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Valence-electron states of $YBa_2Cu_3O_{7-\delta}$ characterized by combined x-ray and photoemission studies

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X-ray-emission (XES), x-ray-excited photoelectron (XPS), and ultraviolet-excited photoelectron spectra of $YBa_2Cu_3O_{7-\delta}$ have been measured and arranged on a common binding-energy scale by XPS core lines. Three main valence-band (VB) structures at 2.7, 3.7, and 4.8 eV relative to the Fermi level ($E_F=0$) could be identified representing hybridized Cu $3d/4p$–O $2p$ states. The VB XES and photoelectron spectra are strongly influenced by correlation and charge-transfer effects and hence reproduce the density of states (DOS) of excited multiple-hole states but not the one-hole ground-state DOS. These processes are responsible for the observed differences between high-energy spectroscopic results and one-electron theory. From the XES compared with calculations we estimate a "local partial correlation shift" of the theoretical Fermi level ($\Delta E_F^{\mathrm{corr}}$) in the energy range 0.6–1.6 eV. Charge transfer and screening processes contribute to the x-ray transitions of the selective-type Cu $2\underline{p}d^{10}\underline{L}\rightarrow d^9\underline{L}$ and O $1\underline{s}p^6$Cu $3d^9\rightarrow d^9\underline{L}$ owing to Cu $L\alpha$ and O $K\alpha$, respectively. With the mechanism of charge transfer and band shift acting in highly correlated electron systems, such as high-temperature superconducting compounds, a possible explanation for the unusually low DOS at E_F in excitation spectra is given.

I. INTRODUCTION

An understanding of the origin of the large superconducting transition temperature T_c of the new class of copper-oxide-based high-temperature superconducting compounds (HTSC's) will require a determination of their electronic structure. So far high-energy spectroscopical studies such as photoemission spectroscopy on the La-Sr-Cu-O, Y-Ba-Cu-O, and related systems have provided a large amount of information about the character of the valence-band (VB) states of these HTSC's. On the other hand, there still exist unsolved questions especially concerning the local partial symmetry of the valence states.

X-ray-emission spectroscopy may provide some answers. Although the resolution is generally not so good as in photoemission spectroscopy, x-ray-emission spectroscopy has some advantages in determining bulk valence-band density of states (DOS): It is less surface sensitive and the choice of corresponding core levels allows selective mapping of local partial DOS of interest. Recently, some x-ray-emission spectra (XES) were measured on the HTCS's (Refs. 1–6) and compared among one another and/or with ultraviolet- and x-ray-excited photoemission spectra (UPS and XPS).[3–5,7,8] Increased information about the character of the valence states is expected by combining and correlating the spectra.

The results and the interpretation of these experiments, however, are not conclusive; they are partly contradictory and seem in some cases somewhat uncertain with respect to the energy calibration and spectra alignment. The aim of this paper is to present well-resolved VB XPS, UPS, and the most principal VB XES of $YBaCu_3O_{7-\delta}$, their order on a common binding-energy scale with the Fermi energy $E_F=0$, and the determination and identification of the spectral features in terms of local partial DOS.

Comparison of the experimental results with calculated DOS for $YBa_2Cu_3O_{7-\delta}$ allows one to make a decision about the validity of the independent particle approximation used in band-structure calculations. For the interpretation of excitation spectra such as XPS, UPS, and XES a satisfactory agreement between experiment and theory requires inclusion of the multiple hole in the final state as well as on-site Coulomb repulsion (correlation effects) and charge transfer.[8–11] Nevertheless, the one-electron local density theory seems to describe adequately the ground-state configuration in highly correlated systems. Hence, in addition to the complexity of electronic structure, the local partial DOS should be judgable by comparison with experimental excitation spectra, if the contributions of correlation and charge-transfer effects in the excited final states are known and can be taken into consideration.

