X-ray spectroscopy of $EuBa_2(Cu_{1-y}Zn_y)_3O_{7-x}$: Suppression of superconductivity

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We have studied the x-ray-absorption near-edge spectra of $EuBa_2(Cu_{1-y}Zn_y)_3O_7$ as a function of Zn and O content. There is clear evidence for the development of Cu^{1+} ions as the O content is reduced to levels sufficient to suppress superconductivity. However, there is no effect on the electronic state of the Cu ion as the Zn content is increased and superconductivity vanishes. We tentatively conclude that the suppression of superconductivity is in both cases due to the preferred occupancy of certain planes by nonmagnetic (filled d subshell) atoms, as proposed in $YBa_2Cu_3O_6$ on the basis of neutron scattering.

The origin of superconductivity in the Cu oxides is intimately related to their electronic properties and physical structure. Numerous theoretical models[1] and band-structure calculations[2] have been reported. The physical structure of $RBa_2Cu_3O_{7-x}$ (where R is a rare-earth metal) as determined by x-ray diffraction[3] and neutron scattering,[4] is a cuprate perovskite with orthorhombic symmetry for $x = 0$. In each cell there are two $Cu-O_2$ planes and another plane (the "chain" plane) containing Cu-O chains, all perpendicular to the c axis. For $x > 0.5$, the orthorhombic splitting vanishes and a tetragonal phase forms[5] with O vacancies in the chain plane.[6] Henry et al.[7] concluded from electron microscopy and neutron scattering that for $x > 0.5$ the number of oxygen ions in the chain planes is reduced. Tranquada et al.[8] using neutron scattering observed magnetic ordering for $x > 0.85$. They propose a magnetic structure in which the two $Cu-O_2$ planes order antiferromagnetically with an ordering temperature $T_N > 500$ K for $x = 1.0$. It was suggested that the formation of magnetically passive Cu-O layers is caused by O depletion, which reduces the Cu ions in these layers to Cu^{1+} (nonmagnetic d^{10} electronic configuration).

Spectroscopic investigations of the electronic properties of the Cu ion by x-ray photoemission spectroscopy[9,10] (XPS) and x-ray-absorption near-edge spectroscopy[9,11,12] (XANES) agree that Cu in the superconducting oxides is nearly divalent as in CuO, that is, in a $3d^9$ configuration. In the $(La_{0.85}Sr_{0.15})_2CuO_4$ system, the Cu valence is not affected by reductions in the Sr concentration sufficient to suppress superconductivity.[11] In the $RBa_2Cu_3O_{7-x}$ compounds, where R may be Y and most rare earths except Ce, Pr, and Tb, the superconducting transition temperature T_c is decreased by O deficiency ($x > 0$). No superconductivity is observed for $x > 0.5$. There is some indication from XANES (Ref. 13) that the Cu valence is reduced in samples with $x > 0$. This is also suggested by core-level[9,10] and valence-band[14] photoelectron spectros-

copy, which is consistent with the presence of Cu^{1+} ions as predicted by the neutron-scattering results. However, due to the surface sensitivity of photoelectron spectroscopy, these results may not be representative of the bulk.[15,16]

We have studied two series of samples, using bulk-sensitive XANES of the high-energy Cu $1s$ (K) edge. In the O-deficient series $EuBa_2Cu_3O_{7-x}$, we find that the Cu valence as measured by XANES decreases systematically as the O concentration is reduced from $x = 0$ to $x = 1$. For $x > 0.5$ the presence of Cu^{1+} ions in the bulk, as proposed by the neutron-diffraction study,[8] is clearly indicated. In the series $EuBa_2(Cu_{1-y}Zn_y)_3O_7$, the addition of even small amounts of Zn, which substitutes for Cu, suppresses superconductivity rapidly; $y = 0.065$ suffices to reduce T_c to below 1.5 K (Ref. 17) while other transition metals have far less effect. Substitution of elements from Ti to Ni at the 10% level was found to merely reduce T_c by at most 50%.[18] We find that Zn doping has no effect on the Cu x-ray-absorption spectra, implying Zn does not suppress superconductivity by changing the electronic state of the Cu. Rather, we suggest this suppression is due to the presence of planes of Zn, with a filled d shell and no magnetic moment, which act like the Cu^{1+} planes in O-deficient samples.

