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Symmetry of holes in high-T_c superconductors

N. Nücker, H. Romberg, X. X. Xi,* and J. Fink
*Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640,
D-7500 Karlsruhe, Federal Republic of Germany*

B. Gegenheimer
Max-Planck-Institut für Festkörperphysik, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

Z. X. Zhao
Institute of Physics, Chinese Academy of Science, Beijing, People's Republic of China
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High-energy electron energy-loss spectroscopy in transmission has been used to obtain information on the symmetry of unoccupied electronic states in the new high-T_c superconductors. In particular, for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$, the O 1*s* and Cu 2*p* absorption edges have been measured for momentum transfer parallel and perpendicular to the *a*,*b* plane. Both σ and in-plane π holes on O, formed upon doping, are compatible with our experimental results. For $YBa_2Cu_3O_7$, in both cases, holes must be in the planes and in the ribbons. Out-of-plane π holes can be excluded for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. In the undoped and doped compounds, the unoccupied states on the Cu sites have predominantly in-plane $3d_{x^2-y^2}$ symmetry. There is an admixture of about 10% of lower-lying states probably with $3d_{3z^2-r^2}$ symmetry.

I. INTRODUCTION

Since the discovery of the new high-T_c superconductors,[1] there has been a massive research effort to understand the electronic structure of these materials both in the superconducting and the nonsuperconducting state. A knowledge of the electronic structure of these compounds is an important first step toward understanding the mechanism of superconductivity which is at present rather unclear. Common to all new high-T_c superconductors with $T_c > 30$ K are two-dimensional CuO_2 planes causing the most important part of the states at the Fermi level by a partially filled antibonding band formed by Cu $3d_{x^2-y^2}$ and O $2p_{x,y}$ electrons. All the single-particle electronic structure calculations yield a metallic state for the undoped materials with the Fermi level close to the middle of the antibonding $dp\sigma$ band.[2–12] This is in contrast to the experimental observation that the undoped compounds, if they exist, are antiferromagnetic insulators with a substantial gap of 1.5 to 2 eV. It is now generally believed that the on-site Cu 3*d* (and possibly O 2*p*) Coulomb interaction is important in these systems. This is also assumed in many theoretical models on high-T_c superconductors.[13–19] Similar to other late 3*d* transition-metal oxides, chalcogenides, and halides the gap is, however, not a pure Mott-Hubbard but a charge transfer gap.[20–23] This means that among the two charge fluctuation processes—the transition of a *d* electron from one Cu atom to the neighboring one, involving the on-site Coulomb energy *U*, or the charge-transfer transition from an O atom to a Cu atom, involving the energy Δ—the latter is more favorable because Δ is smaller than *U*. Thus, due to correlation effects, Cu 3*d* states (in the limit of large *U*, the lower Hubbard band) are pushed away from the Fermi level E_F and the top of the valence band has dominantly O 2*p* character. The lowest states in the conduction band (for large *U*, the upper Hubbard band) have dominantly Cu 3*d* character. The fundamental gap is, therefore, a charge transfer gap. The antiferromagnetic insulating compounds can now be transformed to metallic superconducting compounds by doping, i.e., by charge removal from the CuO_2 planes. This is achieved for La_2CuO_4 by replacement of the trivalent La by divalent Sr or Ba, and for $YBa_2Cu_3O_7$, $Bi_2Sr_2CaCu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ by a charge transfer from the CuO_2 planes to the CuO_3 ribbons, the BiO, and the TlO planes, respectively. According to the model outlined above, the holes created in the CuO_2 planes have dominantly O 2*p* character and almost no Cu 3*d* character. Starting from the Cu $3d^9$ configuration in the semiconducting compound, an additional hole on the Cu atoms (Cu $3d^8$) would cost the Coulomb energy *U* and is, therefore, energetically very unfavorable.

The picture of the electronic structure of the high-T_c superconductors mentioned above was deduced among others from high-energy spectroscopy measurements, e.g., from a comparison of the density-of-states (DOS) measurements by x-ray-induced photoemission spectroscopy (XPS) with calculated DOS curves in a local density approximation (LDA),[24,25] from measurements of satellites via resonant ultraviolet photoemission spectroscopy (UPS),[24,26–30] from XPS studies on the Cu 2*p* core levels,[31–36] from measurements of the Cu L_3VV Auger spectra[25,28,37] and from x-ray-absorption spectroscopy (XAS) on the Cu 2*p* and 1*s* levels.[38–42] The most direct evidence for holes on O sites comes from excitations of O 1*s* electrons into the unoccupied states by electron energy-loss spectroscopy (EELS)[31,43] and by XAS (Refs. 27 and 44) where the DOS of the holes on O sites could be directly probed and where it was shown that the number of holes is roughly proportional to the dopant concentration.

At present, there are considerable speculations on the symmetry of the holes on O atoms. As mentioned before, the LDA band-structure calculations, which neglect short-range correlations, predict holes in the CuO_2 planes which have on the O sites $2p_{x,y}$ character along the Cu-O-Cu axis. Thus, the holes are formed in the $dp\sigma$ band. It is not known whether correlation effects strongly change the symmetry of the holes on O. There are various first-principles quantum chemical calculations on CuO clusters which include short-range correlation effects. Due to the *finite* size of the clusters, these calculations give only approximate information on delocalized band states and an extrapolation to infinite clusters is questionable. Guo, Langlois, and Goddard[45] have derived from such cluster calculations Cu $3d_{x^2-y^2}$ holes for the undoped case. Upon doping, the Cu remains in the $3d^9$ configuration and the O $2p\pi$ $(2p_{y,x})$ orbitals in the plane, but now perpendicular to the Cu-O-Cu axis, are the preferred ones for oxidation. The magnetic frustration model[46] for the magnetic phase diagram and for superconductivity is also based on in-plane π holes. Johnson *et al.*[47] postulate the formation of holes on O in $2p\pi$ (p_z) orbitals perpendicular to the planes. Martin and Saxe[48] reported recently that upon doping, the formation of holes on Cu and on O should be energetically almost degenerate. Finally, McMahan, Martin, and Satpathy[49] have discussed the existence of σ and in-plane π holes on O in doped La_2CuO_4.

