PHYSICAL REVIEW B VOLUME 42, NUMBER 16 1 DECEMBER 1990

Electronic structure and crystal chemistry of $TlBa_2CuO_5$ and related cuprate superconductors

L. F. Mattheiss
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 18 June 1990)

In contrast to the fixed Cu valence ($\sim 2+$) in the Tl-bilayer cuprate superconductors, the average formal valence of Cu in the Tl-monolayer compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ varies as $(2+n^{-1})+$. This characteristic is reflected in linear augmented-plane-wave band-structure results for the simplest $n=1$ member of this Tl-monolayer homologous series, $TlBa_2CuO_5$, where the filling (~ 0.16) of the planar Cu($3d$)-O($2p$) σ^* band is reduced well below one-half. It is shown that the 50-50 Ba-La alloy is an appropriate "parent" compound for this $n=1$ phase since the half-filled-band condition is restored. For any member of this Tl-monolayer series, the optimal doping for high-temperature superconductivity should involve a combination of structural and chemical contributions.

Shortly after the discovery of high-temperature superconductivity in the Tl-Ba-Cu-O (Ref. 1) and Tl-Ba-Ca-Cu-O (Ref. 2) systems by Sheng and Hermann, structural studies showed[3] that these compounds form with a $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ composition and are isostructural with the corresponding body-centered-tetragonal (bct) phases of the Bi-Sr-Ca-Cu-O system.[4,5] However, subsequent studies[6] on this Tl-Ba-Ca-Cu-O system have revealed the existence of a distinct series of Tl-monolayer phases with a modified composition $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ in which the second Tl-O layer is absent and the Bravais lattice is changed from bct to simple tetragonal.

As in the Tl-bilayer series, the superconducting critical temperatures of the Tl-monolayer compounds are found[6,7] to increase with n, the number of CuO_2 layers in the primitive unit cell. The observed[6-8] T_c values vary from ~ 0 K ($n=1$), ~ 80 K ($n=2$), ~ 110 K ($n=3$), ~ 122 K ($n=4$), to ~ 110 K ($n=5$), increasing with n through $n=4$ before turning down slightly.[8] In the early studies, it was reported that the $n=1$ phase, $TlBa_2CuO_5$, did not superconduct.[6] However, quite recent measurements[9,10] have shown that Ba-La alloys with composition $TlBa_{2-x}La_xCuO_5$ do exhibit superconductivity with a maximum $T_c \sim 40$ K near the Ba-rich composition $x \approx 0.8$. Analogous studies of the Tl-Sr-La-Cu-O system[11] have yielded similar T_c's in the isostructural 50-50 compound $Tl_{1-x}SrLaCu_{1+x}O_5$, where excess Cu is believed to substitute at the Tl-deficient sites. In this regard, extensive studies by Morosin *et al.*[12] indicate that deviations from ideal stoichiometry, cation disorder, and oxygen vacancies may be a characteristic feature of these materials, producing the wide T_c and lattice-parameter variations that have been reported for the Tl-Ba-Ca-Cu-O system. For example, the report[10] of ~ 15-K superconductivity in $TlBa_2CuO_{5-\delta}$ may be understood in this context.

These rapidly accumulating results for the Tl-monolayer cuprates raise interesting questions regarding the electronic structure and crystal chemistry of these materials. The basic problem is evident from simple valence considerations. In the case of the Tl-bilayer cuprates, the results of band-structure calculations[13-15] show that the short Tl–apical-O bond lengths (~ 2.0 Å) produce pairs of strongly bonding-antibonding Tls–O$p(z)$ subbands such that the lower of the two antibonding $(sp\sigma)^*$ bands is partially filled. This suggests[13] that the Tl valence is closer to $1+$ than $3+$, while that of the oxygens in the Ba and Tl planes is $1-$ rather than $2-$. Interestingly, recent nuclear-magnetic-resonance studies[16] on the $n=1$–3 Tl-bilayer phases suggest a Tl($3+$) valency in these materials. However, either assumption [Tl($3+$), O($2-$) or Tl($1+$), four O($1-$)] yields an average Cu valence of $\sim 2+$ for all members of the $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ series. This is consistent with the band-structure results for these cuprate superconductors which feature n nearly degenerate planar Cu($3d$)-O($2p$) σ^* bands that are slightly less than half filled as a result of the partial $(sp\sigma)^*$ filling.[14,15]