II. EXPERIMENTAL DETAILS AND RESULTS

All spectra were measured on sintered samples of $YBa_2Cu_3O_{7-\delta}$ at room temperature. The samples were prepared with the usual method which is explained in Ref. 12. The size of these pellets was about 15 mm. The phase of the samples was checked by using x-ray diffraction. The macroscopic homogeneity of the pellets was investigated optically. The oxygen content of the material of interest was not specially determined but the samples were in the orthorhombic metallic phase and showed the superconducting phase transition at about 90 K. Therefore we assume an oxygen deficiency range of $0 \leq \delta \leq 0.5$. For XES measurements the samples were polished mechanically whereas in the case of XPS and UPS they were scraped *in situ* in order to get rid of the possible surface contamination. The Cu $L\alpha$ and O $K\alpha$ emission bands of the HTSC material were measured on an Applied Research Laboratory (ARL) electron microprobe analyzer (EMX-SM) using the RAP spectrometer crystal. The voltage and the current were 8 kV and 50 nA, respectively. The peak positions of the two emission bands were found at 929.3±0.2 eV and 526.1±0.2 eV with reference to the peak positions of the emission bands of metallic copper and SiO_2 (quartz) at 930.1 and 526.0 eV, respectively.[13]

The Cu $K\beta_{2,5}$ valence-band emission was accumulated on a two-crystal x-ray spectrometer using a W tube as the excitation source (40 kV, 40 mA).[14] The energy resolution of the measurement was about 1 eV. Two highly perfect Si(111) crystals in the first-order reflection were used to record the Cu $K\beta_{2,5}$ of $YBa_2Cu_3O_{7-\delta}$ with reference to the $K\beta_{1,3}$ and $K\beta_{2,5}$ of metallic copper.[15] The peak position of Cu $K\beta_{2,5}$ of the HTSC was found at 8978.5±0.3 eV.

With the Si(111) crystals in the third-order reflection the Cu $K\alpha_1$ line of the HTSC material was observed at 8048.06±0.10 eV with a FWHM (full width at half maximum) of 2.61 eV referenced against the Cu_{met} (Ref. 15) with a measured FWHM =2.36 eV. The energy resolution was better than 0.1 eV.

The XPS data were measured with a VG ESCA 3 Mark II spectrometer using monochromatized Al $K\alpha$ excitation at a basic vacuum of 10^{-8} Pa. The energy resolution of the instrument was 0.6 eV. As a reference position the Cu $2p_{3/2}$ peak of metallic Cu was found at 932.7±0.1 eV with respect to the Fermi level at $E_F = 0$.

Using the multifunctional VG spectrometer equipment the UPS spectra at He II excitation were obtained without changing the sample position. In this case the estimated energy resolution was of the order of 0.1 eV. For the alignment of the VB XES, XPS, and UPS in the binding energy (BE) scale the Cu $2p_{3/2}$ and O 1*s* XPS core levels of the $YBa_2Cu_3O_{7-\delta}$ sample were measured. In the BE range of Cu $2p_{3/2}$ a broad asymmetric main line at 933.1-eV peak position with a FWHM of about 2.5 eV was found. At higher BE there appears a comparatively strong satellite structure between 940 and 945 eV. In the O 1*s* region the principal line is observed at 528.8 eV having a FWHM of about 2 eV. In addition a second O 1*s* line is measured at about 531 eV. There still exists a controversy over the existence of a second O 1*s* component at ~531 eV; it is either assumed to exist due to surface or intergranular contaminations, or as an intrinsic part. We performed careful O 1*s* measurements of CuO and $NaCuO_2$ together with the HTSC investigation and obtained evidence for an intrinsic nature of the phenomenon.

The BE of the Cu 1*s* level necessary for adjusting the Cu $K\beta_{2,5}$ emission was determined by the sum of the Cu $2p_{3/2}$ main line BE and the energy of the Cu $K\alpha_1$ emission, resulting in a value of 8981.16 eV. Utilizing this energy parameter for Cu 1*s* the peak of the Cu $K\beta_{2,5}$ emission is placed at about 2.7 eV in the unique BE scale. This position is in excellent agreement with the result obtained by correlating the O 2*s* peak at about 20.4 eV in the VB XPS with the corresponding structure (Cu $K\beta''$) of the Cu $K\beta$ emission.

