

Valence bands and electron correlation in the high- T_c superconductors

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We consider the x-ray photoemission, inverse photoemission, and Cu L_{3VV} Auger spectra of the high- T_c superconductors. We conclude that the on-site correlation energies of the Cu $3d$ electrons are large and that the energy of the Cu d^8 configurations is clearly too high for d^8 configurations to play a significant role in the ground state.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ ($R=\text{Y}$ and all rare-earth elements except Ce, Pr, and Tb) are superconducting at high temperatures.¹ While at the present time there is little, if any, evidence here incompatible with the BCS mechanism² for superconductivity there is no consensus on precisely why the materials exceed the limit previously thought to be set by the McMillan³ equations. The $3d$ electrons in late transition-metal and Cu compounds are known to show strong correlation effects,⁴ in contrast to most high- T_c superconductors.⁵ Briefly, our knowledge of the $3d$ electrons indicates that the on-site correlation energies are large, i.e., the energy U of charge fluctuations, $2d^n \rightarrow d^{n+1} + d^{n-1}$, is comparable to, or larger than, the $3d$ bandwidth. As a consequence of this large correlation energy, band gaps may open up and the activation energy for intrinsic conduction may be dominated by the energy for hopping between d states on different atoms or the charge-transfer energy, Δ , for $d \rightarrow$ ligand or ligand-metal d hopping, or mixtures thereof if the mixing of metal d and ligand orbitals is large.^{4,6} As a consequence of the large U , much theoretical effort has been expended on a search for descriptions which satisfy the London criteria⁷ for the ground state of a superconductor but which take into account the strong correlation effects.⁸⁻¹¹ Our purpose in this paper is to give an account of experimental evidence from high-energy spectroscopies on the size of the effective Coulomb correlation of the Cu $3d$ electrons in the high- T_c superconductors. All the reported photoemission spectroscopy (PS) and bremsstrahlung isochromat spectroscopy (BIS) of the high- T_c materials¹²⁻¹⁶ indicate that La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, have a broad peak in the photoemission centered at about 4 eV which is 4–6 eV wide. All studies of these materials indicate low or nonexistent PS and BIS intensity at and near E_F . This is consistent with

that optical data indicating semiconductorlike behavior, and a gap of about 2 eV at E_F in La_2CuO_4 and perhaps less in $\text{YBa}_2\text{Cu}_3\text{O}_6$.¹⁷ The BIS spectra are dominated by the $4f$ states of La at ~ 9 eV and Ba at ~ 15 eV in these materials, but small peaks and shoulders are found at lower energy. For $(\text{LaSr})_2\text{CuO}_4$ the first shoulder is at ~ 2 eV. Our own data for LaCuO_4 are presented in Fig. 1 to illustrate some of these effects. At first sight the photoemission and inverse photoemission seem to reflect the published density-of-states data (see, e.g., Ref. 18) but on closer examination there are several problems. First, the resonance photoemission shows strong satellites due to transitions to Cu d^8 states at ~ 9 and 12 eV.¹⁶ Secondly, as noted by Fujimori, Takayama-Muromachi, Uchida, and Okai,¹³ the photoemission spectra at most energies should be dominated by the Cu $3d$ states and this should lead to peaking of the spectra at ~ 2 eV below E_F , instead of ~ 4 eV as found. Finally, the photoemission and inverse photoemission at E_F is always very weak.

In contrast to earlier comparisons of x-ray photoemission spectroscopy (XPS) and BIS data of high- T_c materials the calculated spectra in Fig. 1 is a density-of-states curve weighted not only by the atomic cross sections,¹³ but also by matrix elements which include the influence of the solid state¹⁹ because the same potentials are used for the band structure and the matrix elements ($4f$ states are not computed). The calculated XPS peak is much too narrow and far too close to E_F . The oxygen and rare-earth states which dominate the total density of states (DOS) more than ~ 3 eV below E_F contribute only weakly to the spectra. Further the calculation produces intensity at E_F in both XPS and BIS which would certainly have been detected if the calculation had included all the relevant physics.

