Electronic structure studies of high-T_c superconductors by high-energy spectroscopies

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A review of our high-energy spectroscopy studies of the electronic structure of the new high-T_c superconductors is given. X-ray-induced photoelectron spectroscopy, bremsstrahlung–isochromat spectroscopy, Auger electron spectroscopy, and electron energy-loss spectroscopy have been used. Parameters determining the correlated electronic structure have been derived, together with information on the nature and the symmetry of the charge carriers.

1. Introduction

Despite the enormous efforts of the last two years aiming at a microscopic understanding of high-T_c superconductivity [1], the mechanisms involved are not clear. Even the nature of the charge carriers in the high-T_c superconductors is not fully understood. It is therefore a challenge to theorists and experimentalists to obtain more information on the electronic structure of these materials. This work reviews our activities during the last few years directed toward understanding the nature of the electronic states in the neighborhood of the Fermi level (E_F). We have used high-energy spectroscopies such as electron energy-loss spectroscopy (EELS), X-ray-induced photoelectron spectroscopy (XPS), bremsstrahlung–isochromat spectroscopy (BIS), and Auger electron spectroscopy (AES).

A first step toward the understanding of the electronic structure is to examine a single-particle model. It is generally believed that in the high-T_c superconductors with $T_c > 30$ K, the most important part of the states at the Fermi level is formed by electrons in the two-dimensional CuO_2 planes. Starting from an ionic model, the development of the electronic structure in these layers is illustrated in **Figure 1(a)**. The atomic Cu $3d$ level is split due to the cubic crystal field into e_g and t_{2g} states. There is a further splitting due to an octahedral crystal field into $x^2 - y^2$, $3z^2 - r^2$, xy, and xz, yz states. For divalent Cu which has nine $3d$ electrons, the uppermost $x^2 - y^2$ level is half filled, while all other levels are completely filled. There is a strong hybridization of the Cu states, particularly the $x^2 - y^2$ states, with the O $2p$ states thus forming a half-filled two-dimensional Cu $3d_{x^2-y^2}$ – O $2p_{x,y}$ antibonding $dp\sigma$ band. The hybridization of the other $3d$ levels is smaller and is indicated in Figure 1(a) only by a broadening.

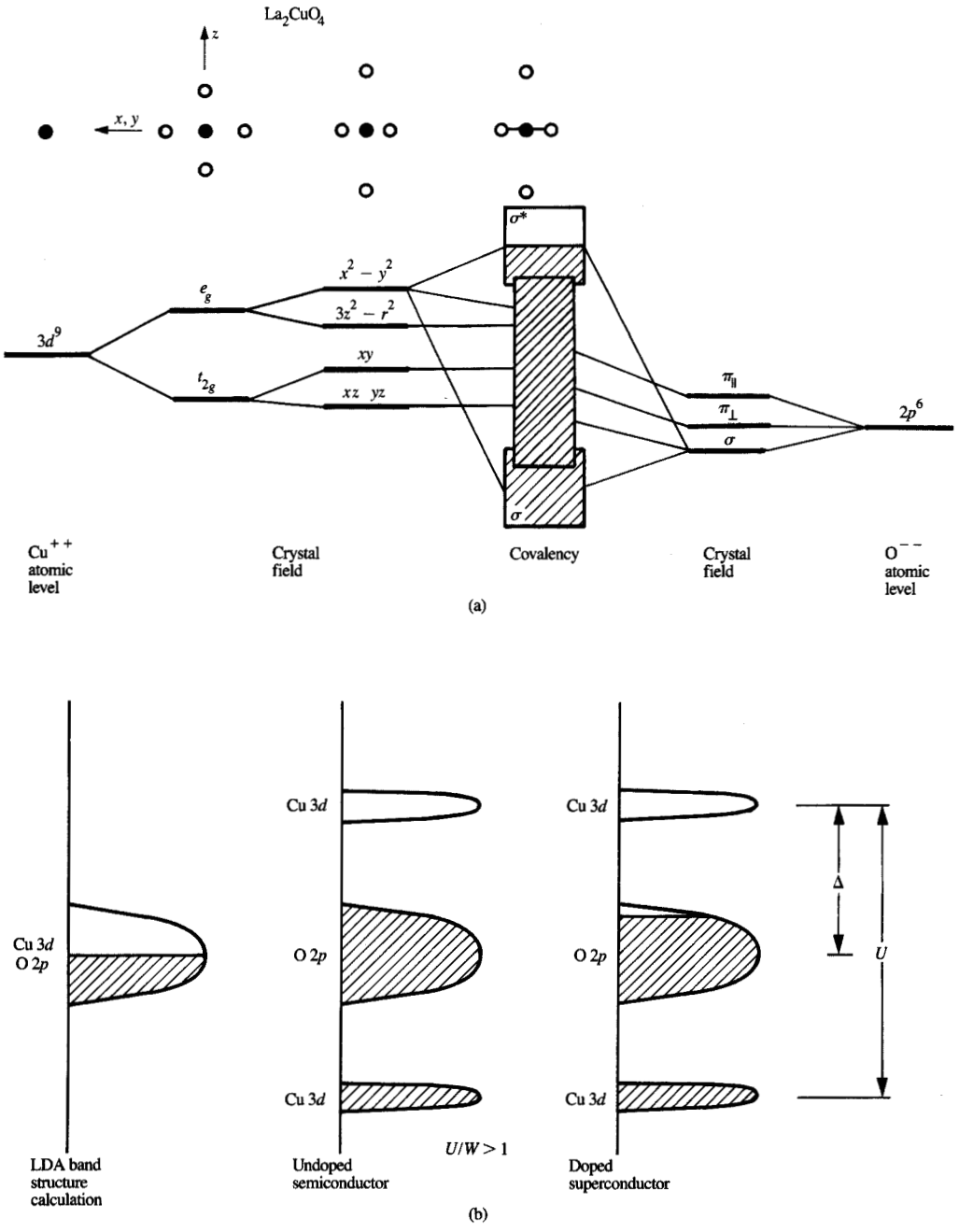

Figure 1

(a) The energy level diagram for a Cu $3d^9$ ion in spherical, cubic, and octahedral crystal field and hybridized with an O $2p$ level. A half-filled Cu $3d_{x^2-y^2}$ band is formed in this single-particle model for CuO_2 planes. (b) Left: Half-filled Cu $3d_{x^2-y^2}$ band (schematic) as derived from LDA band structure calculations. Middle: The same, with $3d$–$3d$ Coulomb energy on Cu sites taken into account; a charge-transfer semiconductor is formed for $U > \Delta$. Right: Upon doping, holes are formed with dominantly O $2p$ character.

