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# Evidence for holes on oxygen sites in the high-$T_c$ superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$

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The local oxygen density of states of $p$ symmetry at the Fermi level of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ has been investigated as a function of $x$ and $y$. Core-level excitations of oxygen 1$s$ electrons into empty states by electron energy-loss spectroscopy have been used. Strong deviations from our calculations of the O 1$s$ edges in the framework of a local density-functional model were observed in the superconducting and in the semiconducting compounds. They can be explained by taking into account on-site correlations of the Cu 3$d$ electrons. The results indicate that for the superconductors, the density of states at the Fermi energy has predominantly oxygen 2$p$ character. In this band the charge carriers in the superconducting compounds are holes. In the semiconducting compounds, the oxygen 2$p$ band is probably completely filled.

## I. INTRODUCTION

The on-site electron-electron correlation is generally accepted to be important for the electronic properties of the oxides, chalcogenides, and halides of the late 3$d$ transition metals (TM), leading frequently to Mott-Hubbard band gaps. In this situation the band gap may have true Mott-Hubbard, charge-transfer, or mixed character.[1-3] There is a widespread (though not necessarily universal) belief that the Cu 3$d$-3$d$ electron correlation is also important[4-16] for the new high-$T_c$ superconductors[17,18] $La_{2-x}M_xCuO_4$ ($M$ = Sr and Ba) and $RBa_2Cu_3O_{7-y}$ ($R$ = Y and most of the rare earths). This follows from the disagreements between observed photoemission or inverse photoemission data and computed density-of-states (DOS) curves,[10,19] from the absence of a recognizable core-hole x-ray photoemission spectroscopy (XPS) signal due to the Cu $3d^8$ configuration[20-23] in XPS spectra, from two-hole energies from Cu $L_3VV$ Auger spectra,[10,23,24] and from satellites in valence-band photoemission.[9,19,25,26] While the importance of the on-site 3$d$ Coulomb interaction is thus well established, there exists almost no spectroscopic information on the influence of these correlations on the DOS near the Fermi level and the nature of the charge carriers in the new high-$T_c$ superconductors. It may be that most of the spectroscopic data reported so far are predominantly sensitive to Cu 3$d$ electrons. For example, the XPS cross section for Cu 3$d$ electrons is about five times larger than that for O 2$p$ electrons. This may explain the puzzling absence of any marked change near the Fermi energy in the photoelectron spectra[20,27] upon variation of $x$ and $y$. Several authors[5,13] have emphasized the role of O 2$p$ states near $E_F$. Hall-effect measurements[28,29] indicate hole conductivity in the high-$T_c$ materials suggesting experimental studies of unoccupied states. Therefore, studies of excitations of O 1$s$ electrons into the local unoccupied part of the DOS at the O atoms is of particular interest. In this paper we report on these O 1$s$-$p$ excitations in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ and their changes upon variation of $x$ and $y$. The experimental data are compared to calculations of O 1$s$ edges in the framework of local density-functional (LDF) band-structure calculations.

## II. EXPERIMENT

The method we use is high-energy electron energy-loss spectroscopy (EELS) in transmission. The energy and momentum resolution of the spectrometer[30] was chosen to be 0.4 eV and 0.2 Å$^{-1}$, respectively. The primary energy of the electrons was 170 keV. The spectra were measured at zero momentum transfer where dipole selection rules apply. For the case of an O 1$s$ core level, this means that the near-edge structure should correlate with the local unoccupied DOS of $p$ symmetry at the O atoms.

The preparation of the bulk samples was described in a previous publication.[20] Films about 1000 Å thick were cut from bulk samples by an ultramicrotome and mounted on standard electron-microscope grids. By measurements with a superconducting quantum interference device (SQUID) magnetometer, it was established that superconducting samples remain superconducting after they were cut with an ultramicrotome. Furthermore, the lattice structure of the films was controlled by electron diffraction measurements. We emphasized that EELS in transmission measures bulk properties and is not surface sensitive like other spectroscopies, such as photoelectron spectroscopy or x-ray absorption spectroscopy (XAS) in the partial-yield mode. This means that in our experiments, the whole of 1000 Å contributes equally to the observed spectrum. Some of the $YBa_2Cu_3O_{7-y}$ films were annealed in O to obtain high O concentrations with $y$ close to 0.2. To increase $y$, the samples were annealed at higher temperatures under ultrahigh vacuum conditions. The sample with $y \sim 0.8$ was annealed at 500 °C. The values of $y$ were estimated from chemical analysis of the bulk samples, from the loss spectra, or from the annealing temperature. It is interesting to note that $y$ can also be increased by radiation damage. Almost the same spectra could be obtained from heated samples and from samples irradiated for longer times in the high-energy electron beam of the spectrometer.

