the maximum energy gain by bending would be estimated at 2 kcal. Thus, hydrogen bonding, which is worth roughly 6 kcal, should dominate the wag angle of water molecules coordinated to ions both in solution and in the solid state.

Valence Fluctuations in the YBa₂Cu₃O₇₋ₓ Superconductor

L. A. Curtiss,* T. O. Brun, and D. M. Gruen

The electronic structures of copper oxide clusters representing the new superconducting materials YBa₂Cu₃O₇₋ₓ and La₂₋ₓMₓCuO₄ (M = Ba, Sr) have been calculated by semiempirical molecular orbital methods. For YBa₂Cu₃O₇₋ₓ the orbital energies indicate that the Cu's located in the CuO₃ "chains" are primarily "trivalent", while the Cu's in the CuO₂ "dimpled planes" are primarily "divalent". The effects of the oxygen breathing mode on the charge distributions and orbital energies are investigated for different electronic configurations. The results indicate that the oxygen breathing modes can cause significant charge fluctuations on the Cu's in the clusters. For certain electron configurations, a double-well type potential may exist for oxygen movement between Cu's in the "chains". This may cause an instability at oxygen stoichiometries near 6.75 and result in a phase separation. A phase diagram is proposed for YBa₂Cu₃O₇₋ₓ, which suggests that the 94 K high-temperature superconducting phase is characterized by an oxygen stoichiometry near 7.0. The phase diagram predicts that a plateau should exist for T_c in the region x = 0.0–0.25 and that in this region two phases are present which are characterized by compositions having oxygen stoichiometries either in the range 6.5–6.75 or close to 7.0.

I. Introduction

The discovery of oxide superconductors with T_c's as high as 94 K has raised questions concerning the mechanism of superconductivity in these materials. One of the remarkable features of the superconducting oxides is that the oxygen stoichiometry requires copper in both La₂₋ₓMₓCuO₄ (M = Ba, Sr) and YBa₂Cu₃O₇₋ₓ to exist in a mixed oxidation state, leading from the outset to the recognition that valence fluctuations may be involved in the superconducting mechanism.[1-3]

The structure of the high-temperature YBa₂Cu₃O₇₋ₓ superconductor has been studied by X-ray diffraction[4] and more recently by neutron diffraction.[5] There are two crystallographically distinct copper atoms in the unit cell: one-third of the copper atoms are in the *b–c* plane consisting of CuO₃ "chains", while two-thirds are in "dimpled" CuO₂ *a–b* planes (see Figure 1). The two planes are separated by yttrium layers without any oxygen, thus minimizing Cu–O–Cu bond overlap between copper-containing planes.[5] The structure suggests that the electronic properties of the material could be highly anisotropic and furthermore raises the possibility that valence fluctuations of the type Cu²⁺ ⇌ Cu³⁺ may occur between copper ions. Such considerations have important consequences, both for the mechanism of superconductivity and the superconducting properties of these materials.

To discuss mixed valency in YBa₂Cu₃O₇₋ₓ, it must be recognized that, of the constituent oxides, only those of Cu can deviate to any appreciable extent from the stoichiometric formulas Y₂O₃, BaO, and CuO since Y₂O₃ and BaO are extremely stable thermodynamically. An oxygen content greater than 6.5, therefore, requires an equivalent amount of Cu to be in the +3 oxidation state. Hence, the average oxidation state of Cu in YBa₂Cu₃O₇₋ₓ is given by $2.33 - 0.66x$ and varies from +2 to +2.33 in going from an oxygen stoichiometry of 6.5 to one of 7.0.
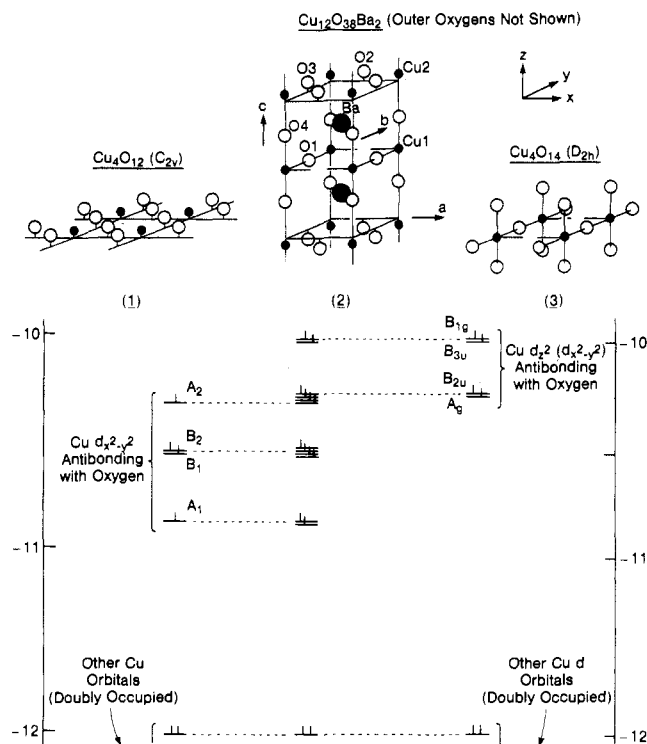
Because of the unique structure of YBa₂Cu₃O₇₋ₓ a question arises concerning the statistical distribution of Cu³⁺ between the