The situation is different in the Tl-monolayer compounds. Here, simple symmetry arguments predict that the similarly short Tl–apical-O bond lengths (~ 2.1 Å) will produce a single $(sp\sigma)$-$(sp\sigma)^*$ pair. This is confirmed by the calculated band results discussed below, which exhibit a single unoccupied $(sp\sigma)^*$ subband well above (~ 1 eV) E_F. In this case, either assumption regarding the Tl-O valence yields an average Cu valence of $(2+n^{-1})+$ that decreases with increasing n. In terms of a band picture, this suggests that the valence-band filling for the $n=1$ compound, $TlBa_2CuO_5$, requires an additional electron to achieve the half-filled σ^* band condition that is characteristic of a cuprate superconductor "parent" compound. Similarly, a combination of structural and chemical contributions determine the average σ^* band filling for $n>1$.

The numerous available options for structural and chemical doping in these $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ phases has produced a wide variety of related alloy phases. These include the $n=1$ parent compounds $TlBaLaCuO_5$ (Refs. 9 and 10) and $TlSrLaCuO_5$ (Ref. 11). For the $n=2$

phase, Y→Ca substitution has produced one type of parent compound, $TlBa_2YCu_2O_7$, which exhibits semiconducting properties.[17] Another alternative involves doping at the Tl site. For example, bulk superconductivity up to 120 K has been observed in the 50-50 Tl-Pb alloys $(Tl,Pb)Sr_2Ca_{n-1}Cu_nO_{2n+3}$ (Ref. 18) and $(Tl,Pb)Ba_2Ca_{n-1}Cu_nO_{2n+3}$ (Ref. 19). In the latter series, phases containing as many as six CuO_2 layers have been prepared, though T_c reaches a maximum value of ~120 K at $n=4$.

In order to understand the basic chemistry of these Tl-monolayer compounds, self-consistent band-structure calculations have been carried out in the local-density approximation with the use of a scalar-relativistic version of the linear augmented-plane-wave (LAPW) method.[20] This study has focused on the simplest $n=1$ member of the $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ series, $TlBa_2CuO_5$, as well as the 50-50 Ba-La alloy, $Tl(Ba,La)_2CuO_5$. The primitive unit cell for this phase is shown in Fig. 1. Since detailed structural results are not yet available for this $n=1$ phase, approximate values for the lattice and atomic position parameters for $TlBa_2CuO_5$ have been estimated from the $n=3$ structural results of Parkin *et al.*[6] The derived $TlBa_2CuO_5$ parameters are summarized in Table I. The same atomic position parameters have been retained in calculations for the 50-50 $Tl(Ba,La)_2CuO_5$ alloy, though the observed[9] reduction in the c-axis lattice parameter (~9.0 Å versus 9.6 Å) has been taken into account.

The present implementation of the LAPW method is free of any shape approximations in calculating the crystalline charge density and potential. The LAPW basis includes plane waves with energies up to 11.25 Ry (~600 LAPW's) and spherical-harmonic cutoffs of $l=8$ within the muffin-tin spheres. The charge density and potential are expanded using ~6500 plane waves (55 Ry) in the interstitial region and by means of lattice-harmonic expansions ($l_{\max}=6$) within the spheres. Brillouin-zone integrations have been carried out into the use of a ten-point k sample in the $\frac{1}{16}$ irreducible wedge. Exchange and correlation effects have been treated with the use of the Wigner interpolation formula.[21]

In the calculations for $TlBa_2CuO_5$, the atomic $Tl(5d^{10}6s^26p^1)$, $Ba(5p^66s^2)$, $Cu(3d^{10}4s^1)$, and $O(2s^2,2p^4)$ states are treated as valence-band electrons, whereas the more tightly bound corelike states are handled using a frozen-core approximation.[20] The corresponding calculations for $Tl(Ba,La)_2CuO_5$ apply the virtual-crystal approximation[22] in which the 50-50 Ba-La distribution is replaced by an average atom containing 56.5 electrons and a balancing nuclear charge. In this case, the valence-band electrons include the atomic Ba-$La(5p^65d^{0.5}6s^2)$ states. This virtual-crystal approximation is expected to have minimal effects on the bands near E_F in the present materials, since the Ba-La constituents are electronically inactive.[13-15] Previous studies on related oxide systems[23-26] have shown that the principal effect of such alloying is to introduce additional structure in the density of states near the cutoff of the nonbonding $O(2p)$ peak, leaving the Fermi-level bands essentially unaffected. These effects will be minimized in the present situation where trivalent dopants are substituted at divalent host sites.

