Electronic structure of the new high-T_c superconductors $Tl_2Ba_2CuO_6$, $Tl_2Ba_2CaCu_2O_8$, $Tl_2Ba_2Ca_2Cu_3O_{10}$, and $Tl_2Ba_2Ca_3Cu_4O_{12}$

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We discuss the electronic structure of the first four members of the high-T_c superconductor family $Tl_2Ba_2Ca_{L-1}Cu_LO_{4+2L}$, where L is the number of CuO_2 layers. Using a simplified BCS-type model, we relate T_c to L using the partial density of states of the CuO_2 layers as the physical link. According to our model, the pure phase of $Tl_2Ba_2Ca_3Cu_4O_{12}$ ($L=4$) would have a value of T_c in the range 135 to 165 K.

INTRODUCTION

Several groups[1-6] have recently reported high values of T_c in a new family of superconductors composed of periodic arrays of double Tl-O layers separated by one or more perovskite layer. This family may be characterized by the chemical formula $Tl_2Ba_2Ca_{L-1}Cu_LO_{4+2L}$, where L is the number of CuO_2 layers in the primitive unit cell, and deviations from ideal stoichimetry are ignored. There have been reports[1-6] that T_c lies between 0 to 85 K for $L=1$; between 90 and 108 K for $L=2$; and between 118 and 125 K for $L=3$. For the closely related Bi-Sr family ($Bi_2Sr_2Ca_{L-1}Cu_LO_{4+2L}$), estimates[6-9] for T_c range from 6 to 22 K for $L=1$; from 80 to 90 K for $L=2$; and from 110 to 120 K for $L=3$. These widely varying estimates for T_c presumably reflect different processing conditions which could, for example, generate admixtures of the $L=1$, 2, and 3 phases on an atomic scale rather than pure phases.

In this paper we will discuss the band structures of the Tl-Ba compounds, emphasizing the special features introduced by the presence of the Tl-O layers. We will also discuss a simple theoretical model which can account in a natural way for the empirical fact that T_c increases as the number of CuO_2 layers increases for many high-T_c superconductors. For the Tl-Ba and related families, we will use the simplified notation 2:2:0:1, 2:2:1:2, 2:2:2:3, and 2:2:3:4 to identify the $L=1$ to 4 members, respectively. For the Tl-Ba family, these symbols denote the proportions Tl:Ba:Ca:Cu.

Our band-structure calculations for the Tl-Ba compounds are based on the first-principles pseudofunction

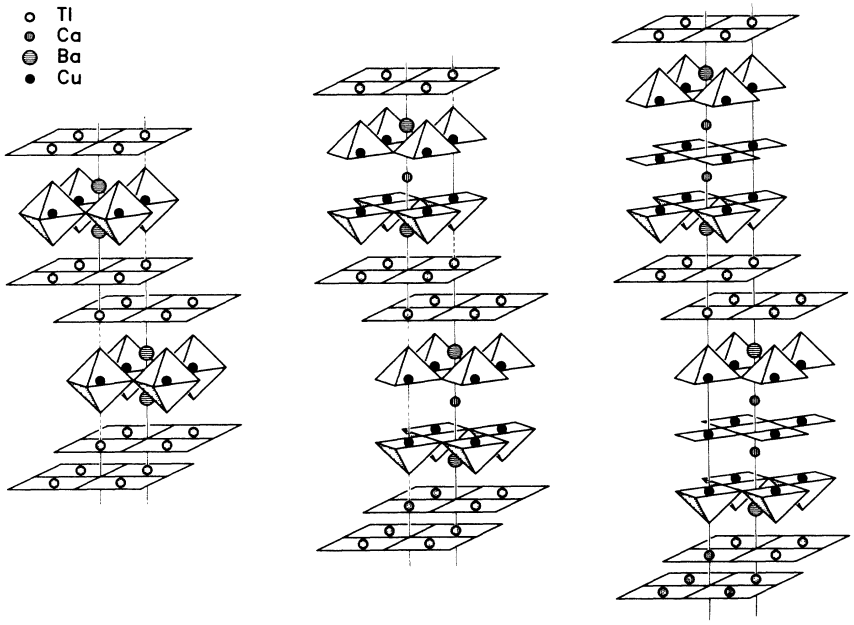

FIG. 1. Crystal structures of $Tl_2Ba_2CuO_6$ (left), $Tl_2Ba_2CaCu_2O_8$ (center), and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (right).

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method, which we used earlier to investigate La_2CuO_4,[10] $YBa_2Cu_3O_7$ (Ref. 11) and related systems,[12,13] as well as $La_2SrCu_2O_6$ and $Bi_2Sr_2CaCu_2O_8$.[14]

CRYSTAL STRUCTURES

The present studies of 2:2:0:1, 2:2:1:2, and 2:2:2:3 Tl-Ba are based on the idealized crystal structures shown in Fig. 1, using the atomic coordinates reported in Ref. 6. For 2:2:0:1 Tl-Ba, the single Cu-O layer is embedded in a distorted, corner-shared CuO_6 octahedra, just as in $(La_{1-x}Sr_x)_2CuO_4$. For 2:2:1:2 Tl-Ba, there are two Cu-O layers formed from the corner-shared square bases of the CuO_5 pyramids, just as in $YBa_2Cu_3O_7$. For 2:2:2:3 Tl-Ba, these two Cu-O layers again appear, plus a third layer which is sandwiched between the first two.