In view of the highly controversial theoretical results mentioned above, O $2p$ holes, having σ, in-plane π, and out-of-plane π symmetry may occur upon doping. In the present contribution we have tried to get experimental information on the symmetry of the holes on O sites. We have used orientation-dependent EELS measurements on the O $1s$ absorption edges on single crystals, which probe the unoccupied electronic orbitals with $2p$ symmetry at O sites and their orientation with respect to the crystal axis. In addition, we have performed similar measurements on the Cu $2p$ edges in order to get information on the symmetry of the unfilled Cu $3d$ states in the undoped and doped compounds. Among the existing new high-T_c superconductors we have concentrated our investigations on $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. Part of the results on $YBa_2Cu_3O_7$ were already published previously.[50] The results on single-crystalline La_2CuO_4 show, at present, strong deviations from the results derived from ceramic materials indicating that the available single crystals probably have a rather inhomogeneous Sr or O distribution. High-quality single crystals of $Tl_2Ba_2Ca_2Cu_3O_{10}$ have not yet been available to us.

II. EXPERIMENT

A. Instrumentation

The absorption edges of the O $1s$ and Cu $2p_{3/2}$ levels were measured by high-energy EELS in transmission through samples about 1000 Å thick. The primary energy of the incoming electrons was 170 KeV. The full width at half maximum (FWHM) energy and momentum resolution was chosen in most cases to be 0.4 eV and 0.2 $Å^{-1}$, respectively. The broadening due to the lifetime of the O $1s$ and Cu $2p_{3/2}$ core levels is 0.2 and 0.6 eV, respectively.[51] Details of the spectrometer are described elsewhere.[52,53]

The cross-section differential in energy loss E and solid angle Ω for excitation from a core-level state $|i\rangle$ into an unoccupied state $|f\rangle$ is given in the Born approximation and the independent electron model by[54]

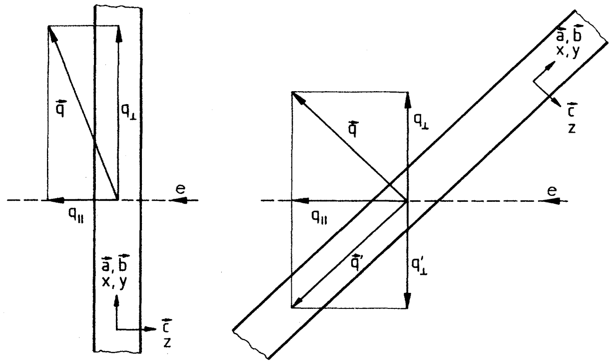
$$\frac{d^2\sigma}{d\Omega\, dE}=\frac{4}{a_0^2 q^4}\,|\langle f|\exp(i\mathbf{q}\cdot\mathbf{r})\,|i\rangle|^2\,,$$

where $\mathbf{q}$ is the momentum transfer and a_0 the Bohr radius. For small $\mathbf{q}$ the exponential function of the operator can be expanded into $1+i\mathbf{q}\cdot\mathbf{r}-(\mathbf{q}\cdot\mathbf{r})^2/2+\cdots$. Since $|i\rangle$ and $|f\rangle$ are orthogonal to each other and provided that $|\mathbf{q}\cdot\mathbf{r}|\ll 1$, the cross section is reduced to the dipole term

$$\frac{d^2\sigma}{d\Omega\, dE}=\frac{4}{a_0^2 q^2}\,|\langle f|\,\epsilon_q\cdot\mathbf{r}\,|i\rangle|^2\,, \qquad (1)$$

where ϵ_q, a unit vector in the direction of $\mathbf{q}$, plays the role of the electric field-polarization vector in the case of XAS. Since the direction of the momentum transfer can be changed, the symmetry of the final state $|f\rangle$ can be probed.

Two different scattering geometries have been used to measure the local density of unoccupied states for q parallel and perpendicular, respectively, to the CuO_2 planes. They are illustrated in Figs. 1(a) and 1(b). For zero scattering angle θ, $\mathbf{q}$ is parallel to the beam axis and is determined by the energy loss to be $\mathbf{q}=q_{\parallel}=k_0E/2E_0$, where k_0 and E_0 are the momentum and the energy of the incoming electron, respectively. At a primary energy $E_0=170$ KeV, corresponding to $k_0=228$ $Å^{-1}$, the parallel momentum transfer for the O $1s$ and for the Cu $2p$ edge are 0.41 and 0.72 $Å^{-1}$, respectively. All our samples had the a,b plane (CuO_2 plane) in the film plane. Thus, in the configuration (a) and with scattering angle equal to zero, q is parallel to the c axis. To turn q more and more into the a,b plane, nonzero scattering angles have to be



(a) (b)

FIG. 1. The two scattering geometries used for orientation-dependent electron energy-loss measurements of absorption edges. (a) Sample perpendicular to the electron beam. (b) Sample tilted 45° against the electron beam.

used giving a $q_\perp = k_0\theta$. For $q_\perp \gg q_\parallel$, the total momentum transfer is almost in the a,b plane. Values of $q_\perp = 1$ Å^{-1} have been used. Higher values were avoided because the intensity decreases with $1/q^2$ and for too large q, dipole selection rules would no longer apply and multiple scattering effects may disturb the results. The mean value of the core-orbital radii of the O 1s and Cu 2p wave functions are both about 0.1 Å and, therefore, for $q = 1$ Å^{-1}, $|\mathbf{q}\cdot\mathbf{r}|$ is still small compared to one. In configuration (b), $|q_\perp|$ was chosen to have the same value as $|q_\parallel|$. With the sample turned 45° against the beam direction and the c axis being in the scattering plane, the total momentum is parallel or perpendicular to the c axis depending on the sign of $q_\perp$. In this configuration, smaller total momentum transfers could be used and, therefore, higher counting rates could be achieved. Because rather small scattering angles are used in EELS (for $q_\perp = 0.4$ Å^{-1}, $\theta = q_\perp / k_0 = 0.002$), there is almost no change in the effective thickness upon changing the sign of $q_\perp$. Therefore, the observed intensity ratios are not obscured by thickness effects. We emphasize that in XAS measurements using the partial yield mode, it is much more difficult to get exact ratios of absorption edges for two different orientations. Finally, we should mention that a rather low momentum resolution of 0.2 Å^{-1} was used in order to increase the counting rate. Therefore, the spectra taken for q in a certain direction (e.g., $q \parallel a,b$) always had contributions from the other direction (e.g., $q \perp a,b$). Thus, the measured spectra $\mathbf{m}(m_\parallel, m_\perp)$ are a superposition of the true spectra $\mathbf{t}(t_\parallel, t_\perp)$, i.e., $\mathbf{m} = \underline{A}\mathbf{t}$ where $\underline{A}$ is a two-dimensional matrix depending on the scattering geometry. In order to obtain the true spectra, the matrix has to be inverted and multiplied with the measured data $\mathbf{m}$. Generally, after correction, good agreement was obtained between data derived from the two different scattering configurations (a) and (b) or from data taken with different angular resolutions.