## III. COMPUTATIONS

The theoretical excitation spectra were obtained within the self-consistent field LDF approximation using the method of linearized muffin-tin orbitals with the atomic-sphere approximation.[31,32] Structural data published in the literature[33,34] were used. The calculated band structure is basically in agreement with published data.[35-39] The matrix elements and thus the transition probability for the O 1$s$ excitations were calculated and these data were broadened by a Gaussian having a total width of $0.5+0.1|E-E_F|$ eV simulating the finite experimental resolution and lifetime effects. The DOS of $La_{2-x}Sr_xCuO_4$ for low values of $x$ would normally require a very large unit cell or supercell calculation. For this reason we had to limit our simulation to calculations in which one out of four La atoms in the unit cell (giving $x=0.5$) was substituted by Sr. The interaction with the core hole was not taken into account. From core-level excitation measurements on similar systems, such as transition-metal carbides and nitrides, we know that the interaction of the 2$p$ final states with the 1$s$ core level is small and that the features in the measured absorption edges are close to the calculated total DOS.[40] Therefore, we believe that also in the present O 1$s$ edges, excitonic effects are small.

For completeness, we mention that in the two compounds there are different O sites contributing to the total DOS and the O 1$s$-$p$ transition probability. In $La_2CuO_4$ there are two sites, the oxygen sites [O(1)] in the basal $CuO_2$ planes of the $K_2NiF_4$ structure and the oxygen sites [O(2)] in the LaO planes. In $YBa_2Cu_3O_7$ there are four different oxygen sites, two containing two O atoms per unit cell in the two-dimensional $CuO_2$ planes perpendicular to the $c$ axis [O(2), O(3)], one in the one-dimensional CuO chains along the $b$ axis [O(1)], and one containing two O atoms per unit cell in the BaO planes [O(4)].

## IV. RESULTS AND INTERPRETATION

We use the O 1$s$ XPS binding energies to define the threshold of the O 1$s$-$p$ excitations in order to allow comparison of theory and experiment. In $La_{2-x}Sr_xCuO_4$, the binding energies of the 1$s$ state of the two inequivalent oxygen atoms were found[20] to be very similar (528.5 eV) and to be independent of $x$. There was an additional peak in the XPS spectra at $\sim 531$ eV which could, however, be strongly reduced by scraping a few tenths of a millimeter of the material from the surface pellet and which was attributed to hydroxides or defects. In $YBa_2Cu_3O_{7-y}$, the situation is more complicated. Two lines at $\sim 528$ and $\sim 531$ eV with intensity ratios varying from 3/1 to 5/6 have been reported in the literature.[23,41-45] We found the 531-eV line to be decreased strongly by scraping. Therefore, we believe it to be due, at least partially, to surface contamination. Also there is practically no change in the XPS spectra[46] when changing $y$ from $\sim 0.2$ to $\sim 0.8$ indicating no variation of the O 1$s$ binding energies upon variation of $y$. At present, we cannot exclude that one or two of the four different oxygen sites [O(1), O(4)] have a O 1$s$ binding energy higher than 528 eV. But we regard 528 eV as the threshold for the important O atoms [O(2), O(3)] in the $CuO_2$ planes.

Figures 1(a) and 1(b) show the oxygen 1$s$ absorption edges of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$, respectively. The solid lines are merely guides to the eye. The O 1$s$ thresholds as defined by XPS are marked by the dashed lines. In general, we find good agreement with the (limited) existing data for the superconducting compounds ($x=0.15$, $y=0.2$) in the literature[25,47] on the O 1$s$ XAS spectra measured in the photoyield mode. In some data, however, there is a second threshold near 531 eV which may be caused, similar to the previous discussion of O 1$s$ XPS spectra, by a surface contamination. The nonexistence of a second threshold at 531 eV in our nonsurface sensitive measurements may indicate that all the four O sites have the same O 1$s$ binding energy. Furthermore, measurements of the O 1$s$ edges at 100 K show no changes compared to room temperature. This may indicate that the reported temperature dependence of the O 1$s$ XPS spectra is also a surface effect.

