Table I. Maximum Absorbance Wavelengths and Corresponding Molar Absorptivities of Neutral and Electrooxidized Fc-(OEP)Ge-Fc in CH_2Cl_2 Containing 0.1 M TBAP

electrode reacn[a]	absorbing species	λ_{max}, nm (ϵ, 10^{-4} cm^{-1} M^{-1})		
none	Fc-(OEP)Ge-Fc	439 (14.1)	569 (0.6)	
1e oxidn	$[Fc-(OEP)Ge-Fc]^+$	435 (8.0)	561 (0.6)	
2e oxidn	$[Fc-(OEP)Ge-Fc]^{2+}$	434 (5.9)	559 (0.9)	
3e oxidn	$[Fc-(OEP)Ge-ClO_4]^+$	408 (6.1)	537 (0.1)	578 (0.04)

[a] See Figure 1.

voltammetric and spectroelectrochemical measurements were carried out at a Pt electrode in dichloromethane (CH_2Cl_2) containing 0.1 M tetrabutylammonium perchlorate (TBAP).

Four reversible oxidations are observed at $E_{1/2}$ = 0.14, 0.32, 1.32, and 1.57 V in CH_2Cl_2 containing 0.1 M TBAP (see Figure 1). The difference between the third and fourth oxidations of Fc-(OEP)Ge-Fc is 0.25 V, which compares to an average separation of 0.29 ± 0.05 V for oxidation of various metalloporphyrins at the porphyrin π ring system.[16] The difference between the first and second oxidation of Fc-(OEP)Ge-Fc is 0.18 V in CH_2Cl_2, and this agrees with separations of 0.17-0.20 V between the two oxidations of $Fc-Si(CH_3)_2-Fc$,[13] Fc-Se-Fc,[2] and $Fc-CH_2-Fc$[2,3] in CH_2Cl_2 or CH_3CN. More importantly, however, the first oxidation of Fc-(OEP)Ge-Fc is shifted negatively by 0.350 V with respect to the Fc/Fc^+ couple in the same solvent. This is the most negatively shifted oxidation of any biferrocene complex and compares to potentials of -0.04 and +0.07 V vs. Fc/Fc^+ for the oxidation of Fc-X-Fc, where X = $Si(CH_3)$[13] and Se,[2] respectively.

Electronic absorption spectra of metalloporphyrins are directly influenced by both the axial ligands bound to the central metal and the charge on the porphyrin ring.[17] The electronic absorption spectrum of Fc-(OEP)Ge-Fc (Figure 2a) is typical of a σ-bonded $(OEP)Ge(R)_2$ complex. This spectrum is virtually identical with that of C_6H_5-(OEP)Ge-C_6H_5 (Figure 2b) but differs from that of C_6H_5-(OEP)Ge-ClO_4 (Figure 2c).

The spectral changes during the first two oxidations of Fc-(OEP)Ge-Fc are shown in Table I and may provide insights into the mechanism of stabilization of singly oxidized Fc-(OEP)Ge-Fc. Apparently, the oxidized ferrocenyl ligand becomes an electron acceptor. This electron-withdrawing effect of the ligand results in a blue shift of the Soret band.[17] The Soret band is further blue-shifted after the second oxidation which generates a second electron-acceptor Fc ligand. Thus, the large decrease in the Soret band intensity after both the first and the second oxidation of Fc-(OEP)Ge-Fc is attributed to a partial delocalization of charge on the a_{1u} and a_{2u} orbitals of the macrocycle. The absorbing species after abstraction of a third electron is assigned as $[Fc-(OEP)Ge-ClO_4]^+$, which results from cleavage of one Ge-Fc bond on the longer spectroelectrochemical time scale (2-5 min). The fourth oxidation is beyond the potential window of CH_2Cl_2, and no spectral changes could be monitored in the thin-layer cell.

