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Nature of empty states in $YBa_2Cu_3O_{7-x}$

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Angle-resolved oxygen K-edge x-ray-absorption spectroscopy measurements were performed on single crystals of $YBa_2Cu_3O_{6.9}$. Measurements were carried out on *in situ* cleaved crystals at 20 K to minimize the loss of oxygen from the surface region of the samples. It was found that there are two distinct transitions between 526 and 531 eV. The peaks in $YBa_2Cu_3O_{6.9}$ show strong orientation dependence, as well as energy dispersion of 2 eV. After the sample is heated to room temperature, there is only one peak visible which shows little energy dispersion or orientation dependence. Comparison of the experimental results to a transition-state calculation of the absorption cross section shows good agreement indicating that there are holes of σ symmetry on all Cu—O bonds.

Since the discovery of high-temperature superconductivity in La_2CuO_4 and $YBa_2Cu_3O_x$ copper oxides, the question of creation of holes by chemical doping has been frequently addressed. It is now a well-known fact that as the oxygen content of $YBa_2Cu_3O_x$ varies between $x=6$ and 7 the material goes from an antiferromagnetic insulator to a superconducting metal.[1] Many theoretical models of the high-temperature superconductors assume that this doping only slightly alters the electronic structure, and therefore the conduction arises from the creation of holes on the oxygen $2p$ band of a variant of the Hubbard model.[2–4] Previous experiments, such as x-ray-absorption near-edge structure (XANES), electron-energy-loss (EELS), and inverse photoemission spectroscopies which can probe the empty levels directly, seemed to support these models.[5–7]

However, it has been shown that $YBa_2Cu_3O_{6.9}$ will lose oxygen from the surface region when subjected to an ultrahigh-vacuum environment, even if cooled to liquid-nitrogen temperatures.[8] This means that results obtained with surface-sensitive techniques such as XANES and inverse photoemission spectroscopy will *not* be representative of the superconducting state. Although EELS probes all of the sample depth as the electron travels through it (about 1000 Å), the oxygen loss might be deep enough to affect an appreciable fraction of the sample volume.

Recent experiments[8] have found that by cleaving the samples while at 25 K, the oxygen loss is much reduced. In this Rapid Communication we report the results of our investigation on the nature of the empty states just above E_F in samples which are superconducting *at the surface* by polarized x-ray-absorption spectroscopy. In this technique, the holes above the Fermi level are filled by promoting an electron from a filled oxygen $1s$ state. The $1s$ hole left behind is filled by electrons from the conduction band, and the ensuing Auger electrons are ejected from the sample, as well as causing a shower of inelastic secondary electrons, which we monitor as a measure of the filling of the empty states above E_F.

Many of the previous XANES and EELS experiments on the oxygen edge have been interpreted without the benefit of comparison to suitable calculations of the absorption cross section. This can be quite misleading, as we will show below. Therefore, here we compare the experimental results to a transition-state calculation of the oxygen K-edge absorption cross section, in which the delocal-

ized empty final states are calculated by the multiple scattering $X\alpha$ method,[9-12] and employing the muffin-tin projection of the self-consistent discrete-variational (DV-$X\alpha$) ground-state periodic potential calculated by Goodman *et al.*[13] Clusters of 59 atoms which center at the four different oxygen sites [O(1) bridging, O(2) and O(3) in plane, O(4) chain] were chosen in the calculation of the continuum final states. A charged spherical boundary was placed around the entire cluster in order to provide an asymptotic $1/r$ potential.[14] The cross section due to empty bound states (those in between the vacuum and Fermi energies) are obtained directly from the (DV-$X\alpha$) calculation in the dipole approximation[14,15] instead of the multiple-scattering procedure.[15]

The experiments were carried out with polarized x rays from the Aladdin Synchrotron, monochromatized by an extended-range Grasshopper monochromator, with an energy resolution of 300 meV. There is an uncertainty of several eV in the absolute photon energy given by the monochromator but relative photon-energy differences within and between individual spectra should be accurate. The samples are single crystals of $YBa_2Cu_3O_{6.9}$, although there is considerable twinning, which makes it impossible for us to distinguish between the *a* and *b* axes. Magnetization measurements were carried out on the samples to confirm that they are of uniform composition, and they exhibit a very sharp (<2 K) superconducting transition at 92 K. The samples were cooled to 24 K *before* cleaving them in a vacuum of 1×10^{-10} Torr, in order to minimize oxygen loss. The measurements are repeated after warming the samples to room temperature, in order to determine the nature of holes in an oxygen depleted sample. In obtaining the data by measuring the total electron yield, we normalized the spectra by subtracting a straight line fitted to the region before the peaks (below 525 eV), and adjusting the intensity of the spectra to coincide at 546 eV. We have found this procedure to yield spectra that can be reasonably compared to each other, although the intensities at one angle relative to another are accurate only up to 20%. The spectra shown in the figures have not been smoothed or filtered in any way.