two crystallographic sites. In particular, the very short Cu(1)–O(4) bond length of 1.843 Å suggests that Cu³⁺ is primarily located in the "chains" rather than the "planes" by analogy with the well-authenticated Cu³⁺ compound KCuO₂ where similar short Cu–O distances have been found.[6] It is the exact distribution of Cu³⁺ between the *a–b* and *b–c* planes and the change in that distribution as a function of oxygen stoichiometry that become very important considerations if Cu²⁺ ⇌ Cu³⁺ valence fluctuations are, in fact, involved in the mechanism of superconductivity in these materials.[1-3]

Band structure calculations[7-15] of varying degrees of sophistication have been reported on the La₂₋ₓMₓCuO₄ and YBa₂Cu₃O₇₋ₓ materials. For YBa₂Cu₃O₇ these calculations have generally shown that the CuO₃ chains contain Cu³⁺ while the

---

*To whom correspondence should be addressed at the Chemical Technology Division.

(1) Bednorz, J. G.; Müller, K. A. *Z. Phys.* **1986**, *B64*, 189.
(2) Chu, C. W.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q. *Phys. Rev. Lett.* **1987**, *58*, 405.
(3) Wu, M. K.; Ashburn, J. R.; Torng, C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Chu, C. W. *Phys. Rev. Lett.* **1987**, *58*, 908.
(4) Cava, R. J.; Batlogg, B.; van Dover, R. B.; Murphy, D. W.; Sunshine, S.; Sunshine, T.; Siegrist, T.; Remeika, J. P.; Rietman, E. A.; Zahurak, S.; Espinosa, G. P. *Phys. Rev. Lett.* **1987**, *58*, 1676.
(5) Beno, M. A.; Soderholm, L.; Capone, D. W.; Hinks, D. G.; Jorgensen, J. D.; Grace, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K. *Appl. Phys. Lett.* **1987**, *51*, 57.
(6) Hestermann, K.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1969**, *367*, 249.
(7) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1829.
(8) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1831.
(9) Whangbo, M.-H.; Evain, M.; Beno, M. A.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1832.
(10) Yu, J.; Freeman, A. J.; Xu, J.-H. *Phys. Rev. Lett.* **1987**, *58*, 1035.
(11) Mattheiss, L. F.; Hamann, D. R. *Solid State Commun.* **1987**, *63*, 395.
(12) Mattheiss, L. F. *Phys. Rev. Lett.* **1987**, *58*, 1028.
(13) Massida, S.; Yu, J.; Freeman, A. J.; Koelling, D. D. *Phys. Lett. A* **1987**, *122A*, 198.
(14) Yu, J.; Massidda, S.; Freeman, A. J.; Koelling, D. D. *Phys. Lett. A* **1987**, *122A*, 203.
(15) Fu, C. L.; Freeman, A. J. *Phys. Rev. B: Condens. Matter* **1987**, *35*, 8861.

Cu₁₂O₃₈Ba₂ (Outer Oxygens Not Shown)

Figure 1. Highest occupied ("high"-spin configuration) molecular orbitals (energies in eV) for a $Cu_{12}O_{38}Ba_2$ cluster (**2**, outer oxygens not shown) composed of one Cu_4O_{14} cluster (**3**, representing the CuO_3 chains) and two Cu_4O_{12} clusters (**1**, representing two CuO_2 "dimpled" planes). The electron configuration is for all Cu's "divalent" (d^9) (the charge on the cluster is −48) in a "high"-spin state. Removal of four of the 12 unpaired electrons corresponds to $x = 0$ in $YBa_2Cu_3O_{7-x}$. The "low"-spin configuration corresponds to the MO's being doubly occupied.

CuO_2 planes contain Cu^{2+}. Some of these studies also indicated that the breathing mode displacement of the oxygens about each Cu in the CuO_2 planes would cause charge fluctuations. In addition, calculations on clusters representing $La_{2-x}Sr_xCuO_4$ have been reported[16] that have been interpreted to support the presence of both Cu^{2+} and Cu^{3+} in the material.

We have carried out semiempirical extended Hückel calculations for CuO clusters choosen to represent $YBa_2Cu_3O_{7-x}$ and $La_{2-x}M_xCuO_4$. While this approach is quite approximate, its computational speed allows the study of problems which could not be easily handled with more sophisticated methods and can provide useful insight into the electronic structure of solids.[17] In the next section we report on such calculations for CuO clusters. The results are very similar to those of the band structure calculations for the valency of the Cu's in the chains and the planes (for $YBa_2Cu_3O_{7-x}$) and for charge fluctuations induced by the breathing vibrational mode (for both materials). We then use these calculations to investigate charge fluctuations for different electronic configurations and, most importantly, to propose in section IV a phase diagram for the orthorhombic form of $YBa_2Cu_3O_{7-x}$ for oxygen stoichiometry in the range 6.5–7.0.

