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Electronic structure of oxygen-deficient high-T_c superconductors: $YBa_2Cu_3O_x$ ($6 \leq x \leq 8$)

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With a view to understanding the relationship between oxygen stoichiometry, oxygen vacancy ordering, electronic structure, and T_c in the $YBa_2Cu_3O_x$ system, we calculated the electronic structure for $x = 6$, 7, and 8 using the first-principles self-consistent pseudofunction method. All three of these crystals contain O vacancies in the yttrium plane. The two O sites in the basal plane are empty in $YBa_2Cu_3O_6$ and occupied in $YBa_2Cu_3O_8$. Only one of these sites is occupied in $YBa_2Cu_3O_7$ (ordered vacancy model). After discussing the essential features of the band-structure and valence charge distribution for $x = 6$, 7, and 8, we explore the consequences of a simple Bardeen-Cooper-Schrieffer (BCS) model which assumes that T_c depends only on the electronic density of states at the Fermi level $N(E_F)$. Using our calculated values of $N(E_F)$ for $x = 6$, 7, and 8, and a simple interpolation scheme, we obtain estimates for $N(E_F)$ for intermediate values of x and for various degrees of oxygen-vacancy disorder at fixed values of x. We can account for at least half of the observed variation of T_c with oxygen stoichimetry in the range $6.5 < x < 7$ using physically reasonable values of the BCS parameters. We can also account for experimental observations that the greater the degree of oxygen-vacancy ordering at a fixed value of x, the higher the value of T_c. Our analysis also provides estimates for T_c for x between 6 and 6.5, but these estimates would apply to the metallic, rather than the semiconducting phase. Our analysis for x between 7 and 8 suggests that it might be possible to enhance the value of T_c beyond present-day values by preparing samples for which the O content is as large as possible, and for which the O vacancies are ordered to the highest possible degree.

I. INTRODUCTION

The 90–100 K high-T_c superconductors first reported by Chu and his colleagues[1] are now known to be triply layered oxygen-deficient perovskites $YBa_2Cu_3O_x$, with x slightly less than 7.[2-9] Although these materials and the La_2CuO_4-type 30–40 K superconductors originally discovered by Bednorz and Müller[10] have different crystal structures, both of these systems contain dimpled two-dimensional (2D) Cu-O networks. These planar networks are coupled only weakly to one another and to intervening cations which do not appear to be involved directly in the superconducting behavior. For the $YBa_2Cu_3O_x$ system, values of T_c in the range 90–100 K can be obtained by a wide variety of isoelectronic cation substitutions, for example, most rare earths in place of Y.[11,12]

The $YBa_2Cu_3O_x$ system exhibits tetragonal-to-orthorhombic structural phase transitions which are associated with the ordering of O vacancies in the basal plane. These transitions can be induced by changes in the temperature or oxygen stoichiometry. In samples showing the highest values of T_c, the oxygen stoichiometry is slightly less than 7, the crystal structure is orthorhombic, and the O vacancies are ordered, giving rise to one-dimensional (1D) Cu-O chains or ribbons first revealed by neutron scattering experiments.[7-9] These 1D Cu-O networks are only weakly bonded to the adjacent 2D Cu-O networks and neighboring cations.

Since the principal structural difference between the La_2CuO_4-type and the $YBa_2Cu_3O_x$-type superconductors is the presence of the 1D Cu-O networks in the latter, it is widely believed that these 1D networks are responsible for the enhanced values of T_c in the $YBa_2Cu_3O_x$ system. This view is supported by substantial evidence that disruption of the 1D Cu-O ribbons by heat treatment or other means tends to lower T_c or to eliminate superconducting behavior altogether. One interpretation is that the enhancement in T_c is due to additional conductivity channels in the 1D Cu-O ribbons, to band-structure (density of states and dimensional) effects, or to interactions between the 1D and 2D Cu-O networks. Another interpretation is that the 1D networks are primarily responsible for the high values of T_c in $YBa_2Cu_3O_x$-type superconductors, and that the 2D networks play only a secondary role in determining T_c in these materials.

According to the first of these interpretations, one might expect T_c to fall from the 90–100 K to the 30–40 K range as the 1D Cu-O ribbons are disrupted, and as the 2D Cu-O networks take over and function as the superconducting medium, as in the La_2CuO_4-type materials. According to the second interpretation, sufficient disruption of the 1D Cu-O ribbons would quench the superconducting behavior altogether, even though the 2D Cu-O networks remain intact structurally. Here, the 2D Cu-O networks might become deactivated due to their coupling with the disrupted 1D chains.

In order to be able to decide which of these interpretations is more nearly correct, and thereby gain some insight into the underlying superconducting mechanisms in these oxides, it is important to understand the relationships between oxygen stoichiometry, oxygen-vacancy ordering, crystal structure, and superconducting transition temperature, as well as the actual role played by the 1D Cu-O networks. In this paper we will attempt to unravel some of these intertwined threads by investigating the electronic structure of $YBa_2Cu_3O_x$ as a function of oxygen content and vacancy ordering. Our objective is to determine the extent to which band-structure effects, particularly changes in the electronic density of states at the Fermi level $N(E_F)$, might be responsible for the enhancement or degradation of T_c.

II. CRYSTAL STRUCTURE

The crystal structure of orthorhombic $YBa_2Cu_3O_7$ (Refs. 7–9) is shown in Fig. 1. Note that there are two O vacancies in the 15-site unit cell. The one lying in the Cu-O plane between the two Ba-O planes will be denoted by $O(y)$, and the other lying in the yttrium plane will be called $O(z)$. These are denoted by heavy dots in the figure. Since the O atoms in the Ba-O planes [O(4)] lie much closer to Cu(1) than to Cu(2), $YBa_2Cu_3O_7$ contains 2D dimpled Cu-O planes [O(2)-Cu(2)-O(3)] which are only weakly coupled to the O atoms at O(4). If the stoichiometry deviates from seven oxygen atoms per unit cell, or if the O vacancies at O(1) and $O(y)$ become disordered, the ribbons will obviously become disrupted and adjacent ribbons could be coupled to one another by intervening O atoms.