Figure 1 shows the O *K* edge as a function of the angle θ between the incident photon beam and the *c* axis of the sample. The samples are oriented such that the photon beam sweeps in angle between the *c* axis and the *a* or *b* axis. At normal incidence (polarization perpendicular to the *c* axis), a small peak at 526.4 eV (labeled *A*) and a prominent peak at 529.2 eV (*B*) precede the edge. The edge itself, starting at ~532 eV, also shows significant structure. As the angle θ is increased by a few degrees, the small peak at 526.4 eV increases in intensity, shifting to ~527.1 eV. The peak at 529.2 eV decreases and also shifts to higher binding energy. Since these are transitions starting from the O 1*s* level, the selection rules of photoemission indicate that we are observing the components of 2*p* symmetry. It should be emphasized that these results do not imply that the holes have *only* 2*p* symmetry.

The behavior of peaks *A* and *B* as a function of angle of incidence can be seen in detail in Fig. 2. There is an increase of peak *A* as well as a decrease of peak *B* as the angle of incidence increases by only 10°. We interpret these results as follows: Peak *A* is due to O(2) and O(3) holes (in the CuO_2 planes), and peak *B* is due to O(4) holes (along the chains). As θ increases by 10°, the x-ray polarization becomes aligned with the O(2),O(3)-Cu axis in the planes, since the O(2)-Cu and O(3)-Cu axes form angles of 10° with the *a* and *b* axes, and the intensity of peak *A* increases. Similarly, as θ increases, the angle between the O(4)-Cu axis and the electric field increases, resulting in a large decrease of peak *B*. Later, comparisons with theory will show that as θ increases different components mix, which causes the intensity of peaks *A* and *B* not to have simple $\cos^2\theta$ variations as one might expect. As θ increases beyond 20°, peak *A* again decreases in intensity.

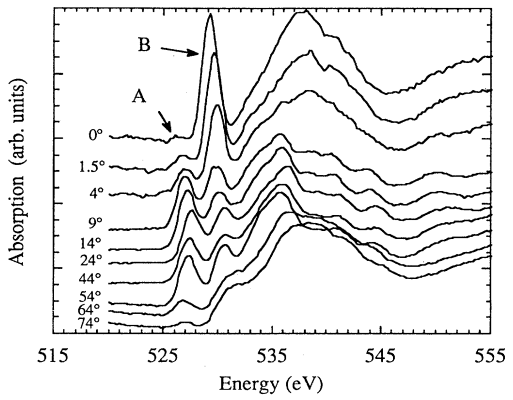

FIG. 1. Total electron yield due to x-ray absorption by O 1*s* electrons as a function of angle between the electric field and the *c* axis of $YBa_2Cu_3O_{6.9}$.

We can better understand the nature of the holes by a comparison with the calculated photoabsorption cross section shown in Fig. 3. The top curve shows the total absorption cross section at $\theta=0°$, when the electric field is perpendicular to the *c* axis. The subsequent curves show the decomposition of the total cross section at $\theta=0°$ into

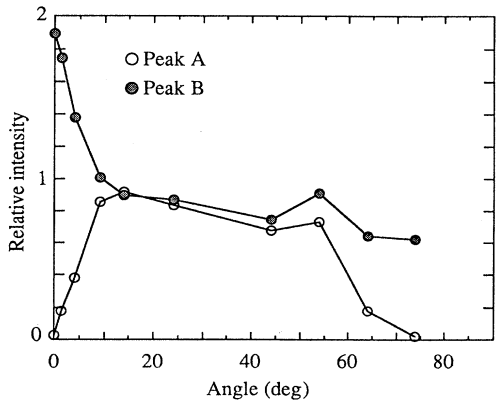

FIG. 2. Angular dependence of the x-ray absorption by O 1*s* electrons as a function of angle between the electric field and the *c* axis of $YBa_2Cu_3O_{6.9}$. The intensities are normalized relative to the intensity of the absorption coefficient at 546 eV.