B. Samples

The preparation of single crystals of $YBa_2Cu_3O_7$ ($T_c = 90$ K) and of $Bi_2Sr_2CaCu_2O_8$ ($T_c = 83$ K) was described elsewhere.[55,56] From the T_c value derived by ac susceptibility measurements and from x-ray diffraction, it was concluded that the $Bi_2Sr_2CaCu_2O_8$ sample was dominantly in the $n = 2$ phase.[57] Films about 1000 Å thick were cut from $YBa_2Cu_3O_7$ crystals along the a,b plane by an ultramicrotome using a diamond knife. Subsequently, the films were mounted on standard electron microscope grids. Thin films of $Bi_2Sr_2CaCu_2O_8$ were obtained by peeling them from the single crystals with a tape. Almost-single-crystalline films of $YBa_2Cu_3O_7$ could be epitaxially grown by sputtering on freshly cleaved CaO single crystals.[58] The films could be removed from the substrate and were mounted on grids. The sputtered films were considerably larger in area compared to the single-crystalline films and, therefore, higher counting rates could be achieved. On the other hand, a small amount of misoriented grains were observed in the sputtered films. As usual, all $YBa_2Cu_3O_7$ samples were twinned and, therefore, a mean value for the a and b directions was measured.

$YBa_2Cu_3O_6$ films were obtained from $YBa_2Cu_3O_7$ films by annealing the films under ultrahigh vacuum conditions at temperatures up to 500 °C. The procedure was controlled by observing the low-energy-loss spectra and by comparing them with optical data.[59,60] The annealing process was ended when a clear gap of about 1.5 eV and a sharp line at 4 eV had developed and did no more change upon further annealing. From the accompanying measurements we conclude that the number of O atoms per unit cell was close to 6.0.

By measurements with a superconducting quantum interference device (SQUID) or by measuring the shielding effect of the film between two small coils, it was verified that the transition temperature of the superconducting samples did not change in the cutting process or in the process of removing them from the substrate. The lattice structure and the orientation of the films was checked by electron-diffraction measurements in the spectrometer, setting the energy loss to zero. In addition, we have measured the low-energy-loss spectra in the range 0.5–40 eV for most of our samples and a Kramers-Kronig analysis was performed to obtain the dielectric functions.[61,62] These data were compared with optical data and confirmed the composition and the quality of our samples. Again, we emphasize that EELS in transmission is not a surface-sensitive method as, e.g., UPS, XPS, or XAS in the partial yield mode. Therefore, a lot of ambiguities due to the problem of preparing surfaces representing bulk properties are avoided.

III. RESULTS

Figure 2(a) shows the O 1s edge of a $YBa_2Cu_3O_7$ single crystal for momentum transfer in the a,b plane and perpendicular to the a,b plane. The solid lines are guides to the eye. The spectra were obtained from measurements in configuration (a) using $q_\perp = 0$ and 1 Å^{-1} and by corrections as described in Sec. II. The uncorrected spectra, not very different from the corrected ones, were shown in Ref. 50. Similar results were obtained from epitaxially grown films measured in configuration (a) and (b). There is a general tendency, for the superconducting compounds, that sputtered films show less pronounced structures compared to single crystals, in particular in the region near the threshold of the absorption edge. In Fig. 2(b), we show the O 1s edges of a $YBa_2Cu_3O_6$ film.

As outlined in our previous work,[31,43] the O 1s absorption edges probe in a first approximation the local unoccupied DOS with 2p symmetry at the O sites. The interaction of the final states with the core hole is probably smaller than the width of the O 2p bands and, therefore, excitonic effects are small. This is supported by core-level measurements on similar systems, such as transition-metal carbides and nitrides, where the measured absorption edges were very close to the calculated total DOS.[63] In addition, the fact that the threshold of the spectra is rather close to the mean value of the binding energies of the O 1s levels of the four different O sites indicates that

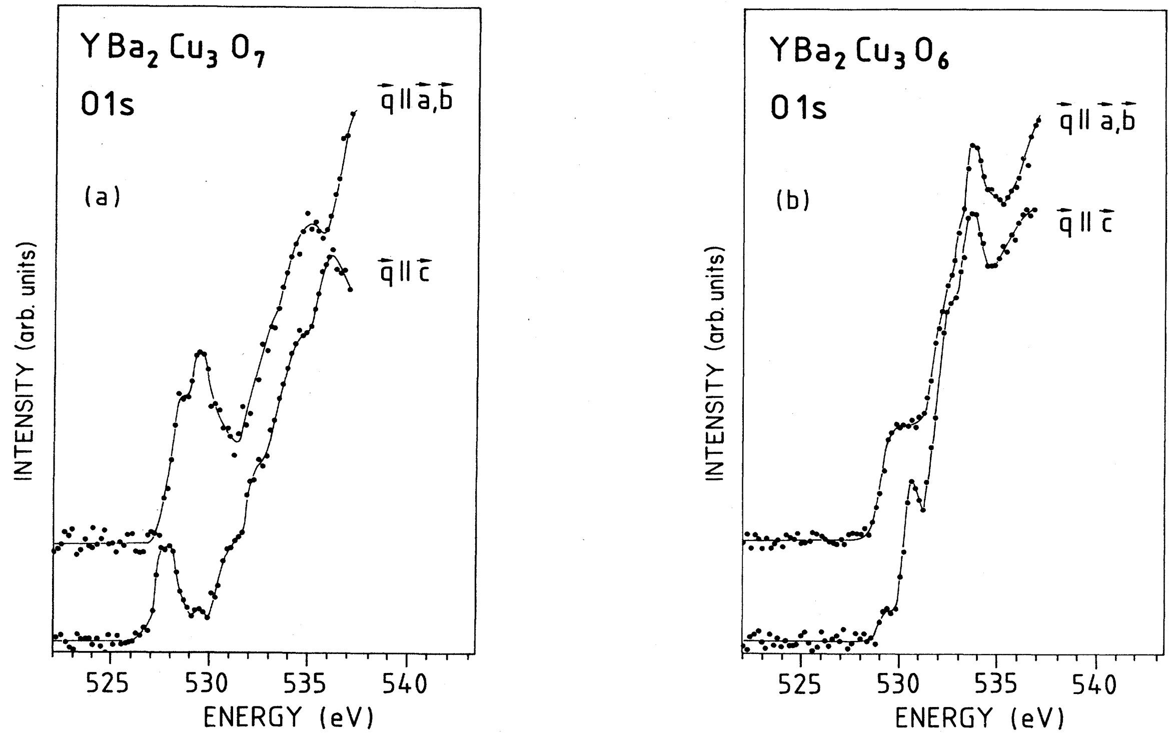


FIG. 2. O 1*s* absorption edges of (a) $YBa_2Cu_3O_7$ and (b) $YBa_2Cu_3O_6$ for momentum transfer parallel to the *c* axis and in the *a*,*b* plane, respectively.

excitonic effects are small. This mean value has been determined by XPS measurements[36,42,64–68] to be at 528.5 eV independent of the O concentration. The width (FWHM) of the O 1*s* line in XPS spectra is about 1.7 eV. We emphasize that due to the poor resolution in XPS a mean value of the O 1*s* binding energy is measured while in EELS, having higher resolution, the onset of the absorption edge in polycrystalline samples corresponds to that O site having the lowest 1*s* binding energy. Usually a second line at 532.5 eV is observed in the O 1*s* XPS spectra. This line has, however, a rather low intensity in "well" prepared surfaces and it is at present not clear, whether this line is completely due to surface contaminations or whether there remains an intrinsic part.[32] A detailed comparison of XPS data on the O 1*s* level in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ is given in Ref. 69.

