Electronic structure of $Bi_2Sr_2CaCu_2O_8$ high-T_c superconductors

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We compare the energy-band structure of the $T_c = 85$ K phase of $Bi_2Sr_2CaCu_2O_8$ with that of nonsuperconducting $La_2SrCu_2O_6$, which has an analogous double-perovskite structure but lacks the Bi-O intergrowths. We also compare the band structures of two alternate $Bi_2Sr_2CaCu_2O_8$ crystal structures to illustrate the consequences of rearranging the O atoms in the Bi-O intergrowth region. Finally, we discuss the effects of Bi-O intergrowths, modulated Bi-O layers, and changes in the number of CuO_2 layers on the band structure and on superconductivity.

The recent discovery by several groups[1-6] of a new family of high-T_c superconductors involving interleaved perovskite and Bi-O layers has prompted us to investigate the electronic structure of representative family members. Our studies are based on the first-principles pseudofunction method, which we used earlier to investigate La_2CuO_4 (Ref. 7) and $YBa_2Cu_3O_7$ (Ref. 8). In the present work, we are particularly interested in new electronic features introduced by the Bi-O intergrowths and their possible role in superconductivity.

Several independent reports[2-6] suggest that there is an 85-K phase of $Bi_2Sr_2CaCu_2O_8$, characterized by alternating double-perovskite layers and double Bi-O "rocksalt" planes. The actual crystal structure is complex and not yet fully understood. X-ray-diffraction measurements[5,6] suggest the simplified crystal structure shown in Fig. 1. We will call this form I. We will adopt the atomic coordinates reported by Tarascon *et al.*[5] except that we will use an occupancy-averaged Bi position, as indicated in Table I, rather than their two partially occupied Bi positions. (The coordinates of Sunshine *et al.*[6] are similar to those in Table I and lead to nearly the same band structure, as we have verified.) The crystal structure is body-centered tetragonal, space group $I4/mmm$.

Before embarking on a study of $Bi_2Sr_2CaCu_2O_8$, it is instructive to consider a simpler and closely related structure, $La_2SrCu_2O_6$,[9,10] which can be derived from $Bi_2Sr_2CaCu_2O_8$ by removing the Bi-O planes, replacing Sr atoms by La atoms and Ca atoms by Sr atoms, and finally closing up the structure vertically so that pyramidal O apex atoms are adjacent to La atoms. It is noteworthy that $La_2SrCu_2O_6$ itself does not appear to be a high-temperature superconductor,[10] while this structure plus the Bi-O intergrowth is. For future reference, we show the reduced zone common to $La_2SrCu_2O_6$ and $Bi_2Sr_2CaCu_2O_8$ in Fig. 2.

In Fig. 3 we show our calculated band structure for $La_2SrCu_2O_6$ based on Nguyen *et al.*'s atomic coordinates.[9] The most significant features are the two broad (nearly degenerate) conduction bands arising from the two two-dimensional (2D) Cu–O networks in the primitive unit cell, and the narrow valence bands arising from the same networks. We do not place great store in the fact that the narrow bands fail to cross E_F, since the atomic coordinates of Nguyen *et al.* are relatively crude, and subsequent refinements could lead to slight shifts in

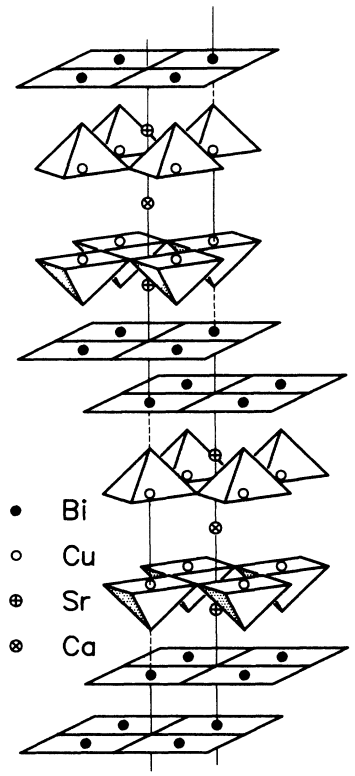

FIG. 1. Idealized crystal structure of $Bi_2Sr_2CaCu_2O_8$ (form I), based on Tarascon *et al.* (Ref. 5) and Sunshine *et al.* (Ref. 6).