A similar picture for the electronic structure was obtained from band structure calculations [2] using the local density approximation (LDA), where the interaction between the electrons is taken into account in an average way. The problem that shows up is that all these single-particle calculations predict compounds such as La_2CuO_4 and

$YBa_2Cu_3O_6$ to be metallic, whereas they are antiferromagnetic semiconductors. It has been well known for many years that the on-site Coulomb interaction (U) of the $3d$ electrons is important in the transition-metal compounds. However, the gap in the high-T_c superconductors is not a true Mott–Hubbard gap. As in other late $3d$ transition-metal oxides, chalcogenides, and halides, the gap is a charge-transfer gap. This means that there are two charge fluctuations. First, there is the charge fluctuation of a $3d$ electron from one Cu atom to the neighboring one involving the on-site Coulomb energy U. Then there is the charge transfer from an O atom to a Cu atom involving the energy Δ. The transformation of the half-filled band derived from band structure calculations to a semiconductor is illustrated (for $\Delta < U$) in **Figure 1(b)**. We also recognize that a conventional Mott–Hubbard picture develops for $\Delta > U$. For the late transition-metal compounds and the high-T_c superconductors, Δ is smaller than U, as shown in Figure 1(b); therefore, the band gap is of a charge-transfer type and the first ionization states are O $2p$ states. Therefore, upon p-type doping, holes are created which should have dominantly O $2p$ character. The Coulomb repulsion between $3d$ electrons strongly suppresses the formation of a second hole on Cu. In the following we describe experiments which may help to determine whether this model is applicable to the electronic structure of the high-T_c superconductors. It is interesting to note that this model was worked out [3] for transition-metal compounds before the discovery of the high-T_c superconductors.

2. Experiment

Most high-energy spectroscopies probe only the first few atomic layers of a surface. For instance, the sampling depth for ultraviolet photoelectron spectroscopy (UPS), XPS, AES, and X-ray absorption spectroscopy in the partial-yield mode (XAS, E = 500–1000 eV) is 5–10 Å, ~20 Å, ~50 Å, ~20 Å, and ~100 Å, respectively. Therefore, all of these methods are highly sensitive to surface contamination.

For high-energy EELS in transmission, films having a thickness of 1000 to 2000 Å are used. Thus, these measurements are not surface-sensitive, but the problem of the preparation of such films arises. XAS for core levels in the keV region can be performed in transmission on samples with a thickness of several μm. The samples used for our XPS, AES, and BIS measurements were bulk ceramic materials with densities between 80 and 95%. They were scraped in ultra-high vacuum (UHV) to get clean surfaces. For EELS, free-standing films about 1000 Å thick were cut from ceramic or single-crystalline bulk samples by an ultramicrotome using a diamond knife. In addition, almost-single-crystalline films of $YBa_2Cu_3O_7$ were epitaxially grown by sputtering on freshly cleaved CaO single crystals. The films were removed from the substrate and mounted on standard electron microscope grids. Thin films of $Bi_2Sr_2CaCu_2O_8$ were obtained by peeling them from single crystals with adhesive tape.

The XPS/BIS spectrometer used in our work is an UHV instrument with a large solid-angle X-ray monochromator. The transmission EELS measurements were performed with a 170-keV spectrometer described elsewhere [4]. The energy and the momentum resolution were chosen in most cases to be 0.4 eV and 0.2 $Å^{-1}$, respectively.

3. Results

• *XPS and BIS on valence and conduction electrons*

In **Figure 2** we show our XPS spectrum on the valence bands and the BIS spectrum on the conduction bands of undoped La_2CuO_4. For comparison we show LDA calculations of XPS and BIS spectra which are a density-of-states curve weighted not only by the atomic cross section but also by matrix elements, which include the influence of the solid state. The BIS spectrum is dominated by the $5d$ states and the $4f$ states (not included in the calculations) of La at 4 and 9 eV above E_F, respectively. The XPS spectrum is dominated by Cu states, since the cross section for Cu $3d$ electrons is about five times higher than that for O $2p$ electrons.

The XPS spectrum indicates a low density of states for Cu $3d$ electrons near E_F. The maximum of the XPS spectrum is shifted by ~2 eV to a lower energy than that shown by the calculations. It was first pointed out by Fujimori et al. [5] that this shift is caused by correlation effects. As shown in Figure 1(b), the Cu $3d$ states appear in the correlated model at lower energy than in the LDA calculations. From the shift, a $3d$ correlation energy U of at least several eV could be derived [6].

In a more refined model [7] the different correlation energies of the $3d$ sublevels should be taken into account, as in recent calculations on the magnetism of $3d$ metals by Oleś and Stollhoff [8]. These authors found that correlations tend to increase the anisotropy in the charge distribution if there is already a considerable anisotropy present in the charge distribution of the uncorrelated system, e.g., in a system with a low d-hole count. Energy is gained by an increase of the phase space for interorbital charge fluctuations if the system is made more anisotropic. A considerable amount of admixture of $3d_{3z^2-r^2}$ holes with the $3d_{x^2-y^2}$ holes is expected. To increase anisotropy, the non-$3d_{x^2-y^2}$ density of states above E_F should be reduced. Thus, mainly the non-$3d_{x^2-y^2}$ states are shifted to lower energy by correlation effects, and these states form the high density of states observed in the XPS spectrum. Of course, the $3d_{x^2-y^2}$ states should also be shifted slightly due to correlation effects.