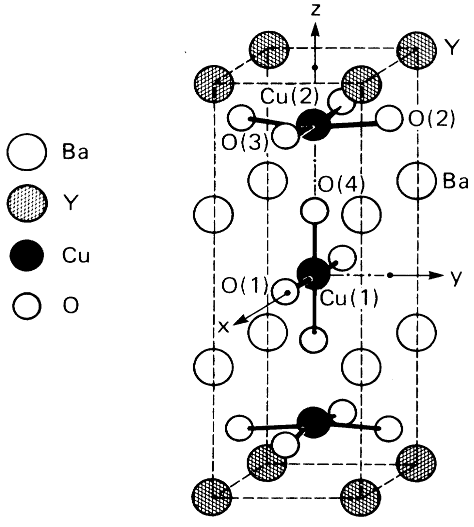

FIG. 1. Crystal structure of orthorhombic $YBa_2Cu_3O_7$ (ordered vacancy model) (Ref. 7). The vacant sites in the Cu(1) and Y planes are denoted by $O(y)$ and $O(z)$, respectively. In $YBa_2Cu_3O_6$, the O(1) site is also vacant. In $YBa_2Cu_3O_8$, the only remaining vacancy is at $O(z)$. See also Table I.

The high-temperature phase (above about 700 °C) is tetragonal because the O vacancies are statistically distributed at the O(1) and $O(y)$ sites. The low-temperature phase (below about 500 °C) is orthorhombic because the vacancies are preferentially ordered along one of the basal axes. This ordering may occur along different directions in different regions, leading to twinning, but this occurs on a scale of 1000 atomic distances and need not concern us here. As the temperature is reduced from about 700 to about 500 °C, the O vacancies gradually order, and the difference between the two basal lattice constants (a and b) becomes progressively larger.[13,14] In the low-temperature phase the orthorhombic distortion is about 2%. Below about 500 °C the vacancies are more or less fully ordered unless rapid quenching or other special processing results in partial ordering, so that samples with a range of orthorhombic distortions can be produced for a given oxygen stoichiometry.

III. RELATIONSHIP BETWEEN T_c AND OXYGEN CONTENT

The values of T_c obtained for $YBa_2Cu_3O_x$ depend sensitively on the method of preparation,[11] and in particular on the oxygen deficiency.[13–15] The highest values of T_c obtained to date correspond to values of x slightly less than seven. For such values of x, the greater the orthorhombic distortion, the higher the value of T_c, and the sharper the superconducting transition becomes.[13] By changing the processing conditions (ambient oxygen atmosphere, quenching, etc.), the oxygen content can be reduced. The dominant effect appears to be removal of O atoms from the chainlike position,[15–18] though there is also some evidence for slight amounts of oxygen removal from the ribbon-edge position as well.[18] The most convincing evidence in favor of chain-link-position removal comes from neutron scattering experiments,[16] which indicate that in the limiting case of $YBa_2Cu_3O_6$, all the O atoms have been removed from the chain-link position, leaving an array of separated O-Cu-O molecules [at upper O(4), Cu(1), and lower O(4) sites].

A reversible structural transformation from orthorhombic to tetragonal occurs as x goes from 7 to 6.[19] Reports differ regarding the sharpness of this transition as a function of oxygen stoichiometry, but there is general agreement that the O-T transition occurs at or near $x=6.5$, where all the Cu ions are nominally Cu^{2+}. There is some evidence that the tetragonal phase (for $x<6.5$) is semiconducting rather than superconducting, but more work remains to be done before it can be stated categorically that $YBa_2Cu_3O_x$ is nonsuperconducting below $x=6.5$.[18–22] In the range of x between 6.5 and 7, T_c rises from low values (possibly as low as 0, possibly as high as 55 K) to 90 K and above. For example, Schuller *et al.*[14] and Tarascon and co-workers[15] have both observed values of T_c in the range 50–55 K for samples with oxygen stoichiometries roughly equal to 6.5. In view of the difficulty of measuring the oxygen stoichiometry accurately, and complications arising from inhomogeneous samples, these results must be regarded as provisional. It would be highly desirable to have accurate experimental measurements of T_c as a function of oxygen stoichiometry in the range 6 to 7.[20–22]

IV. THEORETICAL APPROACH

Since the number and arrangement of the O vacancies apparently play an important role in determining the superconducting properties of $YBa_2Cu_3O_x$, we decided to study the electronic structure of orthorhombic $YBa_2Cu_3O_7$ assuming perfect Cu-O ribbons (ordered vacancies), as well as related structures containing different numbers and arrangements of O vacancies. Since we wish to take full advantage of the powerful band-theoretical computational methods at our disposal, we will carry out detailed calculations only for periodic systems, and then estimate the properties of intermediate nonperiodic systems by interpolation.

Our band-structure calculations of $YBa_2Cu_3O_x$ ($x=6,7,8$) were carried out using the first-principles self-consistent pseudofunction method,[23] which we employed earlier to study orthorhombic La_2CuO_4.[24] For orthorhombic $YBa_2Cu_3O_7$, we used the atomic coordinates obtained by the Brookhaven group using neutron scattering techniques[7] and shown in Table I.

In order to be able to explore the effects of changing the oxygen content, we also investigated the band structures of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_8$, assuming that in the former there are no O atoms at the chain-link position [O(1)], and that in the latter the O(1) and O(y) sites are fully occupied. For simplicity, we assumed that lattice relaxation effects associated with the gain or loss of O atoms at sites O(1) and O(y) can be neglected. Accordingly, in our initial studies we used exactly the same coordinates for these two crystals as we used for orthorhombic $YBa_2Cu_3O_7$. In later studies we also examined the more realistic cases of tetragonal $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_8$ using the same coordinates as before, except that the a and b lattice constants were averaged.

