PHYSICAL REVIEW B VOLUME 41, NUMBER 4 1 FEBRUARY 1990

Density and symmetry of unoccupied electronic states of $Tl_2Ba_2CaCu_2O_8$

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(Received 31 October 1989)

The local density and symmetry of unoccupied electronic states at the O and Cu sites in $Tl_2Ba_2CaCu_2O_8$ single crystals has been investigated by measuring O 1*s* and Cu 2*p* absorption edges. High-energy electron-energy-loss spectroscopy in transmission has been used. There are O $2p_{x,y}$ states at the Fermi level from the CuO_2 planes and O $2p_z$ states from the BaO and TlO layers. The empty Cu 3*d* states have predominantly $3d_{x^2-y^2}$ symmetry. There is an admixture of about 10% probably with $3d_{3z^2-r^2}$ character.

The study of the electronic structure of the high-T_c superconductors is an important goal for the understanding of the mechanism for superconductivity in cuprate superconductors. Generally, it is accepted for *p*-type doped high-T_c superconductors that the essential charge carriers are extra holes in the CuO_2 planes having predominantly O 2*p* character. These holes are created by *p*-type doping due to adjacent layers. In the homologous series $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1,2,3$) which shows superconducting transition temperatures T_c up to 125 K, band-structure calculations[1-3] predict a charge transfer from the CuO_2 planes to the TlO planes. Thus, self doping should lead to holes in the CuO_2 planes and to electron pockets in the TlO layers. On the other hand, the CuO_2 layers are widely believed to display strong correlation effects, leaving the applicability of band-structure calculations in the local density approximation open to question. In addition there are chemical[4] and experimental[5] arguments against the metallic character of the TlO (BiO) layers in $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$). Therefore, experiments investigating the electronic structure of these systems are highly demanded. For the series $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, only very few studies using high-energy spectroscopies are reported[6,7] while for the similar series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, numerous articles have been published. In this contribution, we report on the investigation of the local density of unoccupied electronic states at the O and Cu sites in $Tl_2Ba_2CaCu_2O_8$. This was achieved by measuring transitions from the O 1*s* and Cu 2*p* core levels into unoccupied states using high-energy electron-energy-loss spectroscopy (EELS) in transmission. Performing orientation-dependent measurements on single crystals, information on the symmetry of the unoccupied states could be obtained. Similar work on other high-T_c superconductors has been published previously.[8,9]

For preparation of $Tl_2Ba_2CaCu_2O_8$ single crystals, appropriate amounts of highly pure Tl_2O_3, $Ba(NO_3)_2$, CaO, and CuO fine powders were thoroughly mixed and ground. Pressed pellets, usually 16 mm in diameter and 15 mm in height were arranged in an alumina crucible, together with a Tl_2O_3 source in a gold boat, and covered with a fitting lid. The crucible was heated up to 930 °C with a rate of 600 °C/h and held at this temperature for 5 h, slowly cooled down to 890 °C within 40 h and then cooled to room temperature with 60 °C/h. Free standing single-crystalline platelets had grown at the bottom of the crucible between gold boat and walls with dimensions of about $1\times1\times0.05$ mm^3. By x-ray analysis using the Buerger precession method, no other phases than $Tl_2Ba_2CaCu_2O_8$ could be detected. By dc conductivity measurements, the superconducting transition temperature was determined to be $T_c=101$ K. Films about 1000 Å thick were cut from the single crystals along the **a**,**b** plane by an ultramicrotome using a diamond knife. These films were mounted on standard electron microscope grids. The O 1*s* and Cu 2*p* absorption edges were measured by high-energy EELS in transmission using a dedicated 170-keV spectrometer.[10] The full width at half maximum energy and momentum resolution was chosen to be 0.4 eV and 0.2 Å^{-1}, respectively.