Since the 2:2:3:4 Tl-Ba phase has not yet been isolated, we will assume that its crystal structure is similar to that of 2:2:2:3 Tl-Ba, except that the central CuO_2 layer is replaced by two such layers separated by a plane containing Ca atoms and O vacancies, as shown in Fig. 2. Thus, the x/a and y/a coordinates are the same for all family members. The atomic sites and coordinates for 2:2:0:1, 2:2:1:2, 2:2:2:3, and 2:2:3:4 Tl-Ba are listed in Tables I and II, together with an explanation of our procedure for estimating the lattice constants and atomic parameters of 2:2:3:4 Tl-Ba.

ENERGY-BAND STRUCTURES

The essential features of the calculated band structures for 2:2:0:1, 2:2:1:2, 2:2:2:3, and 2:2:3:4 Tl-Ba are

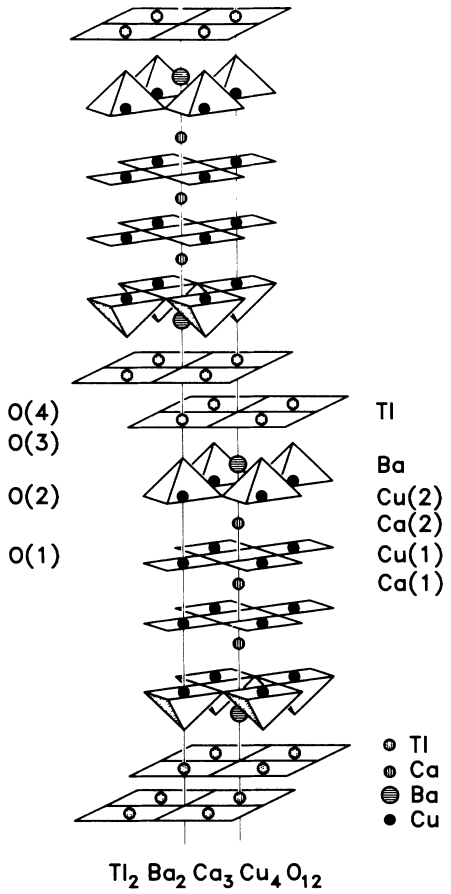

FIG. 2. Crystal structure of $Tl_2Ba_2Ca_3Cu_4O_{12}$. Atomic coordinates are listed in Tables I and II.

TABLE I. Atomic coordinates for Tl-Ba-Ca-O high-T_c superconductors. The atomic sites for 2:2:3:4 are shown at the left using the notation of Fig. 2. Oxygen vacancies are denoted by $O(x)$. All atoms occupying structurally analogous positions are listed in the same row. The coordinates and lattice constants for 2:2:0:1, 2:2:1:2, and 2:2:2:3 are based on Ref. 6. The z coordinates for 2:2:3:4 are estimates (cf. Table II for further details).

Atomic			2:2:0:1		2:2:1:2		2:2:2:3		2:2:3:4	
site	x/a	y/a	z/c	z (Å)	z/c	z (Å)	z/c	z (Å)	z/c	z (Å)
O(4)	0.5	0.5	0.2111	4.906	0.2185	6.406	0.2276	8.166	0.2291	9.608
Tl	0.0	0.0	0.2072	4.709	0.2136	6.262	0.2201	7.897	0.2242	9.405
O(3)	0.0	0.0	0.1168	2.714	0.1461	4.283	0.1588	5.698	0.1752	7.347
Ba	0.5	0.5	0.0830	1.929	0.1218	3.571	0.1448	5.195	0.1593	6.680
Cu(2)	0.0	0.0	0.0	0.0	0.0540	1.583	0.0896	3.215	0.1124	4.715
O(2)	0.5	0.0	0.0	0.0	0.0531	1.557	0.0875	3.140	0.1116	4.681
Ca(2)	0.5	0.5			0.0	0.0	0.0463	1.661	0.0755	3.166
O(x)	0.0	0.0			0.0	0.0	0.0463	1.661	0.0755	3.166
Cu(1)	0.0	0.0					0.0	0.0	0.0362	1.515
O(1)	0.5	0.0					0.0	0.0	0.0362	1.515
Ca(1)	0.5	0.5							0.0	0.0
O(x)	0.0	0.0							0.0	0.0
a (Å)				3.866		3.855		3.850		3.850[a]
$c/4$ (Å)				5.810		7.330		8.970		10.485[b]

[a]Estimated to be the same as for 2:2:2:3 Tl-Ba because of the close structural similarity between 2:2:2:3 Tl-Ba and 2:2:3:4 Tl-Ba.
[b]Average of c for 2:2:2:3 Tl-Ba and the 48-Å repeat period observed for localized inclusions of 2:2:4:5 Tl-Ba in 2:2:2:3 Tl-Ba (cf. Ref. 6).

