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Insufficiency of O and Cu holes for oxide superconductivity: X-ray absorption spectroscopy

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We have studied the electronic properties of $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ superconductors with soft x-ray absorption spectroscopy (XAS) at BESSY. Electronic transitions to unoccupied states (holes) of 2*p* and 3*d* character on O and Cu, respectively, are found in superconducting specimens. In samples with reduced oxygen content, superconductivity is suppressed, and a decrease in the intensity of transitions to these unoccupied states is observed. However, there is little change in these features when Zn sufficient to suppress superconductivity is substituted for Cu. We conclude that O 2*p* and Cu 3*d* holes are necessary but not sufficient for superconductivity.

INTRODUCTION

The electronic properties of the copper oxide superconductors $RBa_2Cu_3O_7$ (1:2:3), where *R* may be Y or most rare earths, have been extensively studied by x-ray absorption spectroscopy[1–4] (XAS) and x-ray photoemission spectroscopy (XPS). This work has focused on the electronic state of the Cu and O ions. These are crucial for superconductivity as calculations[5,6] indicate that the valence band is formed by Cu 2*p* and Cu 3*d* states which therefore determine the transport properties. Hall effect measurements[7,8] show the primary charge carriers in the 1:2:3 compounds are holes, presumably to unoccupied Cu 3*d* and perhaps O 2*p* states, as predicted by various theoretical models.[9–13] In $RBa_2Cu_3O_7$, if O is in a two-oxidation state, charge balance requires Cu to be oxidized to +2.33. However, as discussed below most spectroscopic results imply the Cu valence is not more than 2+. This implies the O valence is more positive than 2 −, i.e., there are unoccupied O 2*p* states, as recent calculations predict.[3]

Spectroscopic measurements in the oxide superconductors, which could determine the oxidation state of the O, are in considerable disagreement. This is because measurements of O present formidable experimental difficulties. Unlike Cu, O has no deep core levels; its deepest level, the 1*s*, has a binding energy of ≈ 530 eV. This precludes conventional XAS, and most measurements have relied on surface-sensitive XPS. In such experiments O adsorbed on the surface or nearby structures in the vacuum system may contribute to the measured spectra. Moreover, in these ceramic materials, it is difficult to obtain surfaces representative of the bulk. These problems have been extensively discussed previously.[14–16] In XPS, peaks are observed at binding energies of 529 and 531 eV,[2,17,18] and sometimes at 533 eV.[2,19] There is evidence that the latter may be due to an irreversible interaction with water.[20] Recent work on well-characterized single crystals[21] seems to be reaching a consensus that the 529-eV peak is due to the bulk, while the 531-eV peak may be due to surface contamination or the loss of O in the surface region.

With reduced O content ($x > 0$ in $RBa_2Cu_3O_{7-x}$), the superconducting transition temperature T_c decreases. Superconductivity is suppressed entirely[22] for $x > 0.5$. It has been shown that this O deficiency causes the formation of Cu^{1+} ions[4,23,24] with a filled *d* subshell (no holes). Electron microscopy,[25] x-ray absorption,[24] and neutron diffraction measurements[26] indicate these monovalent Cu ions are in the so-called "chain planes" [Cu(1) sites[27]] from which the O is preferentially removed.[18(b),28] A similar suppression of superconductivity is caused by the substitution of Zn for Cu [$y > 0$ in $RBa_2(Cu_{1-y}Zn_y)_3O_7$]; $y \approx 0.10$ suffices to induce semiconducting behavior in the normal state.[29] Surprisingly, it was found[23] that in such specimens there was no change in the electronic state of the Cu comparable to that found in O-deficient materials. In view of the strong Cu 3*d*-O 2*p* hybridization,[5,6] it was concluded[23] that the oxidation state of the O was also unaffected by Zn substitution, but direct measurements of the O are clearly desirable.

In this paper we present soft XAS measurements on $RBa_2Cu_3O_{7-x}$, where *R* is Y and Eu, and on Zn-doped $EuBa_2(Cu_{1-y}Zn_y)_3O_7$. In order to maximize sensitivity to bulk electronic properties, these data were taken in a total-electron-yield mode which has been shown to be proportional to the x-ray absorption coefficient.[30] These measurements concentrate on the O 1*s* and Cu 2*p* edges, which probe unoccupied O *p* and Cu *d* states due to the dipole selection rule, and demonstrate that both O 2*p* holes and Cu 3*d* holes are present in superconducting 1:2:3 compounds. Their density is reduced in O-deficient

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samples, but not in Zn-doped samples. We conclude that the presence of such holes may be necessary, but not sufficient, for superconductivity.