Orienting the **a**,**b** plane of the sample 45° relative to the beam direction, the total momentum transfer **q** as composed of the momentum transfer $\mathbf{q}_\parallel$ (due to the energy loss) and $\mathbf{q}_\perp$ (due to a finite scattering angle), could be chosen to be either parallel or perpendicular to the **a**,**b** plane. This can be achieved by setting $q_\parallel=q_\perp$ and changing the sign of $q_\perp$. Details of the measuring geometry are described in Ref. 9. All measurements were corrected for finite momentum-transfer resolution. We emphasize that EELS in transmission is not a surface sensitive method as, e.g., photoemission spectroscopy, inverse photoelectron spectroscopy, or x-ray absorption spectroscopy in the partial yield mode. Therefore, ambiguities due to surface contamination are avoided.

In Fig. 1 we show O 1*s* absorption edges of a $Tl_2Ba_2CaCu_2O_8$ single crystal with momentum transfer parallel ($\mathbf{q}\parallel\mathbf{a},\mathbf{b}$) and perpendicular ($\mathbf{q}\parallel\mathbf{c}$) to the CuO_2 planes. The former probes unoccupied states at the O sites with $2p_{x,y}$ symmetry while the latter probes O $2p_z$ states. A strong anisotropy is observed. The absorption edges are at 527.8 and 529.0 eV for $\mathbf{q}\parallel\mathbf{a},\mathbf{b}$ and $\mathbf{q}\parallel\mathbf{c}$, re-

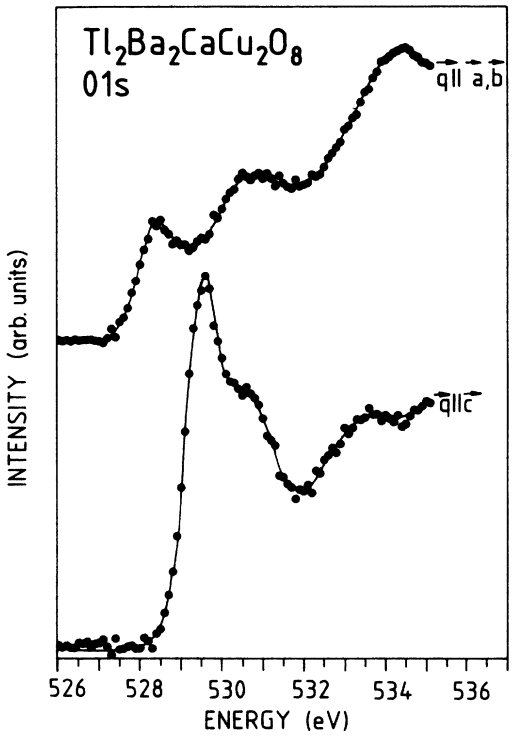

FIG. 1. O 1*s* absorption edges of $Tl_2Ba_2CaCu_2O_8$ for momentum transfer in the **a**,**b** plane and parallel to the *c* axis.

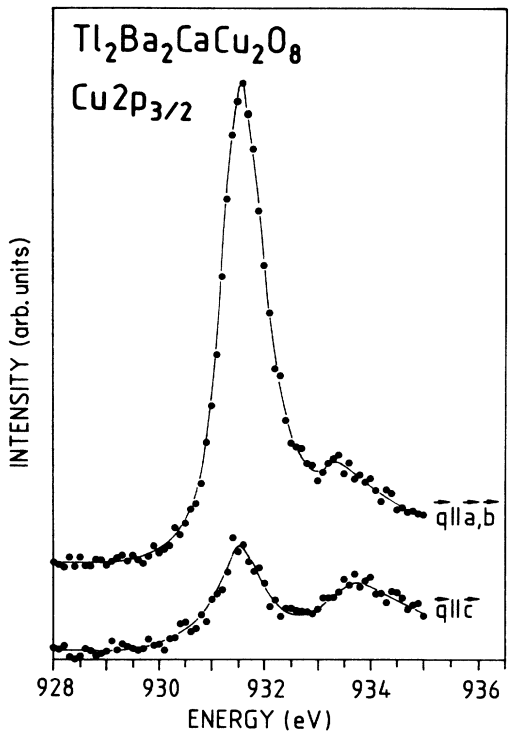

FIG. 2. Cu $2p_{3/2}$ absorption edges of $Tl_2Ba_2CaCu_2O_8$ for momentum transfer in the **a**,**b** plane and parallel to the *c* axis.

spectively. A similarly strong anisotropy is observed for the Cu 2*p* absorption edges as shown in Fig. 2. For **q** ∥ **a**,**b**, a strong excitation into 3*d* orbitals parallel to the CuO_2 planes is observed at 931.6 eV indicating that most of the empty Cu 3*d* states have $3d_{x^2-y^2}$ symmetry. For **q** ∥ **c**, there is a much smaller peak at the same energy indicating empty states in orbitals which are perpendicular to the CuO_2 planes. Additional shoulders are observed at 933.3 eV (for **q** ∥ **a**,**b**) and at ~933.7 eV (for **q** ∥ **c**).