TABLE II. Distances of atomic sites from plane midway between adjacent Tl-O planes, $c/4$-z, in Å. Entries for 2:2:0:1, 2:2:1:2, and 2:2:2:3 are derived from experimental data in Table I. Entries for 2:2:3:4 are estimates.[a]

Atomic site (2:2:3:4)	2:2:0:1	2:2:1:2	2:2:2:3	2:2:3:4
O(4)	0.904	0.924	0.804	0.877
Tl	1.100	1.068	1.073	1.080
O(3) apex	3.096	3.046	3.272	3.138
Ba	3.881	3.759	3.775	3.805
Cu(2) base	5.810	5.746	5.755	5.770
O(2) base	5.810	5.773	5.831	5.804
Ca(2)		7.330	7.309	7.319
O(x) vacancy		7.330	7.309	7.319
Cu(1)			8.970	8.970
O(1)			8.970	8.970
Ca(1)				10.485
O(x) vacancy				10.485

[a]Distances estimated by taking arithmetic averages of corresponding distances for 2:2:0:1, 2:2:1:2, and 2:2:2:3. Cu(1) and O(1) were assumed to be coplanar, and to be 1.515 Å above the Ca(1)-O(x) plane. For 2:2:4:5 Tl-Ba there would be additional Cu and O sites in a plane 1.515 Å below the Ca(1)-O(x) plane, in accordance with the assumed value of c =48 Å for 2:2:4:5 Tl-Ba (cf. Table I, footnote b).

displayed in Figs. 3 to 6. The reduced zone (for space group $I4/mmm$) is shown as an inset in Fig. 5. Total and partial electronic densities of states (DOS) are listed in Table III for the Tl-Ba compounds and analogous (but hypothetical) Tl-Sr compounds which we studied for comparison purposes.

The most distinctive band-structure feature in Figs. 3 to 6 is the presence of L broad Cu-O conduction bands which cross E_F and define the major segments of the Fermi surface. The bands for 2:2:3:4 Tl-Ba are similar to those for 2:2:2:3 Tl-Ba, except that there are four broad CuO conduction bands rather than three. Each of these broad CuO bands arises from one or another Cu-O layer and has two-dimensional (2D) character, as evidenced by the fact that the dispersion in the k_z direction (e.g., Γ to Z) is nearly flat. Even though each of the Cu-O layers has a different crystallographic environment, the various broad Cu-O bands have nearly the same diameter in the equatorial plane (k_z =0). Some of these bands are degenerate along the symmetry directions shown in these figures, but these degeneracies are removed as one moves away from these symmetry directions, the various bands separating from one another.

Another distinctive feature common to all four Tl-Ba crystals is the presence of narrow Cu-O bands which lie very close to and sometimes slightly overlap E_F. If these bands actually intersect E_F, hole pockets are introduced. In view of the flatness and multiplicity of these narrow bands near their maximum, the hole concentration can become quite large even for a very small overlap.

Still another distinctive and common feature is the presence of two Tl-O bands associated with the two Tl-O layers and adjacent pyramidal apex O atoms. One of these Tl-O bands lies at least 1 eV above E_F throughout the zone, while the other dips down and crosses (or just misses crossing) E_F in the neighborhood of the Γ-Z axis in

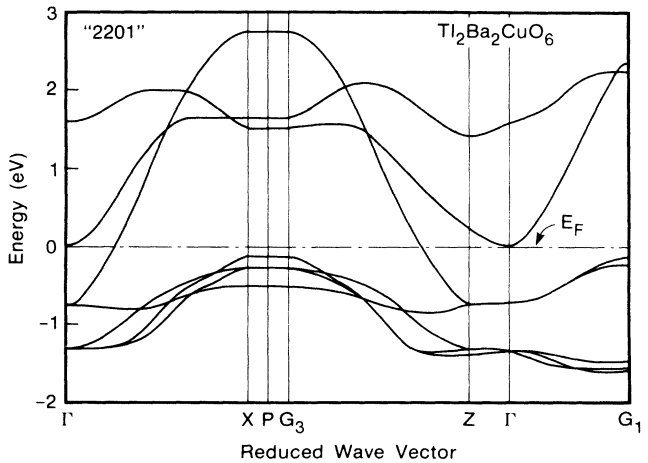

FIG. 3. Energy-band structure of $Tl_2Ba_2CuO_6$ (2:2:0:1).

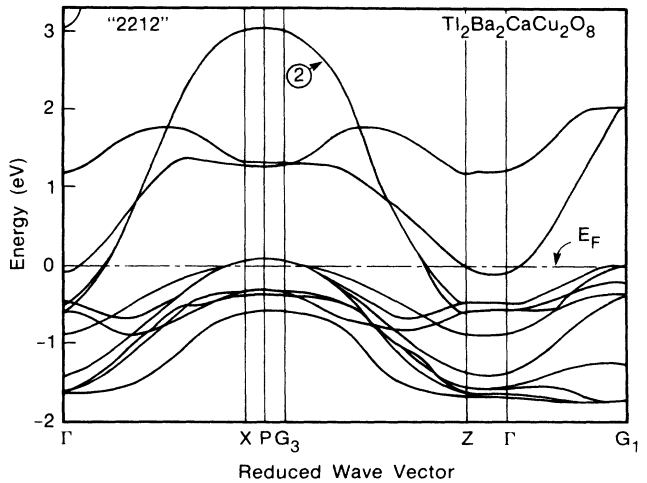

FIG. 4. Energy-band structure of $Tl_2Ba_2CaCu_2O_8$ (2:2:1:2). The circled 2 denotes two degenerate Cu-O bands.