Strong anisotropies of the O 1*s* absorption edges are realized in the low-energy part ($E < 531$ eV) which is related to holes on O sites. At higher energies, where the steep rise of spectral weight is due to Ba 5*d* and 4*f* and Y 4*d* states, hybridized with O 2*p* states,[31,43] the anisotropy is less pronounced. For $q \| c$, the absorption edge starts at 527.2 eV. Small humps are realized at 529.5 and 531.0 eV. For $q \| a,b$, there is an apparent shift to higher energy and the absorption edge is probably near 528.0 eV. A second rise is observed near 529 eV followed by a maximum at 529.5 eV. The difference in the threshold of the absorption edges for the two *q* directions may be related to different binding energies of the O 1*s* level for the four different O sites and/or to different final states for $q \| c$ and $q \| a,b$ having O $2p_z$ and O $2p_{x,y}$ symmetry, respectively. Subtracting for $E < 531$ eV the edges of $YBa_2Cu_3O_6$ from those of $YBa_2Cu_3O_7$, the intensity ratio for $q \| a,b$ to $q \| c$ ($I_{x,y}/I_z$) is about 2.1. For different samples, values between 1.8 and 2.2 were derived, resulting in a mean value of about 2.

When reducing the $YBa_2Cu_3O_7$ sample by heating, the maximum at 528 eV due to the holes with p_z symmetry decreases at first while the $p_{x,y}$ states with the maximum at 529.5 eV decrease more slowly. This has also been observed in our previous measurements[43] as a function of O concentration on polycrystalline materials where the lowest maximum at 528 eV decays very rapidly with decreasing O content and the maximum at 529.5 eV decays less fast. For the insulating single-crystalline $YBa_2Cu_3O_6$, the threshold of the absorption edge is for both *q* directions near 529.0 eV. For $q \| c$, a peak at 530.8 eV is observed, which was already realized in the previous measurements[43] on polycrystalline materials. This again indicates that the present measurements on single crystals are consistent with our previous measurements on ceramics but allow in addition the determination of the symmetry of the final states.

In Fig. 3 we show the O 1*s* edges of $Bi_2Sr_2CaCu_2O_8$, again for $q \| c$ and for $q \| a,b$. For $q \| a,b$, the edge starts at 527.8 eV while the mean binding energy of the O 1*s* levels of the three different O sites as determined by XPS measurements[70,71] was reported to be at 528.7 eV and 529.2 eV. The width (FWHM) of the O 1*s* line measured in XPS spectra was about 1.5 eV. For $q \| c$, there is almost no spectral weight between 527.5 and 529.5 eV. The data indicate that the O 2*p* states just above E_F have almost

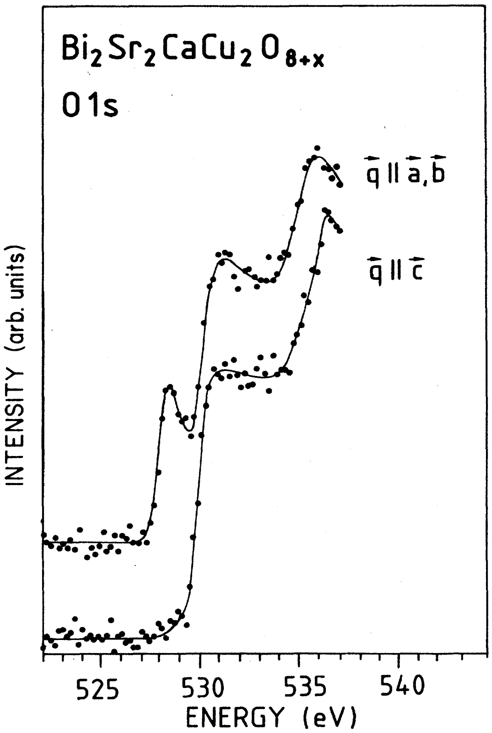


FIG. 3. O 1s absorption edges of $Bi_2Sr_2CaCu_2O_8$ for momentum transfer parallel to the c axis and in the a,b plane.

pure $p_{x,y}$ symmetry. Above 529.5 eV the asymmetry of the spectral weight is much smaller.

In Fig. 4(a) we show the Cu $2p_{3/2}$ edges of $YBa_2Cu_3O_7$ epitaxially grown films for $q \parallel c$ and $q \parallel a,b$. Similar spectra, measured by XAS, were previously reported for ceramics[38,39] and for single crystals.[40] However, the orientation-dependent data on single crystals were normalized to the line at 931.3 eV and, therefore, important information was lost. In addition, we show in Fig. 4(b) for the first time orientation-dependent data on the Cu $2p_{3/2}$ edge for $YBa_2Cu_3O_6$. According to the dipole selection rules, Cu 2p electrons may be excited to either 3d or 4s empty states. The former transition is much stronger than the latter one because the overlap of the 3d with the 2p wave functions is rather large. From previous measurements on Cu compounds, it is well known that the resonancelike line at the onset of the absorption edge is related to transitions into empty 3d states. Due to interactions with the 2p core hole, this line does not, however, represent the details of the unoccupied 3d states but the intensity is a measure of the total amount of unoccupied states.[72,73] In absorption spectroscopy on, e.g., divalent Cu, a $Cu\,2p^63d^9$-$Cu\,2p^53d^{10}$ transition is measured while in XPS two final states ($Cu\,2p^53d^9$ and $Cu\,2p^53d^{10}O\,2p^5$) are reached,[31-36] which are different from that reached in absorption spectroscopy. Therefore, nothing can be learned on the excitonic character of the transition by the comparison of XPS and EELS data. Furthermore, the energy position of the unoccupied d