It is interesting to note that almost no changes of the XPS spectra for La_2CuO_4 were observed [9] upon doping. The reason for this is immediately obvious upon examination of the model for the high-T_c superconductors shown in Figure

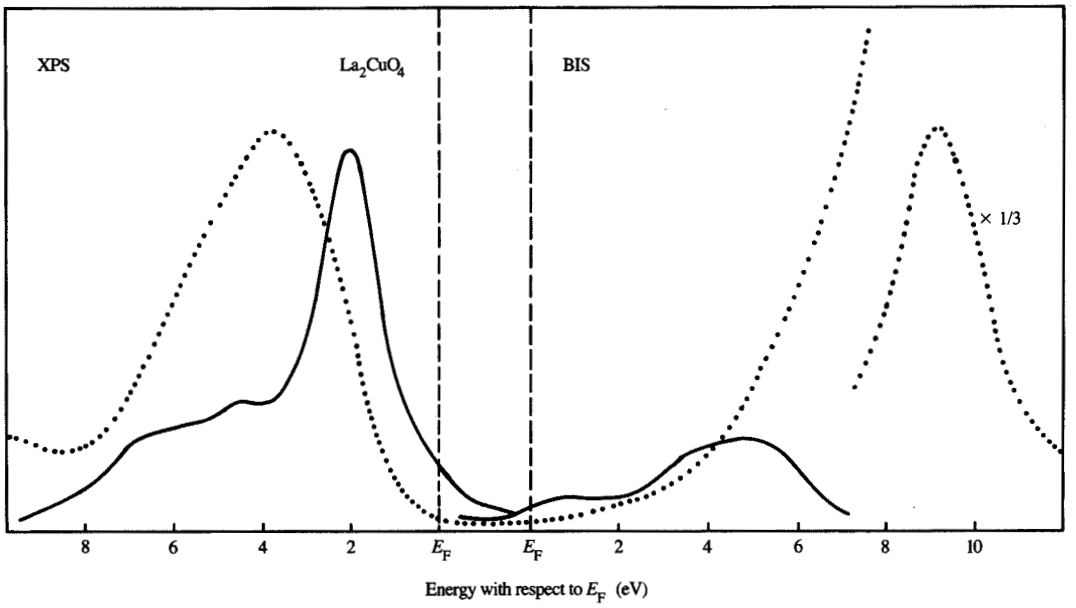

Figure 2

XPS and BIS spectra of undoped La_2CuO_4. Solid line: spectra calculated in the local density approximation. Figure taken from [6].

1(b). Upon doping, holes are formed predominantly on O, and in a first approximation there are no changes on the Cu states. Since the states we probe with XPS are Cu $3d$ states predominantly, we should not observe strong changes upon doping.

• *Cu 2p core-level spectra*

In **Figure 3** we show XPS Cu $2p_{3/2}$ core-level spectra for $La_{1.85}Sr_{0.15}CuO_4$, La_2CuO_4, $YBa_2Cu_3O_7$, and $YBa_2Cu_3O_6$. For comparison, spectra for CuO, CuO_2, and Cu metal are shown as well. For Cu metal and the monovalent Cu_2O, only a main line at 932 eV is seen, corresponding to a Cu $2p^5 3d^{10}$ final-state configuration. For the divalent Cu compounds, the main peak at ~933 eV corresponds to a Cu $2p^5 3d^{10}$ O $2p^5$ state, i.e., a configuration where the Cu core hole is shielded by a charge transfer from an O atom. This supports the picture given in Figure 1(b) in which charge-transfer excitations are possible for small Δ. Besides the main line, there is a satellite at ~943 eV corresponding to a Cu $2p^5 3d^9$ state. The interaction of the $2p$ core hole with the hole in the $3d$ shell leads to a multiplet splitting which is clearly indicated by the trapezoidal form of the satellite line. The shift to higher energy by about 9 eV is caused by the Coulomb repulsion of the two holes. According to an estimate by van der Laan et al. [10], the ratio of the $3d$–$3d$ Coulomb interaction to that of the $2p$–$3d$ holes is about 0.7. From this an on-site Coulomb energy $U = 7$ eV can be derived. The ratio of the area of the satellite to that of the main line in the Cu $2p_{3/2}$ XPS spectra is related to charge fluctuations between O and Cu atoms. For the high-T_c superconductors, this value is similar to that found for CuO (see Figure 3). An analysis [10] for CuO and $CuCl_2$ gave a $3d$ count of 9.4 for the ground state. Thus, a similar value of about 9.4 seems at present to be the most likely value for the high-T_c superconductors.

There have been many discussions on trivalent Cu ions in the high-T_c superconductors. $YBa_2Cu_3O_7$ should have formally 30% trivalent Cu ions. Cu^{+++} ($3d^8$) may give the following final states in the Cu $2p$ XPS spectra: Cu $2p^5 3d^8$, Cu $2p^5 3d^9$ O $2p^5$, and Cu $2p^5 3d^{10}$ (O $2p^5$)^2. The latter may contribute to the main line; indeed, the main line for $YBa_2Cu_3O_7$ is broadened and shows a shoulder at higher binding energies if it is compared with that of $YBa_2Cu_3O_6$. The differences are less pronounced in the La_2CuO_4 system. The changes of the main line as a function of O concentration have been studied in detail by Steiner et al. [11] and Gourieux et al. [12]. From the changes of the spectral weight at the high-binding-energy side of the main line, one cannot conclude that there exists a Cu $3d^8$ configuration in the ground state. According to our model for the electronic structure shown in Figure 1(b), holes created upon doping should have dominantly O $2p$ character