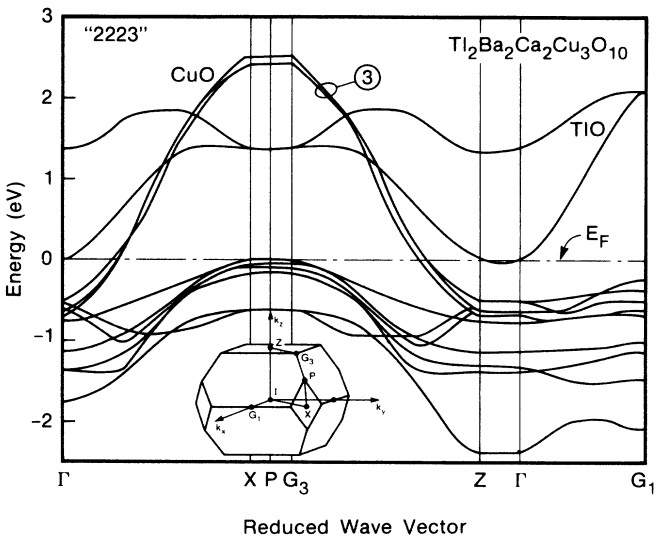

FIG. 5. Energy-band structure of $Tl_2Ba_2Ca_2Cu_3O_8$ (2:2:2:3). The circled 3 identifies the three Cu-O bands. The reduced zone for the body-centered tetragonal structure (space group *I4/mmm*) is shown in the inset.

the reduced zone. If the lower Tl-O band crosses E_F, electron pockets are produced, and the Tl-O layers become metallic. Otherwise, these layers are insulating.

While the broad Cu-O conduction bands are relatively insensitive to small changes in the atomic coordinates, to chemical substitution, and to deviations from ideal stoichiometry, the Cu-O hole pockets and the Tl-O electron pockets are sensitive to all of these factors, as we have found by carrying out various test runs. In actual materials, we would expect the distribution of electrons and holes among the three types of Fermi-surface segments (Tl-O electron pockets, broad Cu-O conduction band, and Cu-O hole pockets) to be sensitive to these factors as well.

As can be seen from Figs. 3 to 6, the sizes of the electron and hole pockets are not monotonic functions of L, that is to say, the relative positions of the band edges and

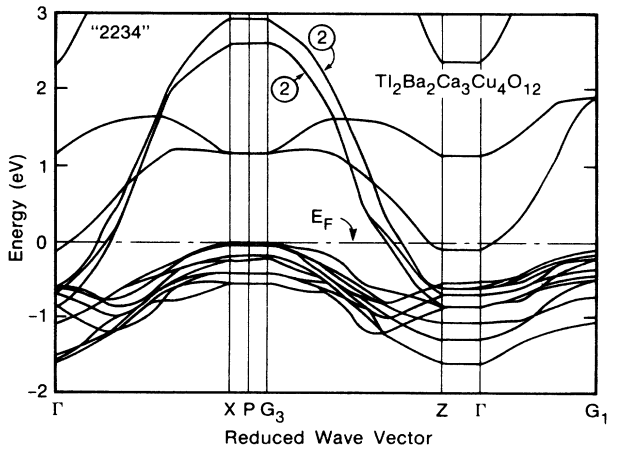

FIG. 6. Energy-band structure of $Tl_2Ba_2Ca_3Cu_4O_{12}$ (2:2:3:4). The circled 2 denotes two degenerate Cu-O bands.

E_F do not vary uniformly with L. This behavior can be traced to the fact that the experimental atomic coordinates[6] are also not monotonic functions of L (cf. Table II). Since the band edges can shift by as much as a few tenths of an eV if the O atoms in the Tl-O planes are shifted from their reported positions by a few tenths of an Å (the experimental uncertainty), the positions of the band edges relative to E_F must be regarded as uncertain to the same extent.

In order to study the effects of chemical substitution in a simple way, we repeated our calculations for the analogous Tl-Sr family. So far as gross features are concerned, the Tl-Sr bands are similar to the Tl-Ba bands near E_F, but corresponding bands become progressively more different above and below E_F, reflecting the fact that even isoelectronic substitutions will affect the valence charge distributions and in turn the band structure. In particular, the relative positions of band edges and E_F change by a few tenths of an eV. These shifts lead to significant changes in the electronic DOS, as can be seen in Table III. Since the highest narrow bands for the Tl-Sr family remain below (or tangent to) E_F, the total and partial DOS at E_F vary more smoothly with L than do their Tl-Ba counterparts. Later, we will exploit this feature and smooth some of our results for 2:2:1:2 Tl-Ba.