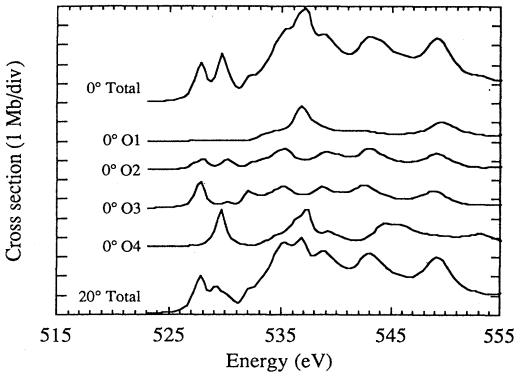

FIG. 3. Calculation of the absorption cross section by O 1*s* electrons as a function of angle between the electric field and the *c* axis of $YBa_2Cu_3O_{6.9}$ at $\theta=0°$ and $\theta=20°$.

the components due to holes along different O-Cu axes. The zero of the theoretical energy scale has been chosen to align with the experimental data. It can be seen that O(2) and O(3) holes contribute to peak *A*, while peak *B* is made up mostly of O(4) holes, although there are also O(2) and O(3) contributions. The calculations show that there is dispersion of the hole states. Although peaks *A* and *B* do in fact show significant dispersion, they are composites of at least two states each, and it is therefore difficult to determine the dispersion of any one state experimentally.

The calculations indicate that the states between the Fermi and vacuum levels are hybrids of O 2*p* with Cu 3*d* orbitals. A trapping-time analysis[14,15] of the final states above the vacuum level (the edge itself) indicates that the peaks following *A* and *B* all derive O 3*p* resonance states.

Figure 4 shows the calculations along $\theta=70°$ and 90°. It can be seen that after 20° both peaks decrease and at $\theta=90°$ a peak due to O(1) dominates the spectra. A decomposition of the total cross section at $\theta=90°$ shows that peak *B* is due almost entirely to O(1) holes, which lie between the apex oxygen along the *c* axis and neighboring Cu atoms on the planes, although small components due to O(2), O(3), and O(4) can still be seen. These calculations confirm our assignment based purely on the intensity behavior shown in Fig. 2, and they also show that holes are present on all O—Cu bonds in the fully oxygenated material. The ratio of intensities of peaks *A* and *B* is somewhat sample dependent, but the angular dependence of each individual peak is the same for all the samples we have studied. It is possible that because the samples are twinned, different proportions of the microcrystallites have their *a* or *b* axes aligned along the electric field direction in different samples. The calculations shown in Figs. 3 and 4 consider equal amounts of crystallites with *a* and *b* axes aligned along the electric field direction.

As can be seen in Figs. 3 and 4 the calculations of the individual contributions of O(1), O(2), O(3), and O(4) at $\theta=0°$ and 90° indicates that the holes are of σ symmetry, as their intensities are maximum when the electric field vector of the incident photon beam is along the Cu—O bonds. This result is in agreement with the interpretation of our experimental results presented above.

We then warm up the sample to 300 K. In this case the spectra are quite different, as shown in Fig. 5: There is only one peak seen for all angles of polarization of the x rays, with very little variation in energy or intensity.

If one takes into consideration the resolution of the experiment, the same features observed in the experiment are reproduced in the calculations for $YBa_2Cu_3O_6$; only one peak is seen at all angles. A decomposition of the cross section reveals that at $\theta=0°$ only O(2) and O(3) contribute, while at $\theta=90°$ only O(1) contributes. Notice also that the peak due to O(1) shifts in energy, such that it now coincides with the peaks due to O(2) and O(3). This also explains the slight disagreement between the energies of the calculated and measured peaks at $\theta=90°$ for the $x=6.9$ sample. Note that the calculation is for $x=7$, while the samples have no more than $x=6.9$, which means that the theoretical peak should be shifted to lower binding energy, in accord with the experiment.

As expected, at $x=6$ there are no O(4) holes. The surprising thing is that the density of states shows that the number of holes in the planes have not changed sig-

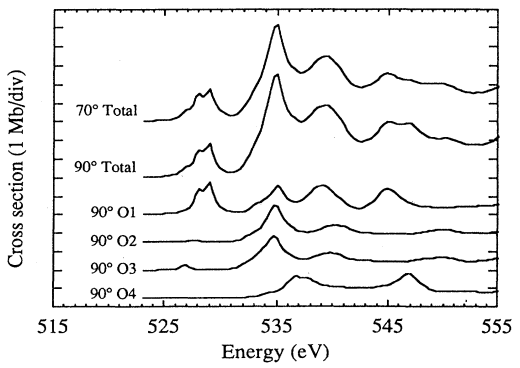

FIG. 4. Calculation of the absorption cross section by O 1*s* electrons as a function of angle between the electric field and the *c* axis of $YBa_2Cu_3O_{6.9}$ at $\theta=70°$ and $\theta=90°$.