The Cu $L\alpha$ and the O $K\alpha$ emission were positioned in the BE scale by means of the Cu $2p_{3/2}$ main line at 933.1 eV and the O 1*s* line at 528.8 eV, respectively. With the above-described correlation of core lines and VB XES, XPS, and UPS spectra a reasonable valence-band ordering could be obtained as in Fig. 1. Our energy-based arrangement of the spectra has been found to be in good

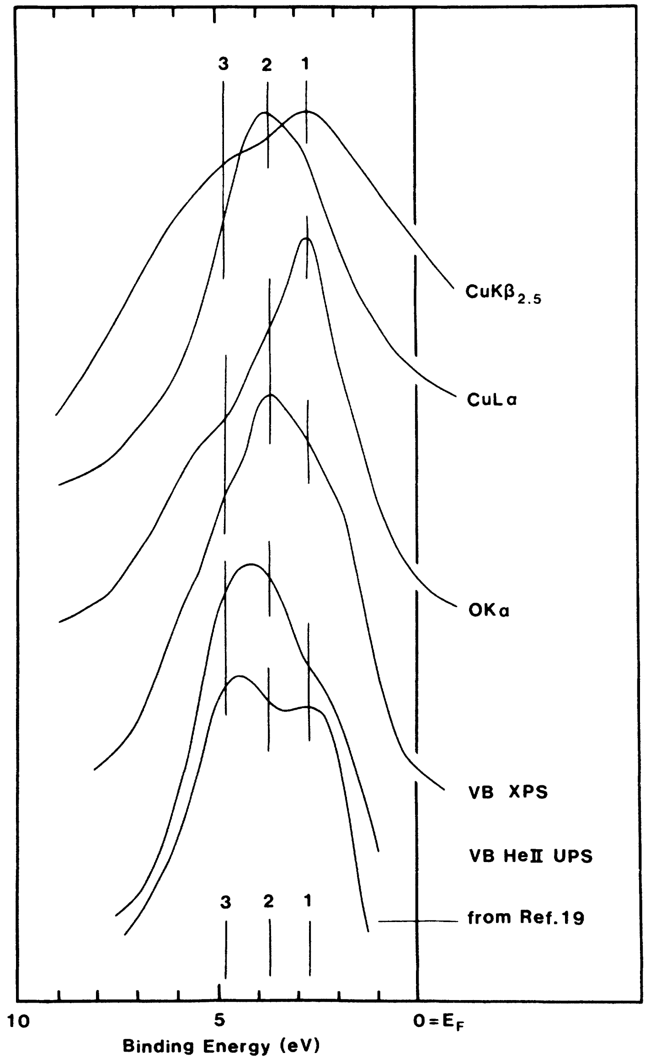

FIG. 1. Experimental x-ray-emission spectra (XES) and photoelectron spectra (XPS and UPS) of the valence band of $YBa_2Cu_3O_{7-\delta}$. All spectra are arranged on a common energy scale with reference to the Fermi energy $E_F = 0$.

agreement with the recently published results of Mariot *et al.*[16]

The usefulness of the spectra correlation and the presented concept of studying the valence-band structure of HTSC material will be discussed in detail below.

III. DISCUSSION OF EXPERIMENTAL RESULTS AND COMPARISON WITH ONE-ELECTRON THEORY

Because of the strong localization of the core orbitals and the dipole selection rules for x-ray transitions, the VB XES are inherently able to map the local partial DOS. For the Cu $L\alpha$ emission one may conclude that the center of gravity at about 3.7 eV determines the position of the main $3d$ band of the $YBa_2Cu_3O_{7-\delta}$ HTSC. Considering the range of the lowest measured FWHM value of about 2.2 eV (Ref. 16) for Cu $L\alpha$ and keeping in mind the energy broadening of the Cu $2p_{3/2}$ core hole of at least 0.7 eV (Ref. 17) together with the Cu $2p_{3/2}$ level spread of the order of 0.4 eV caused by inequivalent sites of the Cu atoms in the HTSC,[18] the existence of a comparatively narrow Cu $3d$ band is evident.