After the present work was completed, we learned that the atomic coordinates of $YBa_2Cu_3O_6$ had just recently been obtained from neutron scattering experiments,[16] and that the experimental coordinates are very close to the ones we used for this crystal. So far as we are aware, $YBa_2Cu_3O_x$ for $x > 7$ has not yet been synthesized in the laboratory, so that for the present $YBa_2Cu_3O_8$ must be regarded as a hypothetical material, but one that can be exploited theoretically, as will be seen below.

Since there is no convincing experimental evidence for the occurrence of O at the O(z) site, we did not consider it worthwhile to explore the consequences of placing O atoms at the site. Similarly, the evidence for depopulation of the O(4) (ribbon-edge) site is considerably weaker than that in favor of the depopulation of the O(1) (chain-link) site, so we ignored the possibility of emptying the O(4) site.

V. ENERGY BAND STRUCTURE $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, AND $YBa_2Cu_3O_8$

Our basis sets include the Cu 4s as well as Y and Ba valence state orbitals. In all cases, however, these orbitals play only a minor role in determining the lower complex of valence and conduction bands, which are determined primarily by the three Cu $3d^5$ orbitals and the six, seven, or eight sets of O $2s^2$, $2p^6$ orbitals. The Cu 4s and Y and Ba orbitals play a major role in determining the higher-lying conduction bands, but these are not of any interest in the present study since they lie well above the Fermi level.

It is convenient to regard the lower complex of bands as being generated only from the Cu 3d and O 2s,2p orbitals. In $YBa_2Cu_3O_6$, this basis set leads to 39 bands of which 38 are (doubly) occupied and 1 is unoccupied. In $YBa_2Cu_3O_7$ we have 41 occupied and 2 unoccupied bands, and in $YBa_2Cu_3O_8$ we have 44 occupied and 3 unoccupied

TABLE I. Atomic coordinates of $YBa_2Cu_3O_7$ in units of a, b, and c. The space group is $Pmmm$ (No. 47). The present work was based on the Cox *et al.* coordinates (Ref. 7). Beno *et al.* coordinates for $YBa_2Cu_3O_7$ (Ref. 8) and Santoro *et al.* coordinates for $YBa_2Cu_3O_6$ (Ref. 16) are also shown for comparison.

Atom	x/a	y/b	z/c[a]	z/c[b]	z/c[c]
			$YBa_2Cu_3O_7$		$YBa_2Cu_3O_6$
Ba	0.50	0.50	0.1839	0.1843	0.1952
Y	0.50	0.50	0.50	0.50	0.50
Cu(1)	0.00	0.00	0.00	0.00	0.00
Cu(2)	0.00	0.00	0.3546	0.3556	0.3607
O(1)	0.50	0.00	0.00	0.00	Vacancy
O(y)	0.00	0.50	0.00	Vacancy	Vacancy
O(2)	0.00	0.50	0.3780	0.3773	0.3791
O(3)	0.50	0.00	0.3783	0.3789	0.3791
O(4)	0.00	0.00	0.1589	0.1584	0.1518
O(z)	0.00	0.00	0.50	Vacancy	Vacancy

[a] Cox *et al.*, Ref. 7 (Brookhaven): $YBa_2Cu_3O_7$: $a=3.817$, $b=3.882$, and $c=11.671$ Å.

[b] Beno *et al.*, Ref. 8 (Argonne): $YBa_2Cu_3O_7$: $a=3.8231$, $b=3.8863$, $c=11.6809$ Å.

[c] Santoro *et al.*, Ref. 16 (National Bureau of Standards and AT&T Bell): $YBa_2Cu_3O_6$: $a=b=3.8570$, $c=11.8194$ Å. These coordinates became available after the present study was completed, and so were not used. The slight differences in atomic positions would not affect the band structure significantly.

bands. This simple discussion shows us just how the numbers of occupied and adjoining unoccupied bands change as the O content increases.

The six highest bands for orthorhombic $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, and $YBa_2Cu_3O_8$, including the highest occupied bands and adjacent unoccupied bands, are shown in Figs. 2–4. The corresponding bands for tetragonal $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_8$ (not shown here) are quite similar to those displayed in Figs. 2 and 4, except that corresponding energy levels at points X and Y are exactly equal to one another. We prefer to display the results for the orthorhombic phases to bring out the small differences in band structure produced by the 2% difference between the lattice constants a and b.

On the other hand, for the ordered vacancy model of $YBa_2Cu_3O_7$, we see from Fig. 3 that the band structure is quite different at points X and Y, demonstrating that the asymmetry of occupancy of sites O(1) (O atom) and O(Y) (O vacancy) produces a band-structure asymmetry that is considerably larger than that produced merely by the 2% difference in a and b. It can also be seen from Fig. 3 that the energy profiles along the line Y-Y' are relatively flat, suggestive of a 1D or 2D band structure. Indeed, many of the bands have the same energy profiles in the upper face of the reduced zone (not shown) as in the basal plane, as expected for 1D bands associated with the Cu-O ribbons and similarly for 2D bands associated with the 2D Cu-O networks.

In $YBa_2Cu_3O_7$, the seven lowest O-2s valence bands lie about 15 eV below E_F, where the zero of energy is placed, and the 36 highest occupied bands span the energy range from -7 to $+2$ eV. Apart from bandwidths, our band-structure results for orthorhombic $YBa_2Cu_3O_7$ agree rather well with those recently reported by Mattheiss and Hamann[25] who used a modified version of Siegrist *et al.* coordinates[5] but a different computational method. The total bandwidth of our Cu 3d–O 2p bands is 7.2 eV, while theirs is only 5.7 eV. Our band-structure results for orthorhombic $YBa_2Cu_3O_7$, including bandwidths, are in general agreement with those recently obtained by Massidda *et al.*[26] using the Beno *et al.* coordinates[8] and still another computational method. However, our energy bands are considerably smoother than those shown in Ref. 26. All three of these calculations for $YBa_2Cu_3O_7$ yield band structures that are roughly similar to one another in the neighborhood of the Fermi level, but there are significant differences in the finer details. Thus, $N(E_F)$, the electronic density of states at the Fermi level, is found to be 9.0, 6.6, and 3.4 states/eV cell in Ref. 25, in our own work, and in Ref. 26, respectively.