II. Cluster Calculations

We have used extended Hückel molecular orbital (EHMO) theory in calculations on hypothetical clusters representing the $YBa_2Cu_3O_{7-x}$ (x = 0.0–0.5, orthorhombic structure) and the $La_{2-x}M_xCuO_4$ superconductor materials. The EHMO method[18] consists of a noniterative (i.e., non self-consistent) scheme that computes the eigenvalues and eigen-

(16) Alp, E. E.; Shenoy, G. K.; Hinks, D. G.; Capone II, D. W.; Soderholm, L.; Schuttler, H.-B.; Guo, J.; Ellis, D. E.; Montano, P. A.; Ramanthan, M. *Phys. Rev. B: Condens. Matter* **1987**, *35*, 7199.
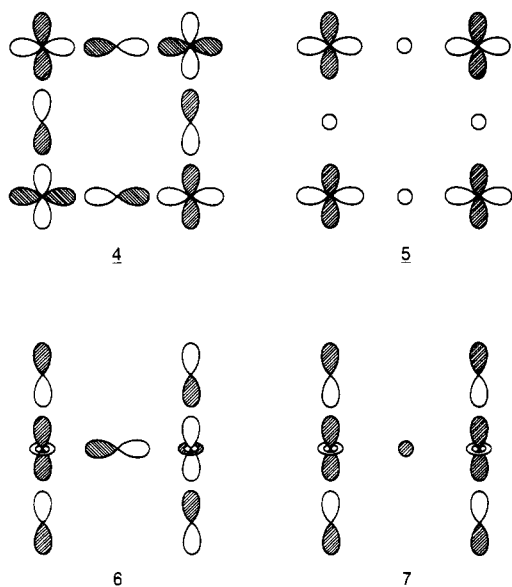
(17) See, for example: (a) Biceramo, J.; Keem, J. E.; Schlegel, H. B. *Theor. Chim. Acta* **1986**, *70*, 265. (b) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150. (c) Companion, A. L.; Liu, F.; Onwood, D. P. *J. Less-Common Met.* **1985**, *107*, 131.

(18) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

Table I. Extended Hückel Parameters[a,b] for Valence Orbitals

	H_{ii}			exptl		
	s	p	d	s	p	d
Cu	−9.32	−3.35	−12.86	1.55	1.55	c
O	−29.86	−13.31		2.275	2.275	
Ba	−5.21	−3.0		1.35	0.80	

[a] Cu and O parameters are from ref 19. The Ba s H_{ii} value is from: Lotz, W. *J. Opt. Soc. A* **1970**, *60*, 206. The Ba p H_{ii} value is estimated. Ba exponents were derived from: Burns, G. *J. Chem. Phys.* **1964**, *41*, 1521. [b] An alternative set of Cu parameters[17a] and oxygen parameters (Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058) gave similar results. [c] The double-δ expansion coefficients are 5.95 and 2.2. The corresponding coefficients are 0.573 32 and 0.574 42.

vectors from an effective one-electron Hamiltonian by a single-matrix diagonalization step. We consider both "high"- and "low"-spin configurations[19,20] of the clusters. If the valence electrons are then placed by pairs into the molecular orbitals (MO's) of lowest energy, this is referred to as a "low"-spin configuration. Alternatively, if the lowest unoccupied orbitals (LUMO's) are close in energy to the highest occupied orbitals (HOMO's), then electronic states in which some or all of these higher energy levels are singly occupied may be possible, because EHMO theory does not include the energy to pair electrons. Although the electrons spins may or may not be unpaired in this case, we will refer to this situation as a "high"-spin configuration. The parameters used in the EHMO calculations are given in Table I. We note that throughout this paper we describe the MO results in terms of common chemical terminology (i.e. valence state, divalent, trivalent, etc.). For example, a neutral Cu_4O_4 cluster, which formally contains four Cu's in a 2+ state and four O's in a 2− state, is described as having a Cu valency of 2 (a Mulliken population analysis gives the charge on Cu and O as +1.42 and −1.42, respectively). Removal of an electron from this cluster comes from all four Cu's as well as the O's (in $Cu_4O_4^+$, the Mulliken charges on Cu and O are +1.57 and −1.32, respectively). In the terminology used here the latter cluster is referred to as having a Cu "valency" of 2.25. The Mulliken charges obtained from these extended Hückel cluster calculations are consistent with those obtained for related CuO clusters by higher levels of theory including ab initio molecular orbital theory[21] and local density methods.[16]

The unit cell of the $YBa_2Cu_3O_{7-x}$ superconductor has been described in the introduction. We have chosen the hypothetical cluster **2** shown in Figure 1 to represent the solid. This is composed of two layers of "dimpled" CuO_2 a–b planes (Cu_4O_{12}, **1**) with a layer of the CuO_3 "chains" (Cu_4O_{14}, **3**) between them. The latter is made up of Cu's in the b–c plane. The Ba atoms separate the "dimpled" planes from the "chain" planes. The Y atoms are not included as they separate two sets of "dimpled" planes from each other and should not effect the energy levels significantly. The $Cu_{12}O_{38}Ba_2$ cluster (**2**) with a charge of −44 represents the $YBa_2Cu_3O_7$ compound with no vacancies. The presence of vacancies gives rise to $x > 0$ in $YBa_2Cu_3O_{7-x}$ and is obtained in this model by the addition of electrons to the $Cu_{12}O_{38}Ba_2$ cluster (addition of four electrons, charge = −48, gives $x = 0.5$). The dimensions given by Beno et. al[5] for $YBa_2Cu_3O_{6.82}$ were used.