The principle effect causing the difference between

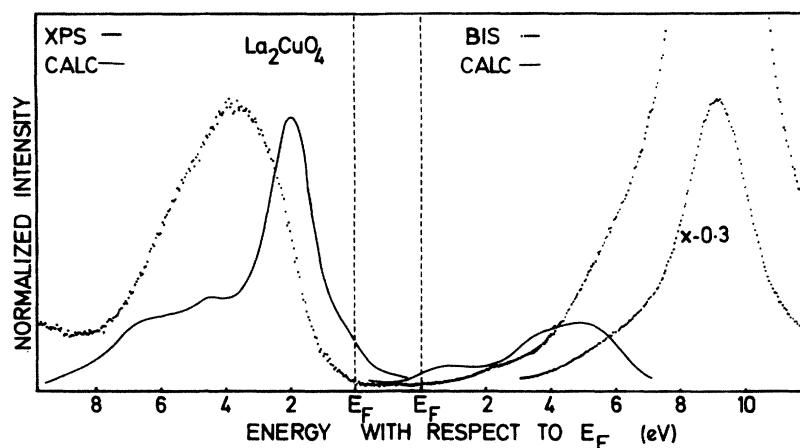


FIG. 1. Experimental and calculated XPS and BIS spectra at 1486.7 eV for La_2CuO_4 .

theory and experiment is use of the independent-particle approximation and the electron-electron correlation energy for the $3d$ states, just as found in transition-metal compounds.^{4,6} The discrepancies illustrated in Fig. 1 are similar to those we find for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ and together with the optical data indicate a $3d$ - $3d$ correlation energy $U_{\text{eff}}(d-d)$ of at least several eV.

Having found these effects of U in comparisons of XPS and BIS data with independent particle theory we turn to Auger spectroscopy and resonant photoemission satellites, because for other systems these have given a quantitative measure of U using the Cini-Sawatzky methodology.²⁰ To understand the spectroscopic data it is desirable to first consider a simple model for the neutral, singly and doubly ionized divalent Cu systems,²¹ such as CuCl_2 , CuO , La_2CuO_4 , or $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. This is a cluster model which is a reasonable zeroth-order approximation for systems in which U is expected to be large and bandwidths, both Cu d and O sp are either neglected, or considered as unimpor-

tant. The basic physics of this model is retained for finite bandwidths, as long as U is larger than the band dispersions.⁴ Neutral copper atoms have the configuration $3d^{10}4s^1$ and oxygen is $2(sp)^6$. Consider first a neutral CuO molecule where the important basis states are Cu $3d^9 4s^0$ O $2(sp)^8$ and Cu $3d^{10} 4s^0$ O $2(sp)^7$. The energy separation of these two states, $3d^9$ and $3d^{10}\underline{L}$, is the ligand-metal transfer energy, Δ (see Fig. 2). As indicated in Fig. 2 the two neutral states mix and "bonding-antibonding" states ensue. Estimates of the relative weights of the d^9 and d^{10} wave functions in the ground state from core-level spectra²¹ exist for chemically divalent Cu compounds and comparison with published XPS and Cu L_3 x-ray absorption spectroscopy spectra for $(\text{LaSr})_2\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (Refs. 12 and 13) suggests the $3d$ count is roughly about 9.3 ± 0.2 per atom for the latter; the precise value is not important here. In the solid the $3d^{10}\underline{L}$ form a band whose width is that of the O $2p$ band.

