Band structures and Fermi surfaces of single- and double-Tl-O-layered high-temperature superconductors

V. V. Tatarskii, M. Paranthaman, and A. M. Hermann
Department of Physics, University of Colorado, Boulder, Colorado 80309-0390
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We present here the complete results of tight-binding calculations of the band structures and Fermi surfaces for the $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1$, 2, and 3) superconducting phases. We show the density of states (partial and total) and three-dimensional Fermi surfaces for each of these six phases. The single-Tl-O-layer Fermi surfaces contain noncylindrical features, and the Fermi surfaces of Tl 2:2:2:3, Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 show pockets corresponding to Tl-O band crossings at E_F.

I. INTRODUCTION

Soon after the discovery of high-temperature superconductivity in the Tl-Ba-Ca-Cu-O system by Sheng and Hermann,[1] two families of Tl compounds were identified.[2–9] They are (i) single-Tl-O-layered compounds with the general formula $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n=1-3$), and (ii) double-Tl-O-layered compounds with the general formula $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1-3$). The crystal structures of these compounds are discussed below. The electronic structures of these compounds are very important for understanding of the normal-state properties and the mechanism of the superconductivity. The electronic band structure of various Tl-compound phases has been investigated by several researchers using different techniques. We address here tight-binding calculations on the six major phases of Tl-Ba-Ca-Cu-O superconductors and compare our results to *ab initio* calculations[10–16] and previous tight-binding calculations[17–25] including those of the density-functional approach that are currently available. The *ab initio* calculations, based on the method of first principles, require very large computational resources to solve the complex structures of the many phases of high-temperature superconductors. Semiempirical methods like tight binding—which do not require large computers and give acceptably accurate results—are very handy. In addition, the reconstruction of the surface spectra is relatively easy using the tight-binding method. The tight-binding method has already been used to calculate the electronic structure of La_2CuO_4 (Ref. 17) and $YBa_2Cu_3O_7$ (Ref. 19) and the results are in good agreement with those of other methods. Similarly, both *ab initio* and tight-binding calculations have been carried out on the major Tl-based superconducting phases.[10–14,20–26]

Experimental evidence on the Fermi surface is extremely important but has been proved to be difficult to obtain. Recently, Barbiellini *et al.*[27] and Peter *et al.*[28] have obtained Fermi-surface parameters from the lifetime and two-dimensional angular correlation of (positron) annihilation radiation (2D-ACAR) studies on untwinned $YBa_2Cu_3O_7$ single crystals. Meyer, Wagener, and Weaver[29] have measured the density of states (DOS) by photoemission and inverse photoemission experiments on Tl 2:2:1:2 and Tl 2:2:2:3 bulk samples and have found good correlation between their results and the DOS calculated by Marksteiner *et al.*[14] using full-potential linearized augmented-plane-wave (FLAPW) calculations of the band structures. Very recently, Fowler *et al.*[30] have investigated the de Haas–van Alphen effect (the component of the magnetic susceptibility periodic in $1/B$) on the oriented bulk $YBa_2Cu_3O_{6.97}$ samples by using a 100-T flux compression system and obtained Fermi-surface orbits. Currently, the same experiment is being conducted on our bulk Tl-based samples. With this as a motivation, we have carried out and present here tight-binding calculations on the single- and double-Tl-O-layered high-temperature superconducting phases. In this paper, we report our method of calculations, choice of atomic parameters, and a complete set of detailed results are presented in the form of density of states (partial and total), and three-dimensional Fermi surfaces for all the Tl compounds with up to three Cu-O sheets per formula unit. We report, for the first time, the Fermi surfaces for the single-Tl-O-layered phases, and three-dimensional Fermi surfaces for all six compounds.

II. TIGHT-BINDING METHOD

The single-Tl-O-layered compounds, $TlBa_2CuO_5$ (hereafter referred as Tl 1:2:0:1), $TlBa_2CaCu_2O_7$ (Tl 1:2:1:2), $TlBa_2Ca_2Cu_3O_9$ (Tl 1:2:2:3), and double-Tl-O layered compounds, $Tl_2Ba_2CuO_6$ (Tl 2:2:0:1), $Tl_2Ba_2CaCu_2O_8$ (Tl 2:2:1:2), $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl 2:2:2:3) are basically intergrowth structures with the conducting $Ca_{n-1}(CuO_2)_n$ layers and the blocking BaO-TlO-BaO (for single-Tl-O layers) or BaO-TlO-TlO-BaO (for double-Tl-O layers) layers. All of these compounds, under consideration for the present study, have tetragonal crystal symmetries.