First we discuss the O 1*s* absorption edges. According to calculations[11] of photoemission, inverse photoemission, and x-ray emission spectra, the three different O sites in $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ have three different binding energies for the O 1*s* level. The atoms with the deepest core level are the O(3) atoms in the Tl_2O_2 layers. The O(2) atoms in the BaO layer have a binding energy of the O 1*s* level which is 1.2 eV smaller. Finally, the O(1) atoms in the CuO_2 layers have the smallest O 1*s* binding energy, about 1 eV smaller than that of the O(2) atoms. The differences in chemical shifts are probably well estimated in the local density approximation (LDA) since the chemical shift is only dependent on the charge distribution in the ground state which is well described in LDA. Unfortunately, the available O 1*s* photoemission spectra[7] provide no detailed information on the binding energies of the O 1*s* level of the different O sites. Assuming that the calculated chemical shifts are correct, the origin of the two absorption edges can be immediately explained. The lowest edge, observed for **q** ∥ **a**,**b**, then corresponds to the O(1) atoms in the CuO_2 planes. Moreover, the energy of this edge is close to that observed[8,9] for O in CuO_2 layers in other cuprate superconductors, e.g., $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_7$, or $Bi_2Sr_2CaCu_2O_8$. At the energy of the O(1) edge (527.8 eV) there is only spectral weight for **q** ∥ **a**,**b**. Within the accuracy of the measurements and the applied corrections, no spectral weight for **q** ∥ **c** is observed. This indicates that the empty states close to the Fermi level at these O sites in the CuO_2 layers have $2p_{x,y}$ symmetry and that there are no hole states on these O sites in $2p_z$ orbitals perpendicular to the CuO_2 layers. This result is the same as that obtained for $Bi_2Sr_2CaCu_2O_8$ by EELS (Ref. 9) and x-ray absorption spectroscopy (XAS).[12,13]

The second edge at 529 eV, observed for **q** ∥ **c**, is ascribed to O(2) atoms in the BaO layers. The energy difference between the two edges is very close to the calculated one. On the other hand, according to these calculations a third edge due to O(3) atoms in Tl_2O_2 layers should be observed at 530.2 eV which is not well pronounced either in the **q** ∥ **a**,**b** or in the **q** ∥ **c** spectrum. Possibly, the shoulder at ~530.5 (for **q** ∥ **c**) and the broad maximum at about the same energy (for **q** ∥ **a**,**b**) is caused by an edge due to O(3) atoms. The width of the two edges at 527.8 and at 529 eV is almost identical. It can be well described by a convolution of a Fermi edge with a Gaussian due to the experimental resolution ($\Delta E_{1/2}$ = 0.4 eV) and a Lorentzian due to the lifetime of the O 1*s* level[14] ($\Delta E_{1/2}$ ~ 0.18 eV). Thus the present experiments clearly reveal a Fermi edge due to O $2p_{x,y}$ states in the CuO_2 planes and due to predominantly O $2p_z$ states from BaO-Tl_2O_2 planes. This is exactly predicted by the band-structure calculations. Electron pockets at the Γ and *Z* point of the Brillouin zone are formed from an antibonding band composed of O(2) and O(3) $2p_z$ orbitals hybri-