In summary, Fc-(OEP)Ge-Fc is the most easily oxidized bridged biferrocene complex studied to date and the first bridged biferrocene complex where delocalization of charge on the bridge can be detected. These effects are attributed to the electron-donating ability of the porphyrin macrocycle which facilitates abstraction of the first and second electron from Fc-(OEP)Ge-Fc. Further stabilization and delocalization of charge on the oxidized species are expected to occur if electron-donating substituents are added to the porphyrin macrocycle, and an evaluation of these data should aid in quantitating the changes in spectra.

Finally, it is also significant to note that Fc-(OEP)Ge-Fc is unusually stable toward light and oxygen. This stability and ease of Fc-(OEP)Ge-Fc oxidation may have interesting properties in terms of the compound's ability to undergo intermolecular photocatalyzed electron-transfer reactions. This application is now under investigation.

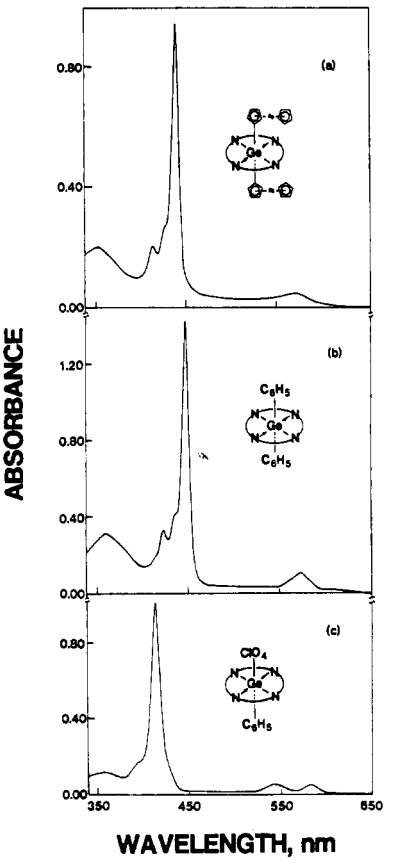

Figure 2. Electronic absorption spectra of (a) Fc-(OEP)Ge-Fc, (b) C_6H_5-(OEP)Ge-C_6H_5 and (c) C_6H_5-(OEP)Ge-ClO_4 in PhCN.

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Differences in the Band Electronic Structures of the Tetragonal and Orthorhombic Phases of the High-Temperature Superconductor $YBa_2Cu_3O_{7-y}$ (T_c > 90 K)

Sir:

Since the first report[1] of ambient-pressure superconductivity above 90 K in a multiphase sample of the Y-Ba-Cu-O system, a number of studies[2-11] have been carried out to identify the

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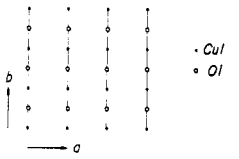
superconducting phase and determine its structure. From several powder neutron diffraction studies,[7-9] it is now known that the Y–Ba–Cu–O phase with the superconducting transition temperature (T_c) greater than 90 K is not tetragonal but orthorhombic, and its composition is $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$).[7] X-ray[10] and neutron powder[11-13] diffraction studies show that above 1023 K orthorhombic $YBa_2Cu_3O_{7-y}$ undergoes a reversible phase transition to tetragonal $YBa_2Cu_3O_{7-y}$ ($y \gtrsim 0.5$),[11] which can be stabilized at low temperatures by fast quenching.[12-14] The resulting tetragonal[10-13] phase appears to exhibit superconductivity at a much lower temperature ($T_c = \sim 50$ K).[10-14] However, it is impossible to state whether or not the tetragonal phase has a ~50 K superconducting transition[10,13,14] and the possibility that this phase is nonsuperconducting cannot be ruled out.[10,14]

The important structural unit of orthorhombic $YBa_2Cu_3O_{7-y}$ is the $Ba_2Cu_3O_{7-y}^{3-}$ slab, which consists of two CuO_2 layers that sandwich one CuO_3 chain and two Ba^{2+} cations per unit cell (e.g., see Figure 1 of our previous paper[15]). In each $Ba_2Cu_3O_{7-y}^{3-}$ slab, the copper atoms (Cu2) of the CuO_2 layers are linked to the copper atoms (Cu1) of the CuO_3 chains via the capping oxygen atoms (O4), thereby forming Cu2–O4–Cu1–O4–Cu2 bridges perpendicular to the slab. The Y^{3+} cations are sandwiched by the $Ba_2Cu_3O_{7-y}^{3-}$ slabs, so that $Ba_2Cu_3O_{7-y}^{3-}$ slabs and layers of Y^{3+} cations alternate along the c axis.