The important energy levels for the Cu_4O_{12} and Cu_4O_{14} clusters are illustrated in Figure 1. In both clusters, the highest lying of these orbitals are Cu d antibonding with oxygen s and p. In the case of Cu_4O_{12} the four highest of these MO's involve Cu $d_{x^2-y^2}$. The A_2 MO is antibonding between all Cu's as well as the oxygens as illustrated by **4** in Figure 2. The A_1 MO is bonding between the four Cu's with only a small amount of O s mixed in (**5** in Figure 2). In between is a nearly degenerate set of orbitals, which is a mixture of bonding and antibonding between the Cu's. In the case of Cu_4O_{14}, which is used to represent the CuO_3 chains, the four highest of these MO's involve Cu d_{z^2} (with some $d_{x^2-y^2}$) antibonding with oxygen s and p. The top two are nearly degenerate and are antibonding between the Cu's (**6** in Figure 2) in each of the two chains in the cluster. The bottom two are $d_{z^2}(d_{x^2-y^2})$ bonding between the two Cu's (**7**) in each chain. The slight splitting in each set is due to the small interaction between the chains which are 3.82 Å apart. The energy levels shift negligibly in the combined cluster **2**. This is due to the long Cu-(2)–O(4) distance (2.42 Å) compared to the short Cu(1)–O(4) distance (1.85 Å). The energy levels in Figure 1 indicate that the antibonding $d_{z^2}(d_{x^2-y^2})$ MO's in the Cu_4O_{14} layer are located significantly higher in energy ($\approx$0.3 eV) than the antibonding $d_{x^2-y^2}$ MO's in the Cu_4O_{12} layer.

(19) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(20) Whangbo, M. *J. Chem. Phys.* **1979**, *70*, 4963.

(21) Curtiss, L. A.; Shastri, A., to be submitted for publication.

Figure 2. Molecular orbitals involving d$_{x^2-y^2}$ orbitals antibonding with oxygen, **4** and **5**, in a Cu$_4$O$_4$ cluster and d$_{z^2}$ orbitals antibonding with oxygen, **6** and **7**, in a Cu$_2$O$_5$ cluster. The Cu$_4$O$_4$ cluster represents the CuO$_2$ planes in YBa$_2$Cu$_3$O$_{7-x}$ and La$_{2-x}$Ba$_x$CuO$_4$. The Cu$_2$O$_5$ cluster represents the CuO$_3$ chains in YBa$_2$Cu$_3$O$_{7-x}$. The MO's in **6** and **7** also contain some d$_{x^2-y^2}$ Cu orbital contribution.

This is reasonable considering the short Cu(1)–O(4) distance in the Cu$_4$O$_{14}$ layer compared to the longer Cu(2)–O(3) and Cu(2)–O(2) distance (1.94 and 1.91 Å, respectively) in the Cu$_4$O$_{12}$ layer.

The electron filling of the energy levels is illustrated in Figure 1 for a "high"-spin configuration and all Cu's in a d^9 Cu configuration (Cu^{2+}); i.e., the 12 highest Cu d MO's are singly occupied. This corresponds to a charge of –48 on the Cu$_{12}$O$_{38}$Ba$_2$ cluster (**2**). An electron configuration equivalent to that of YBa$_2$Cu$_3$O$_7$ is attained by removing four electrons from the energy levels depicted in Figure 1. It is reasonable to suggest on the basis of the energy levels in Figure 1 that the first two electrons would come out of the two d$_{z^2}$(d$_{x^2-y^2}$) antibonding orbitals in the *b–c* plane representing the CuO$_3$ "chains". This would correspond to an average "valence" of 2.5 for the Cu's in the chains. The next two could come out of either the "chains" or the "dimpled" *a–b* planes because of the near degeneracy of the orbitals, indicating that the average "valence" of the Cu's in the chains will be from 2.5 to 3.0, and the Cu's in the dimpled CuO$_2$ planes will have an average "valence" of 2.0–2.25. In a "low"-spin configuration (all MO's doubly occupied), all of the Cu^{3+} would be located in the chains.

Further investigation confirmed the important features of the energy level diagram in Figure 1. Increasing the Cu$_4$O$_{12}$ cluster to Cu$_{16}$O$_{24}$ and the Cu$_4$O$_{14}$ cluster to Cu$_{16}$O$_{44}$ lead to little change in the difference in the energies ($\approx$0.3 eV) of the highest antibonding Cu levels in the two types of clusters. Use of an alternate set of parameters (see Table I) also led to little change in this energy difference.