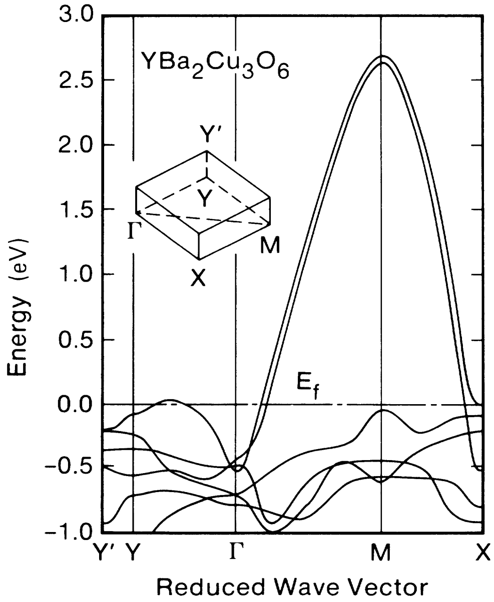

FIG. 2. Energy-band structure of $YBa_2Cu_3O_6$. Only the six highest Cu 3d–O 2p bands are shown.

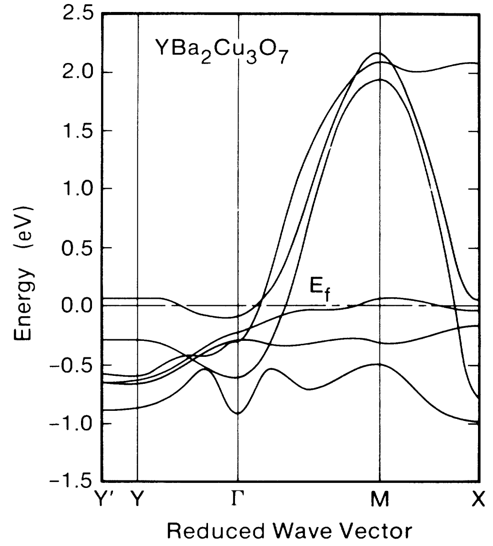

FIG. 3. Energy-band structure of $YBa_2Cu_3O_7$. Only the six highest Cu 3d–O 2p bands are shown.

In the interest of conserving space, we will not duplicate detailed descriptions of the band structure of $YBa_2Cu_3O_7$ since these have already been adequately reported in Refs. 25 and 26. Instead, we will focus on features essential to understanding the changes in band structure arising from changing the O stoichiometry.

Turning to $YBa_2Cu_3O_6$, we see from Fig. 2 that two broad anisotropic bands cross E_F. These bands arise from the two planar Cu-O networks in the unit cell and are formed from antibonding Cu 3d–O 2p orbitals. There are also narrow bands associated with the 2D array of O(4)-Cu(1)-O(4) molecules which is all that is left of the 1D ribbons in $YBa_2Cu_3O_7$. But these narrow bands lie well below E_F and are not of particular interest here.

Some portions of the band structure are expected to have strong 2D character because the O(4)-Cu(1)-O(4) molecular arrays and the O(2)-Cu(2)-O(3) networks have 2D character in real space. Examining the energy bands for $YBa_2Cu_3O_6$ along Y-Y' in Fig. 2, we see that only one of the top four bands is flat, contrary to our expectation for 2D bands. However, this lack of flatness can be attributed to the asymmetry in the a and b coordinates, showing how this small asymmetry can have an important effect on a subtle feature of the band structure such as its 2D character. For tetragonal $YBa_2Cu_3O_6$, the four highest bands along Y-Y' are nearly flat.

In $YBa_2Cu_3O_7$, we see from Fig. 3 that three broad anisotropic bands cross E_F. Two of these correspond to the two planar Cu-O networks, and the third to the 1D ribbons. All of these bands arise from antibonding Cu 3*d*–O 2*p* orbitals. There are also narrow bands arising from nonbonding Cu 3*d*–O 2*p* orbitals, and one of these also crosses E_F. In fact, the position of E_F is partially stabilized by the presence of this top-most narrow band. By populating the O(1) sites (relative to $YBa_2Cu_3O_6$), we have added three bands, one of which corresponds to the top-most broad band crossing E_F. The total bandwidth of the three top-most anisotropic broad bands in $YBa_2Cu_3O_7$ is about 2.5 eV, essentially the same as the total bandwidth of the single top-most anisotropic broad band in orthorhombic La_2CuO_4.[24]

For purposes of comparison, we note that in orthorhombic La_2CuO_4, our recent calculations[24] indicate that there is only one broad band crossing E_F. However, in certain regions of *k* space this band becomes flat and lies very close to E_F, thereby stabilizing E_F.

In $YBa_2Cu_3O_8$, we see from Fig. 4 that four broad anistropic bands and one narrow anisotropic band cross E_F. Two of these bands again correspond to the two planar Cu-O networks, and the remaining three to the cross-linked 1D ribbons, which now form a 2D Cu-O network composed of O(1)-Cu(1)-O(*y*) in the basal plane, and O(4) out of this plane. Some of these bands are described by in-plane antibonding Cu 3*d*–O 2*p* orbitals [O(1)-Cu(1)-O(*y*)], and some by out-of-plane antibonding Cu 3*d*–O 2*p* orbitals [Cu(1)-O(4)]. By populating the O(*y*) site, we have added three bands (relative to $YBa_2Cu_3O_7$), one of which crosses E_F. Examining the band structure along Y-Y' in Fig. 4, we note that the dispersion of the highest occupied band is considerably larger than the asymmetry of *X* and *Y*. Part of this dispersion disappears for tetragonal $YBa_2Cu_3O_8$, but some remains, corresponding to the fact that the basal Cu-O network [O(1)-Cu(1)-O(*y*)-O(4)] is not exactly 2D.