In general, the structure of the tetragonal $YBa_2Cu_3O_{7-y}$ phase is very similar to that of the orthorhombic $YBa_2Cu_3O_{7-y}$ phase. The most important structural difference between the two lies in how the oxygen atoms (O1) are distributed in each plane of the Cu1 atoms. As illustrated in **1**, the O1 atoms of the orthorhombic



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phase connect the Cu1 atoms along the b axis and together with the capping oxygen atoms O4 form the CuO_3 chains. The tetragonal phase is characterized by a random distribution (disorder) of the O1 atoms between all the Cu1–Cu1 linkages along the a- and b-axis directions. Thus, no infinite CuO_3 chains exist in the tetragonal phase. In the present work, we examine the electronic structure of tetragonal $YBa_2Cu_3O_{7-y}$ by performing tight-binding band calculations[15,16] on two ordered model structures designed

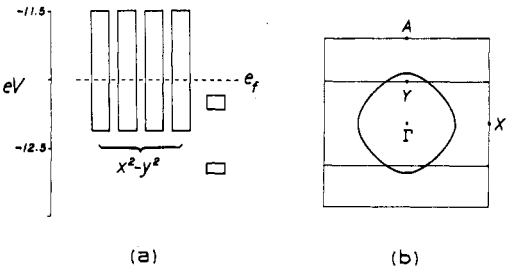


Figure 1. (a) Top six d-block bands calculated for the model **2** of the composition $YBa_2Cu_3O_{6.5}$, where the CuO_2 layer $x^2 - y^2$ bands are each one-fourth filled. (b) Fermi surface associated with each one-fourth-filled $x^2 - y^2$ band, where $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $Y = (0, b^*/2, 0)$, and $A = (0, b^*, 0)$.

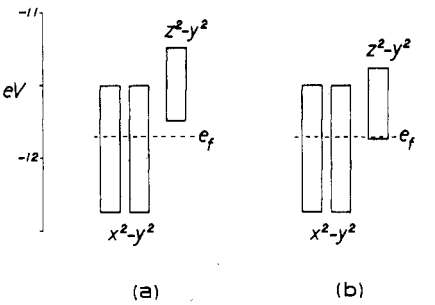
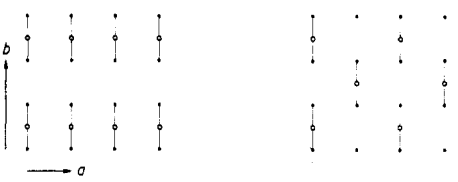


Figure 2. Top three d-block bands calculated for the orthorhombic $YBa_2Cu_3O_7$ phase with the Cu1–O4 distance of (a) 1.850 Å and (b) 1.890 Å. In (a) the CuO_2 layer $x^2 - y^2$ bands are each half-filled, and in (b) they are slightly less than half-filled because the bottom of the CuO_3 chain band is below the Fermi level.

to simulate the tetragonal $YBa_2Cu_3O_{7-y}$ phase and then analyze how the tetragonal and orthorhombic phases differ in their electronic structures.