The XANES measurements were performed in transmission on beam line C1 of the Cornell High Energy Synchrotron Source (CHESS) using a dual Si(111) crystal monochromator with a typical energy resolution of about 3 eV. The energy was calibrated by simultaneous measurements on a Cu foil, defining the first inflection point as a transition energy of 8979 eV.[19] The XANES absorption coefficients, taken to be the logarithm of the incident flux divided by the transmitted flux, are normalized to the increase in absorption far above the edge and plotted as a function of photon energy. Samples were powdered under inert atmosphere and sealed in Kapton tape before exposure to the x-ray beam. Samples were prepared at Los Alamos National Laboratory by conven-

tional ceramic powder techniques. To vary the O stoichiometry, samples of the same batch were heated to 300–600 °C for various times and the weight loss, assumed to be entirely due to O loss, measured.[20] Chemical analysis showed for the starting material $x = 0 \pm 0.1$. From $x = 0$ to 0.47, T_c decreased slowly and then more abruptly so that no superconductivity was observed for $x < 0.5$ for temperatures above 1 K.[20] In the Zn-doped series, T_c was reduced by Zn doping at the rate of -19 K/at.%, and the sample with $y = 0.065$ did not superconduct above 1 K.[17]

Figure 1 shows the Cu 1s x-ray-absorption spectra (XAS) of EuBa$_2$Cu$_3$O$_{7-x}$. For $x = 0$, the spectrum is in good agreement with Refs. 9, 11, and 13. As x is increased (Fig. 1), the edge shifts slightly to lower energy and the magnitude of the absorption peak (C) decreases. For $x > 0.5$, when as mentioned superconductivity is completely suppressed, an additional contribution becomes evident on the low-energy side of the edge. These changes are more clearly shown in the inset of Fig. 1, where we plot the difference between spectra with $x > 0$ and the $x = 0$ spectrum. It is apparent that, particularly for $x > 0.5$, the principal effect of reducing the O concentration is to shift intensity from and above the peak C at about 8990 eV to a range about 8–15 eV below (peaks A and B).

In contrast, doping EuBa$_2$(Cu$_{1-y}$Zn$_y$)$_3$O$_7$ with Zn has almost no effect on the Cu 1s spectra. This is shown in Fig. 2, where we plot the absorption spectra of samples with various concentrations y of Zn. These spectra are essentially all identical, although as noted earlier T_c decreases with increasing y and vanishes entirely for $y = 0.065$. In the inset of Fig. 2 we plot, on the same scale used in Fig. 1, the difference between the pure compound ($y = 0$) and samples with increasing y. No systematic differences are observed, in sharp contrast to the oxygen-

FIG. 2. X-ray absorption spectra of the Cu 1s (K) edge in Cu oxide perovskites doped with amounts of Zn as indicated. In the inset the difference between the spectrum of the $y = 0$ material and the other spectra is plotted on the same scale used in Fig. 1.

deficient series (Fig. 1). This further implies that Zn doping does not affect the O content of the samples. While we have not made a systematic investigation, preliminary results indicate there are also no systematic changes in the x-ray-absorption spectra of the Ba and Eu 2p edges with O or Zn content.