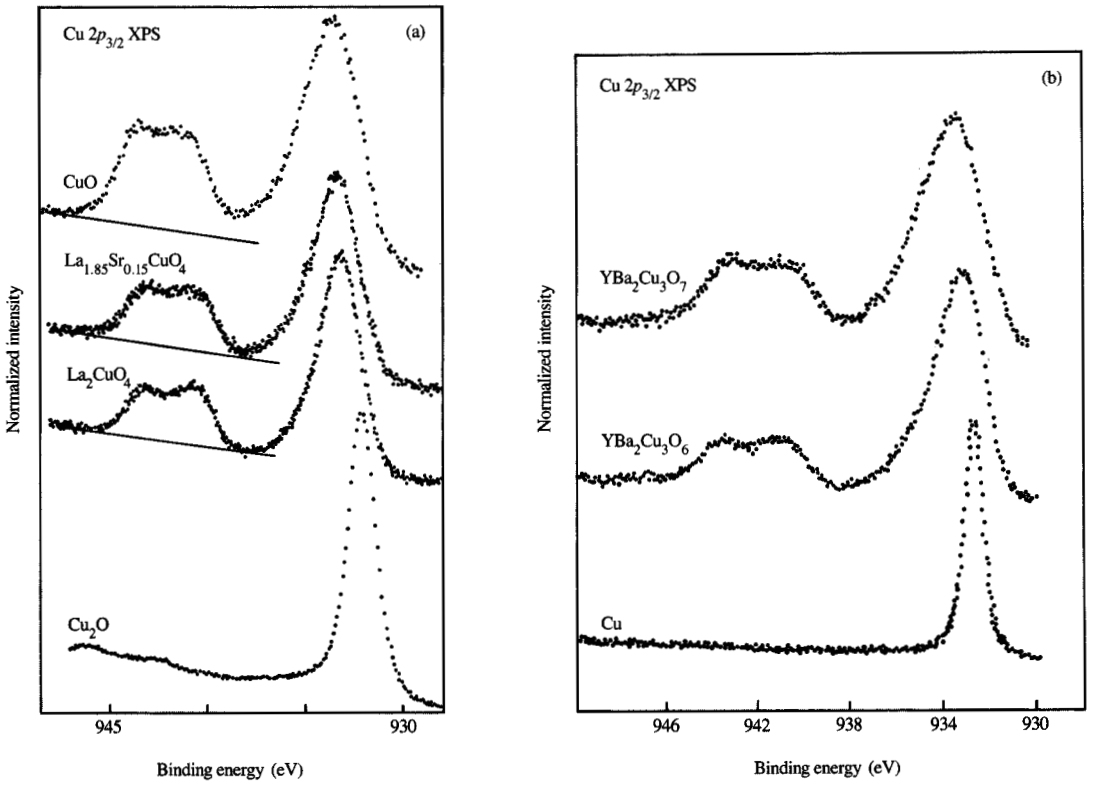

Figure 3

Cu $2p_{3/2}$ XPS spectra. (a) For CuO, $La_{1.85}Sr_{0.15}CuO_4$, La_2CuO_4, and Cu_2O. (b) For $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$, and Cu metal. Figure 3(a) is taken from [9].

and, therefore, the ground-state configuration for formally trivalent Cu should be Cu $3d^9$ O $2p^5$, leading to a final state for the main line in the XPS spectrum of Cu $2p^5 3d^{10}$ (O $2p^5$)^2. To our knowledge, no XPS satellites due to Cu $2p^5 3d^8$ final states, which would be at very high binding energy with respect to the main line, have been reported.

• *Cu L_3VV Auger spectra*

In **Figure 4** we show the Cu L_3VV Auger spectra for Cu metal, Cu_2O, CuO, $YBa_2Cu_3O_7$, and La_2CuO_4. A core hole is created in the $2p_{3/2}$ state which is filled by a transition from the valence band, and the energy of this transition is used to emit a valence electron. Thus, two holes in the valence band are created at the same site, and the kinetic energy (E_{kin}) of the emerging electron must be related to the Coulomb interaction between two valence electrons. In fact, the energy of the Cu L_3VV peak is given by

$$E_{kin} = E_B(2p_{3/2}) - 2E_B(3d) - U^A(3d),$$

where $E_B(2p_{3/2})$ and $E_B(3d)$ are the binding energies for the Cu $2p_{3/2}$ core electrons and the Cu $3d$ valence electrons, respectively. Theoretical treatments by Cini [13] and Sawatzky [14] indicate that U^A approaches the effective Coulomb interaction U asymptotically in the limit of large U. Thus, an estimate of U can be derived from the peak in the L_3VV Auger spectra because $E_B(2p_{3/2})$ and $E_B(3d)$ can be derived from XPS spectra.

For the divalent compounds such as CuO or La_2CuO_4, the final Auger configuration is close to Cu $3d^8$ O $2p^5$ because there is a charge transfer from the O sites to screen the core hole created in the first step of the Auger process. The $3d^8$ configuration has well-defined terms whose energies differ by many eV. The main peak in the Auger spectrum comes from the ^1G term, but the other terms can also be realized in the spectra. Evaluation of the peak position in the Auger spectra estimated U at not less than 4–5 eV [6]. Further detailed calculations on the multiplet structure of these spectra are necessary to obtain accurate values for the Coulomb interaction of the $3d$ electrons in the high-T_c superconductors.

• *EELS O 1s absorption edges*

In **Figure 5** we show the EELS O 1*s* absorption edges for ceramic polycrystalline samples of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$. These are absorption edges which appear due to transitions from the O 1*s* core level (K shell) into the unoccupied states above the Fermi level. The edges appear at about 528 eV because the binding energy of the O 1*s* electrons, as determined by XPS, is close to this energy. For small momentum transfer in the transition, dipole selection rules ($\Delta l = \pm 1$) apply and O 2*p* states are reached. Since the transition starts from a very localized core level on the O sites, only unoccupied states at the O sites are reached; i.e., the *local* density of unoccupied states is probed. We emphasize that, by using this technique, site-selective information on the electronic structure can be obtained. Similar information can be obtained for the Cu sites, starting from the Cu 2*p* states, where the absorption edge appears near 931 eV.