The single-crystal X-ray diffraction data[6] of the tetragonal phase are found to accommodate any $YBa_2Cu_3O_{7-y}$ composition with a y value from 0 to 1. However, recent powder neutron diffraction results[11] have shown that the orthorhombic to tetragonal phase transition of $YBa_2Cu_3O_{7-y}$ which occurs above 1023 K, is accompanied by the loss of oxygen atoms. Namely, the tetragonal phase is observed when $y \gtrsim 0.5$. It is the O1 atoms that are primarily lost during the orthorhombic to tetragonal phase transition. In the tetragonal phase, the occupation number of the O1 atom sites is close to, but less than, 0.25. Thus, in the present study, we represent the tetragonal $YBa_2Cu_3O_{7-y}$ phases by two ordered structures of composition $YBa_2Cu_3O_{6.5}$ that contain no CuO_3 chains. In **2** and **3** we show two different distributions of



2 3

the O1 atoms for the composition $YBa_2Cu_3O_{6.5}$, in which all the Cu1 atoms are equivalent in coordination number and the average occupation number of the O1 atom site is 0.25. These models do not reflect the symmetry of the tetragonal phase but instead try to model the disorder which occurs in that system with ordered supercells. We believe that although these structural models may not exactly reproduce the true shape of the bands associated with the Cu1 atoms, the resultant band widths and band energies will closely reflect those for tetragonal $YBa_2Cu_3O_{7-y}$. It should also be noted that the reported Cu1–O4 distance is slightly shorter

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in the tetragonal phase than in the orthorhombic phase (i.e., 1.829 (11)[12] and 1.795 (2) Å[13] in the former phase and 1.850 (3) Å in the latter phase[7] at room temperature).

Shown schematically in Figure 1a are the top six d-block bands calculated for the model **2** with the Cu1–O4 distance of 1.750 Å,[17] which consist of two narrow d-block bands derived from the Cu1, O1, and O4 atoms and the four wide $x^2 - y^2$ bands derived from the CuO_2 layers. The two Cu1 d-block bands are completely filled, and the four CuO_2 layer $x^2 - y^2$ bands are each one-fourth filled. Therefore, each of the $x^2 - y^2$ bands leads to a closed Fermi surface as shown in Figure 1b. When the Cu1–O4 distance is increased beyond 1.750 Å, the two Cu1 d-block bands are lowered in energy while the CuO_2 layer $x^2 - y^2$ bands remain fixed in energy. Even for the short Cu1–O4 distance of 1.750 Å, the upper Cu1 d-block band is still below the Fermi level by 0.12 eV. Therefore, in tetragonal $YBa_2Cu_3O_{7-y}$ in which the equilibrium Cu1–O4 distance would be close to 1.80 Å at room temperature, any lattice vibrational modes involving the displacements of the O4 atoms are not expected to raise the Cu1 d-block levels above the Fermi level. Our calculations on the model **3** lead essentially to the same results as described above.

Shown in Figure 2a are the top three d-block bands of orthorhombic $YBa_2Cu_3O_7$ (i.e., a stoichiometric model chosen to represent orthorhombic $YBa_2Cu_3O_{7-y}$) calculated for its equilibrium structure.[15] The two $x^2 - y^2$ bands of the CuO_2 layers are each half-filled, and the $z^2 - y^2$ band of the CuO_3 chains is empty. It is clear from Figures 1a and 2a that, in the tetragonal phase $YBa_2Cu_3O_{7-y}$ ($y \gtrsim 0.5$),[11] the low average coordination number of the Cu1 atoms causes all the d-block levels of the Cu1 atoms to lie either below or near the bottom portion of the CuO_2 layer $x^2 - y^2$ band. In contrast, the orthorhombic phase $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$)[7] has one d-block level of each Cu1 atom (i.e., the $z^2 - y^2$ level that forms the $z^2 - y^2$ band of the CuO_3 chains) lying near the top portion of the CuO_2 layer $x^2 - y^2$ band. Consequently, compared with the case for the orthorhombic phases, the tetragonal phase has fewer electrons to fill its $x^2 - y^2$ bands. Thus, each CuO_2 layer $x^2 - y^2$ band is one-forth filled for the model **2** of $YBa_2Cu_3O_{6.5}$ but half-filled for the orthorhombic $YBa_2Cu_3O_{7-y}$.[15] In the two-dimensional $x^2 - y^2$ band, the density of states (DOS) peaks at the Fermi level (e_f) for half-filling. Thus, the DOS value at e_f, $n(e_f)$, is substantially smaller for the model **2** of $YBa_2Cu_3O_{6.5}$ than for the orthorhombic $YBa_2Cu_3O_7$ (i.e., 4.44 vs. 8.85 electrons per three copper atoms per eV). It was found[16] for orthorhombic $YBa_2Cu_3O_7$ that a slight increase in the Cu1–O4 distance (e.g., from 1.85 to 1.89 Å) lowers the bottom of the CuO_3 chain $z^2 - y^2$ band slightly below the Fermi level as shown in Figure 2b. Thus, certain lattice vibrational modes involving displacement of the O4 atom could cause valence fluctuations of the copper atoms.[16] Since the DOS profile of the CuO_3 chain $z^2 - y^2$ band peaks at the top and the bottom of the band, the $n(e_f)$ value of orthorhombic $YBa_2Cu_3O_7$ is enhanced greatly as the bottom of the $z^2 - y^2$ band touches the Fermi level, which already occurs near the DOS peak of the CuO_2 layer $x^2 - y^2$ bands.[16] The Ba^{2+} cations may play a vital role in the positioning of the O4 capping oxygen atoms in the $Ba_2Cu_3O_{7-y}^{3-}$ slab and provide a precise spacing between the CuO_3 chains and the CuO_2 layers.