For the tight-binding calculations, we follow Richert and Allen's simple chemical model[17,18,25] and we take into account *s* and *p* orbitals of oxygen, *s*, *p*, and *d* orbitals of Tl, and *s* and *d* orbitals of Ba, Ca, and Cu. The parameters for Tl are extrapolated from those of Pb and

TABLE I. Values of atomic parameters used in the tight-binding calculations. The atomic energies are referenced to the nominal vacuum level.

Element	ε_s	ε_p	ε_d	r_d
(eV)	(eV)	(eV)	(eV)	(Å)
Tl	−14.8	−8.3	−23.0	1.00
Ba	−4.5		−6.6	1.60
Ca	−5.4		−3.2	1.20
Cu	−12.0		−14.0	0.95
O	−29.0	−14.0		

Bi.[25] We also follow Harrison's parametrization[31] for the intrasite matrix elements (unfitted) which are chosen as atomic energies for orbitals with various symmetries. Intersite matrix elements in the case of overlapping s-s, p-p, and s-p states can be represented as

$$V_{ll'm}=\eta_{ll'm}(\hbar^2/m_e d^2) \quad (l,l'=s \text{ or } p) . \tag{1}$$

Here l,l' are the orbital quantum numbers, m is the magnetic quantum number, d is the interatomic distance, m_e is the electron mass. In the case of d-orbital overlapping with s or p states, the matrix elements are described as

$$V_{ldm}=\eta_{ldm}(\hbar^2 r_d^{3/2}/m_e d^{7/2}) \quad (l=s \text{ or } p) . \tag{2}$$

Here r_d represents an effective radius of the d orbital. Constants $\eta_{ll'm}$ and η_{ldm} are parameters and depend only on the top of the overlapping orbitals. As in Ref. 25, we use the following values: $\eta_{ss\sigma}=-1.1$, $\eta_{sp\sigma}=1.4$, $\eta_{sd\sigma}=1.6$, $\eta_{pd\sigma}=-2.5$, $\eta_{pd\pi}=1.4$, $\eta_{pp\sigma}=1.5$, and $\eta_{pp\pi}=-0.6$. Numerical values of the remaining parameters used in our calculations are listed in Table I. To investigate the validity of atomic parameters in our tight-binding calculations, we used different atomic parameters that are available in the literature[18–21,25,31] for all the elements that are used in the present study. When we follow Richert and Allen's atomic parameters (Table I), we get band structures close to the ones that are expected from the experimental work[32] and nearly identical to those from *ab initio* calculations.[10,12] We will discuss below the results we obtained by using different parameters. The calculations presented here are performed for stoichiometric compounds.

III. RESULTS AND DISCUSSION

Local density of states for the individual atoms in Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 are shown in Figs. 1–3, respectively. For the stoichiometric Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 compounds, both Tl 6s band Cu(3d)-O(2p) bands cross the Fermi level. However, for non-stoichiometric single-Tl-O-layered phases, Jung *et al.*[24] observed only Cu(3d)-O(2p) bands crossing the Fermi level. Even though we used slightly different parameters[25] than those of Meshkov *et al.*,[21] we get the same results on the Tl 1:2:1:2 and Tl 1:2:2:3 phases. Fermi surfaces of Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 are shown in Figs. 4–6, respectively. Local density of states for the individual atoms in Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3 are shown in Figs. 7–9, respectively. Our data on Tl 2:2:0:1 and Tl 2:2:2:3 agree well with Kasowski's *ab initio* calculations.[12] In the Tl 2:2:0:1 case, both sets of calculations, for example, show no Tl-O band crossings at E_F; in the case of Tl 2:2:2:3, Tl-O bands do cross for both calculations. However, in the case of Tl 2:2:1:2, we see no band