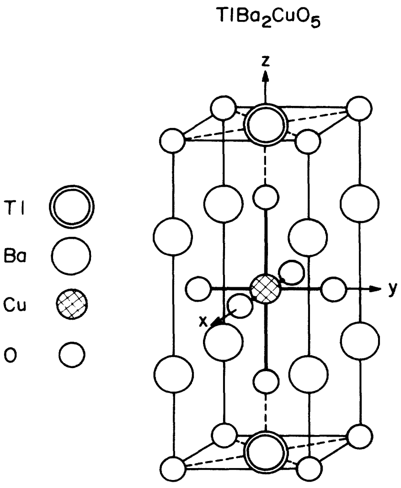

FIG. 1. Primitive simple-tetragonal unit cell for $TlBa_2CuO_5$. Oxygens in the Cu, Tl, and Ba planes are denoted O(1), O(2), and O(3), respectively.

The present LAPW energy-band results for $TlBa_2CuO_5$ are plotted along symmetry lines in the simple-tetragonal Brillouin zone in Fig. 2. The 21 bands that evolve from the $Tl(6s)$, $Cu(3d)$, and $O(2p)$ states span the energy range from about −6 to +3 eV. The uppermost bands (above +4 eV) have $Ba(5d)$ character at Γ and Z and $Tl(6p)$ character at X and R, respectively. Since there are a total of 38 valence electrons in the unit cell, one expects a total of two unfilled valence bands. According to the results in Fig. 2, the $TlBa_2CuO_5$ valence-band filling involves one completely empty band and four partially empty subbands.

Several bands of special interest in Fig. 2 have been highlighted with the use of distinctive symbols, including squares, triangles, and ×'s. The squares denote the bonding (σ) and antibonding (σ^*) combinations of the planar $\mathrm{Cu}\,d(x^2-y^2)$-$\mathrm{O}(1)\,p(x,y)$ states which represent the electronic heart of the cuprate superconductors. The triangles and ×'s identify analogous bands for which the predominant orbital weight involves the $\mathrm{Tl}\,s$-$\mathrm{O}(3)\,p(z)$ and $\mathrm{O}(2)\,p(x,y,z)$ states, respectively.

TABLE I. Atomic position parameters for $TlBa_2CuO_5$ (space group $P4/mmm$) which have been estimated from the structural results of Parkin *et al.* (Ref. 6) for the $n=3$ phase ($TlBa_2Ca_2Cu_3O_9$). The estimated lattice-parameter values for the $n=1$ phase are $a=3.843$ Å and $c=9.586$ Å.

Atom	Site	x/a	y/a	z/c
Tl	1b	0	0	$\frac{1}{2}$
Ba	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.2086
Cu	1a	0	0	0
O(1)	2f	$\frac{1}{2}$	0	0
O(2)	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O(3)	2g	0	0	0.2815