At 3-5 eV above threshold, in all the samples there is a strong increase of spectral weight. For $La_{2-x}Sr_xCuO_4$, this intensity is due to La 5$d$ and 4$f$ states hybridized with O $p$ states. This assignment comes from band-structure calculations and from the calculated O 1$s$ near-edge spectra (see below). According to the discussion to follow, part of the intensity beyond 3 eV above threshold may also be explained by O $p$ states hybridized with the upper Cu 3$d$ Hubbard band. In $YBa_2Cu_3O_{7-y}$, the rise in intensity at 3-5 eV above threshold is related to Ba 5$d$ and 4$f$ and Y 4$d$ states hybridized with O $p$ states.

The region near threshold is of central interest in this paper. According to band-structure calculations[35-39] for $La_2CuO_4$, the intensity in this region should be dominantly related to a two-dimensional, half-filled band composed of Cu $3d_{x^2-y^2}$ electrons hybridized with O $2p_{x,y}$ electrons. The O 1$s$ excitation spectrum of undoped $La_2CuO_4$ shows no intensity near threshold which is in agreement with the semiconducting behavior of this material. The doped $La_{2-x}Sr_xCuO_4$ system with $x=0.15$ shows a triangular-shaped peak near threshold which we know from previous lower resolution studies[20] to have intensity roughly pro-

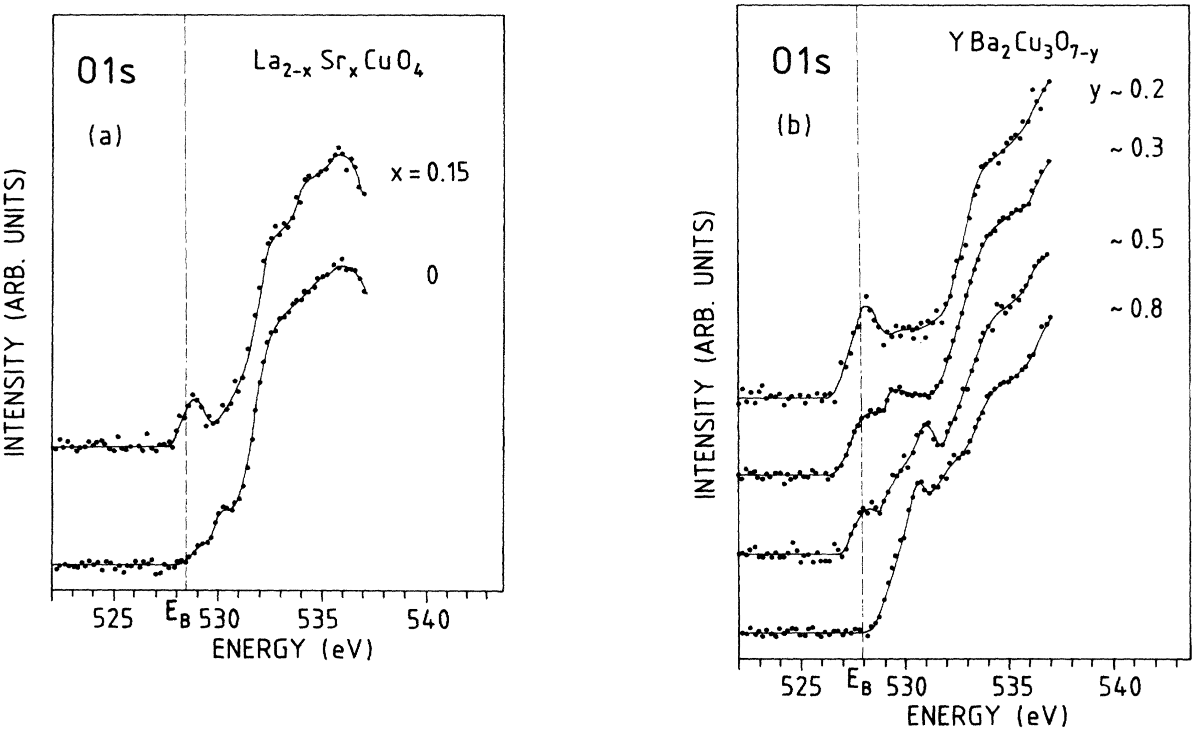

FIG. 1. Oxygen 1*s* absorption edges of (a) $La_{2-x}Sr_xCuO_4$ and (b) $YBa_2Cu_3O_{7-y}$ measured by electron energy-loss spectroscopy. The binding energy of the O 1*s* level, as determined by x-ray-induced photoemission, is shown by the broken line. In the framework of an interpretation of the spectra by the density of unoccupied states, this line would correspond to the Fermi energy.