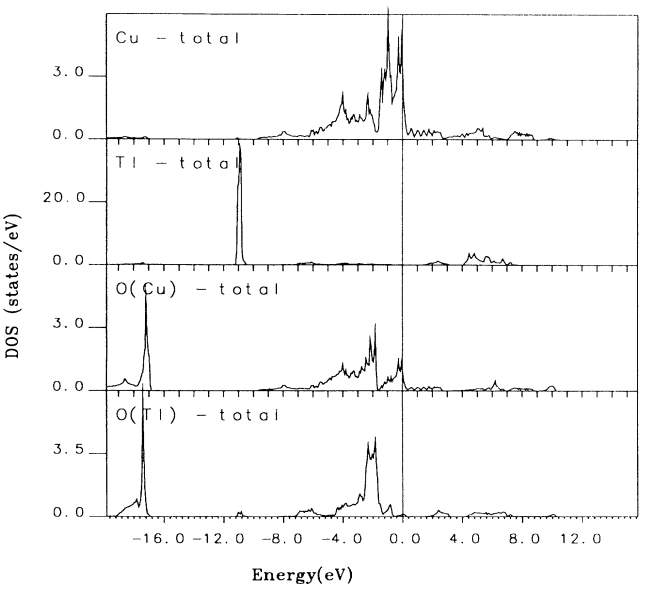

FIG. 1. Local density of states for the individual atoms in $TlBa_2CuO_5$.

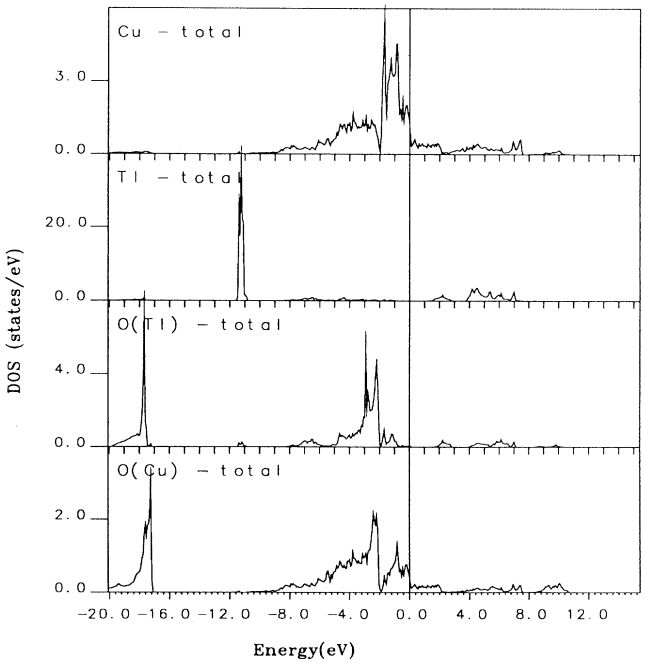

FIG. 2. Local density of states for the individual atoms in $TlBa_2CaCu_2O_7$.

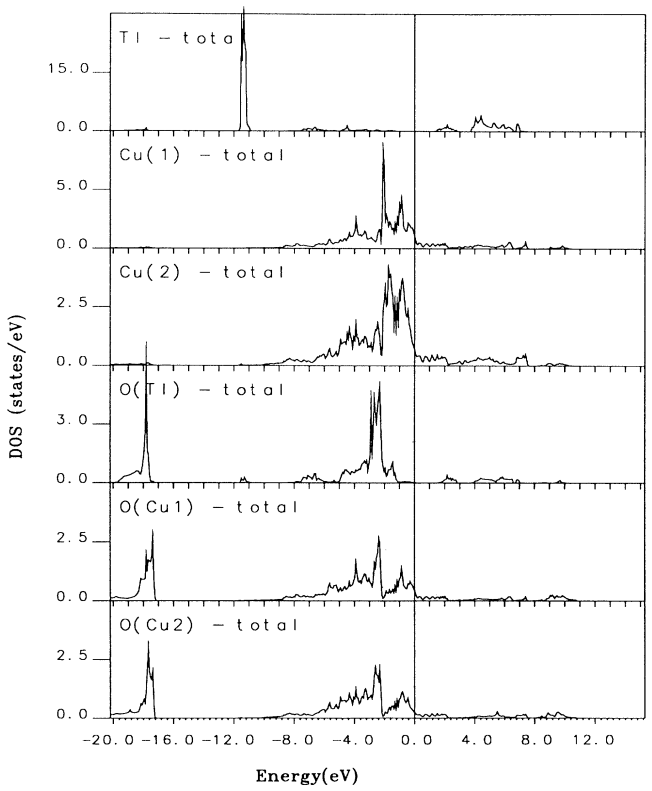

FIG. 3. Local density of states for the individual atoms in $TlBa_2Ca_2Cu_3O_9$.