Hence, these calculations indicate that the "trivalent" Cu's are located primarily in the CuO$_3$ chains while the "divalent" Cu's are located mainly in the CuO$_2$ planes. This is consistent with recent band structure calculations[8,9,14] on YBa$_2$Cu$_3$O$_7$, indicating that the Cu^{3+} ions are located in the chains and the Cu^{2+} ions in the planes. We note that the question of whether oxide oxidation might be favored over formation of Cu^{3+} cannot really be answered at the level of calculation used in our cluster calculations. Higher levels of calculations are needed to resolve this question. Charge-iterative EHMO calculations could also provide insight. However, the results of the present calculations on the valency of Cu in these new materials are in agreement with the formal assignment of charges in these solids and with bond valence arguments.[22]

In both the La$_{2-x}$M$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-x}$ compounds, CuO$_2$ planes and CuO$_3$ chains form "square-planar" networks, a very common CuO configuration. These CuO networks are imbedded in both compounds in such a way that the phonon modes involving oxygen displacements along the Cu–O bonds will be dominated by the Cu–O stretch and as a result couple only weakly to other phonon modes. It is therefore expected that these optical Cu–O stretch phonons are pseudo-two-dimensional for the CuO$_2$ planes and pseudo-one-dimensional for the CuO$_3$ planes. Among these are longitudinal phonons that have their wave vectors in
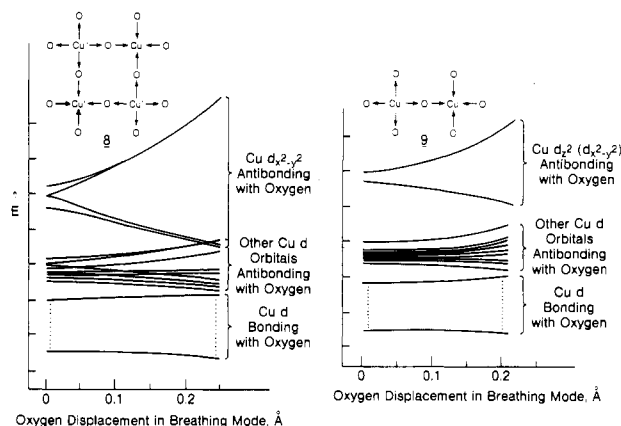
Figure 3. Effect of breathing mode vibration displacement on molecular orbital energy levels in the Cu$_4$O$_{12}$ cluster **8** and a Cu$_2$O$_7$ cluster **9** (half of the Cu$_4$O$_{14}$ cluster in Figure 1). The results for **9** are from the Cu$_{12}$O$_{38}$Ba$_2$ cluster in Figure 1. The results for **8** are from a Cu$_4$O$_{12}$ cluster (D_{4h} symmetry, R(CuO) = 1.89 Å). The arrows in **8** and **9** indicate the motions of the oxygens relative to the Cu's.

the CuO$_2$ or CuO$_3$ planes. At the zone boundary, the oxygen planes (perpendicular to the phonon wave vector) on either side of the plane containing the Cu atoms (also perpendicular to the phonon wave vectors) move closer to or further away from the Cu plane. In the corresponding transverse modes, the oxygen planes shear. At and near the Brillouin zone boundaries, the longitudinal Cu–O stretch phonons can couple to a mixed-valence state of copper. The transverse modes cannot couple to the mixed valence state.

One of the longitudinal modes ($^1/_2$, $^1/_2$, 0) is illustrated for the CuO$_2$ plane in La$_{2-x}$M$_x$CuO$_4$ by **8** in Figure 3. A similar breathing mode is present in the CuO$_2$ planes in the YBa$_2$Cu$_3$O$_{7-x}$ superconductor. Another longitudinal mode (0, $^1/_2$, 0) for the CuO$_3$ chains in this material is illustrated by **9** in Figure 3. In addition, there exist other longitudinal modes such as **10**, corresponding to ($^1/_2$, 0, 0).

10
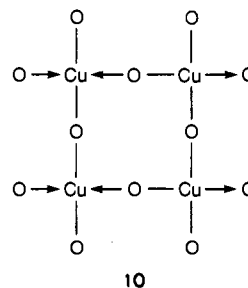
We have examined the coupling between the displacement of oxygen atoms and the valence state of copper atoms for CuO clusters as a function of the average valence of Cu. The effects of the breathing mode displacements on the energy levels of a Cu$_4$O$_{14}$ cluster representing the chains in YBa$_2$Cu$_3$O$_{7-x}$ and a Cu$_4$O$_{12}$ cluster representing the CuO$_2$ planes in La$_{2-x}$M$_x$CuO$_4$ (or YBa$_2$Cu$_3$O$_{7-x}$) are shown in Figure 3. The largest effect for both clusters is splitting of the four highest antibonding d MO's: two of the MO's move upward and two move downward. (These MO's are the ones that are singly occupied in the "high"-spin electron configuration with all Cu's "divalent".) The EH results suggest that deoccupation of the higher of these MO's by pairing of electrons into the low-spin configuration or removal of electrons either by a "doping" mechanism or by oxidation results in oxygen displacement from its symmetrical position, which would suggest that double-well type potentials for oxygen movement between two Cu's may exist. In the "high"-spin configuration, this would occur when two electrons are taken out of the "chain" orbitals in the Cu$_{12}$O$_{38}$Ba$_2$ cluster (Cu valence = 2.5 in the "chains" and x = 0.25). Removal of an additional one (valence = 2.75) or two electrons (valence = 3.0) out of the chains would be necessary to stabilize the symmetrical oxygen position. The possible existence of a double-well type potential in the "chains" under certain conditions may have important implications. We examine one such possibility concerning the stoichiometry of the YBa$_2$Cu$_3$O$_{7-x}$ compound in the next section.