All the special features in the electronic structures of the orthorhombic phase mentioned above arise from the presence of the CuO_3 chains. These special features disappear when the CuO_3 chains are destroyed by partial removal of O1 atoms and random distribution of the remaining O1 atoms in the plane of the Cu1 atoms. Thus, the presence of the CuO_3 chains is essential for the occurrence of high T_c (>90 K) superconductivity in the orthorhombic phase of $YBa_2Cu_3O_{7-y}$.

We have observed[15,16,18] that each $x^2 - y^2$ band of the CuO_2 layers in orthorhombic or tetragonal $YBa_2Cu_3O_{7-y}$ is identical in nature with the $x^2 - y^2$ band of the CuO_4 layers in the superconducting phase $La_{2-x}M_xCuO_4$ (M = Ba, Sr).[19-28] In the latter systems, the T_c value ranges from ~30 to ~40 K for $x \simeq 0.15$. In $La_{2-x}M_xCuO_4$, the occupancy of the $x^2 - y^2$ band is given by $(1 - x)/2$. It has been observed[19,20] that the T_c value of $La_{2-x}M_xCuO_4$ sharply drops when $x \gtrsim 0.2$.[20] Therefore, it appears that the high T_c superconductivity of $La_{2-x}M_xCuO_4$ almost disappears when the occupancy of its $x^2 - y^2$ band is less than $x \approx 0.4$. According to this reasoning, the tetragonal $YBa_2Cu_3O_{7-y}$ phase is not likely to be expected to be superconducting since its $x^2 - y^2$ bands are each one-fourth filled.

In view of the possibility that there may exist another phase with a higher T_c (>100 K)[29] in the L–Ba–Cu–O system (L = lanthanide), it is important to consider some other possible compositions. The superconducting $Ba_2Cu_3O_7^{3-}$ slab can be thought of as a "single-decker sandwich". An interesting variation of this slab is a multidecker (n-decker) sandwich with n chains and $n + 1$ planes, in which every two adjacent CuO_2 planes sandwich one CuO_3 chain and two Ba^{2+} cations per repeat unit. Such an n-decker sandwich has the formula $[Ba_{2n}Cu_{2n+1}O_{5n+2}]^{(n+2)-}$. Then a crystal obtained by alternating these n-decker sandwiches with layers of lanthanide ions L^{3+} would have the formula $[LBa_{2n}Cu_{2n+1}O_{5n+2}]^{1-n}$. One, therefore, obtains the compositions $LBa_2Cu_3O_7$, $LBa_4Cu_5O_{12}^-$, and $LBa_5Cu_6O_{17}^{2-}$ for $n = 1$, 2, and 3, respectively. Of course, the charges on these n-decker structures may be canceled by an appropriate number of oxygen vacancies. Synthetic efforts toward obtaining such compositions are suggested.[30]

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