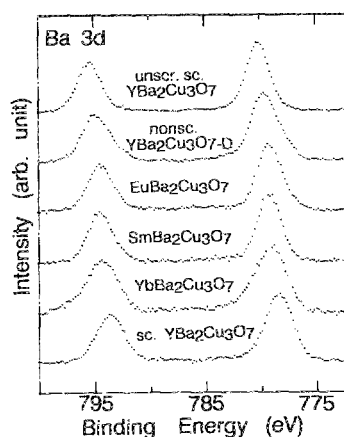


FIG. 2. X-ray photoelectron spectra (XPS) of Ba $3d_{3/2}$ and $3d_{5/2}$ core levels of several superconducting and nonsuperconducting oxide perovskites as noted and described in the text.

TABLE I. The binding energy (B.E.) and relative intensity (R.I.) of indicated peaks in the XPS spectra of the superconducting and nonsuperconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples. Relative intensity was estimated as described in the text, and normalized to make the $\text{Ba } 3d_{5/2}$ intensity equal two. Although intensity estimates are subject to large errors, it is evident that there is more oxygen in the superconducting sample.

	Cu $2p_{3/2}$		O $1s$		Ba $3d_{5/2}$	
	B.E.	R.I.	B.E.	R.I.	B.E.	R.I.
Superconducting	933.1	3.2	532.8	10.0	778.4	2.0
Nonsuperconducting	932.5	2.4	531.1	4.8	779.7	2.0

gy peak at 529 eV with bulk O^{2-} .

We tentatively suggest the following explanation of the high-binding-energy 533-eV O $1s$ peak. To our knowledge, this peak has not been observed by others at room temperature, although it might be related to the 533-eV peak observed below 90 K by Sarma *et al.*,⁸ whose valence-band spectrum differs from others.^{3,9} In the oxygen-deficient Y sample the Cu valence is less than $2+$, reflecting the ability of the bulk oxygen to remain in its preferred 2-formal valence state without fully oxidizing the Cu. On the other hand, in the Y-based material with a full oxygen content, there is insufficient valence electron charge (a "charge shortage") such that the Cu is fully oxidized to $2+$, and yet the oxygen must be content with a charge state less than $2-$, producing a single high-binding-energy O $1s$ peak. Since the Cu valence is not greater than $2+$,⁵ simple charge counting arguments require that in a material with a full seven oxygen ions per unit cell those ions must have a formal charge less than $2-$. Thus this peak is direct evidence of unoccupied $2p$ levels in the oxygen. The Eu-, Sm-, and Yb-based samples then represent intermediate cases. Having been stored in air for some time, they may have lost oxygen. Changes in these high-temperature superconductors over time have been previously observed¹³ and ascribed to loss of oxygen. For Yb, which may be somewhat more stable than the other two materials, this loss was less complete, so that some charge shortage remains, producing a weak Cu satellite and a high-binding-energy O $1s$ peak in the presence of low- and medium-binding-energy peaks representing, respectively, those oxygen ions in a more reduced state and adventitious oxygen. The latter is expected for the Yb-based sample as it was rather small and mounted on a Cu block, making it likely that some emission from the holder was included in the measurements. The same was true of the Sm- and Eu-based samples, while the Y-based sample was large and mounted on a small holder, so the x-ray source and analyzer measured only the sample surface. Other published work is likely affected by similar difficulties. The observed correlation between the Cu valence and the oxygen charge state is reasonable on physical grounds; it is to be expected that an excess of oxygen, which produces a "charge shortage" in the material, will produce oxygen in a lower charge

state and hence at a higher binding energy, while generating Cu in its higher $2+$ valence state. The reduced oxygen charge in the superconducting materials, however, is also predicted by models of superconductivity which rely on O $2p$ holes.

A tentative interpretation of the Ba $3d$ spectra is on similar lines. Steiner *et al.* previously observed two Ba peaks on $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ at 780.4 and 778.7 eV and, noting that the high-binding-energy feature increased with electron escape angle, concluded that it was due to O^{2-} defects associated with the Ba, of which there would be more present at the surface. On an unscrapped surface, the high-binding-energy feature may also be due to formation of another Ba compound, such as BaO, at the surface. We then identify our higher-binding-energy peak observed on the unscrapped surface with their 780.4-eV peak, and the low-binding-energy peak observed on superconducting Y with their 778.7-eV peak. The Sm-, Eu-, and, to a lesser extent Yb-, based samples represent intermediate cases between these extrema. The shift and broadening may then reflect the fact that we are unable to resolve the two peaks. As their relative proportion changes with oxygen concentration, the average peak position will shift accordingly.

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