dized with Tl 6*s* and Tl $5d_{3z^2-r^2}$ orbitals. The strong hybridization is related to the very short Tl-O(3) and Tl-O(2) distances. The experimental results, therefore, clearly indicate the metallic character of the Tl_2O_2 layers [including the O(2) atoms] and support the picture of self-doping due to a charge transfer from the CuO_2 layers to the Tl_2O_2 layers. Recently, similar results were obtained for the $Bi_2Sr_2CaCu_2O_8$ system from angle-resolved photoemission spectroscopy.[15,16] A Fermi surface from both the CuO_2 layers and the BiO layers is observed. Furthermore, it is interesting to note that the calculated contributions[11] to the inverse photoemission from the O_{in} (in the CuO_2 planes) and O_{out} (out of the CuO_2 planes) atoms in $Tl_2Ba_2CaCu_3O_8$ are rather similar to the experimental O 1*s* $\mathbf{q} \parallel \mathbf{a},\mathbf{b}$ and $\mathbf{q} \parallel \mathbf{c}$ spectra, respectively. This is a further indication (see also Ref. 17) that LDA band-structure calculations of doped cuprates are probably not so far from the real electronic structure. Finally, we remark that the observed high density of states with O $2p_z$ symmetry formed by Tl_2O_2 and BaO layers may lead to a considerable coupling between CuO_2 planes.

Recently we have measured an O 1*s* spectrum on polycrystalline $Tl_2Ba_2Ca_2Cu_3O_{10}$. Comparing this spectrum with a spectrum for polycrystalline $Tl_2Ba_2CaCu_2O_8$ calculated from the two spectra shown in Fig. 1, we see almost no difference. This indicates that the electronic structure of these two compounds and in particular the density of states at the Fermi level is almost the same in agreement with the predictions from LDA band-structure calculations.[2]

The Cu $2p_{3/2}$ absorption spectra, besides the shoulders at $\sim$933.5 eV, are very similar to those observed[9] for $Bi_2Sr_2CaCu_2O_8$. Thus we again interpret the spectra in terms of 3*d* holes on Cu having predominantly $3d_{x^2-y^2}$ symmetry and an admixture of about 10% of states having probably $3d_{3z^2-r^2}$ symmetry. This admixture has important consequences for the intensity of valence conserving *d-d* excitations which may lead to a pairing of holes leading to superconductivity.[18] Contrary to recent XAS measurements[19] on $Bi_2Sr_2Ca_2Cu_3O_{10}$, we have never seen any energy shift (within $\sim$50 meV) between the peak measured with $\mathbf{q} \parallel \mathbf{a},\mathbf{b}$ and that with $\mathbf{q} \parallel \mathbf{c}$. This holds for the present measurements but also for EELS measurements on $YBa_2Cu_3O_{7-\delta}$,[9] $Bi_2Sr_2CaCu_2O_8$,[9] $YBa_2Cu_4O_8$,[20] and Nd_2CuO_4.[20] We therefore have no reason to explain the intensity measured for $\mathbf{q} \parallel \mathbf{c}$ in terms of a triplet state between a hole on O sites with x^2-y^2 symmetry and a Cu hole with $3d_{3z^2-r^2}$ symmetry. In addition since our measurements indicate no energy shift between the two polarizations, we have also no indication of a varying crystal field splitting between $3d_{x^2-y^2}$ states and $3d_{3z^2-r^2}$ states. Finally, we remember that in the Cu 2*p*-3*d* excitations, there are interactions between the Cu 2*p* core hole and 3*d* states with an energy of about 10 eV which can seriously distort the ground-state occupation of Cu $3d_{x^2-y^2}$, Cu $3d_{3z^2-r^2}$, and O 2*p* states. Therefore, without detailed theoretical analysis, it is dangerous to extract detailed information on the ground state of cuprate superconductors.

Finally, we remark that the origin of the shoulders at $\sim$933.5 eV in the Cu $2p_{3/2}$ spectra shown in Fig. 2 is not clear. Normally, monovalent Cu compounds show in the Cu $2p_{3/2}$ edges a maximum at this energy. Thus, one explanation could be a contamination of the $Tl_2Ba_2CaCu_2O_8$ single crystals by monovalent Cu compounds. On the other hand, no other phases could be detected by x-ray diffraction. We exclude the formation of Cu^{1+} by radiation damage due to the electron beam because a low flux was used and no changes as a function of exposure time to the electron beam have been detected.

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