Analyzing the spectral distribution of the O $K\alpha$ emission at 3.7 eV with respect to Cu $L\alpha$ we obtain information about the O $2p$ states. It should be noted that the weak shoulder in the O $K\alpha$ emission spectrum is connected with the Cu $3d$–O $2p$ hybridization.

The Cu L peak coincides well with the VB XPS intensity maximum characterizing this structure of the VB photoemission predominantly as $3d$-like states. We observe no coincidence with our He II UPS spectrum and notice the same situation with regard to the UPS spectrum of Steiner *et al.*[19] The UPS results show peak structures at 2.7 and about 4.5 eV, in agreement with the positions of the O $K\alpha$ intensity maximum and the low-energy shoulder, respectively. Hence, we identify the two UPS peak structures and the high- and low-energy shoulders of the VB XPS to be predominantly O $2p$-like. This conclusion is also suggested by the results of the energy-dependent photoemission spectra as discussed in detail by Ramaker.[9]

The two O $2p$ subbands at 2.7 and about 4.8 eV coincide with the corresponding features in the Cu $K\beta_{2,5}$ x-ray emission mapping the Cu $4p$ DOS. Again, this points to a hybridization of the Cu $4p$ and O $2p$ states in HTSC and their splitting into bonding and antibonding states.

In summary, from the correlation of the experimental VB XES, XPS, and UPS spectra on a common BE scale and from the individual specific information content one may derive three fundamental valence-band structures 1, 2, and 3 at about 2.7, 3.7, and 4.8 eV below the Fermi level, respectively. At this structure 1 maps antibonding (with Cu $3d$ and Cu $4p$ states) and/or nonbonding O $2p$ states. Structure 3 represents the bonding O $2p$ states hybridized with Cu $4p$ and to some extent with Cu $3d$ states. In this concept the main structure 2 represents the strongly localized Cu $3d$ states mixed configurationally with O $2p$ states.

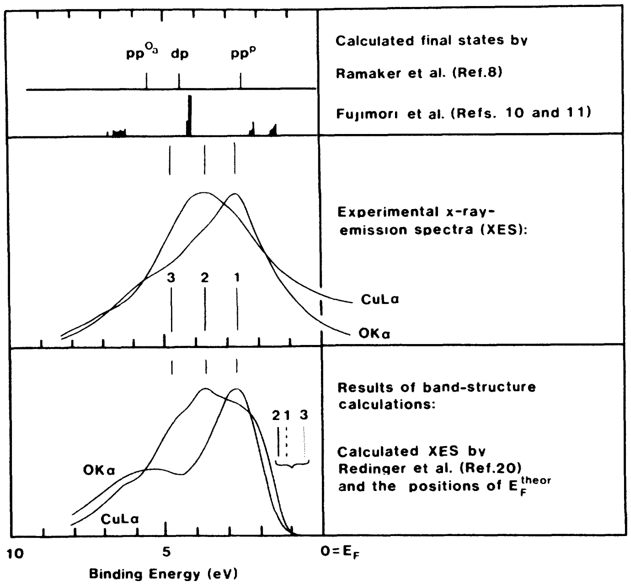

FIG. 2. Comparison of experimental XES spectra and the energy position of the main structures 1, 2, and 3 together with results of the one-electron band calculations (bottom) and cluster calculations including correlation effects (top). In the lower part of the figure the positions of E_F^{theor} are assigned by vertical bars which give coincidence between the experimental structures and the corresponding local partial DOS. The dashed line, solid line, and dotted line indicate structures 1, 2, and 3, respectively.