EXPERIMENT

Samples were prepared using standard solid-state reaction techniques.[31] X-ray diffraction (Cu $K\alpha$) showed no evidence of spurious phases. Samples with $x=y=0$ exhibited bulk superconductivity at about 95 K as determined by resistivity and susceptibility (Meissner effect). In two samples an O deficiency ($x>0$) was induced by vacuum annealing for 2 h at 500 °C. The resistivity and x-ray patterns of all samples were rechecked after the spectrosopic measurements to verify that the transport properties had not been affected by exposure to ultrahigh vacuum (UHV); no differences compared to the previous measurements were observed.

Our spectroscopic measurements were made at BESSY using the He-PGM2,[32] a monochromator with at present a resolving power ($E/\Delta E$) of ≈ 800 in the vicinity of the O K edge and usable flux over the energy range from below 50 eV to over 2000 eV. This uniquely broad energy range facilitated study of core levels of all elements in these compounds in one measurement. In our spectra the total yield is normalized to the incident flux measured by monitoring the total electron yield of a gold grid placed in the beam. This also served as a simultaneous energy reference, due to the presence of a small dip in the incident flux at the O 1s edge. The monochromator was calibrated to the La $3d_{5/2}$ edge in $LaAl_2$, taken to be 834.5 eV (Ref. 32) and corrected for other energies as $E^{3/2}$.[32] This energy scale should be absolutely accurate to ±1 eV, but much smaller relative shifts could be resolved. The total electron yield of the sample was measured by a channeltron electron multiplier mounted in front of it.

A surface layer was removed from the sample *in situ* by scraping with an Al_2O_3 file. During scraping of samples, the pressure rose to the 10^{-9} Torr range, possibly due to loss of O from grain boundaries, although the base pressure was $<2\times10^{-10}$ Torr. Spectral differences were observed between scraped samples and those not previously scraped, probably due to the formation of an O-deficient surface layer during baking.[33] However, after suitable scraping, no further changes were observed in the spectra either after repeated scrapings or exposures of many hours to the ambient pressure in the measurement chamber. This indicates that these measurements are representative of the bulk, as expected given the 100–200 Å sampling depth characteristic of total yield measurements.[34] These results therefore bear directly on the electronic structure of the 1:2:3 materials and should be free of the surface effects which have been shown to be important in more surface-sensitive spectroscopies.[14–21] Our spectra are displayed after removal of a smooth background fitted to the absorption below the edge and are normalized to give unity jump in the absorption well above the edge.

RESULTS

Figure 1 shows the lattice parameters of $EuBa_2(Cu_{1-y}Zn_y)_3O_7$ as a function of y. With increasing Zn concentration the orthorhombic splitting decreases, in contrast to previous work.[29] This splitting vanishes entirely for $y>0.4$. On the other hand, as shown in the inset of Fig. 1, the superconducting transition temperature T_c vanishes with increasing x well before the material assumes a tetragonal structure. Figure 2 shows the resistivity as a function of temperature for samples with various concentrations of Zn. For $y=0.15$ (not shown) the sample exhibits semiconducting behavior down to 4.2 K, the lowest temperature measured. In the inset of Fig. 2 is plotted the resistivity versus temperature of the two O-deficient samples with $y=0$. By comparison with previous measurement[35] we estimate that for the Y-based sample, which does not superconduct down to 4.2 K, $x\approx0.5$, while for the Eu-based material, which shows sharp resistivity drops at 90 and 60 K, $x\approx0.2$.