In the undoped semiconducting antiferromagnetic compounds there is no intensity at the Fermi level (corresponding to the binding energy of the O 1*s* level). This indicates a gap of the order of several eV in agreement with optical data and low-energy EELS data. The steep rise of spectral weight about 3 eV above E_F is due to La 5*d* and 4*f* or Ba 5*d* and 4*f* and Y 4*d* states hybridized with O *p* states. Upon doping ($x > 0$, $y < 0.8$) there appears considerable spectral weight near E_F which has been ascribed to transitions from the O 1*s* level into holes on O sites. Thus, the density of states of the holes, which has according to Figure 1(b) dominantly O 2*p* character, can be directly probed. At present, these measurements give the most direct evidence of the existence of holes on O sites. We have also shown [9, 15] that the number of holes on O sites is roughly proportional to the dopant concentration. In this respect it is also noteworthy that Hall measurements on ceramic superconductors above T_c indicate that the charge carriers are holes [16, 17].

We have also recently measured [18–20] orientation-dependent O 1*s* absorption edges on single crystals. Those spectra are shown in **Figure 6** for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. The direction of the momentum transfer *q* could be changed to be parallel or perpendicular, respectively, to the CuO_2 planes. Thus, information on the symmetry of the holes on O sites could be obtained. For $Bi_2Sr_2CaCu_2O_8$, no O $2p_z$ states are observed near threshold, indicating that there are no holes on O orbitals perpendicular to the CuO_2 and BiO planes. This clearly rules out all models for high-T_c superconductivity based on out-of-plane π holes in the CuO_2 planes [21] or holes in the p_z orbitals of the apex oxygens. Our measurements, however, cannot differentiate between O σ holes (along the Cu–O bond) and in-plane π holes (perpendicular to the Cu–O bond). At energies 2 eV above threshold, a strong rise in intensity is observed due to Bi 6*p* states hybridized with O *p* states.

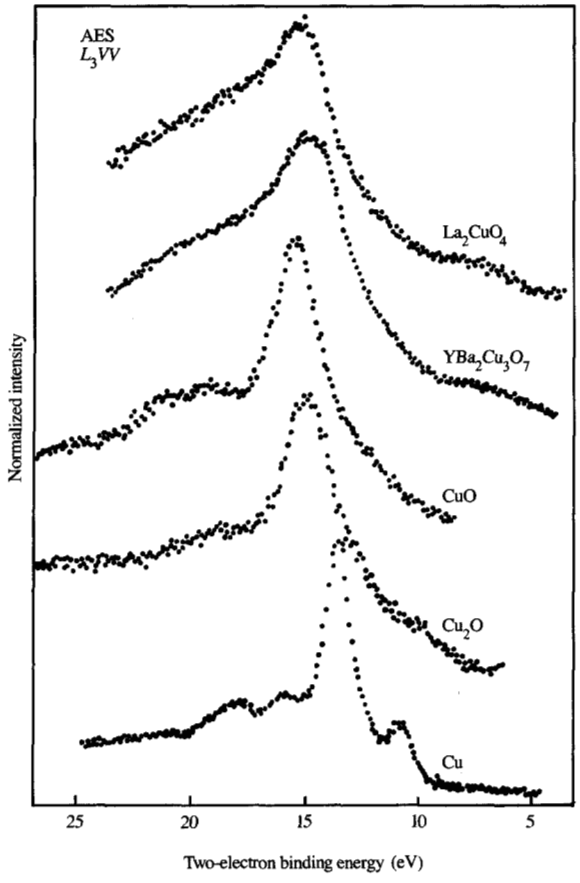

Figure 4

Cu L_3VV Auger spectra of Cu metal, Cu_2O, CuO, $YBa_2Cu_3O_7$, and La_2CuO_4. Figure taken from [6].

In $YBa_2Cu_3O_7$, holes with O $2p_{x,y}$ *and* $2p_z$ symmetry are observed. The threshold energy is slightly lower for $q \parallel c$ than for $q \parallel a, b$. This may result from different O 1*s* binding energies for the four different O sites, or from a different energy position of the final state relative to E_F. When we compare the results shown in Figure 6(a) with measurements on $YBa_2Cu_3O_6$ (not shown), the intensity ratio ($I_{x,y}/I_z$) for the hole states ($E \lesssim 531$ eV) reached for $q \parallel a, b$ and for $q \parallel c$ is about 2. In **Figure 7** we have illustrated the three different types of symmetry for holes on O sites. The σ holes are obtained in a more delocalized picture, e.g., LDA band structure calculations, where on-site Coulomb interaction is small. For a highly correlated system, the hopping in the $dp\sigma$ band is strongly reduced and the $2p\sigma$ states have the highest, the out-of-plane π states have intermediate, and the in-plane π states have the lowest binding energy. Then holes will form