In the lower part of Fig. 2 a comparison of experimental results with one-electron ground-state calculations is presented. It should be mentioned that the comparison between calculated XES and local partial DOS is rough and semiquantitative, because it neglects the influence of lifetime broadening and a possible core level spreading caused by inequivalent Cu and O lattice sites.

This spreading of the Cu $2p_{3/2}$ and O $1s$ core lines has been calculated by Krakauer *et al.*[18] to be ≤ 0.45 and ≤ 0.7 eV, respectively.

In Fig. 2 theoretical Cu $L\alpha$ and O $K\alpha$ emission bands are arranged below the experimental spectra. The spectral distribution was calculated by Redinger *et al.*[20] utilizing data of a local density full-potential linear augmented plane wave (LAPW) calculation of $YBa_2Cu_3O_7$ (Ref. 21) and taking into account the broadening and spreading of the core levels. In view of a sufficient agreement of the structures 1 and 2 between the measured O $K\alpha$ and Cu $L\alpha$ and the theoretical intensity maxima the theoretical Fermi energy E_F^{theor} has to be shifted by ~ 1.1 and ~ 1.4 eV against the experimental E_F, respectively. To obtain a reasonable coincidence of structure 3 a shift of ~ 0.6 eV is necessary. A similar comparison was performed with the O $2p$ and Cu $3d$ DOS obtained from a self-consistent linear muffin-tin orbital (SC LMTO) calculation of $YBa_2Cu_3O_7$.[22] Here the conclusive shifts of E_F^{theor} to give rise to coincidence are about 1.8, 0.3, and 0.8 eV related to the structures 1, 2, and 3, respectively.

In the lower part of Fig. 3 for some other band calculations[3,4,18,23–25] the energy positions E_F^{theor} are shown to provide coincidence of the experimental and theoretical features 1, 2, and 3.

The shifts of the $3d$ derived structure 2 extend over a range between 0.2 and 1.4 eV with the center of gravity at about 0.6 eV for the band calculations considered here.

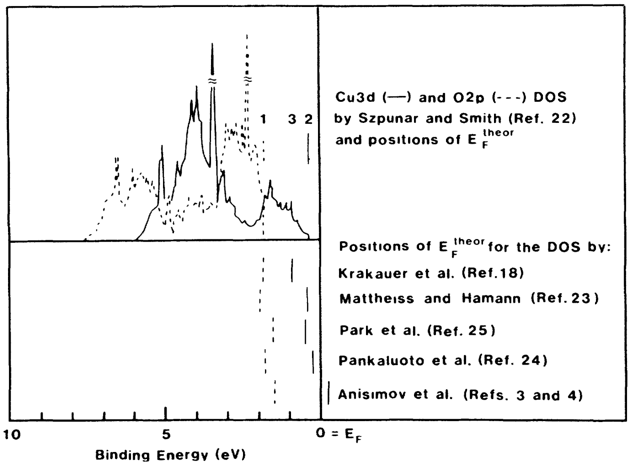

FIG. 3. The one-electron Cu 3*d* and O 2*p* partial densities of states are shown (Ref. 22). The energy positions of the theoretical Fermi levels are described by the same vertical bars as in Fig. 2. These Fermi levels indicate how much the theoretical spectra deviate from the experimental ones as far as the energy positions of the features 1, 2, and 3 are concerned.

The only exception reported is that of Anisimov and coworkers[3,4] where the shift of E_F^{theor} has the opposite direction. The average shifts to fit the O 2*p* derived structures 1 and 3 are 1.6 and 0.8 eV, respectively.

Generally our results agree with those acquired by other methods of high-energy excitation spectroscopy.[26] However, when utilizing XES for systematic investigation one may expect more information about the individual partial shifts of the different subbands in comparison with XPS and UPS where the obtained shifts are more integral and averaged.[27]

One characteristic property of XES is that it is possible to interpret the spectra in terms of one-electron band theory. Comparing theory with experimental spectra one may conclude whether the relative position of the subbands is not correctly calculated or whether the screening of the hole in the final state depends on the character of the subband and causes different shifts in the partial spectra. Both explanations are reasonable as far as the observed shifts are concerned and may be acceptable, at least in principle.