portional to the Sr concentration up to $x = 0.25$. The most important question which arises is whether the observed peak at threshold has dominantly O 2*p* character or whether it is caused by O 2*p* wave functions which are strongly hybridized with Cu 3*d* electrons. Because this peak was never found in photoelectron spectra[10,19,20] where the Cu 3*d* states have a large cross section, we conclude that the peak at threshold on the O 1*s* edge has dominantly O 2*p* character. This is also in line with the observation[10,19] that due to correlation effects, the 3*d* states are pushed to lower energy compared to band-structure calculations thus strongly reducing the Cu 3*d* DOS at $E_F$.

Let us now consider $YBa_2Cu_3O_{7-y}$. For $y \sim 0.8$ no intensity at the binding energy $E_B$ is observed in Fig. 1(b) in agreement with transport measurements which have revealed the semiconducting character for $y \gtrsim 0.5$. With decreasing *y*, the peak at 2.5 eV above $E_B$ decreases and the intensity at threshold increases. At $y \sim 0.2$ there is a narrow peak at $E_B$, about 0.8 eV wide, followed by a constant intensity up to $\sim 4$ eV above $E_B$. We believe that the states near $E_F$ are peculiar to the superconducting material because they appear when the system transforms from the semiconductor to the superconductor. As with the $La_{2-x}Sr_xCuO_4$ material, we conclude that the states at the Fermi level have predominantly O 2*p* character because they are observed in the O 1*s* electron energy-loss spectra and they are not observed by those spectroscopies where the Cu 3*d* cross section is high.[9,19,23] Due to the uncertainties of the O 1*s* binding energies of the four different O atoms, we cannot definitely conclude which of the O sites causes the DOS at $E_F$.

In Fig. 2 we show for comparison the calculated O 1*s* near-edge spectra for $La_{2-x}Sr_xCuO_4$ with $x = 0$ and 0.5 and for $YBa_2Cu_3O_{7-y}$ with $y = 0$ and 1. In addition, we show the calculated contributions of the individual O sites to the total intensity. The fact that the increases in intensity due to La 5*d* and 4*f* states for $La_{2-x}Sr_xCuO_4$ and due to Ba 5*d* and 4*f* and Y 4*s* states for $YBa_2Cu_3O_{7-y}$ are approximately 1-2 eV higher in energy than found in the measured spectra can be attributed to effects of correlation or to the increasing inadequacies of the basis set at higher energies. Comparing the calculated spectra of $La_{2-x}Sr_xCuO_4$ for $x = 0$ with that for $x = 0.5$, the strong reduction of the peak at $\sim 6$ eV above $E_F$ which is related to the replacement of La (with 4*f* electrons) by Sr (without 4*f* electrons) can be clearly seen.

At threshold the calculations predict for undoped $La_2CuO_4$ a finite intensity due to holes in the two-dimensional Cu $3d_{x^2-y^2}$-O $2p_{x,y}$ band typical of a metal. The comparison between theory and experiment (no DOS at $E_F$) is a further very explicit indication that there is a breakdown of the LDF approximation due to *e*-*e* correlations. Upon doping with Sr an increase in the intensity is predicted by the calculation for $x = 0.5$ due to states centered both at the O(1) and O(2) atoms. This increase in intensity near threshold is caused by a lowering of the Fermi level due to the divalent Sr atoms. At $x = 0.5$ the lowering of $E_F$ is so strong that the peak in the DOS due to the band near the $\Delta - U$ midpoint is reached.[35] For