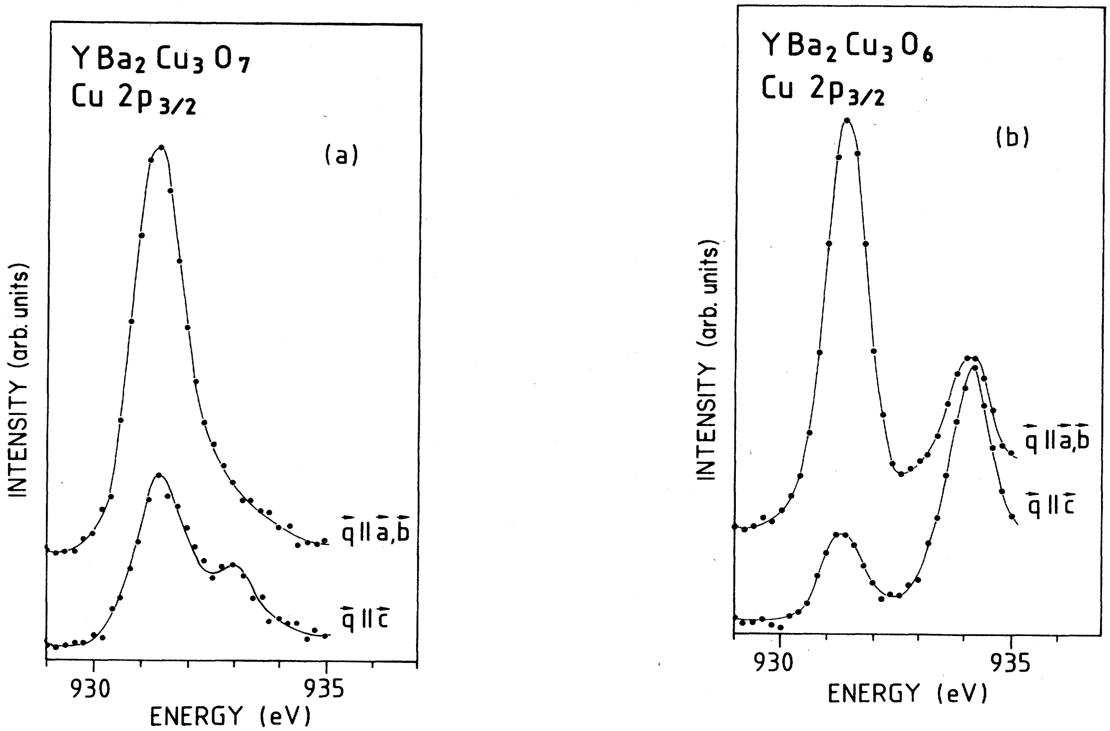


FIG. 4. Cu $2p_{3/2}$ absorption edges of (a) $YBa_2Cu_3O_7$ and (b) $YBa_2Cu_3O_6$ for momentum transfer parallel to the c axis and in the a,b plane.

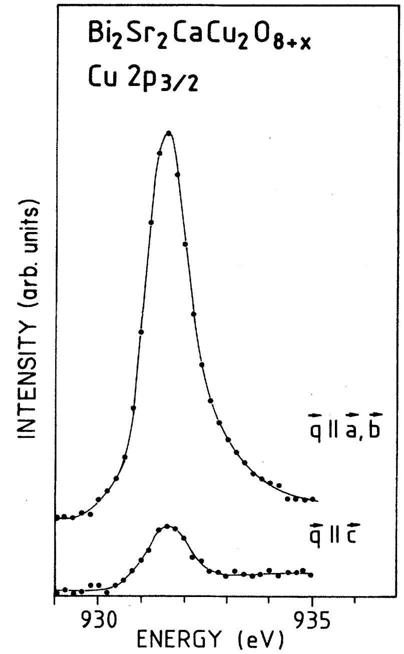


FIG. 5. Cu $2p_{3/2}$ absorption edges of $Bi_2Sr_2CaCu_2O_8$ for momentum transfer parallel to the c axis and in the a,b plane, respectively.

states relative to the Fermi level cannot be derived from these measurements.

In $YBa_2Cu_3O_7$, the main line shows a strong orientation dependence in the intensity and in the spectral form. For $q \parallel a,b$, where dominantly $3d_{x^2-y^2}$ states from the planes and to a lesser extent $3d_{z^2-y^2}$ states from the ribbons are reached, the line is slightly asymmetric with a tail extending to higher energies. For $q \parallel c$, where dominantly $3d_{z^2-y^2}$ states from the ribbons are reached, the total intensity is reduced by a factor of 2 and a more pronounced shoulder at 932.8 eV is realized. The intensity ratio of the main line at 931.3 to the shoulder is about 2.

For $YBa_2Cu_3O_6$ the orientation dependence of the main line has strongly increased. The intensity for $q \parallel c$ is now only 20% of that for $q \parallel a,b$. Both lines are now symmetric. In particular, for $q \parallel c$ the shoulder has disappeared. With decreasing O content a new line at 934.2 eV grows which shows again an orientation dependent intensity with a larger component for $q \parallel c$.

In Fig. 5 we show the Cu $2p_{3/2}$ absorption edges of a $Bi_2Sr_2CaCu_2O_8$ single crystal measured with $q \parallel c$ and $q \parallel a,b$. To obtain a higher counting rate for the small samples, an energy resolution of 0.7 eV was chosen. For $q \parallel a,b$, where dominantly $3d_{x^2-y^2}$ states are reached, the main line appears at 931.5 eV and is again slightly asymmetric. There is also for $q \parallel c$ a non-negligible component of the main line. The intensity is about 15% of that for $q \parallel a,b$. We emphasize that this intensity ratio was measured on several samples and using different angular resolutions. Therefore, we are rather sure that there is a considerable amount of $3d$ states having lobes out of the a,b plane.