For the HTSC material investigated here, however, a third effect seems to be important and may be responsible for the widely observed and reported disagreement between theory and experiment. The difference between the ground state and the excited state for the correlated system seems to be larger than the corresponding difference for the uncorrelated system.[27]

IV. INTERPRETATION OF THE RESULTS IN THE LIGHT OF CORRELATION EFFECTS

Recently, much attention has been paid to correlation effects concerning metal oxides. For instance, Sawatzky and co-workers have interpreted the electronic structure of 3*d* metal oxides in terms of the Anderson Hamiltonian.[28,29] This proposed model seems particularly useful for nearly localized bands, i.e., in the case where correlation energies are large compared to the occupied part of free-electron bandwidth.

It is usually assumed that a Cu $O_n^{(2n-2)-}$ cluster is an adequate description of the basic electronic structure also with respect to the existence of charge-transfer processes.[8] Such a Cu $O_n^{(2n-2)-}$ cluster has one hole belonging to both Cu 3*d* and O 2*p* shells in the ground state, which in other words can be roughly approximated by an admixture of two main configurations d^9 and $d^{10}\underline{L}$ where $\underline{L}$ denotes a hole in the ligand. The d^9 configuration has one hole in the otherwise closed electron shell d^{10} of the Cu atom. For $d^{10}\underline{L}$ the ligand hole $\underline{L}$ is localized in the O 2*p* shell of the O^{2-} ions. Charge-transfer processes cause fluctuations between the two configurations and generate the admixture of the corresponding cluster states.

Excitation spectra involve at least one two-hole final-state configuration. Hence photoexcitation from the valence states of the $CuO_n^{(2n-2)-}$ cluster gives rise to three possible final states: d^8, $d^9\underline{L}$, and $d^{10}\underline{L}^2$ having all two holes. The VB XPS and UPS are connected with the DOS of these two-hole configurations but not the DOS of the one-hole state. In a highly correlated system the two DOS's considered can be very different. This situation explains the well-known differences observed[20] between the theoretical (ground-state) DOS and the photoelectron spectra of HTSC's.

In the case of XES both the initial and final states are two-hole states being strongly influenced by correlation effects and to some extent also by charge-transfer effects. The initial states of Cu $L\alpha$ transitions are in principle $\underline{2p}d^9$ and $\underline{2p}d^{10}\underline{L}$ states ($\underline{2p}$ denotes a Cu 2*p* core hole) identical with the final states in the XPS Cu $2p_{3/2}$ spectra and giving rise to the XPS satellite and main line, respectively.

From the orbital relaxation times and the core level lifetime one can expect as a first approximation a relaxation and screening process of the type $\underline{2p}d^9 \rightarrow \underline{2p}d^{10}\underline{L}$ before the core hole decay. Therefore we believe that only $\underline{2p}d^{10}\underline{L}$ states are the active x-ray initial states and that the Cu $2p_{3/2}$ main line (at 933.1 eV) must be used for the arrangement of Cu $L\alpha$ emission in the BE scale.

Similar considerations for oxygen give rise to the assumption that for the O $K\alpha$ emission the initial-state configuration is O $1\underline{s}$ Cu d^9 and not the other possible configuration O $1\underline{s}$ Cu $d^{10}\underline{L}$. This interpretation leads to an important consequence: The O $K\alpha$ emission seems in a selective way to be connected with the excitation of $O^{2-}(2p^6)$ ions rather than $O^-(2p^5)$ oxygen species. The corresponding 1*s* core level energies we could separate well to 528.8 and 531.0 eV, respectively.[30] Again, in view of the spectra combination we used the former value.