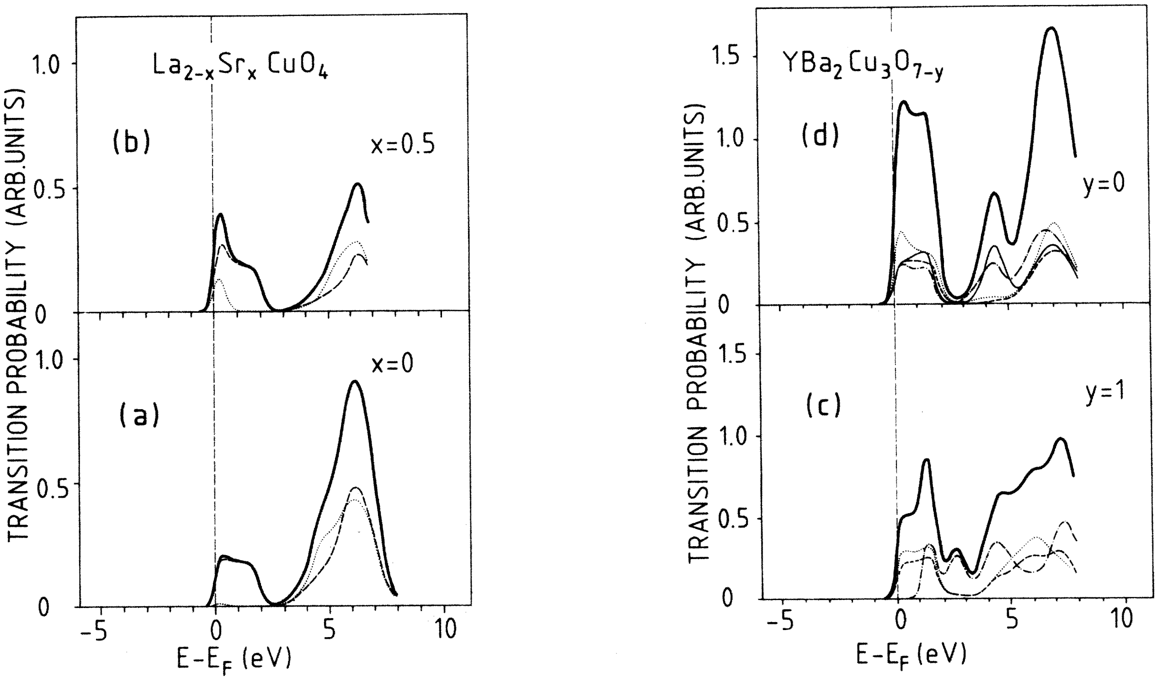

FIG. 2. Calculated oxygen 1*s* absorption edges in the framework of a density-functional formalism for $La_{2-x}Sr_xCuO_4$ [(a) $x=0$ and (b) $x=0.5$] and for $YBa_2Cu_3O_{7-y}$ [(c) $y=1$, (d) $y=0$]. For $La_{2-x}Sr_xCuO_4$: total (solid curve), O(1) (dashed curve), and O(2) (dotted curve). For $YBa_2Cu_3O_{7-y}$: total (thick solid curve), O(1) (thin solid curve), O(2) (dashed curve), O(3) (dotted curve), and O(4) (chain curve). The O sites are explained in the text.

$x=0.15$, however, the peak in the DOS is probably not fully reached and only a broadening of the trapezoidal intensity at threshold is expected together with a small increase of the total spectral weight from 0 to 2.5 eV above $E_F$. Thus the concentration dependence and the spectral shape near threshold is different from that expected from the band-structure calculations, again indicating a breakdown of the single-electron picture in the doped system.

For $YBa_2Cu_3O_{7-y}$ the calculation predicts for $y=1$ a metallic character while in the experiment for $y=0.8$ no DOS at $E_F$ is observed. There is a peak at $\sim$2.5 eV above $E_F$ due to O(4) atoms in the BaO planes which also appears in the measured spectrum. This agreement may be, however, accidental since there are, similar to $La_2CuO_4$, serious discrepancies between theory and experimental data. For $y=0$, the band-structure calculations predict that the DOS at $E_F$ is composed of about equal contributions from all the four O sites. Finally we remark that at least in the calculations the situation is different from that of $La_{2-x}Sr_xCuO_4$. According to recent neutron scattering data, the O vacancies which appear for $y>0$ are not equally distributed on all four O sites, but are created primarily on the CuO linear chains. Therefore, in $YBa_2Cu_3O_{7-y}$ the Fermi level is not just lowered with decreasing *y*. Rather, new states due to the O(1) sites are created and bands are shifted and broadened due to changes in the structure.[32] But also in this system there is a breakdown of the LDF band-structure calculations for the superconducting and the semiconducting compound.