TABLE I. Atomic coordinates and projected and total densities of states (DOS) at E_F for $Bi_2Sr_2CaCu_2O_8$. Coordinates for forms I and II are given in units of $a=b=3.814$ Å and $c=30.52$ Å. The z coordinate is also given in Å. The occupancy-averaged Bi position, ⟨Bi⟩, is used in place of the two partially occupied positions reported in Ref. 5. DOS units are states per eV per formula unit (both spins). All symmetrically equivalent atoms are included in each DOS entry.

Atomic site	x/a	y/b	z/c	z (Å)	DOS I	DOS II
O(3) (form II)	0.5	0.0	0.2500	7.630		0.436
O(3) (form I)	0.5	0.5	0.2050	6.257	0.091	
Bi (occ.=0.13)	0.0	0.0	0.2319	7.078		
⟨Bi⟩	0.0	0.0	0.2022	6.172	0.228	0.767
Bi(occ.=0.87)	0.0	0.0	0.1978	6.037		
O(2) (apex)	0.0	0.0	0.1250	3.815	0.258	0.252
Sr	0.5	0.5	0.1097	3.348	0.042	0.046
Cu	0.0	0.0	0.0544	1.660	1.147	1.380
O(1) (base)	0.5	0.0	0.0540	1.648	4.265	4.834
Ca	0.5	0.5	0.0	0.0	0.031	0.035
O(x) (vacancy)	0.0	0.0	0.0	0.0		
Each Cu–O layer					2.706	3.107
Total DOS					6.065	7.750

the band structure with some of these narrow bands rising slightly above E_F.

Coming now to our main subject, we show the band structure of form I of $Bi_2Sr_2CaCu_2O_8$ in Fig. 4. The Bi 6s bands lie very deep, roughly 13 eV below E_F, while the Bi 6p bands lie a few eV above E_F. The Bi electronic structure found here generally resembles that found earlier[11] for bismuth ruthenate ($Bi_2Ru_2O_7$), a pyrochlore material closely related to the perovskites. Comparing Figs. 3 and 4, we can clearly distinguish the broad and narrow Cu(3d)-O(2p) bands, which occur in both structures, as well as the additional conduction bands in Fig. 4 arising from the Bi-O layers. Most of these lie at higher energies, between 1 and 4 eV above E_F. In Fig. 4, only one of the two lowest Bi-O conduction bands actually crosses E_F, creating an electron pocket. There is also a hole pocket produced by the intersection of the highest narrow Cu-O bands with E_F.

In Figs. 3 and 4, the two broad Cu(3d)-O(2p) bands cross E_F between Γ and X and between Z and G_3.[12] These two bands are nearly degenerate and lie so close together that they appear as one band over most of their range. Since they cross E_F well inside the reduced zone, their Fermi surfaces will be considerably larger than those for the Bi-O bands, for which the intersection occurs near the G_1 face point. We wish to emphasize that there is often considerable hybridization between Bi 6p, Cu 3d, and the various types of O 2p orbitals, so that in some energy ranges the bands are not strictly Bi-O or Cu-O, but admixtures.

In order to study the sensitivity of the band structure to the location of the O atoms in the Bi-O region, we decided to investigate an alternate crystal structure, form II, which differs from form I only in the arrangement of O(3) atoms. In form II, the Bi_2O_2 region has the same puckered structure as is known to exist in bismuth titanates.[1,13] In contrast to these titanates, where the Bi atoms act as

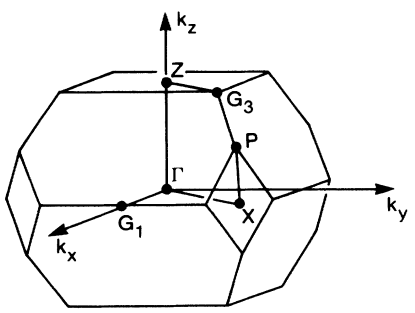

FIG. 2. Reduced zone for body-centered tetragonal structure.

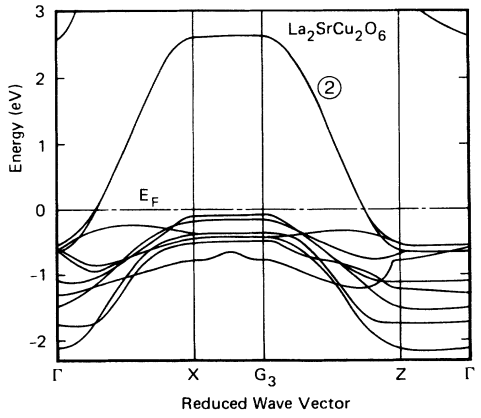

FIG. 3. Energy band structure of $La_2SrCu_2O_6$. The circled 2 denotes two degenerate bands.