By comparing our band structures for 2:2:1:2 Bi-Sr (Ref. 14) and 2:2:1:2 Tl-Ba (cf. Fig. 4), we see that both families have broad Cu-O conduction bands, Cu-O hole pockets, and Tl-O or Bi-O electron pockets in common. However, owing to the fact that the Bi-O bands arise from Bi(6*p*)-O(2*p*) orbitals and the Tl-O bands from Tl(6*s*)-O(2*p*) orbitals, the lowest Bi-O and Tl-O bands dip down and intersect E_F in different regions of the reduced zone. In all cases, however, the Fermi surface is dominated by the broad Cu-O bands, with the Cu-O hole pockets and Bi-O or Tl-O electron pockets contributing relatively small segments to the overall Fermi surface.

BAND STRUCTURES AND SUPERCONDUCTIVITY MECHANISMS

The band structures computed here and in earlier works[10,11,14] are consistent with the plasmon mechanism.[15,16] The necessary requirement for this mechanism is the coexistence of broad and narrow electronic bands intersecting the Fermi surface (light and heavy holes) to facilitate the formation of acoustic plasmons. It is interesting to note that the narrow bands (heavy holes) are absent at the Fermi surface of nonsuperconducting $La_4BaCu_5O_{13}$ (Ref. 12) and $La_2SrCu_2O_6$.[14]

Band structures such as those shown in Figs. 3 to 6 are also of considerable interest to theoreticians exploring exciton,[17] interlayer pairing,[18] and interlayer coupling[19] mechanisms. Apart from the challenge of demonstrating that such mechanisms are operative in these materials, there is now the further challenge of relating T_c to the number of CuO_2 layers within these respective theoretical frameworks. There have also been speculations[20] concerning the relationship between T_c and how metallic the Tl-O or Bi-O interlayers are. However, preliminary calculations[21] dealing with single Tl-O layer high-T_c materi-

TABLE III. Projected and total densities of states at E_F in states per eV per formula unit (both spins). In the upper section, the atomic sites for 2:2:3:4 are listed in the first column, and the number of atoms per primitive unit cell (for $L=1$ to 4) are listed in the next four columns. The remaining columns list the partial DOS at E_F for the various atomic sites, with analogous sites appearing in the same row, and all symmetrically equivalent atoms included for each site. The Tl-Sr-Cu-O columns refer to hypothetical comparison compounds. In the section immediately below the "Total DOS" line, the entries represent the partial DOS at E_F for the various Cu-O planes. In the interest of clarity, we have arranged these entries in the same way that the corresponding planes are arranged in space for the various compounds.

		Partial density of states						
Atomic	Atoms	Ti-Sr-Cu-O			Tl-Ba-Cu-O			
site (2234)	per cell	2:2:0:1	2:2:1:2	2:2:2:3	2:2:0:1	2:2:1:2	2:2:2:3	2:2:3:4
O(4)	2 2 2 2	0.16	0.16	0.17	0.15	0.12	0.16	0.19
Tl	2 2 2 2	0.09	0.09	0.08	0.08	0.16	0.08	0.11
O(3)	2 2 2 2	0.33	0.35	0.40	0.30	0.46	0.39	0.42
Sr or Ba	2 2 2 2	0.05	0.03	0.02	0.04	0.02	0.01	0.02
Cu(2)	1 2 2 2	1.69	1.96	1.30	1.45	2.60	0.72	2.49
O(2)	2 4 4 4	2.62	4.58	3.85	2.11	4.63	3.40	4.60
Ca(2)	0 1 2 2		0.05	0.09		0.06	0.08	0.08
Cu(1)	0 0 1 2			0.57			0.52	1.20
O(1)	0 0 2 4			2.39			2.30	3.51
Ca(1)	0 0 0 1							0.06
Total DOS		4.94	7.22	8.87	4.13	8.05	7.67	12.68
Partial DOS								
Top or bottom Cu-O plane for 2:2:3:4								3.55
Top or bottom Cu-O plane for 2:2:2:3				2.58			2.06	
Top or bottom Cu-O plane for 2:2:1:2; intermediate Cu-O plane for 2:2:3:4			3.27			3.61		2.35
Central Cu-O plane for 2:2:0:1 and 2:2:2:3		4.31		2.96	3.56		2.82	
Top or bottom Cu-O plane for 2:2:1:2; intermediate Cu-O plane for 2:2:3:4			3.27			3.61		2.35
Top or bottom Cu-O plane for 2:2:2:3				2.58			2.06	
Top or bottom Cu-O plane for 2:2:3:4								3.55
All Cu-O bands		4.31	6.54	8.12	3.56	7.23	6.94	11.80
Narrow Cu-O bands removed						5.66		
Broad Cu-O bands only (extrapolation or scaling)								7.94

als[4,5] suggest that in such materials the Tl-O layer is insulating, so that metallic interlayers may be irrelevant to high-T_c superconductivity. In any event, we hope that the detailed information presented in Table III will prove useful to theoreticians concerned with multilayer high-T_c mechanisms.[22]