We have also investigated the effect of the breathing modes on the Mulliken[23] charges of the Cu's and find that the antibonding and bonding

---

(22) Siegel, S., private communication.

(23) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

Table II. Mulliken Population Analysis for a Cu_4O_{12} Cluster[a] and Effects of Breathing Mode Displacements in **8**

electrons removed[b]	configuration[c]	charges[d] on Cu	$q(Cu') - q(Cu'')$,[e] e
0	HS	1.40[f]	0.02[f]
0	LS	1.35	1.16
1	HS	1.54[g]	0.28[g]
1	LS	1.51	0.85

[a] D_{4h} structure with $R_{CuO} = 1.89$ Å as in $La_{2-x}Ba_xCuO_4$: Jorgensen, J. D.; Schuttler, H.-B.; Hinks, D. G.; Capone, D. W.; Zhang, K.; Brodsky, M. B.; Scalapino, D. J. *Phys. Rev. Lett.* **1987**, *58*, 1024. [b] Electrons removed from the highest occupied orbital of a $Cu_4O_{12}^{16-}$ cluster. The −16 cluster corresponds to all "divalent" Cu's. [c] HS = singly occupied $d_{z^2-y^2}$ MO's as illustrated for a Cu_4O_{12} cluster (**1**) in Figure 1. LS = low-spin configuration with double occupation of all MO's unless there is an odd number of electrons, in which case there is a singly occupied orbital. [d] Charges on Cu in the D_{4h} structure. [e] For breathing mode displacement of 0.05 Å (**8** in Figure 3). Similar charge fluctuations occur for the dimpled CuO_2 plane in $YBa_2Cu_3O_{7-x}$. [f] For a $Cu_{16}O_{24}^{16-}$ cluster, the charges on the center four Cu's are 1.39e and the $q(Cu') - q(Cu'')$ is 0.14e. [g] For a $Cu_{16}O_{24}^{15-}$ cluster, the charges on the center four Cu's are 1.52e and the $q(Cu') - q(Cu'')$ is 0.28e.

Table III. Mulliken Population Analysis for a $Cu_{12}O_{38}Ba_2$ Cluster (**2**) and Effects of Breathing Mode Displacement in **9** in Chains

electrons removed[a]			charges[b]		$q(Cu') - q(Cu'')$,[c] e	
Cu_4O_{12}[d]	Cu_4O_{14}[e]	Cu_4O_{12}[d]	Cu(1)	Cu(2)	Cu_4O_{12}[d]	Cu_4O_{14}[e]
0	0	0	1.30	1.30	0.00	0.01
0	1	0	1.45	1.30	0.00	0.27
0	2	0	1.60	1.30	0.00	0.53
0	3	0	1.77	1.30	0.00	0.27
0	4	0	1.94	1.30	0.00	0.02
			(1.93)[f]	(1.26)[f]		
0	3	1	1.73	1.38	0.00	0.27

[a] Electrons removed from energy levels filled, as depicted in Figure 1. [b] Cu(1) is the Cu in the CuO_3 chains and Cu(2) is the Cu in the CuO_2 plane (see Figure 1). [c] For breathing mode displacement of 0.05 Å (**9** in Figure 3). [d] Represents the CuO_2 dimpled plane. [e] Represents the CuO_3 chains. [f] Results for low-spin configuration (all doubly occupied MO's) of remaining electrons.

MO's have a nearly equal and opposite effect on the populations of the two types of Cu's (Cu' and Cu'', Figure 3) in the distorted cluster. Hence, deoccupation (oxidation) of the highest orbital of the Cu_4O_{12} cluster, which is $d_{x^2-y^2}$ antibonding between all Cu's, gives rise to a difference in charge on the Cu's where the oxygens are close (Cu') and on those that have the oxygens moved out (Cu''). As shown in Table II the charge difference is about 0.28e with the removal of one electron for a displacement of 0.05 Å. In the "low"-spin configuration, significant charge fluctuation (1.16e) occurs without removal of an electron since in this case the highest antibonding orbitals are unoccupied. We also find that other phonon modes like the transverse "scissors" mode, where each Cu has two short Cu–O bonds and two long Cu–O bonds, do not give rise to charge fluctuations. Band structure calculations have also indicated that the breathing vibrational mode causes Cu charge fluctuations in the CuO_2 planes.[7,15]