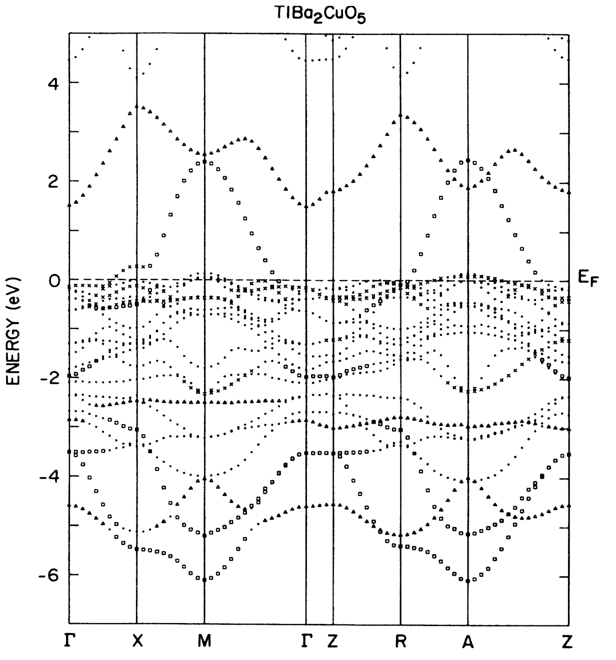

FIG. 2. Energy-band results for TlBa$_2$CuO$_5$ along symmetry lines in the Brillouin zone. Bands with special orbital characteristics are identified with squares, triangles, and ×'s. The squares bands have at least 30% Cu $d(x^2-y^2)$–O(1)$p(x,y)$ orbital weight within the corresponding muffin-tin spheres. The triangles and ×'s denote analogous bands with 30% Tl s–O(3)$p(z)$ and O(2)$p(x,y,z)$ orbital weight, respectively.

As is well known, the squares-designated Cu $d(x^2-y^2)$–O(1)$p(x,y)$ σ^* band is exactly half filled in a typical parent compound such as stoichiometric La$_2$CuO$_4$ (Ref. 27). This produces a material that is both antiferromagnetic and insulating. Metallic behavior and superconductivity are observed when the band filling is changed so that extra carriers (electrons or holes) are introduced into the CuO$_2$ planes. It is evident in Fig. 2 that the band filling of this σ^* band is well below one half ($\sim$0.16 according to the density-of-states results discussed below) in TlBa$_2$CuO$_5$ and the Fermi level falls within the energy range of the nonbonding O(2p) manifold.

The highest and lowest "triangles" bands in Fig. 2 represent $(sp\sigma)^*$ and $(sp\sigma)$ combinations of Tl s–O(3) $p(z)$ orbitals while the corresponding band at intermediate energies (~ -2 to -3 eV) represents a nonbonding combination of O(3) $p(z)$ orbitals with different symmetry. For example, the $(sp\sigma)^*$-$(sp\sigma)$ pair has Γ_{1+} symmetry at the zone center, while the intermediate nonbonding $p(z)$-type state has Γ_{2-} symmetry.[28] It is clear from Fig. 2 that there is a single $(sp\sigma)^*$ triangle band well above E_F in the Tl-monolayer compounds. This is in contrast to the Tl-bilayer compounds, where a pair of $(sp\sigma)^*$ bands occur and one is partially occupied.[13–15] As in the Tl-bilayer materials,[13] the lower-energy $(sp\sigma)$ band has enhanced Tl(6s) character relative to its $(sp\sigma)^*$ counterpart. Averaged over the six symmetry points in Fig. 2, the Tl(6s) LAPW orbital weight within the Tl muffin-tin sphere ($R \approx 2.02$ a.u.) for the $(sp\sigma)$ and $(sp\sigma)^*$ bands is 0.21 and 0.14, respectively. Again,[13] this suggests that the Tl valence is closer to 1+ than 3+ while that of O(3) is 1− rather than 2−. In tight-binding language, this 6s admixture suggests that the Tl(6s) orbital energy is somewhat below that of the O(3) $p(z)$ states, namely, $\sim$2.5–3.0 eV below E_F.

The TlBa$_2$CuO$_5$ valence bands in Fig. 2 are much less two dimensional than those of typical cuprate superconductors. A comparison of results in the basal (ΓXM) and top (ZRA) faces of the Brillouin zone indicates c-axis dispersion as large as 0.5 eV. These dispersion effects will be reduced for $n>1$ in the TlBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+3}$ series as extra Ca and CuO$_2$ layers are inserted into the primitive unit cell. The extra layers will also increase the filling of the valence-band manifold, decreasing the average valence of Cu from 3+ for $n=1$ to 2.5+, 2.33+, 2.25+, etc. As noted earlier, this is paralleled by enhanced superconducting properties as the observed T_c's increase from $n=1$ through 4. However, the actual Cu valence in each phase is also affected by materials deficiencies such as deviations from stoichiometry, disorder, site interchange, and vacancies.[12]

Although it is difficult to grow single-phase samples of the TlBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+3}$ materials, specific problems with the $n=1$ compound, TlBa$_2$CuO$_5$, have led to the study of TlBa$_{2-x}$La$_x$CuO$_5$ (Refs. 9 and 10) and TlSr$_{2-x}$La$_x$CuO$_5$ (Ref. 11) alloys. Here, T_c's in the $\sim$40-K range have been observed for roughly 60-40 Ba-La and 50-50 Sr-La compositions. The band results for the 50-50 Ba-La alloy are shown in Fig. 3. As noted above, these calculations have incorporated the reduced