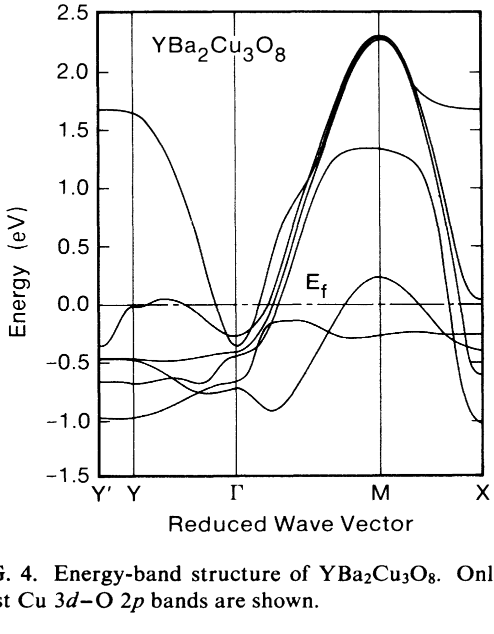

FIG. 4. Energy-band structure of $YBa_2Cu_3O_8$. Only the six highest Cu 3*d*–O 2*p* bands are shown.

After the present work was completed, we learned that the band structures of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_8$ were also investigated by Fujiwara and Hatsugai[27] using the linear muffin-tin orbital atomic sphere approximation method. In spite of differences in computational approach, it is gratifying that some key results are quite similar in both sets of calculations. For example, for $YBa_2Cu_3O_8$ their value of $N(E_F)$ is 8.34 states/eV cell, while our value is 7.02 in the same units. They do not quote the corresponding result for $YBa_2Cu_3O_6$.

To recapitulate, $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, and $YBa_2Cu_3O_8$ all have metallic band structures. As the O content increases, the number of bands crossing E_F increases, greatly complicating the shape of the Fermi surface. This degree of complexity is of considerable interest to theoreticians who have developed models according to which T_c can be enhanced by multiband effects.[28,29] The present work cannot validate such theories, but does serve to dramatize the degree of complexity of the band structure at the Fermi surface.

Our work also indicates that a 2% orthorhombic distortion has only a minor effect on the gross features of the band structure, shifting energy levels at the zone faces up or down by about 0.1 eV. We found that $N(E_F)$ was nearly the same for tetragonal and orthorhombic $YBa_2Cu_3O_x$ ($x=6,8$). However, the orthorhombic distortion can have a more profound effect on subtle features such as two-dimensional character. In contrast, the asymmetry associated with ordered vacancies in $YBa_2Cu_3O_7$ can have a profound effect on the band structure, as can be seen by comparing the energy levels at *X* and *Y* in Fig. 3.

VI. DISTRIBUTION OF VALENCE ELECTRON CHARGE

The total density of states (DOS) was obtained by computing the energy bands at 12 points in the irreducible sector of the reduced zone, and broadening the individual points with a Gaussian function of 0.25 eV half width. The total valence charge was decomposed into portions which lie inside suitably chosen atomic spheres, and a residual portion lying outside all the spheres. The sphere radii and enclosed charges are listed in Table II. These radii were also used in our earlier work on La_2CuO_4 (Ref. 24) and were chosen to yield the lowest total energy for that system.[30] Note that about 21% of the total valence charge lies outside all the atomic spheres. The partial DOS for the various atoms were obtained by weighing the total DOS by the valence charge contained inside the corresponding atomic spheres. For simplicity, we did not attempt to attribute the residual charge outside these spheres to particular atoms, and so we ignored the residual charge in computing the partial DOS. In subsequent work, we hope to deal with the residual charge in a more sophisticated manner.[31]

The most striking feature of Table II is that, in spite of

TABLE II. Valence charge distributions. R denotes the atomic sphere radius (in atomic units), M the site multiplicity, and Q the charge enclosed in atomic sphere. Columns headed $Q(O_6)$, $Q(O_7)$, and $Q(O_8)$ correspond to $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, and $YBa_2Cu_3O_8$. The residual charge is denoted by Res. In contrast to Ref. 25, we regard Ba $5p$ orbitals as core orbitals, so the corresponding charges are not included here.

Atom	R	M	$Q(O_6)$	$Q(O_7)$	$Q(O_8)$	Site description
Y	2.81	1	1.44	1.44	1.42	
Ba	2.81	2	0.36	0.32	0.32	
Cu(1)	1.84	1	9.16	8.93	8.86	Ribbon (node)
Cu(2)	1.84	2	8.90	8.96	8.94	Cu-O plane
O(1)	1.62	1	Empty	5.13	5.00	Ribbon (chain link)
O(y)	1.62	1	Empty	Empty	5.00	Ribbon (cross link)
O(2)	1.62	2	5.30	5.12	5.14	Cu-O plane (above vacancy)
O(3)	1.62	2	5.13	5.23	5.17	Cu-O plane (above chain)
O(4)	1.62	2	5.17	5.15	5.04	Ribbon edge
Res			15.67	16.91	18.51	Outside all spheres
Total			76.00	82.00	88.00	Total valence charge

their large atomic volumes, the Y and Ba spheres contain very little valence charge. The Y and Ba atomic orbitals do not hybridize strongly with the occupied Cu and O orbitals, and hence do not interact much with the Cu and O atoms in the ground state. The Y and Ba atoms play a more important role in defining the unoccupied bands. They also serve as electron donors, contributing electrons to the O atoms. The Y and Ba atoms help to establish the crystal structure both through electrostatic and steric effects.

Another striking feature of Table II is the similarity of the enclosed charges for each of the different types of O sites, in each of the three crystals. (The same is true for the two Cu sites.) In spite of the different local environments, the enclosed O and Cu charges are nearly the same under all circumstances. There are systematic changes from crystal to crystal, and from site to site, but these are generally rather small. If we examine the partial DOS for Cu(1) and Cu(2), which are given in Fig. 5, we see that these are quite different from one another in the same and in different crystals. These differences are direct consequences of the differences in chemical bonding associated with different O coordinations.