In Fig. 3 the normalized total electron yield, which as noted above is proportional to the x-ray absorption coefficient, of various samples is plotted as a function of incident photon energy. Shown are spectra of the O 1s core level of Y- and Eu-based 1:2:3 samples having a full

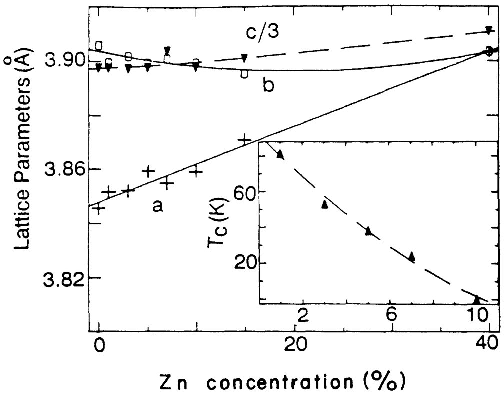

FIG. 1. Lattice parameters (a, b, and $c/3$) of $EuBa_2(Cu_{1-y}Zn_y)_3O_7$ as a function of y. The orthorhombic splitting decreases and vanishes entirely for $y\gtrsim0.4$. Plotted in the inset is the superconducting transition temperature T_c as a function of y.

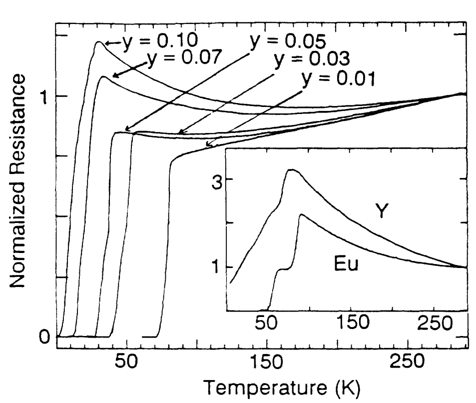

FIG. 2. Resistance (normalized to value at 300 K) of $EuBa_2(Cu_{1-y}Zn_y)_3O_7$ as a function of temperature for representative values of y. Plotted in the inset is the resistance of two O-deficient samples $RBa_2Cu_3O_{7-x}$ with $R=Y$ and Eu as described in the text.

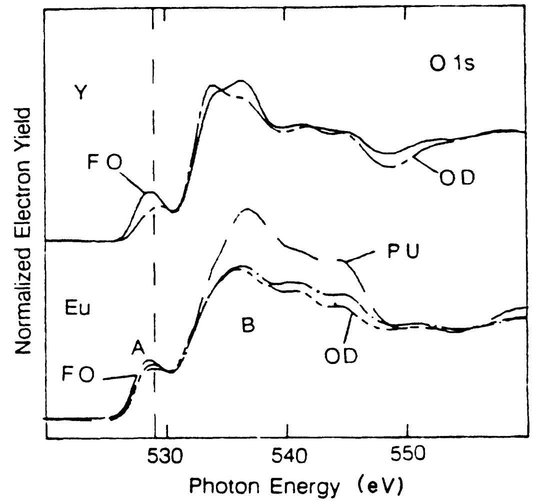

FIG. 3. Total electron yield (proportional to the absorption coefficient) of $R\mathrm{Ba_2Cu_3O_{7-x}}$, with $R = \mathrm{Y}$ and Eu and with $x = 0$ (full O or FO), $x \approx 0.2$ (O deficient or OD) and a previously unscraped (PU) sample as described in the text, in the vicinity of the O 1*s* edge. The binding energy of the O 1*s* level as determined from XPS is indicated by the vertical dashed line.

$\mathrm{O_7}$ content and spectra of the O-deficient samples described above. Plotted for comparison is the spectrum of the Eu-based sample measured before the surface layer was removed by scraping. As remarked above, this previously unscraped layer is probably deficient in O. The main edge (*B*) has an excitation energy of about 533 eV, with a smaller feature (*A*) at 528.5 eV, very close to the XPS binding energy of the O 1*s* core level (529 eV; see discussion above) indicated in the figure. Peak *A* is most intense in the Eu-based and Y-based full-O samples; it is smaller in the O-deficient specimens and the previously unscraped sample. There are also significant changes in the features above peak *B* between full O and O-deficient samples. This presumably reflects changes in the local environment of the absorbing O ions.

In Fig. 4 the total yield of a series of scraped Zn-doped samples in the vicinity of the O 1*s* core level is plotted. Remarkably, for small additions of Zn ($y \lesssim 0.07$) peak *A* actually increases slightly, although the superconducting properties become progressively poorer as described above. In contrast to the O-deficient samples shown in Fig. 3, there is no substantial decrease in the amplitude of peak *A* even when enough Zn ($y = 0.10$) is added that the material no longer superconducts. Zn doping causes no significant changes in the features above peak *B*, which presumably have the same origin as those observed in Fig. 3. These differences between Zn-doped and O-deficient samples indicates that Zn doping did not cause a loss of oxygen.