Charge fluctuations are also found in the clusters representing the chains in $YBa_2Cu_3O_7$ as shown in Table III. In the "high"-spin configuration the presence of all 2+ Cu ions in the chains (singly occupied d_{z^2} MO's as in Figure 1) gives little charge fluctuation as the contributions from the antibonding and bonding orbitals approximately cancel. The removal of one, two, and three electrons leads to charge differences between the two Cu's of 0.27e, 0.53e, and 0.27e, respectively, in the Cu_4O_{14} cluster. Finally, the presence of all Cu^{3+} ions in the chains also gives little charge fluctuations for the breathing mode. The results in Table III also indicate that there is no charge fluctuation in the CuO_2 planes as a result of the breathing mode in the "chains"; i.e., the chains and the planes are basically uncoupled. This is also consistent with the results of band structure calculations.[9,14]

There are a number of approximations in these calculations, in addition to those in the EH method, that should be mentioned. Among these are that our representation of the vacancies ($x > 0$) is done by adding electrons with no oxygens being removed. Also, we have not considered the possibility that electrons from a doubly occupied MO may
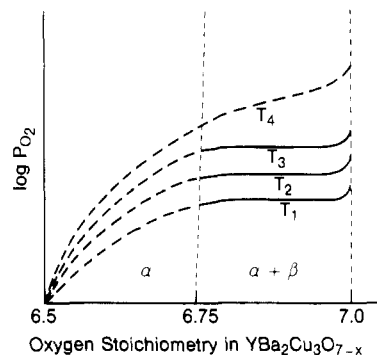
Figure 4. Phase diagram for oxygen stoichiometry in $YBa_2Cu_3O_{7-x}$ as a function of O_2 pressure.

be excited into an empty MO's created by oxidation such as in the case of "trivalent" Cu.

III. Discussion

The results of the EHMO calculations on the $Cu_{12}O_{38}Ba_2$ cluster will be discussed in relation to properties of bulk $YBa_2Cu_3O_{7-x}$, although the approximate nature of the calculations makes the discussion of bulk properties somewhat speculative. Nonetheless, some of the interesting consequences of the changes in electronic structure attending changes in oxygen stoichiometry appear to find support in recent work on oxygen site ordering.[24] These experimental results will be discussed in light of the theoretical calculations.

Removal of two electrons from the $Cu_{12}O_{38}Ba_2$ cluster is formally equivalent to going from a value of $x = 0.5$ to $x = 0.25$ in $YBa_2Cu_3O_{7-x}$, while removal of two more electrons (a total of four) is equivalent to going from $x = 0.25$ to $x = 0$. A recent detailed study[25] of oxygen ordering in $YBa_2Cu_3O_{7-x}$ has shown that the orthorhombic superconducting phase exists over the range $x = 0$–0.5 and that the transition to a tetragonal structure occurs very near the $x = 0.5$ stoichiometry. The 0, $^1/_2$, 0 site for oxygen along the "chains", which is fully occupied when $x = 0$, becomes unoccupied with decreasing oxygen content. The transition to the tetragonal structure is characterized by increasing occupation of the $^1/_2$, 0, 0 site for oxygen.

We suggest that the structural situation is more complicated than has hitherto been recognized, with possibly profound implications for the mechanism of superconductivity in $YBa_2Cu_3O_{7-x}$. On energetic grounds, as already discussed, oxidation of $YBa_2Cu_3O_{6.50}$ to $YBa_2Cu_3O_{6.75}$ would occur with conversion of Cu^{2+} to Cu^{3+} in the "chains" ("high"-spin configuration). In this region of oxygen stoichiometries, addition of oxygen could proceed in a continuous manner by filling of vacancies at the 0, $^1/_2$, 0 sites. At the 6.75 stoichiometry, the structure may become unstable with respect to oxygen displacement from its symmetrical position due to the development of a double-well type potential. The instability can be relieved by the removal of additional electrons from the cluster. Removal of two electrons would be formally equivalent to going from the $YBa_2Cu_3O_{6.75}$ stoichiometry to $YBa_2Cu_3O_{7.0}$. The situation that has just been described could give rise to the phase diagram for the $YBa_2Cu_3O_{6.5}$-O_2 system schematically depicted in Figure 4. The phase diagram consists of regions spanning oxygen stoichiometries from 6.5 to 6.75 (α) and 6.75 to 7.0 (α and β). The α-phase region results from the gradual filling of oxygen vacancies along the "chains" with the oxygen stoichiometry at a given temperature fixed by the oxygen pressure. At oxygen stoichiometries greater than 6.75, the α phase is converted to the β phase with the conversion completed at the composition 7.0. This region of the phase diagram is characterized by a "plateau", meaning that the oxygen stoichiometry at a fixed temperature is *independent* of oxygen pressure. Structurally, the difference between the α and β phases resides in the degree of

(24) Jorgensen, J. D.; Beno, M. A.; Hinks, D. G.; Soderholm, L.; Volin, K. J.; Hitterman, R. L.; Grace, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K.; Kleefisch, M. S. *Phys. Rev. B: Condens. Matter* **1987**, *36*, 3608.