crossings at E_F. Usually, *ab initio* calculations do show Tl-O crossings at E_F for double-Tl-O-layered phases, but the energy uncertainty of our calculations are within the spreads of values seen in *ab initio* calculations.

The essential feature of the ideal Tl 2:2:0:1 band structure is the broad Cu($3d_{x^2-y^2}$)-O($2p_{x,y}$) band crossing the

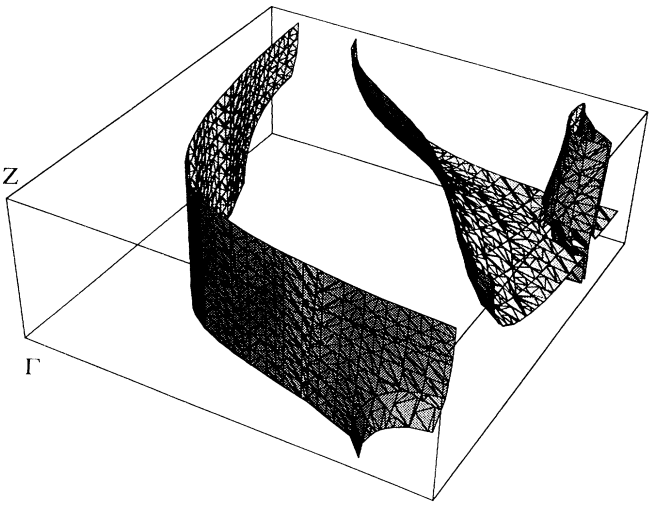

FIG. 4. Fermi surface of $TlBa_2CuO_5$.

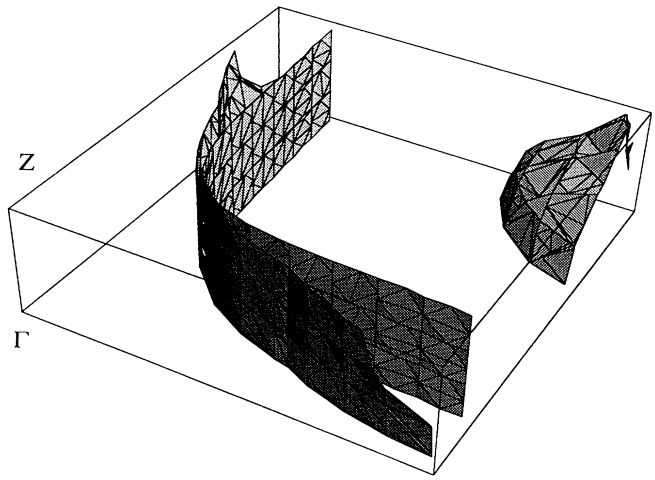

FIG. 5. Fermi surface of $TlBa_2CaCu_2O_7$.

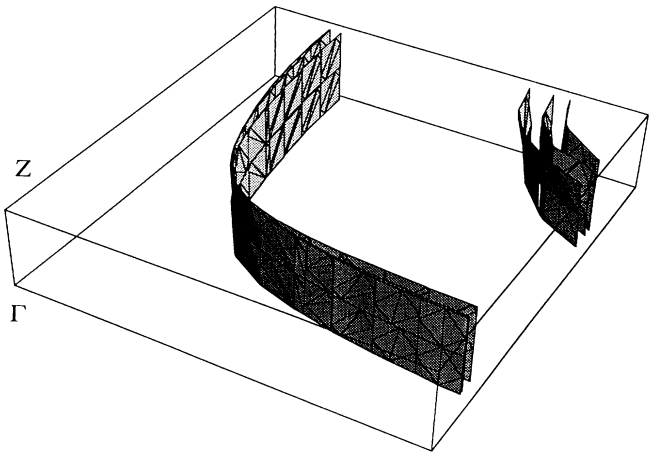

FIG. 6. Fermi surface of $TlBa_2Ca_2Cu_3O_9$.