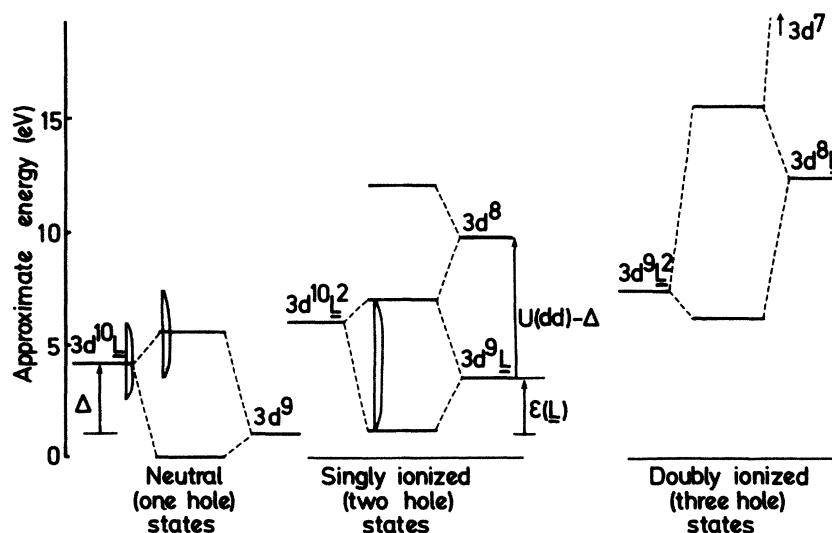
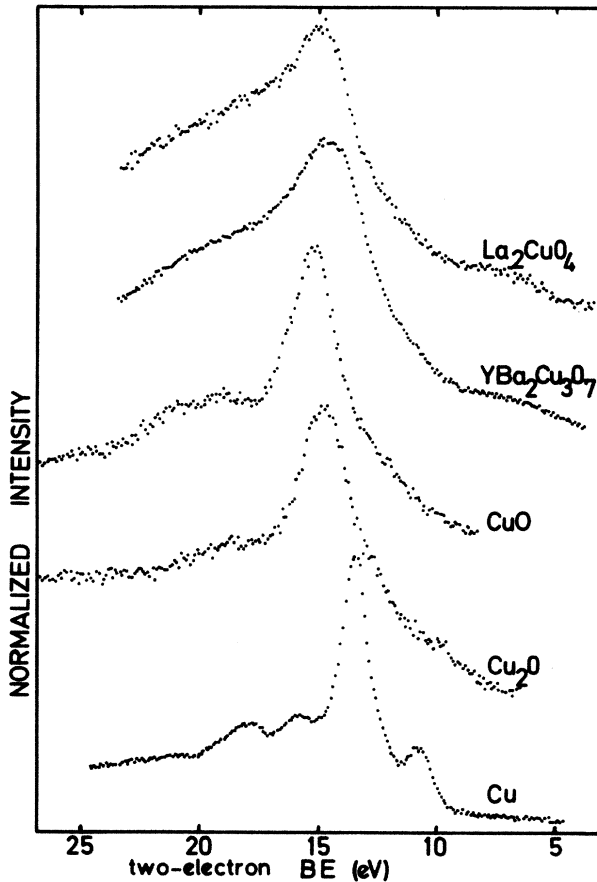


FIG. 2. Schematic energy-level diagram for divalent Cu compounds. The bandwidths are indicated only schematically and only for some configurations.

FIG. 3. Cu L_3VV Auger spectra of Cu compounds.

Photoemission of a single electron from these systems leads us to consider the singly ionized (2-hole) basis states $3d^{10}\underline{L}^2$, $3d^9\underline{L}$, and $3d^8$. The separation of the $3d^{10}\underline{L}^2$ and $3d^9\underline{L}$ states will be similar to that in the neutral state and they will mix, and again in the solid should be broadened into bands. The position of the $3d^8$ states is determined mainly by U , which for Ni and Cu oxides is of the order of 6 eV.^{6,21,22}

In Auger spectroscopy the final states are doubly ionized, i.e., they are three-hole states for these systems. The relevant basis states are $3d^9\underline{L}^2$, $3d^8\underline{L}$, and $3d^7$. The latter is at an energy $\sim 3U - \Delta$ above the ground state, which is so high as not to concern us, and $d^{10}\underline{L}^3$ does not directly couple with $d^8\underline{L}$ via a one-electron hopping matrix element. The $3d^9\underline{L}^2$ state is expected $\sim E(\underline{L})$ above the $3d^9\underline{L}$ state and the $3d^8\underline{L}$ state is $\sim E(\underline{L})$ above the $3d^8$ states, as shown in Fig. 2. The mixing between the $d^8\underline{L}$ and $d^9\underline{L}^2$ states is large because the transfer integral is large (~ 1.85 eV, see Ref. 18). The holes in the ligand bands may lead to some width of spectral features associated with these states.