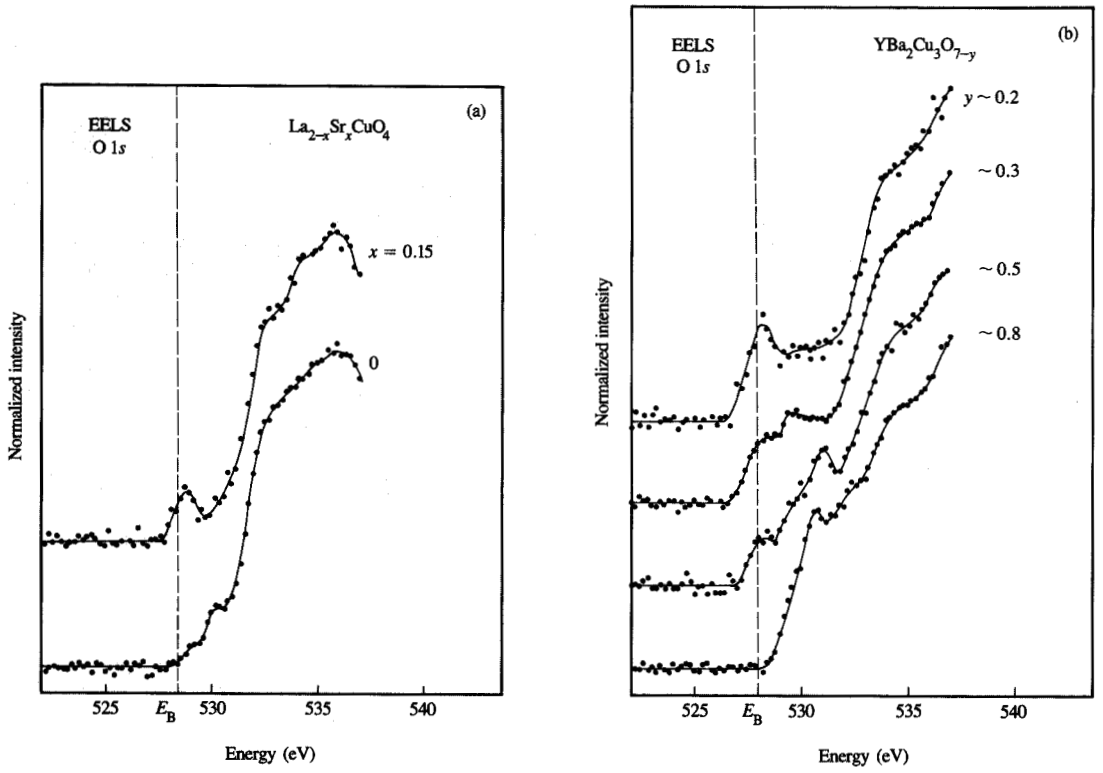

Figure 5

O 1*s* absorption edges for ceramic samples measured by electron energy-loss spectroscopy. (a) La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$. (b) $YBa_2Cu_3O_{7-y}$. Figure taken from [15].

on the latter orbitals [22, 23]. The magnetic frustration model [24] for the magnetic phase diagram and for superconductivity is also based on in-plane π holes.

Let us assume σ holes and an equal distribution of holes among the four different O sites [O(2) and O(3) in the planes, O(4) in the ribbons on the *c* axis, and O(1) in the ribbon on the *b* axis]. Then only the two O(4) atoms contribute to the $q \parallel c$ spectrum, and the two O(2) and O(3) atoms and the O(1) atom contribute to the $q \parallel a, b$ spectrum. The ratio $I_{x,y}/I_z$ should be 1.25. By calculating this ratio with the help of LDA calculations and including matrix elements [15], the ratio $I_{x,y}/I_z$ is increased to 2.1, in excellent agreement with the experimental results. According to these calculations, 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. It is interesting to note that the LDA band structure calculations predict for the absorption edges for the four different O sites almost the same trapezoidal form, with a width of about 2 eV. Indeed, this trapezoidal form is observed for $q \parallel c$. 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. Then the width of the $dp\sigma$ band may be considerably reduced. 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 1*s* level for the O(1) and O(2, 3) atoms. Unfortunately, the present O 1*s* XPS spectra show only a 1.5-eV-wide line at 528.5 eV, and the individual O sites could not be resolved. It is interesting to note that in a recent work on $YBa_2Cu_3O_7$ single crystals [25], a line-shape asymmetry of the O 1*s* XPS line was analyzed in terms of two different binding energies for O sites in the ribbons (lower binding energy) and the planes (higher binding energy), in agreement with the interpretation of our O 1*s* edges assuming σ holes.

Assuming in-plane π holes, only the O(1) sites would contribute to the $q \parallel c$ spectrum, while the other sites would contribute to the $q \parallel a, b$ spectrum. With an equal distribution of holes among the four O sites, the ratio $I_{x,y}/I_z$