SUPERCONDUCTING TRANSITION TEMPERATURES, ELECTRONIC DENSITIES OF STATES, AND NUMBER OF CuO_2 LAYERS

It is an empirical fact that in optimized materials T_c becomes larger as L, the number of CuO_2 layers, becomes larger. The two best known and most widely studied examples are $(La_{1-x}Sr_x)_2CuO_4$, for which $L=1$ and $T_c=40$ K,[10] and $YBa_2Cu_3O_7$, for which $L=2$ and $T_c=95$ K.[11] (We will take the point of view that the CuO_2 planes, rather than the CuO_3 chains, are the seat of high T_c in $YBa_2Cu_3O_7$.) Combining this information with that already given for the Bi-Sr and Tl-Ba families at the outset of this paper, it seems likely that there is a causal connection between T_c and the number of CuO_2 layers, as we suggested earlier.[14]

The most obvious connecting link between T_c and the number of CuO_2 layers is the total DOS, $N(E_F)$, or more precisely, the partial DOS of the CuO_2 layers, $N_{CuO}(E_F)$, since these layers are now generally believed to play the central role in high-T_c superconductivity. Earlier band-structure calculations for $YBa_2Cu_3O_x$, $x=6$, 7, and 8,[11] more recent studies of the Bi-Sr family,[14] and the present studies of the Tl-Sr and Tl-Ba families (cf. Table III) all indicate that $N(E_F)$ and $N_{CuO}(E_F)$ increase progressively as L increases. The reason is simply that each additional CuO_2 layer introduces another broad CuO band which crosses E_F, enlarging the size of the Fermi surface.[14]

Before pursuing this idea further, it is important to bear in mind that the occurrence of high T_c depends on many

factors other than the mere existence of CuO_2 layers. For example, pure La_2CuO_4 and $YBa_2Cu_3O_6$ are nonsuperconducing antiferromagnetic insulators[23] which become high-T_c superconductors only after being suitably doped or heat treated. Another case in point is metallic $La_2SrCu_2O_6$,[12] whose normal electronic, magnetic, and structural properties are very similar to those of known high-T_c superconductors, but is itself not superconducting above 5 K.[24]

As long as we calculate band structures within a nonspin-polarized framework, we will necessarily obtain metallic solutions instead of antiferromagnetic insulator solutions in crucial cases, such as pure La_2CuO_4. There have been several recent attempts to obtain antiferromagnetic insulator solutions using the local-spin-density-functional approximation, but so far these have not yielded such solutions, presumably because of shortcomings in this approximation.[25] Further improvements in numerical methods and underlying physical approximations are expected to remove this difficulty, so that we should soon be able to distinguish between metals and antiferromagnetic insulators within the framework of one-electron theory. Even so, we still have to contend with strongly correlated electron systems and Mott-Hubbard as well as antiferromagnetic insulators.[26]

SIMPLIFIED THEORETICAL MODEL

In the absence of a fundamental theory of high-T_c superconductors, it is instructive to construct a simple heuristic model that relates T_c to L using $N_{CuO}(E_F)$ as the connecting physical link. With this in mind we introduce the BCS expression

$$T_c = 1.13\hbar\omega \exp[-1/N_{CuO}(E_F)V] ,$$

where the energy $\hbar\omega$ and interaction strength V are taken to be the same for all layers for all values of L. This expression occurs in many theories based on an electron pairing mechanism.[26] We will assume that the pairing takes place in the CuO_2 planes, and that the pairs populate primarily the broad CuO_2 bands. Accordingly, we will ignore the contributions to the total $N(E_F)$ from the narrow Cu-O bands (hole pockets) and the Tl-O bands (electron pockets).

It would be of great interest to develop a multiband model for overlapping, nearly degenerate bands following the examples of Suhl, Matthias, and Walker,[27] and Lee and Ihm,[28] who treated two dissimilar overlapping bands. In fact, the general theory for an arbitrary number of overlapping bands has already been outlined by Suhl *et al.*[27] At the present stage, such theories would be based on a large number of interband and intraband parameters, and would not be particularly instructive since possible enhancements of T_c would depend on these unknown parameters. It is expedient, therefore, to assume the most optimistic outcome of such a theory, and simply use the sum of the $N_{CuO}(E_F)$ for the various CuO_2 layers as the relevant electronic density of states in the BCS expression.[14,21]

We will proceed on the assumption that our analysis will apply only to metallic systems, and that electron correlation effects will affect the electronic structure of metallic members of the Tl-Ba family in a similar fashion, so that the actual DOS at E_F will change from member to member in the same way that the band DOS changes. As long as our objective is to study systematic trends, we can regard the band DOS as indicators of these trends. If, for example, the ratio of the actual and band DOS has the common value S for all metallic family members, then we can use the BCS expression as it stands, with the understanding that the actual DOS is $N_{CuO}(E_F)S$ and the actual interaction strength is V/S.