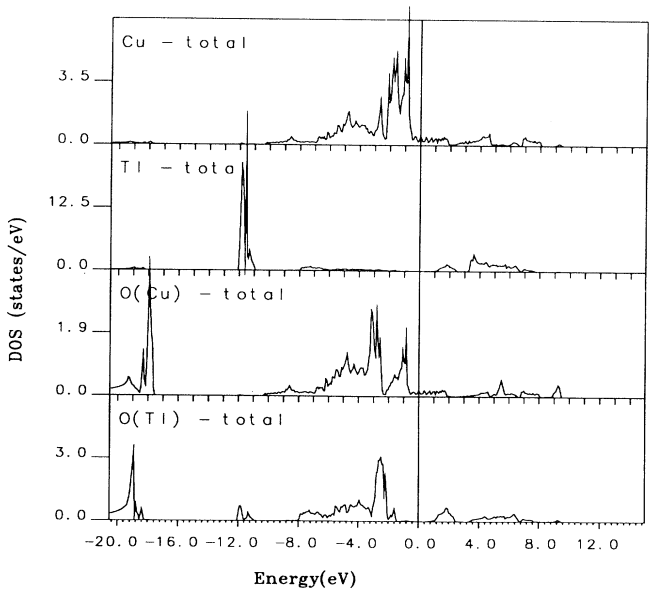

FIG. 7. Local density of states for the individual atoms in $Tl_2Ba_2CuO_6$.

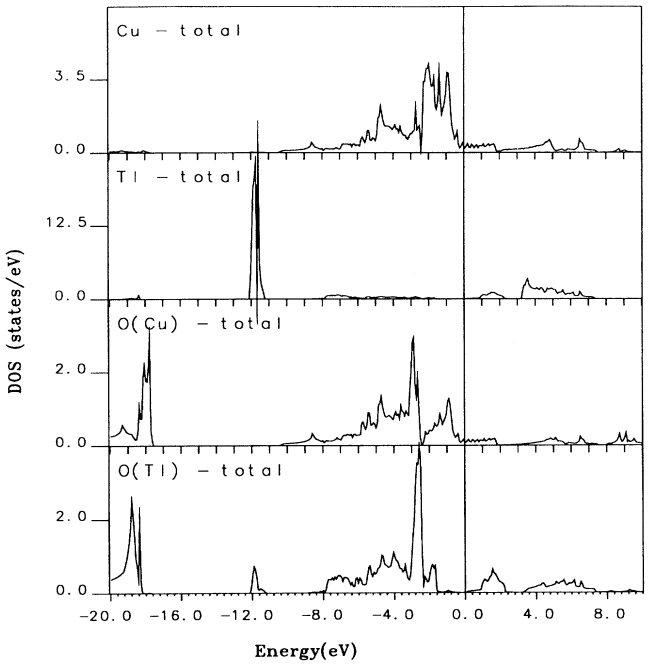

FIG. 8. Local density of states for the individual atoms in $Tl_2Ba_2CaCu_2O_8$.