The total electron yield near the Cu 2*p* absorption edge is plotted in Fig. 5 for the Eu-based full O, O-deficient, and previously unscraped samples as described above. Two prominent features are observed some 20 eV apart, which correspond to the spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ core levels. These features are just below the XPS binding energy of the Cu 2*p* core levels indicated in the figure (see discussion below). Evidently, the intensity of particularly the $2p_{3/2}$ peak has decreased in O-deficient samples, so that the $2p_{3/2}$:$2p_{1/2}$ ratio is larger for the superconducting full O sample. These relatively sharp features appear on a gradually increasing yield extending over ≈ 100 eV as illustrated in the inset of Fig. 5. The shape of this slow rise was sample dependent, making background removal somewhat ambiguous for these spectra.

There is, in contrast, relatively little change in the Cu 2*p* spectra in Zn-doped samples. In Fig. 6 we plot the spin-orbit split Cu $2p_{3/2}$ and $2p_{1/2}$ absorption edges measured on $\mathrm{EuBa_2(Cu_{1-y}Zn_y)_3O_7}$ samples with $y = 0.01$ (indistinguishable from the $y = 0$ spectrum), 0.03, and 0.10 as described above. Superconductivity is entirely suppressed in these samples with $y \lesssim 0.10$. Nevertheless, there is no change in either the peak amplitude or the $2p_{3/2}$:$2p_{1/2}$ ratio within the limits imposed by the ambiguous background.

The Cu 2*s* edge, which should be at about 1095 eV, is

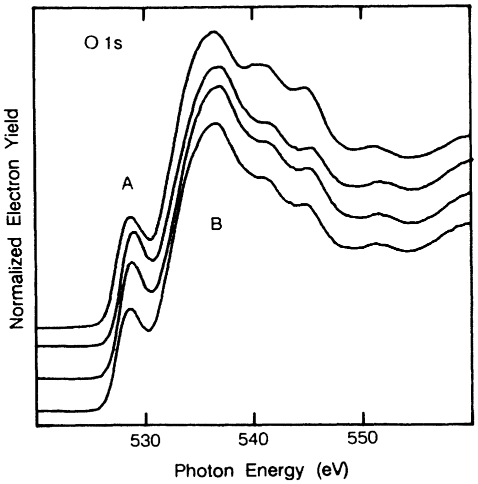

FIG. 4. Total electron yield of $\mathrm{EuBa_2(Cu_{1-y}Zn_y)_3O_7}$, for *y* values (top to bottom) 0.0, 0.05, 0.07, and 0.1, in the vicinity of the O 1*s* edge. See also Fig. 3.

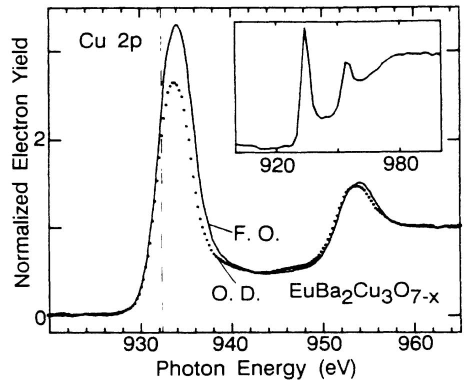

FIG. 5. Total electron yield (proportional to the absorption coefficient) of $\mathrm{EuBa_2Cu_3O_{7-x}}$, with $x = 0$ (full O or FO), $x \approx 0.2$ (O deficient or OD) and a previously unscraped FO sample (PU) as described in the text, in the vicinity of the Cu 2*p* edge. The binding energy of the well-screened Cu 2*p* level as determined from XPS is indicated by the vertical dashed line.