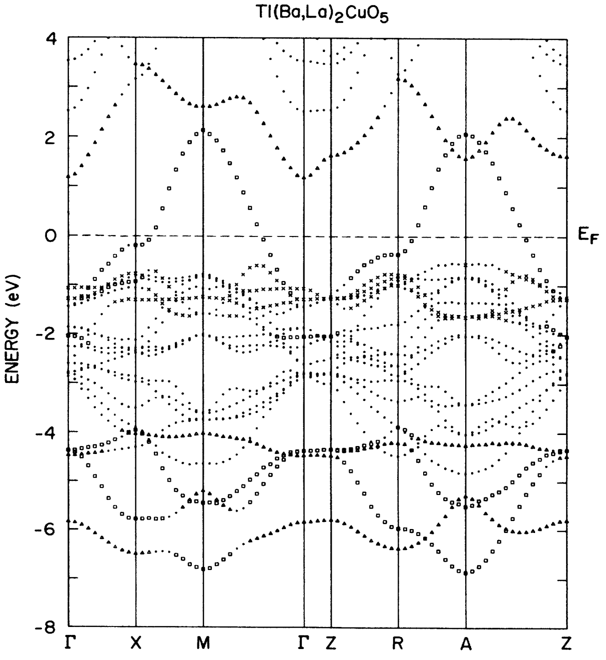

FIG. 3. Energy-band results for Tl(Ba,La)$_2$CuO$_5$ along symmetry lines in the Brillouin zone. Different symbols identify bands with specific orbital character (see Fig. 2).

c-axis lattice parameter $c \approx 9.0$ Å, scaled atomic position parameters (Table I), as well as the virtual-crystal approximation to treat the Ba-La admixture.

According to the results in Fig. 3, the added valence electron in $Tl(Ba,La)_2CuO_5$ raises the Fermi level to the extent that there is now a single half-filled σ^* band which originates from the CuO_2 plane. This demonstrates that stoichiometric $Tl(Ba,La)_2CuO_5$ is an appropriate parent compound for the $n=1$ phase. A comparison with the $TlBa_2CuO_5$ results of Fig. 2 shows that the alloying effects involve more than strict rigid-band filling. In fact, several of the more prominent band-structure changes appear to be due to the reduced *c*-axis parameter of the 50-50 Ba-La alloy.

In particular, the reduced Tl-O(3) bond length (1.97 versus 2.09 Å) increases the $(sp\sigma)$-$(sp\sigma)^*$ splitting of the $Tl\,s$-$O(3)p(z)$ triangle subbands from ~ 6 eV in $TlBa_2CuO_5$ to ~ 7 eV in $Tl(Ba,La)_2CuO_5$. As expected, the overall planar CuO_2 $d(x^2-y^2)$-$p(x,y)$ σ^*-σ bandwidth (squares) is essentially unchanged. Relative to the σ^* band, there is an overall shift (~ 0.5 eV) of the nonbonding O(2*p*) bands to higher binding energies in the Ba-La alloy. In both materials, the O(2) *p* bands (i.e., those denoted by ×'s) are concentrated near the low-binding-energy edge of the nonbonding O(2*p*) manifold.

A comprehensive overview of the $Tl(Ba,La)_2CuO_5$ electronic structure is provided by the density-of-states (DOS) results, including its projected contributions within the individual muffin-tin spheres. These results, which are shown in Fig. 4, have been calculated with the use of tetrahedral interpolation involving LAPW results at 63 *k* points within the irreducible wedge of the Brillouin zone. For the projected results, the total DOS is weighted by the integrated LAPW charges within the Tl, (Ba,La), Cu, and O spheres (volume ratios $\sim 1.8{:}4.6{:}1.6{:}1$). Unlike the Tl-bilayer compounds[13,14] where the planar CuO_2-derived states dominate the DOS for the first 2 eV below E_F, the Tl-layer O(2) *p* bands are concentrated in this energy range in the Tl-monolayer materials. However, the DOS near E_F originates almost entirely from the σ^* $d(x^2-y^2)$-$p(x,y)$ subband of the CuO_2 plane in both the Tl-monolayer and Tl-bilayer materials. Madelung-type corrections to the virtual-crystal approximation in $Tl(Ba,La)_2CuO_5$ are expected to occur within the O(3) manifold, well below E_F.