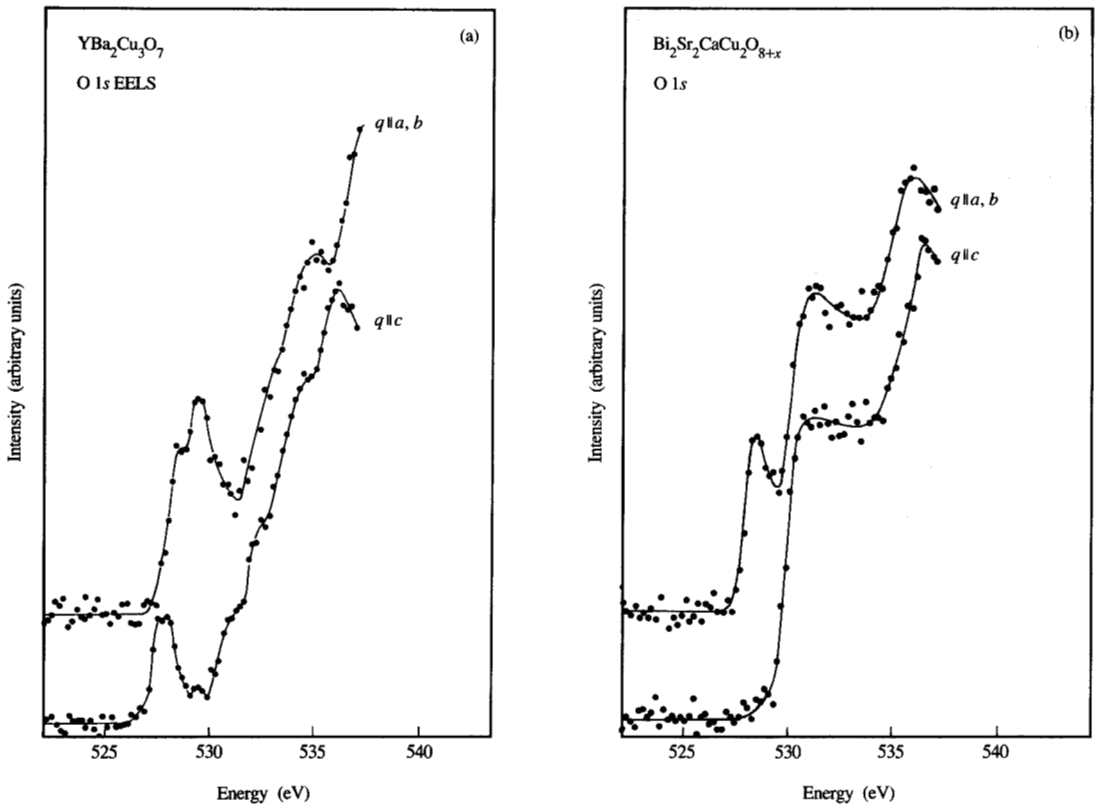

Figure 6

EELS O 1*s* absorption edges for high-T_c superconductors for momentum transfer parallel ($q \| a, b$) and perpendicular ($q \| c$) to the CuO_2 planes. (a) $YBa_2Cu_3O_7$, (b) $Bi_2Sr_2CaCu_2O_8$. Figures taken from [20].

should be three. 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.

Finally, for holes with only out-of-plane symmetry, O(2) and O(3) sites would contribute to the $q \| c$ spectrum, and O(2) and O(4) sites would contribute to the $q \| a, b$ spectrum. Assuming again an equal distribution of the holes among the four O sites, the intensity ratio $I_{x,y}/I_z$ should be 3/8, which is very far from the experimental ratio of 2. To obtain agreement with the experimental value, almost no holes should be in the planes and almost all the holes should be in the ribbons, which is very unlikely. Therefore, we exclude, as in $Bi_2Sr_2CaCu_2O_8$, 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. Many experimental facts favor holes with σ symmetry. On the other hand, we cannot exclude holes with in-plane π symmetry. A calculation of the hole distribution among the four O sites could help to decide whether or not the model with in-plane π holes is realistic. In addition, determination of the binding energies of the four different O sites may be crucial for the interpretation of the absorption edges and thus for the final decision between σ and in-plane π holes.

4. Concluding remarks

High-energy spectroscopy has significantly contributed to the understanding of the electronic structure of the high-T_c superconductors. Nevertheless, it is at present not clear whether these materials are very localized systems or whether the truth lies somewhere between the localized and more delocalized picture worked out by the LDA band structure calculations. The values of the parameters (U, Δ) determined by these measurements show a considerable

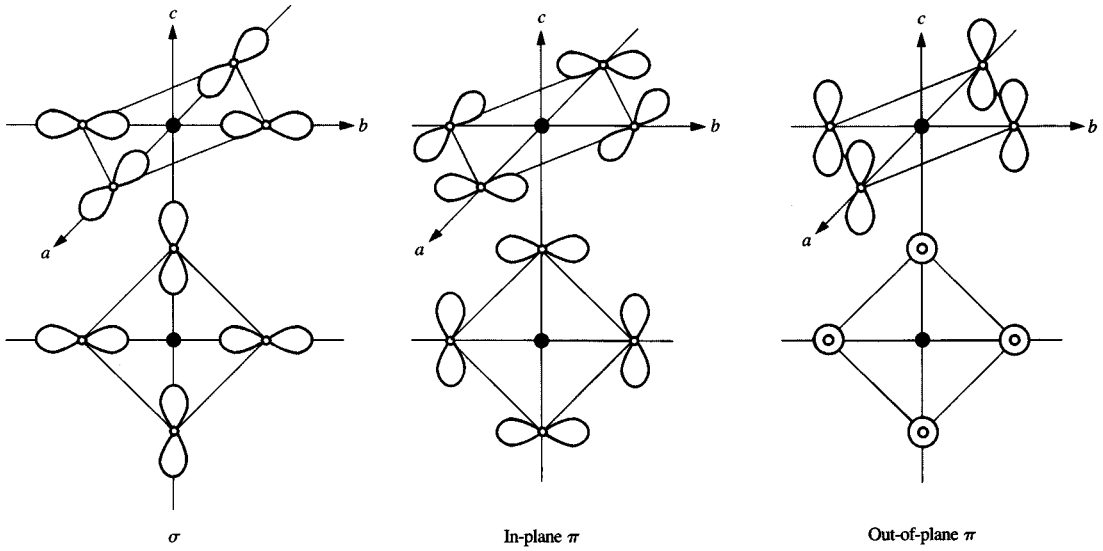

Figure 7

Different symmetries for holes in O for $YBa_2Cu_3O_7$: σ holes along the Cu–O bond, in-plane π holes and out-of-plane π holes perpendicular to the Cu–O bond. For each type of hole, a square of the CuO_2 planes and a square of the CuO_3 ribbons are shown. Closed circles: Cu atoms; open circles: O atoms.

scattering and must be considered at present as estimated values. Furthermore, there exist various important questions which are still open. Are there really no Cu $3d$ holes ($3d^8$) in these systems, or is the correlation energy U not sufficiently high to allow a *small* mixing of the Cu $3d^8$ configuration into the ground state? Is the symmetry of the holes on O σ-like or in-plane π-like? How big are the correlation effects on the oxygen sites? What is the effective mass of the holes on O?