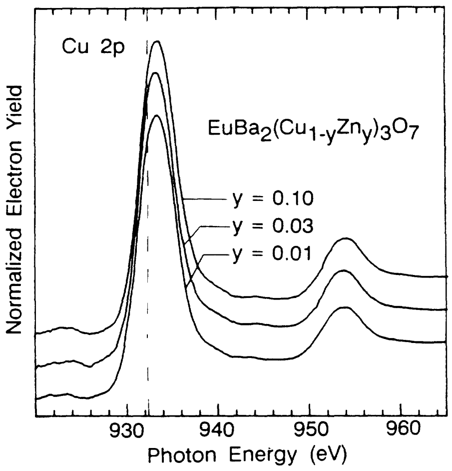

FIG. 6. Total electron yield of $EuBa_2(Cu_{1-y}Zn_y)_3O_7$, for various values of y as indicated, in the vicinity of the Cu $2p$ edge. See also Fig. 5.

not apparent in these measurements. This is probably due to the fact that the yield in that energy range is dominated by the larger Ba $3p_{3/2}$ edge at about 1070 eV. Nevertheless, we conclude from the absence of a strong $2s$ feature in our spectra that in contrast to the $2p$ edges there is no prominent "white line" at the $2s$ edge. This is expected if the former are due to transitions to unoccupied $3d$ states, transitions dipole forbidden from an s initial state except in tetrahedrally coordinated systems.[36]

The Ba, Y, and Eu $3d$ edges are all dominated by a $3d^{10}4f^n \rightarrow 3d^9 4f^{n+1}$ transition which results in an intense white line due to the high density of unoccupied $4f$ states. The peaks are displaced to lower energy than expected in a single-electron picture by the strongly attractive Coulomb interaction of the highly localized $4f$ states with the core hole.[37] The intensity of the lines therefore reflects the number of unfilled f states and the energy position the screening interaction of the localized f states with the core hole. On unscraped samples we observe a shift of ≈ 1 to 2 eV to higher binding energy relative to scraped samples, and a larger $3d_{5/2}$:$3d_{3/2}$ ratio, consistent with photoemission and other results[17,18,38] indicating Ba enrichment at the surface. Spectra taken from scraped surface show little change between the full-O and O-deficient samples, as is also true for Zn-doped samples. This reflects the fact that these elements are not direct participants in the charge rearrangements which accompany changes in O content. These results will be further described elsewhere.[39]

DISCUSSION AND CONCLUSIONS

If we adopt a simple one-electron interpretation of the XAS in terms of the density of unfilled states and take 529 eV as the XPS binding energy in bulk 1:2:3 as discussed above, peak A in Figs. 3 and 4 involves transitions to states directly at the Fermi level (E_F). This is in agreement with XAS results of Yarmoff *et al.*[40] on $YBa_2Cu_3O_7$. A similar peak, whose intensity increased with z, was observed in the O $1s$ spectrum of $La_{2-z}Sr_zCuO_4$ by Sondericker *et al.*[41] They interpreted this result as indicative of defect states forming in the gap as Sr doping increased. However, in 1:2:3, a stoichiometric compound, there is not likely to be a high density of defect states. Two possible interpretations of peak A are as follows. (1) It may be similar to the "edge singularities" frequently observed in the x-ray absorption spectra of metals, which have been described by Mahan[42] and von Barth and Grossman[43] and extended to the Auger process by Ramaker.[44] In this case the many-body effects responsible for an edge singularity produce an absorption peak at E_F. However, measurements and calculations indicate that in Li, these effects in fact produce a rounding at the edge.[45] (2) Following Yarmoff *et al.*,[40] peak A may be due to dipole transitions from the $1s$ initial core state to unoccupied O $2p$ states in the ground state. This is consistent with the observation that in the light elements ($Z < 10$) the absorption edge closely resembles the calculated local density of states above E_F.[46] Nücker *et al.*, using electron energy-loss spectroscopy (EELS), have observed a peak at E_F in $La_{2-z}Sr_zCuO_4$ (Ref. 47) and in $YBa_2Cu_3O_{7-x}$ with $x \approx 0.2$ (Ref. 48). No measurements were reported with $x = 0$, possibly due to the difficulty of preventing the loss of O from the thin (≈ 1000 Å) samples required in EELS. Nücker *et al.*[48] calculated the O $1s$ absorption edge and concluded that the peak at E_F was due to transitions to unoccupied $2p$ states.