As in the case of the other cuprate-superconductor parent compounds, stoichiometric $Tl(Ba,La)_2CuO_5$ is expected to be an antiferromagnetic insulator rather than the metal predicted by the local-density approximation. This is generally attributed to strong electron-electron correlation effects in the $Cu\,d(x^2-y^2)$-$O(1)p(x,y)$ σ^* band. Nevertheless, the charge density, electrostatics, and overall level distribution should be accurately described by this scheme. As observed experimentally,[9-11] the 50-50 $Tl(Ba,La)_2CuO_5$ and $Tl(Sr,La)_2CuO_5$ alloys must be doped with excess Ba or Sr in order to provide additional holes in this σ^* band before they become metallic and superconducting.

Since the relatively short Tl-O (apical) bond length persists for the $n>1$ phases,[6] one can anticipate that the $(sp\sigma)^*$ triangle band remains well above E_F for the remaining members of the $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ series. This implies that for all *n*, a single extra valence electron is required to achieve the half-filled-band condition for the *n* nearly degenerate σ^* bands that originate from the individual CuO_2 planes. Since this can be achieved by a variety of doping alternatives, there is no unique parent compound for this series. One alternative is the 50-50

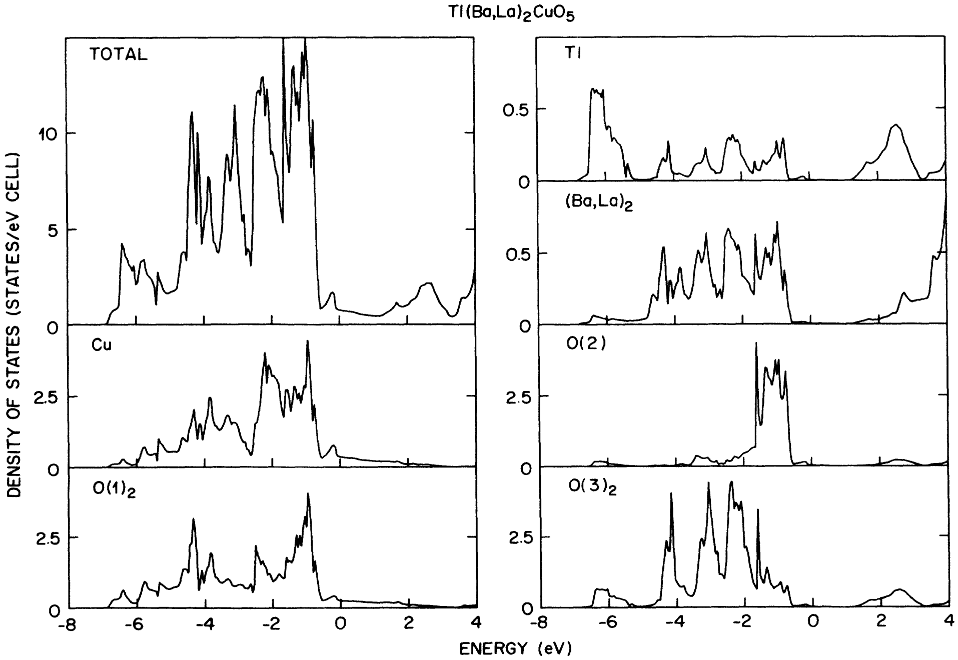

FIG. 4. Total and muffin-tin projected density-of-states results for $Tl(Ba,La)_2CuO_5$.

Ba-La alloy,[9,10] which has been investigated thus far only for the $n=1$ phase. For $n=2$, a second approach involves Y→Ca substitution,[17] yielding the isostructural compound $\mathrm{TlBa_2YCu_2O_7}$. The situation is less clear in the case of the 50-50 Tl-Pb alloys,[18,19] since the atomic Pb(6s) binding energy is ~2.5 eV greater than that of Tl. This could reduce the energy and cause partial occupancy of the $(sp\sigma)^*$ subband, thereby altering the filling of the crucial σ^* bands.