The x-ray final states of the VB XES spectra should be the same as those of the VB photoemission. Fujimori and co-workers[10,11] calculated appropriate final states on CuO_6^{10-} cluster taking into account the configuration interaction and the intra-atomic Coulomb and exchange interaction between the 3*d* electrons. Again three possible final configurations can be arrived at by photoexcitation: d^8, $d^9\underline{L}$ and $d^{10}\underline{L}^2$. With regard to the inherent XES mechanism the $d^9\underline{L}$ configuration is relevant only because of the Cu $\underline{2p}d^{10}\underline{L} \rightarrow d^9\underline{L}$ and the O $1\underline{s}p^6$ Cu

$3d^9 \rightarrow d^9\underline{L}$ transitions owing to the Cu $L\alpha$ and O $K\alpha$ emission, respectively.

At the top of Fig. 2 the electronic states of the $d^9\underline{L}$ two-hole final configuration are shown. Evidently, the energy positions agree with the gross spectral distribution, i.e., the final states at about 4 eV with feature 2 while the calculated results at about 2 and 6.5 eV can be linked with the experimental features 1 and 3, respectively. Moreover, it should be noticed that the center of gravity of the calculated states referring to E_F agrees substantially better with the measured features compared to the one-electron results. As a further result we can state that our experimental data in general coincide with the calculated energies of Ramaker *et al.*[8,9] at a highly correlated CuO_n cluster. The authors used an extended Hubbard model including the intersite correlation parameters U_{dp} and U_{ppo} for neighboring Cu-O and O-O atoms, respectively. Relevant values of the Hubbard parameters were estimated empirically by means of Cu $2p$ and VB UPS data as well as XES, x-ray-absorption, and Auger spectra. The final states as two-hole states in the VB are described by d (Cu $3d$) or p (O $2p$) showing how the holes are located. If the two holes belong to the oxygens then the authors make a distinction between the holes on orthoneighboring O atoms (pp^O) or on para-atoms (pp^P). It is also necessary to assume the two holes to be in bonded (pp^{Ob}) and antibonded (pp^{Oa}) O pairs as far as the neighboring (pp^O) holes are concerned.

Finally, in the upper part of Fig. 2 the calculated energy positions after Ramaker *et al.* in terms of two-hole final states for UPS and XES are shown: pp^P at 2.5 eV, dp at 4.5 eV, and pp^{Oa} at 5.5 eV, relative to E_F.

Following this theoretical level ordering our Cu $L\alpha$ peak (structure 2) at 3.7 eV would be identified as the dp final state, which will be attained by the transition $cp \rightarrow dp$ (in this case c denotes the Cu $2p$ core hole). Using our notation above this transition is Cu $2\underline{p}d^{10}\underline{L} \rightarrow d^9\underline{L}$. Structure 1 at a BE 2.7 eV (position of the O $K\alpha$ peak) is probably produced by the $cp^P \rightarrow pp^P$, i.e., the transition from the initial-state configuration O $1\underline{s}p^6$ with the second hole on para-O atoms to the final-state configuration p^5 of the radiating O atom and with the second hole located as before (i.e., in a state p^P).

Consequently, structure 3 at about 4.8 eV can be interpreted by transitions to the final state pp^{Oa} calculated at 5.5 eV. It can be reached from the initial state cd (O $1\underline{s}d^9$) by an x-ray transition to pd ($=dp$ at 4.5 eV) and a simultaneous relaxation process of the type $pd \rightarrow pp^{Oa}$ (charge-transfer process).

Our interpretation of O $K\alpha$ deviates from that given by Ramaker *et al.*[8] in the sense that with respect to O $K\alpha$ we suppose the oxygen core level energies of both initial states cd and cp^P to be equal and to be given by the O $1s$ main line at 528.8 eV.

V. CONCLUSIONS

The localization of the core orbitals and dipole selection rules indicate the highly selective character of the XES reproducing local partial DOS by their intensity. Therefore the arrangement of the XES spectra on a common energy scale by means of the XPS core lines allows one to analyze the character of the valence-band states. The experiments aim at proving the accuracy of one-electron band-structure calculations in comparison with spectroscopic data.