In Fig. 3, we compare the Cu 1s spectra of superconducting EuBa$_2$(Cu$_{1-y}$Zn$_y$)$_3$O$_{7-x}$ ($x = y = 0$) with those of nonsuperconducting samples with $x = 0.5$ and $y = 0.065$. Spectra of CuCl and CuCl$_2$ are also plotted as representatives of formally monovalent and divalent Cu, respectively. The ~ 10-eV shift observed between the
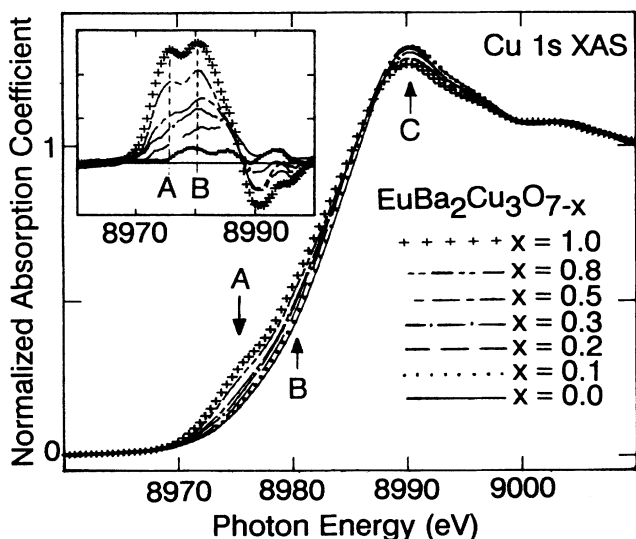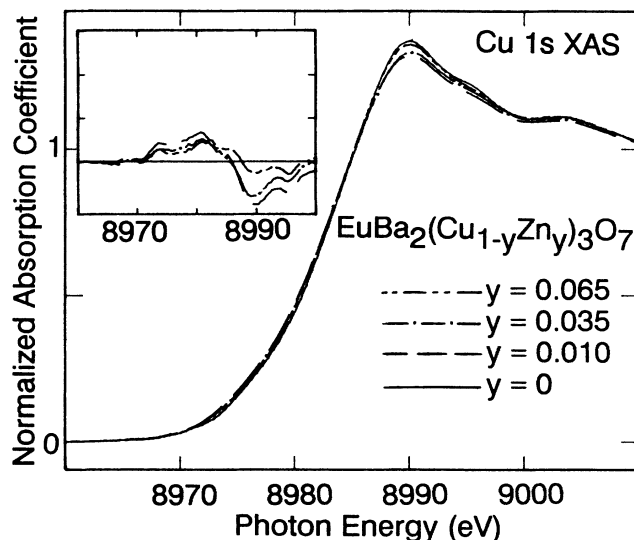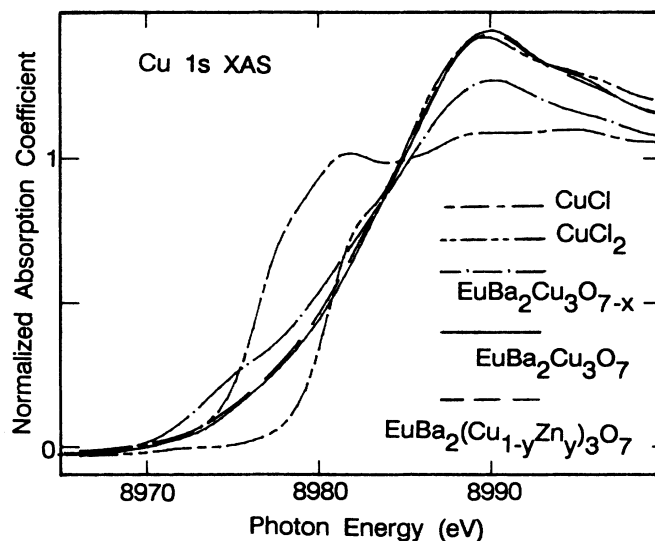

FIG. 1. X-ray absorption spectra of the Cu 1s (K) edge in copper oxide perovskites with various O contents as indicated. In the inset we plot the difference between the spectrum of the $x = 0$ material and the other spectra. Peaks A, B, and C are discussed in the text.

FIG. 3. X-ray absorption spectra of the Cu 1s (K) edge of reference compounds CuCl and CuCl$_2$ compared to superconducting EuBa$_2$Cu$_3$O$_7$ and nonsuperconducting materials with reduced O content ($x = 1$) and doped with Zn ($y = 0.065$).

peaks in the latter two spectra is consistent with other measurements[11,21-23] and with calculations comparing the energy of a Cu $1s$ hole in divalent and monovalent Cu.[12] The spectrum of the undoped superconductor, particularly the energy position of the major peak C, closely resembles that of $CuCl_2$ except for a low-energy tail, and is at significantly higher energy than that of $CuCl$, showing, consistent with other measurements,[11,12,23] that Cu in the superconducting material is primarily divalent.