In the latter interpretation, the XAS final state corresponding to peak A is $\underline{1s}2p^6$, where $\underline{1s}$ indicates an O $1s$ hole, and its intensity should depend on the density of unfilled O $2p$ states (holes) in the initial state. This important result is valid even if the mechanism causing peak A is an edge singularity, since an edge singularity can only occur if there is significant density of states at E_F at the O site, and such unoccupied states must necessarily have $2p$ character. This interpretation is confirmed by a survey of O $1s$ absorption edges; in a variety of materials in which O if formally divalent, the $1s$ edge appears at or above 531 eV,[49,50] and no feature corresponding to peak A in Fig. 3 is present. Thus we conclude that peak A in Figs. 3 and 4 measures the density of O holes near E_F in the bulk of the sample. As already noted, the energy position of peak A coincides with the $1s$ binding energy as determined by XPS, which implies that the XAS and XPS final states are similar. This is expected as, with O in a nearly $2-$ oxidation state, the preferred XPS final state will be $\underline{1s}2p^6$. The absence of a $\underline{1s}2p^5$ final state (corresponding to a $1s2p^5$ initial state, i.e., a $2p$ hole) in XPS could mean either that this feature is too low in intensity to be observed or that such a state is effectively screened by charge transfer resulting in a $2p^6$ final state.

Figure 3 shows that in the Y-based material, the intensity of peak A is greatly reduced by an O deficiency sufficient to completely suppress superconductivity, indicating a reduction in the density of O $2p$ holes near E_F. This is expected: O ions are electron acceptors. As O ions are removed, more charge becomes available per remaining O ion and the number of empty O $2p$ states is reduced. With sufficient O deficiency, the material will become a semiconductor as the hybridized Cu $3d$-O $2p$ band is entirely filled. An analogous reduction in the intensity of peak A is apparent in the Eu-based materials. However, the decrease is less, as expected since the O deficiency of this specimen is smaller. A larger intensity decrease is also apparent between the scraped 1:2:3 superconductor, representative of the bulk properties, and the initially unscraped material, which as noted above is presumably O deficient.

It is natural to ascribe to the charge carriers, which are known to be holes,[7,8] the character and symmetry of the empty state near E_F. We accordingly identify the empty $2p$ states with at least part of the charge carriers (holes). This is supported by the observation that as the O concentration is decreased, Hall effect measurements[8] show that the number of charge carriers also decreases, consistent with the present data showing a reduction in the number of O $2p$ states at E_F.

The decrease in O hole density is not proportional to the change in O concentration. When x changes from 0 to 0.5, corresponding to about a 7% reduction in the O content, peak A in Fig. 3, which measures the hole concentration, has decreased by much more than 7%. This indicates either that there is charge transfer between different O ions, in order to redistribute the additional charge among the remaining O ions, or that the O holes are preferentially associated with those O ions which have been removed. As it is well known that O removal depletes primarily the O sites in the Cu-O planes, the disproportionate reduction in the O hole intensity suggests either (1) the O holes are preferentially associated with the O in these sites, or (2) charge transfer occurs from the "chain" planes to the O ions in the CuO_2 planes. Spectroscopic measurements[51] show that doping on the rare-earth site with Pr, which has a valence higher than +3 in these materials, apparently does not cause charge transfer to the adjacent CuO_2 plane. Thus charge transfer, if it occurs, must take place preferentially along Cu—O bonds. While some band-structure calculations[5,6] do suggest that unoccupied O $2p$ states are primarily on the "chain" sites, other calculations by Nücker *et al.*[47] imply the holes are uniformly distributed over all the O ions. This could be resolved by studies of single crystals or oriented grains using polarized radiation as states at each site have a different spatial orientation in the crystal.[5]

Peak B in Figs. 3 and 4 is due to transitions to other O p-like empty states, and the spectral shape at higher energies is determined by multiple scattering of the ejected photoelectrons from surrounding atoms,[52] and may be described in a Korringa-Kohn-Rostocker[53] (KKR) formalism. This near-edge x-ray absorption fine structure (NEXAFS) may be used to determine the local environment of the absorbing atom.[54] The changes in the NEXAFS observed in Fig. 3 thus indicate that O deficiency causes significant modifications of the local environment of the remaining O. We have not yet carried out a quantitative analysis of these features to determine what these changes might be; this is a formidable task, as there are four distinct O sites.