IV. DISCUSSION

First, we discuss the results on $Bi_2Sr_2CaCu_2O_8$, because this system is simpler having only two-dimensional CuO_2 planes and no chains. We believe that the edge for $q \parallel a,b$ at 527.8 eV corresponds to the Fermi level. This is supported by the fact that the width of the edge can be attributed to our experimental energy resolution. The LDA band-structure calculations[8–11] predict besides the Cu $3d_{x^2-y^2}$-O(1) $2p_x$-O(1) $2p_y$ $dp\sigma$ band from the CuO_2 planes also a wide antibonding Bi $6p_{x,y,z}$-O(2) $2p_{x,y}$-O(3) $2p_z$ band crossing in the lower part the Fermi level. Near E_F, this band has a dominantly two-dimensional Bi $6p_{x,y}$-O(2) $2p_{x,y}$ character. Thus, near the Fermi level, DOS with O $2p_{x,y}$ character are expected both from the CuO_2 and BiO planes. If both cause a DOS at E_F of the same order of magnitude, we conclude that O(1) and O(2) atoms have within some tenths of eV the same $1s$ binding energy because there is only one absorption edge. For $q \parallel c$, there is no spectral weight in the first 2 eV above threshold. A 2-eV higher binding energy of one of the three O atoms can be excluded because this would cause a well-separated second line in the O $1s$ XPS spectrum which is not observed.[70,71] We conclude, therefore, that the O $2p$ states at E_F due to CuO_2 planes and BiO planes have dominantly $2p_{x,y}$ character and, within error limits, no $2p_z$ character. This excludes out-of-plane π holes in the CuO_2 planes and clearly rules out all models for high-T_c superconductivity based on holes with O $2p_z$ character in the CuO_2 planes. Our measurements, however, cannot differentiate between O σ or in-plane π holes for $Bi_2Sr_2CaCu_2O_8$. It is interesting to note that in the LDA band-structure calculations,[8–11] the Cu $3d_{x^2-y^2}$-O(1) $2p_{x,y}$ band extends up to 2 eV above E_F. At energies above 2 eV, strong O $2p_{x,y}$ and O $2p_z$ DOS are expected on the O(2) and O(3) atoms, respectively, due to the hybridization with Bi $6p$ bands. This is in agreement with our experimental absorption edges which show almost no anisotropy for energies higher than 2 eV above threshold.

Our measurements also complement recent angle-resolved resonant photoemission data[74] on $Bi_2Sr_2CaCu_2O_8$ which gave information on the density and the character of occupied states near E_F. In agreement with our previous results[25,43] on $YBa_2Cu_3O_7$, almost no Cu $3d$ but dominantly O $2p$ density of states at E_F was observed for $Bi_2Sr_2CaCu_2O_8$.

We now turn to the Cu $2p_{3/2}$ spectrum of $Bi_2Sr_2CaCu_2O_8$. The observed asymmetry of the main line for $q \parallel a,b$ may be explained by the influence of holes on O sites. A weak asymmetry of the main line was also realized in XAS (Ref. 75) measurements on $La_{1.85}Sr_{0.15}CuO_4$ and was interpreted in the same way. The problem of the influence of holes on O on the Cu $2p_{3/2}$ absorption edge will be treated below in more detail, when discussing the results on $YBa_2Cu_3O_7$. For $q \parallel c$, no intensity would be expected for unoccupied states having only $3d_{x^2-y^2}$ character. In the experiment, however, spectral weight is observed with an intensity of about 15% of that observed for $q \parallel a,b$. Thus, we must assume some admixture of $3d_{3z^2-r^2}$ states to the unoccupied states. Then, for $q \parallel a,b$ we obtain, using Eq. (1), contributions from $2p_{x,y}$-

$3d_{x^2-y^2}$ and $2p_z$-$3d_{3z^2-r^2}$ transitions with a relative weight of $\frac{1}{2}$ and $\frac{1}{6}$, respectively. For $q \parallel c$, the $2p_z$-$3d_{3z^2-r^2}$ transitions have a relative weight of $\frac{2}{3}$. This gives the result that about 10% of the unoccupied $3d$ states have $3d_{3z^2-r^2}$ character and the rest have $3d_{x^2-y^2}$ character. We point out that in this evaluation only e_g states were taken into account and the lower lying t_{2g} states were neglected. We cannot exclude the admixture of $3d_{xy}$, $3d_{zx}$, or $3d_{yz}$ states. However, the t_{2g} states are considerably lower in energy than the e_g states and, therefore, the admixture of these states should be lower.

The fact that there is a 10% admixture of states with another symmetry implies that the Cu $3d$ states are not completely localized due to correlation effects and that covalency to the O atoms is larger than the crystal-field splitting between $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ states which is about 1 eV. In addition, the result that there are empty states with $3d_{3z^2-r^2}$ symmetry in the upper Hubbard band may have important consequences for theoretical models for the pairing of electrons leading to superconductivity. Having these states near E_F, low-lying $3d_{3z^2-r^2}$-$3d_{x^2-y^2}$ excitations may occur which will always result in a coupling to vibrations of the distorted or incomplete O octahedra. A model for high-T_c superconductivity based on d-d excitations was worked out by Weber.[76]

In the following we discuss the results on the more complicated compound $YBa_2Cu_3O_7$, starting with the O $1s$ absorption edges. LDA band-structure calculations[4-7] predict that the Cu and O atoms in the CuO_2 planes form a roughly half-filled Cu(2) $3d_{x^2-y^2}$-O(2) $2p_x$-O(3) $2p_y$ $dp\sigma$ band. Furthermore, in $YBa_2Cu_3O_7$ the one-dimensional ribbons, composed of CuO_3 squares with Cu(1) atoms in the center and O(1) atoms (on the b axis) and O(4) atoms (connecting chains and planes) at the corners form a similar Cu(1) $3d_{z^2-y^2}$-O(1) $2p_y$-O(4) $2p_z$ $dp\sigma$ band which is less than half filled. In addition, there exists a Cu(1) $3d_{z,y}$-O(1) $2p_z$-O(4) $2p_y$ $dp\pi$ band which just crosses the Fermi level and which may be filled for small O deficiency. In this case, the O $2p$ orbital is in the plane of the ribbons and points perpendicular to the Cu—O bond. In the band-structure calculations of Temmermann *et al.*,[5] the relative number of holes on the O(1), O(2), O(3), and O(4) sites is 1.7, 1.4, 1.6, and 1.0, respectively. Including matrix elements for the $1s$-$2p$ transition, the ratios of transition probabilities change[43] to 2.5, 1.2, 1.8, and 1.0, respectively. The calculations predict dominant σ character for the O $2p$ holes. Then, for $q \parallel a,b$ O(2), O(3), and O(1) sites should contribute to the spectral weight for $E < 531$ eV. For $q \parallel c$, only contributions from the O(4) atoms are expected. This yields an intensity ratio $I_{x,y}/I_z$ of 2.1 in excellent agreement with the experimental value of about 2. An equal distribution of holes among the four O sites and the assumption of only σ holes would yield a value of 1.25 which is not compatible with the experimental value. To achieve agreement with the experimental value, the number of holes on the O(4) sites has to be considerably reduced compared to those on the other sites. We also mention that the LDA calculations for the absorption edge[43] yield for the four different O sites almost the same trapezoidal form with a width of about 2 eV. The trapezoidal form is observed for $q \parallel c$ indeed. The width of this structure is, however, only about 1.3 eV which may be caused by a slightly higher Fermi level. Moreover, strong correlation effects may reduce the hopping between Cu and O sites. Therefore, a considerable reduction of the width of the $dp\sigma$ band is expected, but even for very strong correlation effects, there remains a finite width for the O $2p$ states due to the hopping between O sites. According to band-structure calculations,[2] this width is about 4 eV. The correlation effects on the O sites were not taken into account in this estimate. For $q \parallel a,b$, the absorption edge near threshold may be a superposition of two trapezoidal structures separated by about 1 eV due to a different binding energy of the $1s$ level for the O(1) and O(2,3) atoms.