REMOVAL OF NARROW Cu-O BAND CONTRIBUTIONS

In order to proceed, we must extract the total $N_{CuO}(E_F)$ arising from the broad CuO bands. For all the Tl-Sr and Tl-Ba compounds studied, except 2:2:1:2 Tl-Ba, the narrow Cu-O bands make a negligible contribution to the partial DOS for the Cu and O atoms at E_F. For these compounds, there is no ambiguity, and we can obtain the $N_{CuO}(E_F)$ for the broad CuO bands directly from the partial atomic DOS, as indicated in Table III. In the case of 2:2:1:2 Tl-Ba, the highest narrow Cu-O bands intersect E_F, as can be seen in Fig. 4, so that the partial atomic DOS include contributions from both the broad and narrow Cu-O bands. By comparing the partial and total DOS for 2:2:1:2 Tl-Sr and 2:2:1:2 Tl-Ba, and interpolating between adjacent family members, we can estimate the narrow Cu-O band contributions and subtract these for 2:2:1:2 Tl-Ba. Nearly identical results can be obtained by using simple scaling arguments.[29] Accordingly, for 2:2:1:2 Tl-Ba, we replace the broad plus narrow Cu-O band value of $N_{CuO}(E_F)$, 7.23, by the broad Cu-O band only value of 5.66.

If we begin with 2:2:0:1, 2:2:1:2, and 2:2:2:3 Tl-Ba and extrapolate to 2:2:3:4 Tl-Ba, or use scaling arguments, we obtain a value of 7.94 for $N_{CuO}(E_F)$, which is considerably smaller than the directly calculated value of 11.80. If we examine the contributions from the individual planes in either the Tl-Sr or Tl-Ba families, we see that these contributions are different from layer to layer and from crystal to crystal, though they exhibit distinct patterns (cf. Table III). The only entry that does not fit the general pattern is that for the outermost plane in 2:2:3:4 Tl-Ba, which is 3.55 rather than smaller values such as 1.3 to 1.6, as would be given by extrapolation or scaling. As can be seen from Table II, the uncertainties in our estimates of the atomic coordinates for 2:2:3:4 Tl-Ba are not sufficiently large to account for this entry being two to three times larger than expected. Accordingly, we believe that this anomalously large entry is correct, though unexpected.

PREDICTION OF T_c FOR 2:2:0:1 Tl-Ba AND 2:2:3:4 Tl-Ba

Let us now determine the BCS parameters $\hbar\omega$ and V by fitting the BCS expression to the two most reliable experimental values for T_c for the Tl-Ba system:[4,5] $T_c = 108$

K for 2:2:1:2 and $T_c = 125$ K for 2:2:2:3. This fit yields $\hbar\omega = 211$ K and $V = 0.22$ eV, comparable to the values $\hbar\omega = 298$ K and $V = 0.134$ eV obtained earlier for the Bi-Sr system.[14,30] If 2:2:0:1 Tl-Ba were metallic and superconducting, our model would predict that $T_c = 68$ K. The best available experimental evidence from Parkin and coworkers[4,5] is that 2:2:0:1 Tl-Ba is an insulator rather than a superconductor ($T_c = 0$ K), or at best a superconductor with $T_c < 4.2$ K. On the other hand, the best available evidence from Ref. 6 is that $T_c = 85$ K for this material.

It remains to be seen whether suitable doping or processing will render an otherwise pure phase of 2:2:0:1 Tl-Ba superconducting and whether its optimized value of T_c will be close to our predicted value of 68 K. Of course, two experimental values of T_c are required to determine the two BCS parameters, so the predictive power of the present model remains to be tested. The situation is the same for the double Bi-O layer Bi-Sr-Cu-O (Ref. 14) and the single Tl-O layer Tl-Ba-Cu-O (Ref. 21) systems.

Turning to 2:2:3:4 Tl-Ba, we will treat the estimate for $N_{CuO}(E_F)$ obtained by extrapolation or scaling as a lower limit, and that obtained by direct calculation as an upper limit. This leads to 136 K as the lower limit for T_c and 163 K as the upper limit. If 2:2:3:4 Tl-Ba could be isolated as a single phase, if its crystal structure is that shown in Fig. 2, and if it is metallic, our best estimate for T_c is 150 ± 15 K.

We do not know of any direct observations of 2:2:3:4 Tl-Ba though 2:2:4:5 Tl-Ba has been observed[6] as isolated inclusions in 2:2:2:3 Tl-Ba. Even though 2:2:3:4 and 2:2:4:5 Tl-Ba apparently can be generated locally as edge dislocations, with one or two extra CuO_2 layers inserted next to the central CuO_2 layer in 2:2:2:3 Tl-Ba, it is conceivable that these and still higher family members would not be stable as separate phases having such crystal structures.

Of course, 2:2:3:4 Tl-Ba (and higher family members) might exist in crystal forms other than that imagined here. Four CuO_2 layers per primitive unit cell could be formed by adjoining the perovskite structures of 2:2:0:1 and 2:2:2:3, or doubling the perovskite structure of 2:2:1:2. In view of the significant difference between the extrapolated and directly calculated values for $N_{CuO}(E_F)$ for 2:2:3:4 Tl-Ba, it is difficult to estimate what T_c would be for these alternate structures without carrying out detailed calculations. We would be greatly surprised, however, if T_c for such alternate four-layer structures would fall outside the range 135 to 165 K, since we believe that our earlier estimate for $L = 4$ would also apply to these alternate four CuO_2 layers structures.