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References

1. J. G. Bednorz and K. A. Müller, "Possible High-T_c Superconductivity in the Ba-La-Cu-O System," *Z. Phys. B* **64,** 189 (1986).
2. L. F. Mattheiss, "Electronic Band Properties and Superconductivity in $La_{2-y}X_yCuO_4$," *Phys. Rev. Lett.* **58,** 1028 (1987).
3. J. Zaanen, G. A. Sawatzky, and J. W. Allen, "Band Gaps and Electronic Structure of Transition-Metal Compounds," *Phys. Rev. Lett.* **55,** 418 (1985), and references therein.
4. J. Fink, "Recent Development in Energy-Loss Spectroscopy," *Adv. Electron. Electron Phys.* **75,** 121 (1989).
5. A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, "Spectroscopic Evidence for Strongly Correlated Electronic States in La-Sr-Cu and Y-Ba-Cu Oxides," *Phys. Rev. B* **35,** 8814 (1987).
6. J. C. Fuggle, P. J. W. Weijs, R. Schoorl, G. A. Sawatzky, J. Fink, N. Nücker, P. J. Durham, and W. M. Temmerman, "Valence Bands and Electron Correlation in the High-T_c Superconductors," *Phys. Rev. B* **37,** 123 (1988).
7. F. U. Hillebrecht, J. Fraxedas, L. Ley, H. J. Trodahl, J. Zaanen, W. Braun, M. Mast, P. Petersen, M. Schaible, L. C. Bourne, P. Pinsukanjana, and A. Zettl, "Experimental Electronic Structure of $Bi_2CaSr_2Cu_2O_{8+\delta}$," *Phys. Rev. B* **39,** 236 (1989).
8. A. M. Oleś and G. Stollhoff, "Correlation Effects in Ferromagnetism of Transition Metals," *Phys. Rev. B* **29,** 314 (1984).
9. N. Nücker, J. Fink, B. Renker, D. Ewert, C. Politis, P. J. W. Weijs, and J. C. Fuggle, "Experimental Electronic Structure Studies of $La_{2-x}Sr_xCuO_4$," *Z. Phys. B* **67,** 9 (1987).
10. G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, "Satellite Structure in Photoelectron and Auger Spectra of Copper Dihalides," *Phys. Rev. B* **23,** 4369 (1981).
11. P. Steiner, S. Hüfner, V. Kinsinger, I. Sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Müller, R. Hoppe, S. Kemmler-Sack, and C. Kunz, "The Hole Concentration on Oxygen Sites in the High-T_c Superconductor Y_1-Ba_2-Cu_3-O_{7-x}," *Z. Phys. B* **69,** 449 (1988).
12. T. Gourieux, G. Krill, M. Maurer, M. F. Ravet, A. Menny, H. Tolentino, and A. Fontaine, "Oxygen-Stoichiometry Dependence of the Electronic Structure of $YBa_2Cu_3O_{7-\delta}$ with $\delta(0 < \delta < 0.7)$: Possibility of a Highly Correlated Mixed-Valent State," *Phys. Rev. B* **37,** 7516 (1988).
13. M. Cini, "Density of States of Two Interacting Holes in a Solid," *Solid State Commun.* **20,** 605 (1976).

14. G. A. Sawatzky, "Quasiatomic Auger Spectra in Narrow-Band Metals," *Phys. Rev. Lett.* **39,** 504 (1977).
15. N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, "Evidence for Holes on Oxygen Sites in the High-T_c Superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$," *Phys. Rev. B* **37,** 5158 (1988).
16. M. F. Hundly, Z. Zettl, A. Stacy, and M. L. Cohen, "Transport Properties of Superconducting Oxide $La_{1.85}Sr_{0.15}CuO_4$," *Phys. Rev. B* **35,** 8800 (1987).
17. N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, "Hall Effect of $La_{2-x}Sr_xCuO_4$: Implications for the Electronic Structure in the Normal State," *Phys. Rev. B* **35,** 8807 (1987).
18. J. Fink, N. Nücker, H. Romberg, J. C. Fuggle, P. J. W. Weijs, R. Schoorl, P. J. Durham, W. M. Temmerman, and B. Gegenheimer, "Electronic Structure of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$," *Proceedings of the International Discussion Meeting on High-T_c Superconductors*, Schloss Mauterndorf, Austria, 1988.
19. N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, "Electronic Structure of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$," *Physica C* **153–155,** 119 (1988).
20. N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, "On the Symmetry of Holes in High-T_c Superconductors," submitted to *Phys. Rev. B.*
21. K. H. Johnson, M. E. McHenry, C. Counterman, A. Collins, M. M. Donovan, R. C. O'Handley, and G. Kalonji, "Molecular Orbital Basis for Superconductivity with Applications to High-T_c Materials," *Novel Superconductivity*, Stuart A. Wolf and Vladimir Z. Kresin, Eds., Plenum Publishing Co., New York, 1987, pp. 563–576; *Physica C* **153–155,** 1165 (1988).
22. Y. Guo, J.-M. Langlois, and W. A. Goddard III, "Electronic Structure and Valence-Bond Band Structure of Cuprate Superconducting Materials," *Science* **239,** 896 (1988).
23. F. Adrian, "Implications of Crystal-Field and Intra-Atomic Interactions for the Electronic Structure of High-T_c Superconductors," *Phys. Rev. B* **37,** 2326 (1988).
24. A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, "Magnetic Phase Diagram and Magnetic Pairing in Doped La_2CuO_4," *Phys. Rev. Lett.* **60,** 1330 (1988); R. J. Birgeneau, M. A. Kastner, and A. Aharony, "Magnetic Frustration Model for Superconductivity in Planar CuO_2 Systems," *Z. Phys. B* **71,** 57 (1988).
25. J. H. Weaver, H. M. Meyer III, T. J. Wagener, D. M. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, "Valence Bonds, Oxygen in Planes and Chains, and Surface Changes for Single Crystals of M_2CuO_4 and $MBa_2Cu_3O_x$ (M = Pr, Nd, Eu, Gd)," submitted to *Phys. Rev. B.*

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