XPS measurements on divalent Cu compounds show two sets of multiplets corresponding to $2p_{1/2}$ and $2p_{3/2}$ final states, separated by the spin-orbit splitting of ≈ 21 eV. In each set, one multiplet corresponds to transitions to a $\underline{2p}^5 3d^9(s,p)^*$ final state,[55] where $\underline{2p}$ indicates a $2p$ hole and $(s,p)^*$ a screening electron of sp character, and another multiplet to $\underline{2p}3d^{10}\underline{L}$ final states (shakedowns), where $\underline{L}$ indicates a ligand hole. The latter ("well-screened") configuration has a lower binding energy due to the better screening of the more localized d electron, and corresponds closely in energy to the $\underline{2p}^5 3d^{10}$ XPS final state of Cu^{1+}. Similar multiplets are observed in the 1:2:3 superconductors.[2,18,56–58] The XPS binding energies of the spin-orbit-split well-screened $\underline{2p}3d^{10}\underline{L}$ configurations indicated on Fig. 5 evidently coincide in energy with the prominent peaks in our spectra at $\sim$934 and 955 eV. In view of this agreement and the dipole selection rule which favors $p \rightarrow d$ transitions, we assign the main peaks to $\underline{2p}3d^{10}$ final states similar to the XPS final states. We conclude that the Cu is predominantly in a 2+ oxidation state, consistent with previous spectroscopic measurements.[56]

The amplitude of the $2p$ features should be proportional to the Cu $3d$ hole density, subject to the following cautions. (a) These features appear on a large background due to continuum states as shown in the inset of Fig. 5, somewhat obscuring the comparison of intensities between different samples. (b) Similar features are also observed[59] in Cu_2O, in which Cu is formally monovalent (filled d subshell), uniquely among compounds with formally monovalent Cu. Their presence in Cu_2O is evidently due to an excitonic mechanism[59] peculiar to the unusual Cu-O chain structure of Cu_2O, which facilitates the localization of a d-symmetry state below the Fermi level in the presence of a $2p$ hole. However, this process is unlikely to occur in the 1:2:3's because Cu_2O is a semiconductor while the 1:2:3's are metallic and would not be expected to support excitons. We therefore conclude that the peak intensities in Fig. 5 are proportional to the density of unfilled Cu d states near E_F.

The fact that these peaks are smaller on previously unscraped surfaces and on O-deficient samples is consistent with earlier measurements[60] and can be understood as follows. In earlier work we concluded[23] that O deficiency causes the formation of Cu^{1+} ions in Cu(1) sites. As the d shell of these ions is filled they do not contribute to the white-line intensity. However, since the excitation energy of Cu^{1+} and Cu^{2+} ions is almost identical (because both involve $3d^{10}$ final states close in energy, as discussed above in the context of XPS) both contribute to the edge jump to which our spectra are normalized. This effectively reduces the white-line intensity as the Cu^{1+} content of the sample increases, and its observed decrease therefore does not necessarily imply a homogeneous valence decrease of all the Cu ions, some of which might well remain divalent. However, we conclude that there is a decrease in the density of unoccupied Cu $3d$ states associated with O depletion. This important result is expected, as O vacancies replace sites with negative charge by sites with zero charge, thus adding electrons to or reducing the number of holes on the Cu ions.[61]

We note parenthetically that the change in d occupancy inferred from the decrease in peak intensity is not as large as that previously inferred from surface-sensitive XPS (Refs. 2 and 56) and appearance potential spectroscopy[14]

(APS) measurements on oxygen-depleted samples. As previously noted,[14] this large decrease was shown to be inconsistent with bulk-sensitive x-ray absorption measurements, implying that the XPS and APS work was not representative of the bulk. The present measurements, on the other hand, are consistent with bulk-sensitive XAS measured in transmission,[4,23,24] confirming that they measure bulk properties.