It is interesting to note that in a recent work[77] on $YBa_2Cu_3O_7$ single crystals, a line-shape asymmetry of the O $1s$ XPS line was analyzed in terms of two different binding energies for O sites in the ribbons and in the planes. According to their data, the O atoms in the chains [in particular the O(4) atoms] should have a lower $1s$ binding energy by 0.7 eV relative to that of the O atoms in the planes. Although this analysis should not be taken to be too conclusive, the agreement to the assignment of the orientation-dependent O $1s$ edges, assuming holes with σ symmetry, is remarkable. As mentioned before, the threshold with the lowest energy (for $q \parallel c$) is caused in this case by O(4) atoms while the threshold ascribed to O(1,2,3) atoms (for $q \parallel a,b$) appears at 1.2-eV higher energy.

As mentioned in the Introduction, holes on O having in-plane π symmetry have also been predicted.[45] This is a model where correlation effects are very strong, thus strongly reducing hopping in the $dp\sigma$ band. Then, due to the Coulomb repulsion of the O orbitals between neighboring O sites, the binding energy is strongest for the $2p\sigma$ states, intermediate for the out-of-plane π states and weak for in-plane π states. Then, holes will form on the latter orbitals.[78] Assuming *only* in-plane O π-holes, only O(1) sites would contribute to the $q \parallel c$ spectrum and assuming an equal distribution among the four O sites, the ratio $I_{x,y}/I_z$ should be 3, which is larger than the experimentally observed value. To achieve agreement with our experimental data, the number of holes on the O(1) sites should be increased by about 50% compared to the average number of holes on the other three sites. We emphasize that our data are then also compatible with models predicting holes with in-plane π symmetry. Unfortunately, no detailed description of the distribution of holes among the four O sites was given in Ref. 45. A calculation of this distribution could help to decide whether the in-plane π hole model is realistic or not.

Finally, for holes with only out-of-plane π symmetry, O(2) and O(3) sites would contribute to the $q \parallel c$ spectrum and O(1) and O(4) sites would contribute to the $q \parallel a,b$ spectrum. Assuming again an equal distribution of the holes among the four O sites, the intensity ratio $I_{x,y}/I_z$ should be then 0.38 which is very far from the experimental ratio of two. To explain the experimental value with only out-of-plane π holes, there should be almost no holes in the planes and almost all holes in the ribbons which is very unlikely. Therefore, we exclude, as in Bi_2Sr_2-

$CaCu_2O_8$, holes with out-of-plane symmetry.

To summarize our measurements on $YBa_2Cu_3O_7$, we cannot definitely decide whether there are holes on O with σ symmetry or in-plane π symmetry. There are many experimental facts which are in favor of holes with σ symmetry. On the other hand, we cannot exclude holes with in-plane π symmetry or holes on O having σ *and* in-plane π symmetry.

In the following, we discuss the Cu $2p_{3/2}$ absorption edges. In the LDA band-structure calculations[4–7] for $YBa_2Cu_3O_7$, a valency for Cu between 1^+ and 2^+ is derived. The $3d$ count is about 9.4. According to the calculations by Mattheiss and Hamann[4] for $YBa_2Cu_3O_7$, the Cu holes have in the planes dominantly $3d_{x^2-y^2}$ and in the ribbons dominantly $3d_{z^2-y^2}$ character. These are the same orbitals but turned 90° because the plane of the ribbons is turned against the planes by 90°. The number of holes in the $3d$ shell should be roughly the same for the Cu(1) and Cu(2) atoms. Therefore, we would expect from the LDA band-structure calculations an intensity ratio of the main line for $q \parallel a,b$ to $q \parallel c$ of 2.5. This is not far from the experimental value of 2. The reduction may indicate slightly more holes per Cu atoms on the ribbons than in the planes caused by, e.g., a larger bonding-antibonding splitting of the $3d_{z^2-y^2}$ states in the ribbons or $3d_{zy}$ states forming the π bonding to the in-plane O $2p$ π-holes. Increasing the correlation effects, less Cu^{1+} and more Cu^{2+} is expected, i.e., the Cu electronic configuration should turn closer and closer to a $3d^9$ configuration. Also in this case, the intensity ratio would probably be close to 2.5 because dominantly in-plane and in-ribbon $3d$ states would form the upper Hubbard band, in agreement with the cluster calculations of Ref. 45. Therefore, we cannot conclude from these measurements whether correlation effects are important or not. Furthermore, a small admixture of lower-lying $3d$ states would not, in a first approximation, change the intensity ratio. From our results, however, we can conclude that there is no strong rearrangement of empty $3d$ states due to correlation effects.

The shoulder at higher energy which is particularly pronounced in the $YBa_2Cu_3O_7$ spectrum for $q \parallel c$ and which appears only in the superconducting (doped) samples, has been ascribed by Bianconi *et al.*[38] and Sarma *et al.*[39] to a $Cu\,2p^6 3d^9 O\,2p^5$-$Cu\,2p^5 3d^{10} O\,2p^5$ transition, i.e., a transition in which a hole on O, created upon doping, is involved. The energy difference between the main line and the shoulder would then be the difference of the shielded Coulomb repulsion between a Cu $3d$ hole and an O $2p$ hole and that of a Cu $2p$ hole and an O $2p$ hole. Although this assignment and its implication demand further investigations, it is strongly supported by the fact that the $Cu\,2p^5 3d^{10} O\,2p^5$ final state observed in XPS spectra on divalent Cu compounds lies at the same energy where the shoulder is detected. Furthermore, it was observed[39] that in XAS spectra on formally trivalent $NaCuO_2$, the main line is observed again at 932.8 eV. This is expected because the formally trivalent Cu is dominantly a Cu $3d^9$, O $2p^5$, and not a Cu $3d^8$ configuration and, therefore, the final state in the XAS spectrum should be dominantly a $Cu\,2p^5 3d^{10} O\,2p^5$ state.