Table IV. Fractional Occupation of the $(0, \frac{1}{2}, 0)$ Site as a Function of Oxygen Partial Pressure[a]

% oxygen content of gas phase	fractional site occupation		
	650 °C	600 °C	450 °C
100	0.53	0.64	0.80
20	0.37	0.52	0.78
2		0.40	0.75

[a] Data taken from ref 24.
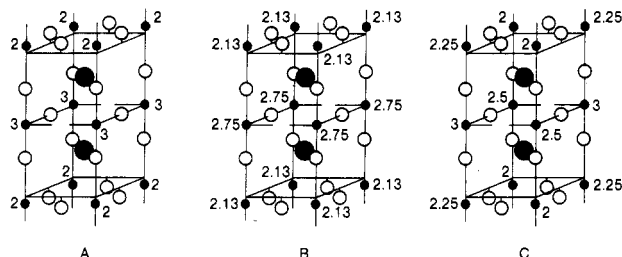
Figure 5. Illustration of charge fluctuation on Cu's in $Cu_{12}O_{38}Ba_2$ clusters (outer oxygens not shown): (A and B) the last two configurations in Table III; (C) effects of oxygen breathing mode on charges in the B configuration. The charges are for illustration purposes only, not calculated. Formal charges of 2– and 2+ for O and Ba, respectively, are used in this figure.

occupation of the $0, \frac{1}{2}, 0$ site. It is fully occupied in the β phase and only partially so in the α phase. Very high resolution neutron or X-ray diffraction studies will be required to resolve the structural differences between these phases.

A careful examination of the data recently reported on oxygen ordering[24] can be interpreted as lending support to the conjecture embodied in the proposed phase diagram. The numbers in Table IV are derived from the data presented in Figure 7a–c of ref 24. It can be seen that the fractional site occupancy of the $0, \frac{1}{2}, 0$ site is strongly oxygen pressure dependent when the site occupancy is less than ~ 0.75 but only very weakly pressure dependent at higher values. It turns out that the oxygen stoichiometries and fractional site occupations are very closely related in the 6.5–7.0 region. The suggested phase behavior of $YBa_2Cu_3O_{7-x}$ is consistent with the molecular orbital calculations and is supported by experimental results. The behavior implies that the 94 K high-temperature superconducting phase is characterized by an oxygen stoichiometry near 7.0. Material whose overall stoichiometry is less than 7.0, but greater than 6.75, would display an onset of superconductivity at 94 K. Only at oxygen stoichiometries less than 6.75 would one expect a lowering of T_c. These considerations then do not predict a *value* for T_c but do predict a plateau in T_c between $x = 0.0$ and $x = 0.25$.

We now consider possible contributions to the mechanism for the high-temperature superconductivity on the basis of the cluster

calculations. The $YBa_2Cu_3O_7$ stoichiometry required the removal of four electrons from the $Cu_{12}O_{38}Ba_2$ cluster. The two most likely ways of doing this for the "high"-spin configuration are represented by the last two rows of Table III. One of them (configuration A) requires that all four electrons come from the chains and none from the planes as illustrated in Figure 5. We have shown that the breathing mode induces little charge fluctuation in either the chains or the planes in this case (see Table III). However, configuration A also corresponds to the "low"-spin state in which the breathing mode does induce large charge fluctuations in the planes (see Table II). The other configuration, B, requires that three electrons come from the chains and one electron comes from the planes. As shown in Tables II and III, substantial charge fluctuations are induced by the breathing mode in both the chains and planes for configuration B. The charge fluctuation caused by the breathing mode in configuration B is illustrated by C in Figure 5. Also since configurations A and B are close in energy, charge transfer of the type $Cu^{2+} \rightleftarrows Cu^{3+}$ could occur via some type of electron-hopping mechanism. Therefore, a subtle interplay of phonon-mediated charge fluctuations and electron hopping between the chains and the planes may contribute to the mechanism for superconductivity in $YBa_2Cu_3O_7$.

IV. Conclusions

The following conclusions can be drawn from this study:

(1) The results for the $Cu_{12}O_{38}Ba_2$ cluster suggests that a valence of 2.5 in the chains may lead to a double-well type potential for oxygen movement between the Cu's in the "chains" in the $YBa_2Cu_3O_{7-x}$ compound. This may cause an instability at stoichiometries around 6.75 and result in a postulated phase change (Figure 4), which implies that the 94 K high-temperature superconducting phase is characterized by an oxygen stoichiometry near 7.0. Only at stoichiometries less than 6.75 would one expect a lowering of T_c.

(2) Calculations on the $Cu_{12}O_{38}Ba_2$ cluster indicated that in $YBa_2Cu_3O_{7-x}$, the valency of Cu's in the CuO_3 chains is close to three, while the valency of Cu's in the dimpled CuO_2 planes is close to two. This is consistent with recent band structure calculations.

(3) The existence of mixed-valence states in the "high"-spin configuration leads to increased charge fluctuations with the breathing vibrational mode in the planes or the chains. Charge fluctuations are present in the "low"-spin configuration (CuO_2 planes) without mixed-valence states. These charge fluctuations, as well as electron hopping between the planes and the chains, may contribute to the mechanism for superconductivity in $YBa_2Cu_3O_{7-x}$.