The spectral changes observed may be understood by comparison with previous Cu $1s$ XANES. Bair and Goddard[24] have investigated the $1s$ edge in $CuCl_2$ and concluded that the main peak C is due to dipole transitions into Cu p orbitals, while the shoulder B is due to a shakedown effect resulting from a $1s$-to-$4p$ transition plus the simultaneous transfer of one electron from a ligand orbital (Cl $4p\sigma$ or $4p\pi$) to a Cu d orbital. Thus, the final state of peak C is $\underline{1s}3d^9p^*$, while that of peak B is $\underline{1s}3d^{10}p^*\underline{L}$, where $\underline{1s}$ ($\underline{L}$) refers to a hole in the Cu $1s$ state (ligand) and p^* indicates an excited p like state. These final states differ by approximately $\delta = U_{cd} - U_{dd} - \varepsilon_L$, where U_{cd} (U_{dd}) is the Coulomb energy between a core hole and a d electron (between two d electrons on the same atom) and ε_L is the excitation energy of the ligand electron. Measurements show $\delta \sim 7.5$ eV. Transitions to similar final states based on a $2p$ hole are observed in XPS, where $\delta \sim 8$ eV,[25] in fair agreement. Calculations[12] indicate that $U_{cd} - U_{dd} \sim 10$ eV, which implies $\varepsilon_L \sim 3$ eV. In CuO, Grunes[26] identifies two pre-edge peaks at 6 and 12 eV below the main edge, and concludes they are due to similar shakedown processes, but at other energies as ε_L varies with the bonding configuration. We similarly identify peak C in the $EuBa_2Cu_3O_7$ spectrum with direct transitions and peak B, which appears 7 eV lower, with a shakedown. Figure 1 indicates that peak B increases in intensity and shifts to lower energy as the O content is reduced. The energy shift may be due to a decrease in ε_L and the intensity increase due to greater overlap between the ligand orbital and the Cu core states as decreasing O content reduces the binding energy of a ligand electron and shifts the center of gravity of the bond charge distribution towards the Cu ions. As the O content is further reduced, another peak A appears. We propose that this peak is due to Cu^{1+} (d^{10}) ions in the initial state, as previously proposed for O-deficient materials.[9,13] The final state $\underline{1s}d^{10}p^*$ reached by a dipole transition from a Cu^{1+} initial state is lower in energy by ε_L than the shakedown final state $\underline{1s}d^{10}p^*\underline{L}$ (peak B) of a Cu^{2+} (d^9) initial state. Since $E(B) - E(A) \sim 4$ eV, this yields $\varepsilon_L \sim 4$ eV, in good agreement with the estimate above. No shakedown is expected for a d^{10} initial state. The observation that the Cu spectrum is unchanged by Zn doping implies that the Zn has no effect on the electronic state of the Cu.

Our measurements imply that O deficiency causes a decrease in the Cu valence, adding electrons to or decreasing the number of d holes on the Cu ions. This valence change may be homogenous, with all Cu ions in a valence state intermediate between 2 and 1, or heterogenous, with Cu ions on different sites adopting different valences. Our measurements cannot distinguish between these two possibilities, but XAS work on oriented samples[27] suggests

heterogeneity, as the Cu ions responsible for the monovalent spectral component evidently are twofold coordinated, and hence, are in the chain planes. This possibility is reinforced by the neutron-diffraction results[8] mentioned above which imply the chain plane Cu ions do not order magnetically. This does not necessarily require these ions are in a nonmagnetic (d^{10}) configuration, but it suggests they are, especially since O deficiency removes primarily the adjacent O ions in this plane. If the O ions all have the same valence, as is indicated by photoemission measurements which show a single peak corresponding to O in a single charge state,[28] the fact that a Cu^{1+} component appears as soon as x exceeds zero implies that the Cu valence at $x = 0$ is not greater than $2+$. If we assume there is no charge transfer between the planes, so that O removal from the chain planes affects only the ions within those planes, all the Cu in the chain planes must be monovalent at $x \gtrsim 0.5$, while the other Cu are unaffected. However, the Cu^{1+} spectral component continues to increase for $x > 0.5$, and we conclude that charge transfer from the chain planes to the CuO_2 planes does occur. They may happen in two ways: either all chain plane Cu ions are monovalent for $x \sim 0.5$ and the continued increase in the Cu^{1+} feature for larger x is due to charge transfer to the CuO_2 planes and an associated change in the valence of its Cu ions, or charge transfer to the CuO_2 planes begins when x is less than 0.5 and not all chain plane Cu ions are monovalent yet for $x \sim 0.5$. In either case, it is appealing to relate this change in the Cu valence to the suppression of superconductivity. When, on the other hand, the material is doped with Zn sufficient to completely suppress superconductivity, we observe no change in the Cu valence.