Concerning T_c for still higher family members, we see from the present study that extrapolation and/or scaling lead to estimates that already diverge from first-principle estimates for 2:2:3:4 Tl-Ba. Accordingly, simplified estimates for T_c for $L \geq 4$ should be treated with caution. The more serious question, of course, is whether prospective higher family members can actually be isolated and stabilized.

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[29]A simple relationship between $N_{CuO}(E_F)$ and L can be derived by assuming that all the broad Cu-O bands have nearly the same size and shape near the Fermi level, as can be verified by comparing Figs. 4 to 6. Then $N_{CuO}(E_F)$ is proportional to L/c, where the band multiplicity L is a measure of the total perimeter of these two-dimensional bands in the equatorial plane of the reduced zone. Here $1/c$ is a measure of their thickness, and c itself is the length of the primitive unit cell. Now let $c(L)=Lc_{CuO}+c_{TlO}$, where c_{CuO}, the thickness of a CuO_2 layer, is defined by $c(L)-c(L-1)$, and c_{TlO} is the thickness of TlO portion of the primitive unit cell. Then $N_{CuO}(E_F)$ is proportional to $(Lc_{CuO})/(Lc_{CuO}+c_{TlO})$. This simple derivation leads to the same relationship between $N(E)$ and L as that obtained earlier by P. M. Grant [Brazilian J. Phys. (to be published)] using more lengthy arguments. Thus, the density of states at the Fermi level is proportional to the fraction of the unit cell that contains the CuO_2 layers, and this fraction saturates as L becomes large.
[30]In the absence of a fundamental theory of high-temperature superconductivity, these values for $\hbar\omega$ and V should be regarded as model parameters, rather than as actual physical pairing and interaction energies.

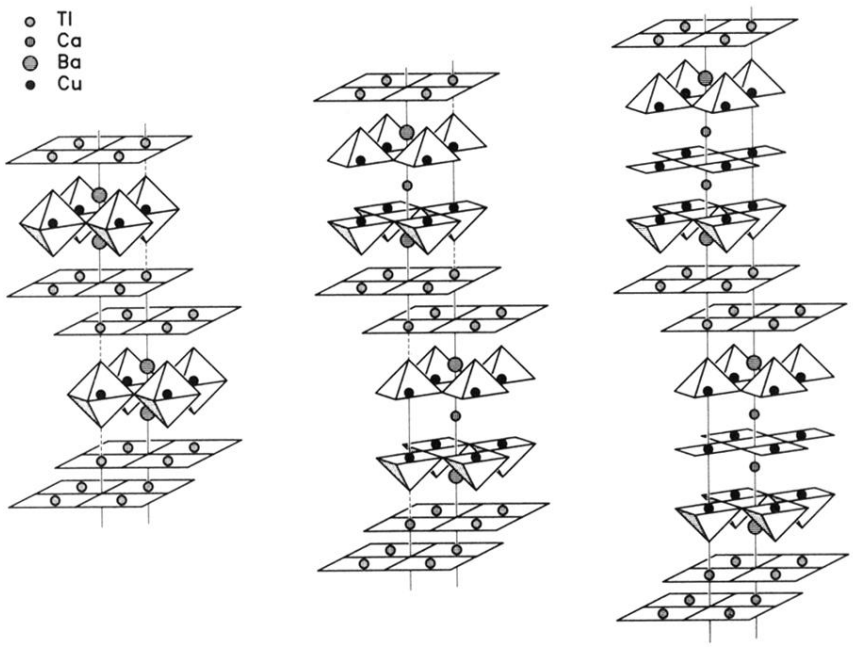

FIG. 1. Crystal structures of $Tl_2Ba_2CuO_6$ (left), $Tl_2Ba_2CaCu_2O_8$ (center), and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (right).

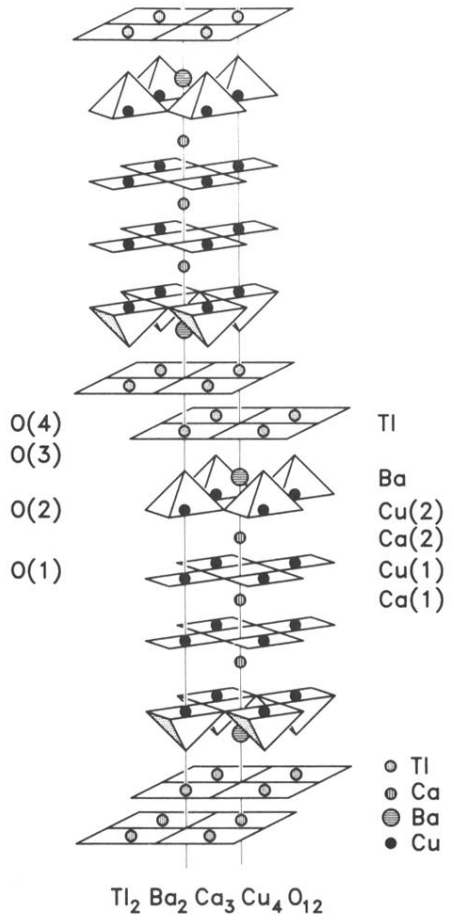

FIG. 2. Crystal structure of $Tl_2Ba_2Ca_3Cu_4O_{12}$. Atomic coordinates are listed in Tables I and II.