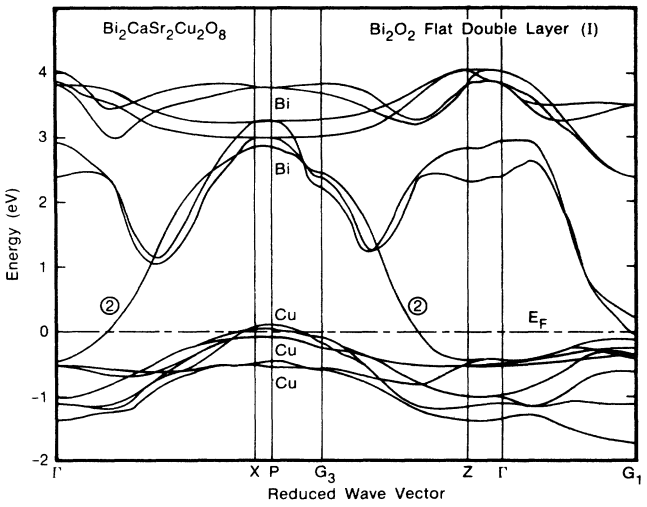

FIG. 4. Energy band structure of $Bi_2Sr_2CaCu_2O_8$ (form I). The circled 2 denotes two degenerate bands.

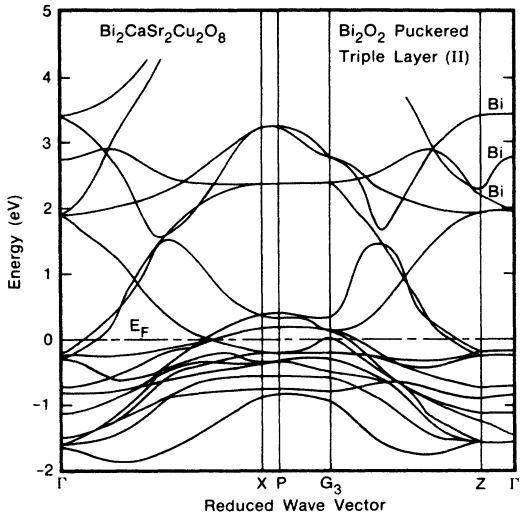

FIG. 6. Energy band structure of $Bi_2Sr_2CaCu_2O_8$ (form II).

substitutes for adjacent perovskite cations, the Bi atoms in form II lie above O(2), the perovskite apex atoms, as illustrated in Fig. 5, and the O(3) atoms lie above the basal O(1) atoms. As can be seen from Fig. 6, the band structure of form II differs dramatically from that of form I in that many of the Bi-O bands have been lowered considerably in energy, with more of these Bi-O bands intersecting E_F.

Although there is no experimental evidence for the existence of form II as a separate (minority) phase, the positionally and compositionally modulated Bi-rich layers revealed by recent high-resolution electron-diffraction studies[4(c),14] can be regarded as superlattices which alternate between forms I and II.[14] Modulated Bi-O layers will generate modulated band structures whose average is intermediate between those for forms I and II. Since the actual displacement of the O atoms out of the Bi-O planes may not be as extreme as suggested by form II, the average band structure should more nearly resemble that of form I, but with lowered Bi-O bands. In any event, the increased coupling between the Bi-O and Cu-O bands produced by the modulated Bi-rich layers increases the total $N(E_F)$ and more particularly the partial density of states (DOS) for the CuO_2 layers, $N_{CuO}(E_F)$, as shown in Table I. (Possible effects on T_c are discussed in the final paragraph.)

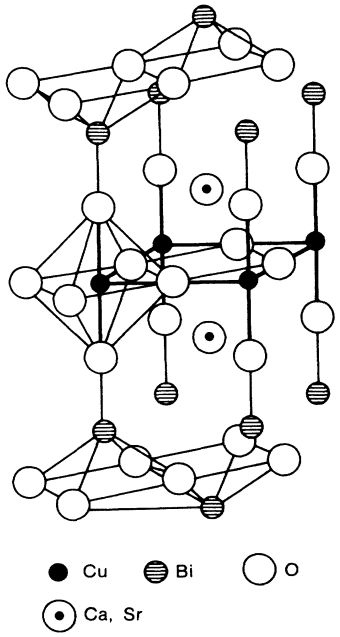

FIG. 5. Crystal structure of hypothetical form of $Bi_2Sr_xCa_{1-x}CuO_6$ illustrating puckered Bi-O structure with Bi atoms lying above perovskite O apex atoms.