## V. DISCUSSION

The present experimental results give a very direct evidence that the charge carriers in the new high-$T_c$ superconductors are holes with dominant O 2*p* character. There have been other experimental studies such as, for example, resonant photoemission experiments[19] or XPS investigations[48] which come indirectly to the same conclusions. Our results support theoretical models[5] for the cuprate perovskites which were previously developed for other transition-metal compounds.[1] In order to explain the insulating state of $La_2CuO_4$ and $YBa_2Cu_3O_6$ we may use the Mott-Hubbard theory in which charge fluctuations of the type $d_i^n d_j^n - d_i^{n-1} d_j^{n+1}$ (where *i* and *j* label transition-metal places) are considered which involve the *d*-*d* Coulomb and exchange interaction $U_{\text{eff}}$. When $U_{\text{eff}}$ is much larger than the bandwidth, these charge fluctuations are strongly suppressed and for a half-filled band, a gap with an energy of about $U_{\text{eff}}$ is formed. This Mott-Hubbard gap is, however, rather large and it is difficult to understand the metallic character of various transition-metal compounds. Besides the above mentioned fluctuations, there exist charge fluctuations of the type $d_i^n - d_i^{n+1}\underline{L}$ involving the energy $\Delta$, where $\underline{L}$ denotes a hole in the anion valence band. When $U_{\text{eff}}$ is large and $\Delta$ is small, an anion (oxygen) band is formed between the lower Hubbard (Cu 3*d*) "band" and the upper Hubbard (Cu 3*d*) "band." Electrons are transferred from the Cu sites to the O sites thus stabilizing a Cu configuration which is close to $3d^9$ (half-filled band) and a filled O $2p$ band. In this case, the simple Mott-Hubbard model is no more valid and we obtain the so-called charge-transfer semiconductor with a gap between the filled O band and the upper Cu $3d$ Hubbard "band." By Sr doping or O intercalation, light holes are introduced in the O $2p$ band but not in the Cu bands formed by heavy $3d$ electrons. The gap (for $x=0$ and $y=1$) and the partial DOS of these holes on the O sites can be directly observed in the O $1s$ edges shown in Fig. 1.

This "band" model is supported by various other measurements. XPS studies[20,23] on the Cu $2p$ level show dominantly a Cu $3d^9$ ($Cu^{2+}$) configuration and no formation of a Cu $3d^8$ ($Cu^{3+}$) configuration and almost no change upon variation of $x$ and $y$. It should not be concealed, however, that very recently a small amount of Cu $3d^8$ ($Cu^{3+}$) was observed[48] in $YBa_2Cu_3O_{7-y}$ for $y < 0.2$. According to LDF calculations, the photoemission spectra should have a maximum at $\sim 2$ eV below $E_F$ while in the experiment a maximum at $\sim 4$ eV was found.[10,19,25] Since, as mentioned above, these spectra are dominated by Cu $3d$ states this indicates a high on-site correlation energy for the $3d$ electrons which shifts the Cu $3d$ states to lower energies. This explains why in photoemission spectra, apparently a very low DOS at $E_F$ is observed which is considerably smaller than that calculated in the single-particle approximation.[20] It also explains that there is almost no change of spectral weight at $E_F$ upon variation of $x$ and $y$. In the above-mentioned model, the DOS at $E_F$ has dominantly O $2p$ character, and since the cross section for these states is much lower than that of the Cu $3d$ states, the spectral weight at $E_F$ should be strongly reduced. Furthermore, almost no changes are found in recent Cu $2p$ XAS spectra[49,50] upon variation of $x$ and $y$. In a first approximation, these spectra give a measure for the density of unoccupied states and thus for holes on Cu sites. Finally, the existence of holes in the superconducting compounds was already found by Hall effect studies[28,29] and optical spectroscopy.[51,52]

## VI. SUMMARY

We have investigated the local DOS on the O sites in the high-$T_c$ perovskite cuprates. Core-level spectroscopy on the O $1s$ level was used which to our knowledge is the only method revealing directly the strong changes in the electronic structure near the Fermi level which occur upon doping or changing the O concentration. Strong deviations from local density-functional calculations have been obtained in the superconducting and in the semiconducting compounds. For the insulating compounds, the present results favor a model of a charge-transfer semiconductor with an almost completely filled O $2p$ valence band. In the superconducting compound, holes are created in the O $2p$ band, the DOS of which can be seen directly in the O $1s$ edges.

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