Returning to Table II, we note that in $YBa_2Cu_3O_6$, twofold O-coordinated Cu(1) and fourfold O-coordinated Cu(2) enclose 9.16 and 8.90 charges, while in $YBa_2Cu_3O_7$, where Cu(1) and Cu(2) are both fourfold coordinated, the corresponding enclosed charges are more nearly equal (8.93 and 8.96). Finally, in $YBa_2Cu_3O_8$, where Cu(1) and Cu(2) are sixfold and fourfold O coordinated, the enclosed charges are more disparate (8.86 and 8.94) but still nearly equal. Although we have not yet attempted to make detailed estimates of how the residual charge in the region outside all the spheres should be apportioned among the various atoms, the indications are that the distribution is determined by the radial charge density and its radial derivative at the sphere boundaries.[31] These quantities are not drastically different for corresponding atoms in the various crystals, though small systematic differences do occur.

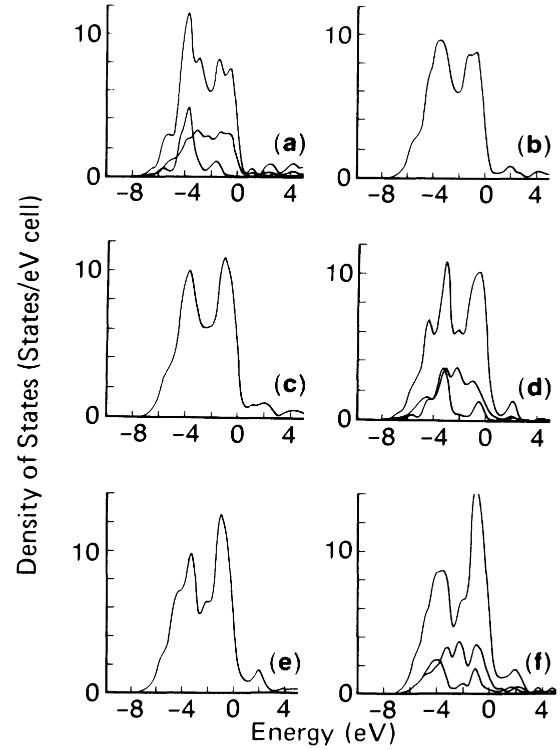

FIG. 5. Total electronic densities of states for (a) tetragonal $YBa_2Cu_3O_6$, (b) partially ordered vacancy model for $YBa_2Cu_3O_{6.5}$, (c) disordered vacancy model for $YBa_2Cu_3O_7$, (d) ordered vacancy model for $YBa_2Cu_3O_7$, (e) partially ordered vacancy model for $YBa_2Cu_3O_{7.5}$, and (f) tetragonal $YBa_2Cu_3O_8$. The zero of energy indicates the Fermi level in all panels. The projected densities of states for Cu(1) (Cu-O ribbon) and Cu(2) (Cu-O plane) are also shown for some cases. The curves for Cu(1) and Cu(2) can be identified by noting that the area under Cu(2) is twice as large as that under Cu(1) since there are two Cu(2) and one Cu(1) in the unit cell. For further details see Table III.

We must conclude, therefore, that though there are differences in the charge that can be assigned to Cu(1) and Cu(2), these differences are small, considerably less than the unit difference implied by the nominal ionicities Cu^{3+} and Cu^{2+} [which correspond to Cu(1) and Cu(2) in $YBa_2Cu_3O_7$]. All of this is reminiscent of the situation in the $T_c = 10-14$ K mixed valence Ba-Bi-Pb-O system, where Bi^{3+} and Bi^{5+} have nearly the same charge.[32]

VII. TREATING PARTIAL OXYGEN FILLING AND ORDERING

We have already indicated how the band structure changes as we increase the O content by unit amounts. These band-structure changes are very complex indeed, involving not only the shifting and distortion of existing bands, but also the creation and interposition of new bands arising from the newly introduced O atoms. The simplest way to deal with an O content intermediate between 6 and 8 is to consider the electronic density of states, which we can interpolate, as opposed to the energy bands, which we cannot because of their changing number.

We can see from Fig. 5 and more clearly from Table III that $N(E_F)$ becomes progressively larger as we proceed from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_8$. To deal with intermediate cases, let us assume that the O(1) and O(y) sites are progressively filled, on an equal basis, as we move from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_8$. Thus, the occupancy of each of these sites is $(x-6)/2$, as x ranges from 6 to 8. With these considerations in mind, we can estimate $N(E)$ and $N(E_F)$ for an intermediate value of x simply by interpolating between out total DOS for the end members of this sequence ($x=6$ and 8). The results of such interpolations are shown in Fig. 5, and some specific numerical results for $N(E_F)$ are listed in Table III.

Although this interpolation scheme is relatively crude, ignoring localized lattice relaxation effects and localized electronic states associated with O insertion and withdrawal, it is, nevertheless, considerably more realistic than the rigid-band filling model used by some authors.[26] The simplistic rigid-band model assumes that the band structure remains the same as the O content changes, which is manifestly incorrect. Our scheme can be used over a wide O range, and can be used to estimate $N(E)$ and $N(E_F)$ for partially disordered as well as totally disordered vacancies. This can be done by forming suitably weighted averages of $N(E)$ involving $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, and $YBa_2Cu_3O_8$, as indicated in Fig. 5 and Table III.

It is clear from Table III that $N(E_F)$ increases with increasing oxygen content x, and that for a given value of x, $N(E_F)$ is larger the more ordered the vacancies are. These calculated results parallel recent experimental observations[13-15] that T_c increases with increasing content as x increases from 6.5 to 6.9, and that T_c at $x=6.9$ is higher the greater the orthorhombic distortion, and, by implication, the more ordered the vacancies.

VIII. BCS MODEL

In view of this correlation between theory and experiment, it is instructive to go a step further and attempt to make the correlation more quantitative. Accordingly, let us assume that changes in oxygen content and vacancy ordering affect the lattice vibrational spectrum and the electron-lattice interaction much less strongly than they do changes in $N(E_F)$, so that we can simplify the problem by assuming that T_c depends only on $N(E_F)$. In this spirit, let us adopt the simple BCS expression

$$T_c = 1.14\langle\omega\rangle\exp[-1/N(E_F)V] \, ,$$

where $\langle\omega\rangle$ is an average phonon energy (expressed in degrees K), and V is an interaction parameter. We will not attempt to draw distinctions between weak and strong coupling BCS theory, nor will we consider more complicated formulas, such as McMillan's. It will be sufficient for our purposes to evaluate $\langle\omega\rangle$ and the coupling coefficient $N(E_F)V$ for various choices of T_c for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, and then consider the implications.