An independent measure of the changes in Cu *d* hole concentration may be obtained by examining the relative intensity of the $2p_{3/2}$ and $2p_{1/2}$ levels. It is evident from Fig. 5 that the $2p_{3/2}$:$2p_{1/2}$ intensity ratio in the full O sample is different from that in the O-deficient and previously unscraped samples. The $2p_{3/2}$ level is reduced in intensity by O deficiency much more than the $2p_{1/2}$ level, so that the $2p_{3/2}$:$2p_{1/2}$ intensity ratio in O-deficient samples is closer to, but still larger than, the 2:1 value expected on the basis of the initial-state occupation. Nonstatistical intensity ratios have been previously found in the $2p$ absorption spectra of most of the transition metals,[62] and have been explained using $2p$-$3d$ exchange interactions[63] or multiconfiguration Dirac-Fock calculations[64] which show that the ratio is sensitive to the initial-state charge configuration or *d*-state occupancy of the absorbing ion. Thus, for Mn the calculated $2p_{3/2}$:$2p_{1/2}$ ratio was 3.25 for Mn^{2+} but 2.25 for Mn^{4+}.[64] The change in the intensity ratio apparent in Fig. 5 therefore implies, consistent with our earlier conclusion, that the Cu valence is higher in the full-O material than in O-deficient materials. However, the previously discussed background difficulties and the fact that the Cu^{1+} and Cu^{2+} edges are energetically very close prevent sufficiently precise measurement of the $2p_{3/2}$:$2p_{1/2}$ ratio to determine whether a homogeneous valence change occurs.

Our data imply that the suppression of superconductivity in O-deficient samples is related to a reduction in the density of O $2p$ states which we associate with charge-carrying holes. In contrast, Figs. 4 and 6 show that there is very little change in the intensity of the O $1s$ and Cu $2p$ features when Zn sufficient to suppress superconductivity is added. This indicates first of all that Zn substitution does not cause O deficiency in the samples, as such a deficiency would cause spectral changes similar to those observed in the samples known to be O deficient. The lack of changes in the Cu spectra also indicates that Cu is divalent in Zn-doped samples, as the Zn is expected to be divalent. Most importantly, the absence of spectral changes indicates that the density of O $2p$ and Cu $3d$ holes has not been affected by the addition of Zn, and we conclude that the density of such holes, that is, the charge carrier density, is not the sole decisive factor in superconductivity.

A number of electronic pairing mechanisms have been proposed in the high-temperature superconductors. These are usually described in a Hubbard model, which takes into account electronic correlations due to the large electron-electron repulsive interaction. The resonating valence-bond model of Anderson and co-workers[12] is based on a single-band Hubbard model, in which it is assumed that the addition of O beyond 6.5 causes the formation of some Cu^{3+} ions. On the other hand, many descriptions[10,11,13] assume that the additional oxygen causes the formation of O holes and describe the system in a two-band Hubbard model. The clear evidence in our data for O holes is consistent with such two-band models.

Several of these models are consistent with the observed persistence of such unoccupied states in Zn-doped materials while superconductivity is suppressed. The feature of divalent Zn which distinguishes it from divalent Cu is its filled *d* shell. Weber[65] suggests that O $2p$ holes pair via *d*-*d* orbital excitations within a Cu^{2+} ion. Such excitations have been observed in Cu by optical spectroscopy,[66] but are expected to be absent for Zn with a filled *d* shell. Emery[11,67] postulates O $2p$ holes paired by polarization of a neighboring Cu ion, which increases the Cu-Cu superexchange interaction in the vicinity of this O hole, making it energetically favorable for a second O hole to be nearby. This effect will, of course, be absent for a Zn ion. The reduction of T_c with increasing Zn concentration is also consistent with models which assume a pairing mechanism based on a hole-magnon interaction such as that due to Guo, Langlois, and Goddard,[13] as the introduction of nonmagnetic Zn on Cu sites is expected to perturb the magnetic coupling between ions. In all these models it is not difficult to understand that Zn suppresses superconductivity, since the specific properties of Cu^{2+} are essential to all of them. The discovery of a new oxide superconductor[68] without Cu suggests that magnetism does not hold the key to superconductivity in these materials. It is, however, interesting to note the presence in all known oxide superconductors of ions with unfilled subshells. In the present case, the substitution of such ions by closed subshell ions leads to a rapid decrease in superconductivity.

SUMMARY

These spectroscopic measurements demonstrate directly the existence of unoccupied states of O $2p$ character and Cu $3d$ character (holes) in the superconducting Cu oxide perovskites. However, measurements on analogous nonsuperconducting Zn-doped perovskites show a similar density of such holes, and indeed a very similar overall electronic structure. This implies that not merely the existence of these holes but other factors as well, presumably including their mobility, are important to achieve the superconducting state.

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