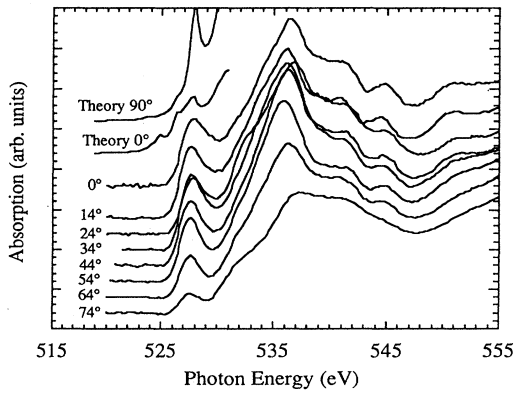

FIG. 5. Total electron yield due to x-ray absorption by O 1*s* electrons as a function of angle between the electric field and the *c* axis of $YBa_2Cu_3O_6$.

nificantly as the oxygen concentration is reduced from $x=7$ to $x=6$, contrary to what one might expect. It is the hole between O(1) and the planes which is affected the most. However, this does not mean that the band structure has not changed. The two materials, $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, are indeed different. The $x=6$ material does show the characteristics of a highly correlated insulator, but the $x=7$ material is a good metal,[8] which is not obtained by just doping an O $2p$ band in the $x=6$ material, as is also shown by valence-band photoemission experiments.[16] In our model calculations, the charge difference in going from $x=7$ to $x=6$ is accommodated mostly by the Cu(1) atoms, with almost no change in O(2) and O(3).[13] The experiments seem to confirm this picture, which is contrary to predictions of models which are variants of the Hubbard model.[2]

In summary, we have determined that holes with σ symmetry are present in all Cu—O bonds at $x=6.9$, and that it is the O(4) and O(1) holes which are affected the most as oxygen is lost, while the holes in the planes remain mostly unperturbed. There is significant dispersion of the hole states, although we have not been able to quantify it experimentally as yet.

We thank N. Rivier for explaining to us how our measurements can determine dispersion.

[1]J. D. Jorgensen, H. Shaked, D. G. Hinks, B. Dabrowski, B. W. Veal, A. P. Paulikas, J. L. Nowicki, G. W. Crabtree, W. K. Kwok, L. H. Nuñez, and H. Claus, Physica C **153-155**, 578 (1988).

[2]V. Emery, Phys. Rev. Lett. **58**, 1196 (1987).

[3]J. C. Fuggle, P. J. Weijs, R. Schoorl, G. A. Sawatzky, J. Fink, N. Nücker, P. J. Durham, and W. M. Temmerman, Phys. Rev. B **37**, 123 (1988).

[4]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[5]J. Fink, N. Nücker, H. Romberg, and J. C. Fuggle, IBM J. Res. Dev. (to be published).

[6]N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B **39**, 6619 (1989), and references therein.

[7]P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. Weijs, F. M. F. de Groot, G. A. Sawatzky, H. Verweij, L. F. Feiner, and H. Petersen (unpublished).

[8]R. S. List, A. J. Arko, Z. Fisk, S.-W. Cheong, S. D. Conradson, J. D. Thompson, C. B. Pierce, D. E. Peterson, R. J. Bartlett, N. D. Shinn, J. E. Schirber, B. W. Veal, A. P. Paulikas, and J. C. Campuzano, Phys. Rev. B **38**, 11966 (1988).

[9]D. Dill and J. L. Dehmer, J. Chem. Phys. **61**, 692 (1974).

[10]K. H. Johnson, in *Advances in Quantum Chemistry,* edited by P. O. Lowdin (Academic, New York, 1973), Vol. 7, p. 143.

[11]J. L. Dehmer and D. Dill, Phys. Rev. Lett. **35**, 231 (1975); J. Chem. Phys. **65**, 5327 (1976).

[12]S.-H. Chou, J. Guo, and D. E. Ellis, Phys. Rev. B **34**, 12 (1986).

[13]G. L. Goodman, D. E. Ellis, E. E. Alp, and L. Soderholm, J. Chem. Phys. **91**, 2983 (1989).

[14]J. Guo, D. E. Ellis, E. E. Alp, L. Soderholm, and G. K. Shenoy (unpublished).

[15]J. Guo, D. E. Ellis, G. L. Goodman, E. E. Alp, L. Soderholm, and G. K. Shenoy, Phys. Rev. B **39**, 6125 (1989).

[16]J. C. Campuzano, G. Jennings, M. Faiz, L. Beaulaigue, B. W. Veal, A. P. Paulikas, J. Z. Liu, K. Vandervoort, R. S. List, A. J. Arko, and R. J. Bartlett (unpublished).