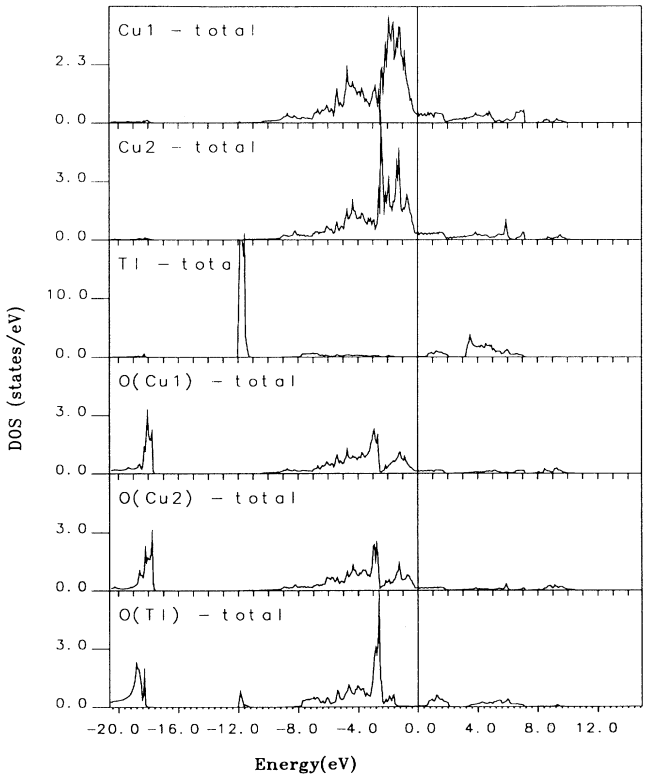

FIG. 9. Local density of states for the individual atoms in $Tl_2Ba_2Ca_2Cu_3O_{10}$.

Fermi level. Similarly, for Tl 2:2:1:2, two equivalent Cu-O bands, and for Tl 2:2:2:3, a Tl 6*s* band, two equivalent and one nonequivalent Cu-O bands cross the Fermi level. However, Jung *et al.*[24] have found for the nonstoichiometric compound $Tl_{2-y}Ba_2CuO_{6-x}$, the Tl 6*s* band lies significantly below the Fermi level so that there is a large electron pocket to remove electrons from the $d_{x^2-y^2}$ bands of the CuO_2 layers. Our Figs. 7–9 reveal that the O(2*p*) and Cu(3*d*) states are responsible for the dominant contribution to the total density of states at the Fermi level for Tl 2:2:0:1 and Tl 2:2:1:2. But for Tl 2:2:2:3, Tl 6*s* bands are equally important with O(2*p*) and Cu(3*d*) states contributing to the Fermi energy. Fermi surfaces of Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3 are shown in Figs. 10–12, respectively. The calculated band structure for all the double-Tl-O-layered compounds turns out to have a quasi-two-dimensional nature and strongly resembles that of La_2CuO_4.

The new three-dimensional Fermi-surface results presented in Figs. 4–6 and 10–12 afford an opportunity to compare the electronic structure of the various phases. Tl 2:2:0:1 and Tl 2:2:1:2 show featureless cylinders (see Figs. 10 and 11) which are nearly identical to each other. The simplicity arises from the (only) Cu-O bands crossing at the Fermi level. On the other hand, we do see unusual features for Tl 2:2:2:3 compounds (Fig. 12). Figure 12 shows a cylinder at the center, and a cylinder near the corner of the zone. However, for Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3, we see features near the corner of the zone. In the Tl 1:2:0:1 compound, one near-cylindrical shell and a prolate spheroidlike surface are seen near the corner, and a near-cylinder with tubelike features is seen near the edge. In Tl 1:2:1:2, one near-sphere and a near-cylindrical shell are seen at the corner, and a cylinder, and another near-cylinder are shown. In Tl 1:2:2:3, three small near-cylindrical shells are seen near the corner, and large right cylindrical surfaces are seen. The appearance

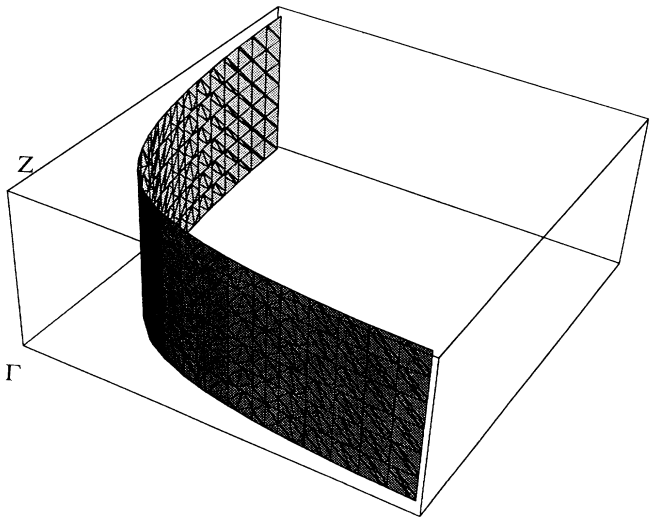

FIG. 10. Fermi surface of $Tl_2Ba_2CuO_6$.