In summary, the results of LAPW calculations for $\mathrm{TlBa_2CuO_5}$ and $\mathrm{Tl(Ba,La)_2CuO_5}$ show that a single $(sp\sigma)^*$ subband that originates from an antibonding combination of Tl s–O(3) $p(z)$ orbitals is raised well above E_F in both compounds. La doping increases the filling of the planar Cu(3d)–O(2p) σ^* band from about 0.16 in $\mathrm{TlBa_2CuO_5}$ to exactly one half in the 50-50 alloy, $\mathrm{Tl(Ba,La)_2CuO_5}$. For ideal stoichiometric materials with composition $\mathrm{TlBa_2Ca_{n-1}Cu_nO_{2n+3}}$, one extra valence electron is required for all n to achieve this half-filled-band condition within the n nearly degenerate σ^* bands that evolve from the $\mathrm{CuO_2}$ planes. This suggests that the optimal doping for high-temperature superconductivity in these Tl-monolayer cuprates involves a combination of chemical and structural contributions.

---

[1] Z. Z. Sheng and A. M. Hermann, Nature **332**, 55 (1988); Z. Z. Sheng *et al.*, Phys. Rev. Lett. **60**, 937 (1988).

[2] Z. Z. Sheng and A. M. Hermann, Nature **332**, 138 (1988).

[3] R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1657 (1988); M. A. Subramanian *et al.*, Nature **332**, 420 (1988).

[4] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L209 (1988).

[5] M. A. Subramanian *et al.*, Science **239**, 1015 (1988); J. M. Tarascon *et al.*, Phys. Rev. B **37**, 9382 (1988); S. A. Sunshine *et al.*, *ibid.* **38**, 893 (1988); H. W. Zandbergen *et al.*, Nature **332**, 620 (1988).

[6] S. S. P. Parkin *et al.*, Phys. Rev. Lett. **61**, 750 (1988); S. S. P. Parkin *et al.*, Phys. Rev. B **38**, 6531 (1988).

[7] H. Ihara *et al.*, Nature **334**, 510 (1988); H. Ihara *et al.*, Phys. Rev. B **38**, 11952 (1988).

[8] S. Nakajima *et al.*, Physica C **158**, 471 (1989).

[9] T. Manako *et al.*, Physica C **158**, 143 (1989).

[10] H. C. Ku *et al.*, Jpn. J. Appl. Phys. **28**, L923 (1989).

[11] T. Mochiku *et al.*, Jpn. J. Appl. Phys. **28**, L1926 (1989).

[12] B. Morosin *et al.*, Physica C **161**, 115 (1990).

[13] D. R. Hamann and L. F. Mattheiss, Phys. Rev. B **38**, 5138 (1988).

[14] J. Yu, S. Massidda, and A. J. Freeman, Physica C **152**, 273 (1988).

[15] R. V. Kasowski, W. Y. Hsu, and F. Herman, Phys. Rev. B **38**, 6470 (1988).

[16] F. Hentsch *et al.*, Physica C **165**, 485 (1990).

[17] T. Manako *et al.*, Physica C **156**, 315 (1988).

[18] M. A. Subramanian *et al.*, Science **242**, 249 (1988).

[19] H. Kusuhara, T. Kotani, H. Takei, and K. Tada, Jpn. J. Appl. Phys. **28**, L1772 (1989).

[20] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).

[21] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[22] J. S. Faulkner, in *Progress in Materials Science,* edited by J. W. Christian, P. Haasen, and T. M. Massalski (Pergamon, Great Britain, 1982), Vol. 27.

[23] W. E. Pickett, H. Krakauer, D. A. Papaconstantopoulos, and L. L. Boyer, Phys. Rev. B **35**, 7252 (1987).

[24] L. F. Mattheiss and D. R. Hamann, Phys. Rev. Lett. **60**, 2681 (1988).

[25] M. J. DeWeert, D. A. Papaconstantopoulos, and W. E. Pickett, Phys. Rev. B **39**, 4235 (1989).

[26] D. A. Papaconstantopoulos, A. Pasturel, J. P. Julien, and F. Cyrot-Lackmann, Phys. Rev. B **40**, 8844 (1989).

[27] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[28] A. W. Luehrmann, Adv. Phys. **17**, 1 (1968).