This method commonly used in solid-state spectroscopy has a substantial drawback as it compares calculated ground states with an excited final state having at least one hole in the final-state configuration. In the case of strongly correlated systems such as the HTSC materials, however, profound differences may appear between these two states leading also to unsatisfactory results in the comparison of experiment and theory.

From our valence-band analysis of $YBa_2Cu_3O_{7-\delta}$ utilizing the XES it follows that the calculated local partial DOS and hence the corresponding Fermi energy E_F^{theor} has to be shifted to higher binding energy for giving rise to coincidence between measured spectra and calculated DOS. Furthermore, the shifts are not unique but depend on the character and the energy of the subbands. Therefore the information content of the XES with respect to such "correlation shifts" is larger than that of the VB XPS or UPS where only an integral shift can be stated. The most important result from our XES experiments is that the relative positions of the subbands as measured by the excitation spectra are in general different from the positions calculated for the ground state. Or, in other words, the measured positions used in the discussion in Chap. 3 are those of the excited final states but not the positions of the ground-state structures.

This result can be used to define and estimate special correlation parameters, for example a "local partial correlation shift" which may be noted ΔE_F^{corr}. It can be estimated by comparing spectral structures with corresponding local partial DOS's. Such special correlation data may also be useful for the calculation of more principal correlation parameters like the on-site Coulomb energy U on the basis of the appropriate theories. It should be mentioned that Costa-Quintana *et al.*[31] have made band calculations by including the Coulomb repulsion U_d between the $3d$ electrons. They found that the energy of the Fermi level will be about 0.4 eV larger for $U_d = 4$ eV than for $U_d = 0$. However, the other U's were omitted.

Inversely, the ground-state electronic structure could be reconstructed from the XES excitation spectra if the corresponding correlation parameters are known from other experiments or from theory. With the $\Delta E_F^{\text{corr}} = 1.6$, 0.6, and 0.8 eV obtained above for structures 1, 2, and 3, respectively, one would have the results: Structure 1 at 2.7 eV $\xrightarrow{\Delta E_F^{\text{corr}}=1.6 \text{ eV}}$ 1.1 eV (ground state DOS of upper O $2p$ band); structure 2 at 3.7 eV $\xrightarrow{\Delta E_F^{\text{corr}}=0.6 \text{ eV}}$ 3.1 eV (Cu $3d$ band); structure 3 at 4.8 eV $\xrightarrow{\Delta E_F^{\text{corr}}=0.8 \text{ eV}}$ 4.0 eV (lower O $2p$ band). This example demonstrates only the general procedure and reproduces the mean positions of the DOS from which we started. The above discussion is related to the question of small or vanishing density of states as measured at $E_F = 0$ for most of the HTSC's by XPS or UPS. Considering the different "correlation shifts" as estimated from XES or the integral shift from the VB XPS and UPS we can roughly assume that the DOS as measured at $E_F^{\text{expt}}=0$ in the excitation spectra is *in fact the ground state DOS positioned above* E_F^{theor} according to Fig. 3. But, there the one-electron states are unoccupied. This would explain the numerous useless attempts to detect the density of states at E_F of HTSC's by excitation spectroscopy. One may expect a nonvanishing DOS at E_F, if (i) at least one DOS component at E_F has a finite value and (ii) the band exhibits no "correlation shift." These two conditions seem to be filled in the case of the Bi 6*p* band in $Bi_2Sr_2CaCu_2O_8$ (see, e.g., Figs. 10 and 11 in Ref. 27). We believe the observable edge at E_F^{expt} to be produced by uncorrelated electrons in the extended Bi 6*p* band.

On the other hand, a careful inspection of the He II spectrum of $Bi_2Sr_2CaCu_2O_8$ (Ref. 27) gives evidence for a second edgelike structure with the BE at about 1.2 eV which should be attributed to the DOS of the other correlated electrons (Cu 3*d* and O 2*p*) at E_F^{theor}.

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