Note that the precise energies of the basis states indicated in Fig. 2 are not physical observables. The states formed by mixing are observables and their energies can be determined by photoemission or Auger spectroscopy if the models are appropriate. The models have been shown to be applicable for a number of Ni and Cu compounds

TABLE I. Energies of Cu d^8 , $d^8\underline{L}$, and $d^9\underline{L}^2$ states.

Material	$E(d^8)$ (resonant PS)	$E(d^8\underline{L})$ (Auger)	$E(d^9\underline{L}^2)$
Cu	14.6	13.9	
Cu ₂ O	15.3	14.8	
CuO	12.9	15.2	~ 6.7
La ₂ CuO ₄	~ 12 (Ref. 16)	14.8	~ 7.7
La _{1.8} Sr _{0.2} CuO ₄		14.8	
YBa ₂ Cu ₃ O ₇	~ 12 (Ref. 16)	14.6	~ 6.8

(see, e.g., Refs. 4, 5, and 20–23). The energies of the one-hole states are normally referred to as the binding energies (E_b) in photoemission (i.e., $E_b = h\nu - E_K$, where E_K is the electron kinetic energy). The energies of the two-hole final states of the Cu L_3VV process are given by

$$E(2\text{-hole}) = E(\underline{L}_3) - E_K,$$

where $E(\underline{L}_3)$ is the L_3 binding energy derived from XPS. The intensities in the various spectra features are beyond the scope of this publication²¹ but the energy of the main “ $3d^8$ ” state is found in resonance photoemission to be at ~ 12 eV in Y₁Ba₂Cu₃O_{7- γ} and (LaSr)₂CuO₄ (Refs. 15 and 16).

The $3d^8\underline{L}$ states dominate the L_3VV Auger spectra of Cu compounds illustrated in Fig. 3 and Table I. For the oxides the Auger peaks are broader than for Cu metal, probably as a result of the continuum of holes in the L band and crystal-field effects. However, they are still much narrower than peaks due to d^7 final states which have a much broader envelope due to multiplet splittings.^{24,25} The energies of the $d^8\underline{L}$ final states from Auger and the main d^8 -like states from resonant photoemission are tabulated in Table I. In contrast to Cu metal, the Auger-derived “ $d^8\underline{L}$ ” energies for Cu oxides are ~ 3 eV higher than the resonant photoemission satellite energies because of the energy associated with L . Both resonant PS and Auger spectra of the superconducting oxides show the d^8 configurations to lay far too high to play a significant role in the ground state. This is also true for chemically trivalent Cu in NaCuO₂. This is in agreement with XPS data for these materials¹⁴ and clearly shows that the presence of chemically trivalent Cu does not indicate the presence of Cu³⁺, $3d^8$ ions. Determination of the precise values of U and Δ from spectroscopic data is not possible without detailed calculations²⁶ but it is clear from the Auger data that $U > \Delta$ and not less than 4–5 eV for the Cu $3d$ states. Analysis of the oxygen levels with similar methods is more complicated because the transfer integrals involved are larger. We suspect that the states near E_F in (LaSr)₂CuO₄ and Y₁Ba₂Cu₃O_{7- γ} have a strong oxygen character.