There are three possible explanations of these results. (a) The mechanism for the suppression of superconductivity is different in O-deficient and Zn-doped samples. (b) The change in Cu valence is not the primary cause of the suppression of superconductivity, but a reduction of the O (i.e., a change in O valence) is the determining factor in both cases. (c) The electronic state of the O and Cu ions is not important to superconductivity. Interpretation (c) seems unlikely as the Cu-O planes and possibly the Cu-O chains evidently are important in the mechanism of superconductivity and changes in the electronic state of either of these ions must affect the superconducting properties. In favor of option (b) one can argue that doping with Zn may affect only the O valence, which was not investigated here. However, since band-structure calculations[2] show these materials have a strongly hybridized (Cu $3d$)-(O $2p$) band, large changes in the electronic state of the O would necessarily affect the Cu. Furthermore, we have recently obtained spectroscopic data[29] indicating that Zn doping ($y \lesssim 0.1$) has little or no effect on the electronic state of the O. This also implies that the Zn does not donate more charge to the lattice, and we conclude that the doped Zn is divalent, with a filled d^{10} subshell, as is chemically expected. This leaves option (a), that two different mechanisms are involved. However, the development of the macroscopic properties as a function of x and y are suggestively similar. For example, the pure compound is metallic (electrical resistivity decreasing linearly

with temperature) while both specimens with large x and specimens with large y are semiconducting and both become more magnetic.[30]

Although Zn doping evidently does not affect the electronic state of the Cu, it nevertheless involves a decrease in the number of $3d$ holes because divalent Zn has a filled d shell: in this context, an increase in the Hall coefficient, implying a reduction in either the mobility or the concentration of the carriers, has been observed for Zn-doped samples.[31] Indeed, it is remarkable, but nevertheless implied by this experiment, that 7% Zn doping causes only a 7% reduction in the $3d$ hole concentration, as we observe no change in the Cu valence, and no reduction in the O $2p$ hole concentration.[29] This modest reduction in the charge carrier density seems insufficient to produce a semiconductor from a metal. Thus we surmise that Zn doping must reduce the carrier mobility, or, equivalently, acts as a hopping barrier to localize the $3d$ holes. Such hole localization should also be present in O-deficient samples, with the Cu^{1+} ions adopting the role of divalent Zn (both have a filled d shell).

As we have just noted, it is surprising that a relatively low Zn concentration has such large effects on both the normal and superconducting properties. If the Zn is statistically distributed among the three Cu planes, these effects would be produced by less than 2–3% Zn in each plane; this seems unlikely and suggests that the Zn distribution is not, in fact, statistical. The Zn might preferentially occupy either (a) the CuO_2 planes or (b) the chain plains. Possibility (a) is suggested by the widely held belief that conductivity occurs in the CuO_2 planes and by some neutron-scattering measurements.[32] Possibility (b) is attractive for these reasons: (i) The concentration of

Zn in this plane would be higher, and hence more influential, as there is only one chain plane per cell. (ii) The structure thus formed is reminiscent of that proposed by the neutron-scattering measurements mentioned above,[8] with Zn^{2+} adopting the role of Cu^{1+}. These transition-metal ions, in a filled $3d$ configuration with no magnetic moment, might suppress superconductivity and facilitate the formation of the long-range (anti)ferromagnetically ordered structure observed in O-deficient samples.[8] This proposed preferential occupancy could be tested by neutron-diffraction measurements which could also investigate possible magnetic ordering in these Zn-doped materials.