In order to establish the scale, we will set T_c equal to

TABLE III. Electronic density of states at the Fermi level (E_F) for $YBa_2Cu_3O_x$ as a function of oxygen content x and occupancy of sites O(1), O(y), and O(z). Cases (a) through (f) correspond to panels in Fig. 5. Values for $N(E_F)$ were obtained from crystal calculations and from interpolations between the cases indicated. The units are states/eV cell.

Case	$N(E_F)$	x	O(1)	O(y)	O(z)	Crystal	Interpolation
(a)	5.04	6.0	0	0	0	$YBa_2Cu_3O_6$	
	5.54	6.5	$\frac{1}{4}$	$\frac{1}{4}$	0		(a) and (f)
(b)	5.81	6.5	$\frac{1}{2}$	0	0		(a) and (d)
(c)	6.03	7.0	$\frac{1}{2}$	$\frac{1}{2}$	0		(a) and (f)
(d)	6.61	7.0	1	0	0	$YBa_2Cu_3O_7$	
	6.53	7.5	$\frac{3}{4}$	$\frac{3}{4}$	0		(a) and (f)
(e)	6.81	7.5	1	$\frac{1}{2}$	0		(d) and (f)
(f)	7.02	8.0	1	1	0	$YBa_2Cu_3O_8$	

100 K for the ordered vacancy model for $YBa_2Cu_3O_7$. Since the 1D chains are totally absent in $YBa_2Cu_3O_6$ we are left only with 2D Cu-O networks, not unlike the situation in La_2CuO_4-type superconductors. Accordingly, let us set T_c equal to 40 K for $YBa_2Cu_3O_6$, this being the upper range of measured transition temperatures in La_2CuO_4-type superconductors. With these two adjustments, we can obtain values for $\langle\omega\rangle$ and $N(E_F)V$, and thereby estimate T_c for the remaining cases, as indicated in Table IV. (If the reader feels that $T_c=100$ K is too high a value to use for $YBa_2Cu_3O_7$, the T_c entries in Table IV can be read as percentages of T_c for $YBa_2Cu_3O_7$, rather than as actual temperature values.)

In this way we find that as x is raised from 6 to 7, T_c increases from 40 to 100 K (by design), and that at $x=6.5$, T_c is 57 K if the vacancies are totally disordered, and 67 K if they are partially ordered. These estimates bear a resemblance (most probably fortuitous) to the experimental results of Schuller *et al.*[14] and Tarascon and coworkers,[15] both of whom reported values of T_c of about 55 K at roughly $x=6.5$. Referring to Table IV, we see that at $x=6.5$, 7.0, or 7.5, the more ordered the vacancies, the higher the value of T_c. This theoretical conclusion is consistent with the experimental results of Beyers,[13] who found that for values of x just below 7, the greater the orthorhombic distortion, and by implication the more ordered the vacancies, the higher the value of T_c.

Taking this model at face value, we would predict that T_c can be increased by about 19% (relative to ordered $YBa_2Cu_3O_7$) if we could synthesize $YBa_2Cu_3O_8$. Since this may not be feasible, we could at least try to increase the O content as much as possible, keeping the O vacancies as nearly ordered as possible, since both of these strategies would tend to enhance T_c.

It is conceivable that O vacancy ordering for $7 \le x \le 8$ might lead to ordered structures that are related to that shown in Fig. 1 but having a larger unit cell. For example, if we place an O atom at alternate O(y) positions, we would create double ribbons in place of the single ribbons appearing in Fig. 1. The unit cell now has 30 sites and contains three oxygen vacancies, two at the two O(z) positions, and one at alternate O(y) positions, so that the chemical formula is $YBa_2Cu_3O_{7.5}$. Note that there are two other substances with the same formula listed in Tables III and IV, but these have partially ordered O vacancies. We already see that partially ordered $YBa_2Cu_3O_{7.5}$ has a theoretical T_c of 109 K , 13 K higher than that for disordered $YBa_2Cu_3O_{7.5}$. It is possible that an ordered version would have T_c in the 110–120 K range.

Setting $T_c=100$ K for the ordered vacancy model of $YBa_2Cu_3O_6$, and T_c equal to various values for $YBa_2Cu_3O_6$, as indicated in Table IV, we can evaluate $\langle\omega\rangle$ and $N(E_F)V$ for the various fits and decide whether these parameters assume physically reasonable or unreasonable values. For the fit already discussed: $T_c=40$ K for case (a) and 100 K for case (d), the interaction parameter $NV=0.34$, which is unremarkable (physically reasonable), but $\langle\omega\rangle=1661$ K, which is considerably higher than phonon frequencies for this class of materials, which range up to 600 $cm^{-1}=863$ K.[17] If one regards $\langle\omega\rangle$ not as an ordinary phonon frequency, but as a plasmon-enhanced[33] or an exciton-enhanced[34] phonon frequency, then the outcome is reasonable.

Turning to the other fits, we see that as the fitted value of T_c for $YBa_2Cu_3O_6$ is increased, the effective phonon frequency falls while the interaction parameter NV rises. On the other hand, if one attempts to fit T_c to values much lower than 40 K for $YBa_2Cu_3O_6$, the effective phonon frequency rises dramatically and becomes unphysically large. We must conclude, therefore, that while our simple theoretical analysis can account for observations such as Schuller's[14] and Tarascon's[15] that T_c is about 55 K at $x=6.5$, our analysis cannot account for considerably lower values of T_c at $x=6.5$ and below if we insist on using physically reasonable parameters in the BCS expression.