It is an empirical fact that T_c in optimized materials becomes larger as L, the number of CuO_2 layers, becomes larger: $T_c = 40$ K for $(La_{1-x}Sr_x)_2CuO_4$ ($L=1$) (Ref. 7); $T_c = 85$–95 K for $Bi_2Sr_2CaCu_2O_8$ (Refs. 4 and 15), and $YBa_2Cu_3O_7$ (Ref. 8) ($L=2$); and $T_c = 110$ K for $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Ref. 15) ($L=3$). Avoiding obvious pitfalls, such as antiferromagnetic insulators (pure La_2CuO_4) and metallic but nonsuperconducting $La_2SrCu_2O_6$,[9,10] it is reasonable to assume that there is a causal connection between T_c and the number of CuO_2 layers. Detailed band calculations for the Bi-Sr-Ca-Cu-O and closely related Ti-Ba-Ca-Cu-O families[16] indicate that $N(E_F)$ increases progressively as L increases, simply because each additional CuO_2 layer introduces another broad CuO band which crosses E_F, enlarging the size of the Fermi surface.

In the absence of a fundamental theory of high-T_c superconductors, it is instructive to construct a simple heuristic model[8] that relates T_c to L using $N_{CuO}(E_F)$, the partial DOS arising from the CuO_2 layers, as the connecting physical link. With this in mind, we introduce the Bardeen-Cooper-Schrieffer (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. For simplicity, let us assume

that all the broad Cu-O bands have nearly the same size and shape near the Fermi level (cf. Fig. 4) so that $N_{CuO}(E_F)$ is proportional to L/C, where their multiplicity L is a measure of the total perimeter of these 2D bands in the equatorial plane of the reduced zone, $1/C$ is a measure of their thickness, and C itself is the length of the primitive unit cell.

To illustrate this model, set $T_c = 85$ K for $L = 2$ and $T = 115$ K for $L = 3$.[15] Using our value for $N_{CuO}(E_F)$ for $L = 2$ from Table I, we obtain $\hbar\omega = 296$ K, $V = 0.134$ eV, $T_c = 38$ K ($L = 1$), 131 K ($L = 4$), and 196 K (L large). Somewhat different results can be obtained using different experimental values for T_c or different ways of relating $N_{CuO}(E_F)$ to L.[17] If one could choose the experimental values of T_c with confidence (avoiding results based on samples containing admixtures of $L = 1$, 2, and 3, etc.), such semiempirical fits could provide useful clues regarding high-T_c mechanisms.

Returning to Table I, and noting that $N_{CuO}(E_F)$ is slightly larger for form II than for form I, similar reasoning based on the BCS model suggests that the increased coupling between the Bi-O and Cu-O bands produced by the modulated Bi-rich layers could increase T_c by as much as 5–10 K. Enhancement of T_c by compositionally and positionally modulated intergrowths is a new feature not previously encountered in high-T_c superconductors.

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[13]See, for example, A. F. Wells, *Structural Inorganic Chemistry,* 3rd ed. (Clarendon, Oxford, 1962), p. 672. Compare Fig. 233 with our Fig. 5.

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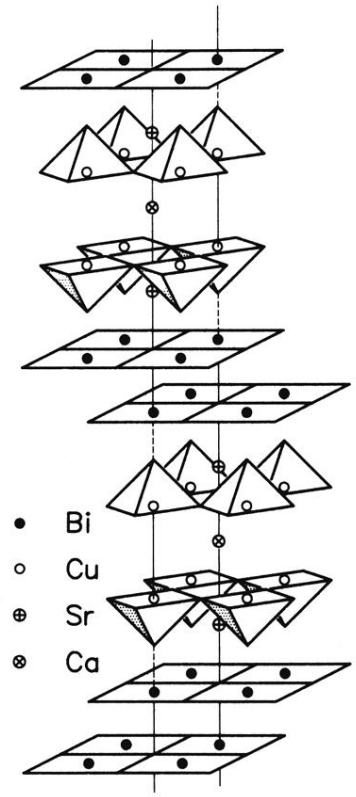

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