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- ¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986); C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58**, 405 (1987).
- ²J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957); **108**, 1175 (1957).
- ³W. L. McMillan, *Phys. Rev.* **167**, 331 (1986).
- ⁴J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985), and references therein.
- ⁵See, e.g., J. L. Smith and E. A. Kmetko, *J. Less-Common Met.* **90**, 83 (1983).
- ⁶J. Zaanen, Ph.D. thesis, University of Groningen, 1986 (unpublished); J. Zaanen and G. A. Sawatzky, *Can. J. Phys.* (to be published).
- ⁷F. London and H. London, *Physica* **2**, 341 (1935); F. London, *Phys. Rev.* **74**, 562 (1948), and references therein.
- ⁸P. W. Anderson, *Science* **235**, 1196 (1987); P. W. Anderson, G. Baskaran, Z. Zou, and H. Hsu, *Phys. Rev. Lett.* **58**, 2790 (1987).
- ⁹S. Kivelson, D. Rokhsar, and J. Sethna, *Phys. Rev. B* **35**, 8865 (1987).
- ¹⁰V. J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987); C. M. Varma, G. Schmitt-Rink, and E. Abrahams, *Solid State Commun.* **62**, 681 (1987).
- ¹¹C. Gros, R. Joynt, and T. M. Rice, *Z. Phys. B* (to be published).
- ¹²P. Steiner, *Z. Phys. B* **66**, 275 (1987); P. Steiner *et al.*, *ibid.* **67**, 19 (1987); *Appl. Phys. A* **44**, 326 (1987); T. Takahashi *et al.*, *Jpn. J. Appl. Phys.* **26**, L349 (1987); H. Ihara *et al.*, *ibid.* **26**, L460, 463 (1987).
- ¹³A. Fujimori, E. Takayama-Murmachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).
- ¹⁴N. Nücker, J. Fink, B. Renker, D. Ewert, C. Politis, P. J. W. Weijs, and J. C. Fuggle, *Z. Phys. B* **67**, 9 (1987).
- ¹⁵B. Reihl, T. Reisterer, J. G. Bednorz, and K. A. Müller, *Phys. Rev. B* **35**, 8804 (1987); P. D. Johnson *et al.*, *ibid.* **35**, 8811 (1987).
- ¹⁶K. L. Kurtz *et al.*, *Phys. Rev. B* **35**, 8818 (1987); P. Thiry *et al.*, *Eurphys. Lett.* (to be published); J. A. Yarmoff *et al.*, *Phys. Rev. B* **36**, 3967 (1987).
- ¹⁷S. Etemad *et al.* (unpublished); J. Orenstein *et al.*, *Phys. Rev. B* **36**, 8892 (1987); in *Novel Superconductivity*, Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, 1987, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987); K. Kamarás *et al.*, *Phys. Rev. Lett.* **59**, 919 (1987); S. Tajima *et al.*, *Jpn. J. Appl. Phys.* **26**, L432 (1987).
- ¹⁸L. F. Mattheiss, *Phys. Rev. Lett.* **58**, 1028 (1987); J. Yu, A. J. Freeman, J. H. Xu, *ibid.* **58**, 1035 (1987); K. Takegahara, H. Harima, and A. Yanase, *Jpn. J. Appl. Phys.* **26**, L352 (1987); R. A. de Groot, H. Gutfreund, and M. Weger, *Solid State Commun.* **63**, 451 (1987).
- ¹⁹W. M. Temmerman, G. M. Stocks, P. J. Durham, and P. A. Sterne, *J. Phys. F* **17**, L135 (1987).
- ²⁰M. Cini, *Solid State Commun.* **24**, 681 (1977); *Phys. Rev. B* **17**, 2788 (1978); G. A. Sawatzky, *Phys. Rev. Lett.* **39**, 504 (1977).
- ²¹G. van der Laan, Ph.D. thesis, University of Groningen, 1982 (unpublished); G. van der Laan, C. Westra, and G. A. Sawatzky, *Phys. Rev. B* **23**, 4369 (1981).
- ²²G. A. Sawatzky, in *Narrow Band Phenomena*, edited by J. C. Fuggle, G. A. Sawatzky, and J. W. Allen (Plenum, New York, in press).
- ²³A. Fujimori, F. Minari, and S. Sugano, *Phys. Rev. B* **29**, 5225 (1984); **30**, 957 (1984).
- ²⁴S. Aksela, T. Pekkalte, H. Aksela, M. Wallenius, and H. Hakola, *Phys. Rev. A* **35**, 1426; **35**, 1522 (1987).
- ²⁵ d^7 -like final states do contribute to the broad shoulders indicated between 10 and 20 eV in Fig. 3. However, they are the result of decay of the L_{3d^9} XPS shake up states and their two-electron binding energy (BE) is about 20–30 eV. The assignment of that d^7 contribution to XPS shake up can be supported by XPS-Auger coincidence measurements in H. Haak, G. A. Sawatzky, and T. D. Thomas, *Phys. Rev. Lett.* **41**, 1825 (1978).
- ²⁶G. A. Sawatzky and J. Zaanen (unpublished).