Assuming the validity of our analysis, however, the present study suggests a specific strategy for obtaining higher values of T_c in $YBa_2Cu_3O_x$: increase the O content while keeping the vacancies as ordered as possible. There could well be a maximum in T_c at values of x somewhat above 7 if one could maximize the degree of ordering of

TABLE IV. Estimates for the superconducting transition temperature T_c based on the BCS expression $T_c=1.14\langle\omega\rangle\exp[-1/N(E_F)V]$. Adjusted values of T_c are indicated by asterisks. Values of NV (at 100 K) and $\langle\omega\rangle$ in various units are given at bottom.

Case	T_c (K)					x	Vacancies
(a)	30*	40*	50*	60*	70*	6.0	Ordered
	47	57	65	73	80	6.5	Disordered
(b)	59	67	74	80	85	6.5	Partially ordered
(c)	69	75	81	86	90	7.0	Disordered
(d)	100*	100*	100*	100*	100*	7.0	Ordered
	95	96	97	98	99	7.5	Disordered
(e)	112	109	107	105	103	7.5	Partially ordered
(f)	125	119	114	110	107	8.0	Ordered
$N(E_F)V$	0.26	0.34	0.45	0.61	0.87		(at 100 K)
$\langle\omega\rangle$	4184	1661	820	515	314		(K)
$\langle\omega\rangle$	2908	1154	570	358	218		(cm^{-1})
$\langle\omega\rangle$	0.36	0.14	0.07	0.04	0.03		(eV)

the O vacancies at this composition. However, the increase in T_c over present-day values would only be about 10% to 20%, which might or might not be worth pursuing. Of course, this analysis is based only on the values of $N(E_F)$, and ignores finer details such as the effects of disrupting the 1D Cu-O ribbons or coupling adjacent ribbons by populating the intervening $O(y)$ sites.

IX. DISCUSSION

Our (spin unpolarized) electronic structure calculations clearly show that $YBa_2Cu_3O_x$ ($x=6,7,8$) are all metals, whether the structure is tetragonal or orthorhombic. Although we have not dealt directly with intermediate compositions, we would expect $YBa_2Cu_3O_x$ to be metallic over the entire range of x between 6 and 8 within the framework of spin-unpolarized one-electron band theory. If it proves to be true that $YBa_2Cu_3O_x$ is a semiconductor in the range of x between 6 and 6.5, one would have to explore the possibility that the band gap arises from an antiferromagnetic spin arrangement, or from electron correlation effects. In either case, semiconducting behavior below $x=6.5$ would limit the applicability of our theory to values of x larger than 6.5.

Assuming that the semiconducting band gap has an antiferromagnetic origin, it would be interesting to find ways of suppressing the antiferromagnetism experimentally. One would then be able to see whether T_c still falls to zero below $x=6.5$, or whether it approaches values appropriate to the 2D Cu-O networks in the La_2CuO_4-type superconductors, as mentioned at the beginning of the paper.

If it proves to be true that T_c is zero at $x=6.5$ and rises more or less linearly to values in the 90–100 K range at $x=7$, we would have to conclude that the present analysis, taking only changes in $N(E_F)$ into account, accounts for at least half of the variation of T_c with oxygen stoichimetry above $x=6.5$. In order to account for the remaining variation, we would in all likelihood have to consider the effects of structural disorder on the lattice vibrational spectrum and electronic structure. That is to say, we would have to consider localized vibrational modes, localized vacancy states, and the manner in which these features affect the electron-lattice coupling. All of this still assumes conventional or nearly conventional BCS theory. One could also explore the possibility of depopulating the ribbon-edge sites,[35] but we doubt that this would change the present theoretical picture significantly. If such attempts fail, one is still left with a wide variety of exotic mechanisms to consider.

In summary, then, we have shown that, within the framework of BCS theory, changes in the electronic density of states at the Fermi level[36] can account for at least half of the variation of T_c with oxygen stoichiometry in the range $6.5 < x < 7.0$. Our analysis also indicates that at a fixed oxygen stoichiometry, T_c becomes larger as the O vacancies become more fully ordered, consistent with experimental observations. The present study is confined to metallic $YBa_2Cu_3O_x$, and so would not apply to the range $6.0 < x < 6.5$, where there are indications of semiconducting behavior.

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[35] For a discussion of the possible consequences of depopulating the ribbon-edge sites, see Ref. 20.

[36] The present study of the electronic structure of the $YBa_2Cu_3O_x$ system is based on one-electron theory and so neglects electron correlation effects. Since the crucial quantity from our point of view is the electronic density of states at the Fermi level, $N(E_F)$, it would be important to know how our theoretical predictions for $N(E_F)$ compare with experiment as a function of oxygen content x. Unfortunately, not enough experimental work has yet been done to answer this question, even in the vicinity of $x = 7$. It is reasonable to expect, however, that the conclusions drawn from the present study would remain valid provided the effects of electron correlation on $N(E_F)$ are relatively insensitive to oxygen content. Present indications are that electron correlation effects are significant but not overwhelming. For example, in a recent study of the magnetic properties of this system, with x close to 7, S. S. P. Parkin, E. M. Engler, V. Y. Lee, and R. B. Beyers (unpublished) find that the magnitude of the magnetic susceptibility, after correction for ion core diamagnetism, is enhanced by a factor of approximately 2 over the Pauli susceptibility estimated from band-structure densities of states such as our own. This factor of 2 is attributed to electron correlation effects. Such an analysis based on magnetic measurements is less ambiguous than one based on experiments

involving electronic excitations, which bring many other physical factors into play. Although there appear to be significant differences between theoretical and experimental photoemission spectra [cf. R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, Phys. Rev. B **35**, 8818 (1987); M. Onellion, Y. Chang, D. W. Niles, R. Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon, Phys. Rev. B **36**, 819 (1987); J. Redinger, A. J. Freeman, J. Yu, and S. Massidda (unpublished); P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Huefner, and C. Politis, Z. Phys. B **67**, 19 (1987)], it is not yet clear whether the differences in the vicinity of the Fermi level are due to experimental surface effects, or to shortcomings in band-theoretical treatments of electronic excitation processes.