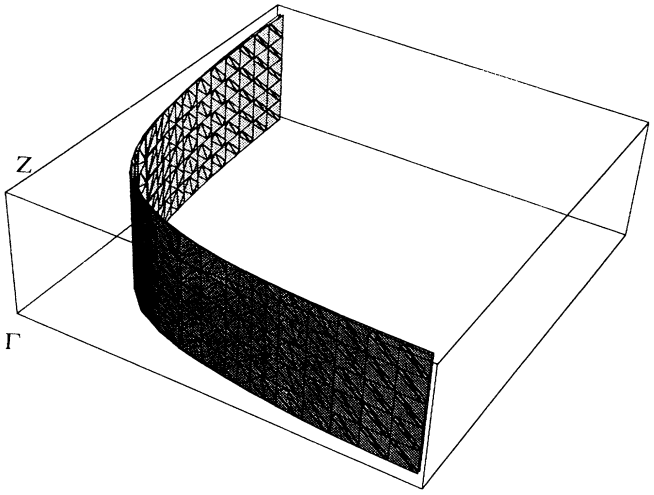

FIG. 11. Fermi surface of $Tl_2Ba_2CaCu_2O_8$.

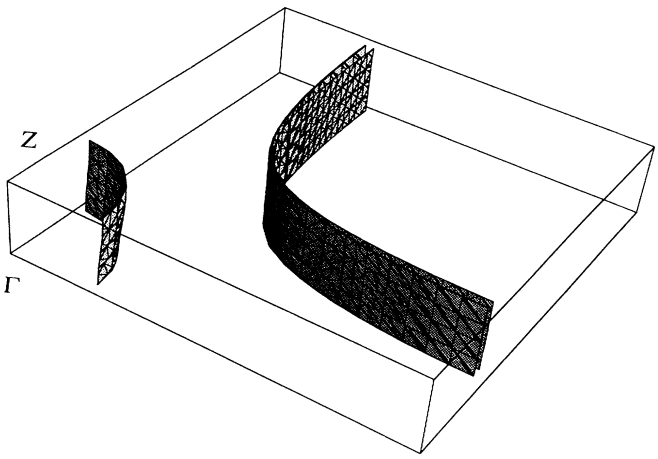

FIG. 12. Fermi surface of $Tl_2Ba_2Ca_2Cu_3O_{10}$.

and shape of the Fermi-surface features, especially those near the corner of the zone, are unexpected and may be experimentally verifiable due to their small areas. High-field de Haas–van Alphen measurements similar to those reported in Ref. 30 on a number of the Tl-based superconducting phases are currently underway.

During our tight-binding calculations, we used different atomic parameters[18–21,25,31] for all the elements Tl, Ba, Ca, Cu, and O. Between Allen's[25] and Harrisons parameters,[31] mostly Tl parameters vary greatly from -14.8 to -9.9 for ε_s orbitals, -8.3 to -4.5 for ε_p orbitals, and -23.0 to -14.7 for ε_d orbitals. Cu parameters vary only from -12.0 to -13.0 for ε_s orbitals. Ca parameters vary from -5.4 to -5.5 for ε_s, and -3.2 to -7.0 for ε_d orbitals. Ba and O parameters are quite similar. When Harrison's atomic parameters[31] are used for our calculations, we see features at the center of the Fermi surface for Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3. We did not see any features for Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3, and their Fermi surfaces were similar. But, when Allen's parameters[25] are used, we obtained the results that are reported in the present study, and are convincingly similar to the *ab initio* calculations.[10,12] Hence, the choice of parameters for tight-binding calculations is critical and the Fermi surfaces vary accordingly.

In summary, we have presented here the results of our tight-binding calculations for the density of states (partial and total) and the Fermi surfaces of single- and double-Tl-O-layered compounds. The observation of noncylindrical features for the Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 phases shows the need for three-dimensional representations for the single-Tl-O-layered compounds. Pockets are seen in the Fermi surfaces of Tl 2:2:2:3, Tl 1:2:0:1, Tl 1:2:1:2, and Tl 1:2:2:3 compounds corresponding to Tl-O band crossings at E_F.

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