In a recent paper, Bianconi *et al.*[40] have reported that the shoulder at 932.8 eV appears *mainly* for $q \parallel c$ and they concluded that the holes on O are not formed in $2p_{x,y}$ but in $2p_z$ orbitals, either in the planes on O(2) or O(3) atoms or in the ribbons on the O(4) atoms. This is in clear contradiction to our O $1s$ spectra, where we have observed holes on O with $2p_z$ *and* $2p_{x,y}$ character. Furthermore, in our spectra for $q \parallel a,b$, the main line is asymmetric, too and may be also decomposed into two lines at 931.3 and 932.8 eV, respectively. Another possible explanation for the orientation dependence of the shoulder may be that due to the shielding of the above-mentioned Coulomb repulsion, the shift of the shoulder depends on a high power of the distance between a hole on O and the Cu atom. Then the holes on O(4) should cause the strongest energy shift since the Cu(1)-O(4) distance is only 1.84 Å while the other Cu(1)-O(1) and Cu(2)-O(2,3) distances are about 1.94 Å. A further explanation may be that holes localized in the squares of the ribbons cause a larger energy shift than the more delocalized holes in the planes. Finally, we cannot exclude that the shoulder may be related to holes in the $dp\pi$ band which crosses the Fermi level only for the electrons in the ribbons. All these explanations would ascribe the shoulder in the $q \parallel c$ spectrum to transitions on Cu atoms in the ribbon influenced by holes on O(1) or O(4) atoms. This is supported by the spectra on $Bi_2Sr_2CaCu_2O_8$ which has no ribbons and where no pronounced spectral weight at 932.8 eV has been detected for $q \parallel c$. Assuming for $YBa_2Cu_3O_7$ that $\frac{1}{3}$ of the Cu atoms should be linked to an O $2p$ hole ($\frac{1}{3}$ of the Cu atoms are formally trivalent, i.e., they are in a $Cu\,3d^9 O\,2p^5$ state), the intensity ratio of the main line to the shoulder should be 2, which is in excellent agreement with the experimentally observed value.

In the nonsuperconducting $YBa_2Cu_3O_6$ samples, the shoulder and the asymmetry of the white line in the Cu $2p_{3/2}$ spectra both have disappeared indicating that they are caused by the formation of holes due to self-doping with O. In the above given discussion on $YBa_2Cu_3O_7$, we have assumed that all the $3d$ states which are reached in the $q \parallel c$ spectrum belong to Cu(1) atoms and have $3d_{z^2-y^2}$ character. It is generally believed (except Ref. 79) that on going from $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_6$, the Cu(1) atoms transform from divalent to monovalent Cu. Therefore, for $q \parallel c$, there should be no intensity at 931 eV. In the experiment, however, for $q \parallel c$ there is some remaining intensity which is about 20% of the main line. One could argue that our samples have not exactly the $YBa_2Cu_3O_6$ composition and that some of the Cu(1) atoms are still divalent. Our O $1s$ spectra, and the comparison of our low-energy-loss spectra with optical data, on the other hand, indicate that there is only a very low concentration of O holes in our heat-treated $YBa_2Cu_3O_7$ samples indicating a composition very close to $YBa_2Cu_3O_6$. Therefore, a possible explanation for the remaining intensity for $q \parallel c$ may be also a 15% admixture of $3d_{3z^2-r^2}$ states to the $3d_{x^2-y^2}$ states in the CuO_2 planes as already discussed for $Bi_2Sr_2CaCu_2O_8$.

Assuming that the above given interpretation of the $YBa_2Cu_3O_6$ spectra is correct it is interesting to note that the amount of admixture of the lower lying $3d$ states to the antibonding Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ band is almost the same for the undoped semiconducting $YBa_2Cu_3O_6$ and the doped superconducting $Bi_2Sr_2CaCu_2O_8$. In the framework of a single-particle model, the formation of holes on Cu upon doping may strongly change the amount of admixture, because then bands other than the $dp\sigma$ band may be emptied. Therefore, these results again support previous results[25,43] that upon doping no further holes are formed on Cu due to the high Coulomb interaction between two holes on the Cu sites. Instead, the holes formed upon doping must be on O sites, in agreement with the model for the electronic structure of the high-T_c superconductors having dominantly O $2p$ character.

The strong spectral weight at 934 eV in the $YBa_2Cu_3O_6$ spectra, implies the transformation of Cu(1) from divalent ($3d^9$) to monovalent ($3d^{10}$), because in monovalent Cu compounds, always a line near 934 eV is observed.[80] The resonancelike structure indicates that also for monovalent Cu there is a considerable amount of unoccupied $3d$ states. This was already postulated in a band-structure calculation[81] on Cu_2O, where a considerable amount of unoccupied $3d$ states with $3d_{3z^2-r^2}$ symmetry along the O-Cu-O axis was realized. These calculations also corroborate the present results that for $q \parallel c$ the intensity at 934 eV is considerably larger than for $q \parallel a,b$. In $YBa_2Cu_3O_6$, there remain from the ribbons CuO_2 molecules [Cu(1) and O(4)] which are oriented along the z axis. When the unoccupied states of these molecules have predominantly $3d_{3z^2-r^2}$ character, the intensity at 934 eV for $q \parallel c$ should be larger than for $q \parallel a,b$ in agreement with the experiment.

V. SUMMARY

We have investigated the symmetry of unoccupied states in the high-T_c superconductors $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. Electron energy-loss spectroscopy has been used to perform orientation-dependent excitations of O $1s$ and Cu $2p$ core electrons into unoccupied local states. In $YBa_2Cu_3O_7$, our results of the O $1s$ absorption edges can be explained by holes on O with σ symmetry and with a distribution of holes among the four O sites which is very close to that obtained in band-structure calculations, i.e., a reduced number of holes on the O(4) sites compared to the other three O sites. The experimental results are also compatible with in-plane π holes on O with an increased number of holes on O(1) sites compared to the other three O sites. A calculation of the hole distribution among the four O sites could help to decide whether the model with in-plane π holes is realistic or not. For $Bi_2Sr_2CaCu_2O_8$, we cannot differentiate between σ and in-plane π holes on O atoms. In both compounds, out-of-plane π holes on O can be excluded. The Cu $2p$ absorption edges reveal for the undoped and doped compounds dominantly unoccupied in-plane $3d_{x^2-y^2}$ states. There is a 10%–15% admixture of low-lying states probably with $3d_{3z^2-r^2}$ symmetry.

Note added in proof. Recently, similar results on the O $1s$ absorption edges of $Bi_2Sr_2CaCu_2O_8$ measured by x-ray absorption spectroscopy were obtained by F. J. Himpsel *et al.* [Phys. Rev. B **38**, 11 946 (1988)] and by P. Kuiper *et al.* [Physica C (to be published)].

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*Permanent address: Peking University, Beijing, China.

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