In conclusion, x-ray-absorption measurements indicate that the suppression of superconductivity in $EuBa_2Cu_3O_7$ due to O deficiency or Zn doping may not be due to an overall change in the electronic state of Cu but that a significant common factor seems to be the presence of ions with a filled $3d$ subshell. We speculate that Zn ions in $EuBa_2(Cu_{3-y}Zn_y)O_7$ occupy preferentially one kind of CuO plane; if this is the chain plane as for the Cu^{1+} ions in $YBa_2Cu_3O_6$, the same mechanism may be responsible for the loss of superconductivity in both systems.

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[1]T. M. Rice, Z. Phys. B **67**, 141 (1987), and references therein.

[2]L. F. Matheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987); S. Massidda, *et al.*, Phys. Lett. A **122**, 198 (1987).

[3]R. J. Cava, *et al.*, Phys. Rev. Lett. **58**, 1676 (1987).

[4]Q. W. Yan, *et al.*, Phys. Rev. B **36**, 5599 (1987).

[5]J. M. Tarascon, *et al.*, **36**, 226 (1987).

[6]R. J. Cava, *et al.*, Phys. Rev. B **36**, 5719 (1987).

[7]J. Y. Henry, *et al.*, Solid State Commun. **64**, 1037 (1987).

[8]J. M. Tranquada, *et al.*, Phys. Rev. Lett. **60**, 156 (1988).

[9]S. Horn, *et al.*, Phys. Rev. B **36**, 3895 (1987).

[10]A. Fujimori, *et al.*, Phys. Rev. B **35**, 8814 (1987); Zhi-xun Shen, *et al. ibid.* **36**, 8414 (1987); A. Bianconi, *et al.*, Solid State Commun. (to be published); P. Steiner, *et al.*, Z. Phys. B **67**, 497 (1987).

[11]J. M. Tranquada, *et al.*, Phys. Rev. B **35**, 7187 (1987).

[12]J. M. Tranquada, *et al.*, Phys. Rev. B **36**, 5263 (1987).

[13]F. Baudelet, *et al.*, Z. Phys. B **69**, 141 (1987).

[14]N. G. Stoffel, *et al.* (unpublished).

[15]J. Halbritter (unpublished).

[16]S. Horn, *et al.*, in *Thin Film Processing and Characterization of High-Temperature Superconductors*, edited by J. M. E. Harper, R. F. Cotton, and L. C. Feldman, AIP Conference Proceedings series, Vol. 165 (American Institute of Physics, New York, 1988) p. 311; A. G. Schrott, *et al.*, *ibid.*, p. 349.

[17]H. A. Borges, *et al.*, Physica B **148**, 346 (1987).

[18]Gang Xiao, *et al.*, Phys. Rev. B **35**, 8782 (1987).

[19]*X-ray Data Booklet* (Lawrence Berkeley Laboratory, Berkeley, 1985), and references therein.

[20]R. S. Kwok, *et al.*, Physica B **148**, 411 (1987).

[21]E. E. Alp, *et al.*, Phys. Rev. B **35**, 7199 (1987).

[22]Y. Jeon, *et al.*, Phys. Rev. B **36**, 3891 (1987).

[23]J. B. Boyce, *et al.*, Phys. Rev. B **36**, 5251 (1987).

[24]R. A. Bair and W. A. Goddard, Phys. Rev. B **22**, 2767 (1980).

[25]G. van der Laan, *et al.*, Phys. Rev. B **23**, 4369 (1981).

[26]L. A. Grunes, Phys. Rev. B **27**, 2111 (1983).

[27]J. Tranquada, *et al.*, Bull. Am. Phys. Soc. **33**, 772 (1988).

[28]N. G. Stoffel, *et al.*, Phys. Rev. B **37**, 7952 (1988).

[29]M. L. denBoer, *et al.*, (unpublished).

[30]S. H. Bloom, *et al.*, Bull. Am. Phys. Soc. **33**, 689 (1988).

[31]Z. Z. Wang, *et al.*, Phys. Rev. B **36**, 7222 (1987).

[32]Gang Xiao, *et al.* (unpublished).