Oxygen–Oxygen Pair Potentials and the Origin of Nonstoichiometry in $YBa_2Cu_3O_{7-\delta}$

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The use of different types of pair potentials is explored in an effort to mimic the energetics of the interplanar oxygen atoms in $YBa_2Cu_3O_{7-\delta}$. It is shown how the Sterne–Wille V_i parameters obtained from the Connolly–Williams formalism are dependent upon the identity of the structures included in the process. Simple two-atom pair potentials derived from calculations where there is no choice of structure or stoichiometry are used to view the oxygen motion. Even within this scheme there are three types of pair potentials. Two are appropriate for the study of processes where atoms or ions are lost from the structure. The third pair potential which uses two merged densities of states is appropriate for the study of ordering processes in materials of fixed stoichiometry. The d count variation of these three parameters leads to useful insights into the behavior of the oxygen atoms in the interplanar region of $YBa_2Cu_3O_{7-\delta}$. Plane-to-chain electron transfer in this compound (and thus an increase in the d count of the chain oxygen atoms above 8) is a vital ingredient in leading to repulsive oxygen–oxygen potentials which lead to oxygen loss and hence nonstoichiometry.

I. Introduction

In addition to their interesting transport properties, the series of high-T_c cuprate superconductors which have been discovered in recent years have provided chemists with a fascinating crystal chemistry to unravel. It is clear that structure and properties are as intimately related in this field as in many others, and encourages us to seek a detailed understanding of the complex chemistry the area presents. We are particularly fortunate to have an unparalleled set of new compounds and structures which have been studied in enormous detail by several different groups of workers. One system of pivotal importance in the field is the 1-2-3 compound, $YBa_2Cu_3O_{7-\delta}$. Although T_c is highly dependent on oxygen stoichiometry in both compounds, its dependence is much more complex in 1-2-3 (see, for examples, refs 1 and 2) than in the oxygen-rich 2-1-4 compound[3] $La_2CuO_{4+\delta}$. In both materials some of the oxygen atoms are mobile at room temperature. The way the oxygen atoms in the interplanar region are ordered has been shown to be crucial in controlling the details of interatomic distances and the superconducting transition temperature.[1,2,4] We have shown[5] how the extent of chain-to-plane electron transfer, which directly determines the number of holes in the planes, and also T_c, is critically determined by the interplanar oxygen stoichiometry and ordering pattern. The energetics which control this problem have been the object of much thought. The generation of computed interatomic pair potentials[6] has led to construction of the phase diagram[7,8] (compound stability as a function of temperature and δ) and a model[9] leading to correlation of T_c with δ. This paper will be concerned with the validity of pair potentials of various types for these systems and what they tell us about the behavior of the oxygen atoms in the interplanar region of this material.

II. Pair Potentials

The idea of representing the energy of a system in terms of the sum of a set of potentials between clusters of atoms of various sizes has been used in several different forms for many years with a spectrum of results. "Ionic" materials, for example, have long been described in terms of sums of pairwise attractive and repulsive (Coulombic and van der Waals) interactions between ions. Van der Waals solids and clusters have been usefully described by Lennard-Jones potentials or similar. The validity of such pairwise approaches for systems where the bonding is "delocalized" is frequently debated, although it often seems to work well in metal alloys. Perhaps the most general picture of the many-atom potential problem is that of Connolly and Williams,[10] who wrote the total energy of the system as the sum

$$E(r) = \sum\nolimits_n \Phi_n(r)\,\xi_n \qquad (1)$$

Here the Φ_n are the many-atom interaction potentials and ξ_n are the multisite correlation functions defined on the nth order cluster. The ξ_n clearly define the frequency of the occurrence of that function in the structure. By the choice of a set of M structures then the problem may be inverted to generate a set of M values of v_n, viz.

$$\Phi_n(r) = \sum\nolimits_{m=1,M} \xi^{-1}{}_{n,m} E_m(r) \qquad (2)$$

Presumably the energetics of any structure may be modeled if a sufficiently large number of $\Phi_n(r)$ are included (but see ref 11), but the advantages of being able to describe the energetics of a system in terms of a small number, and especially pairwise, or two-atom, potentials, is a particularly attractive one. We have shown,[12] for example, how such parameters are useful in describing the energetics of small molecules. How the pair potentials are

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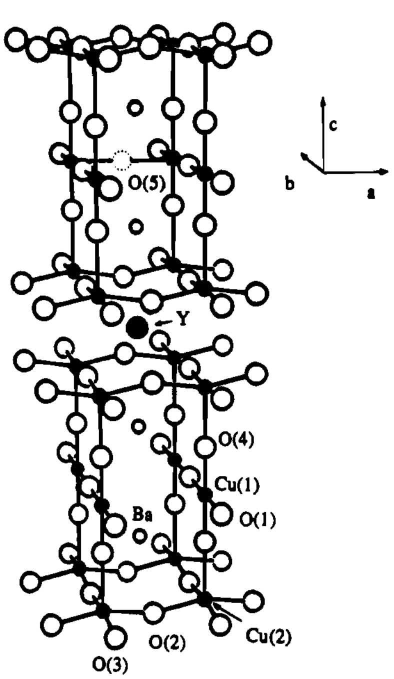

Figure 1. Structure of the 1-2-3 superconductor, $YBa_2Cu_3O_{7-\delta}$. The stoichiometry shown is for $\delta = 0$ and shows the location of the O(1) and O(5) sites.

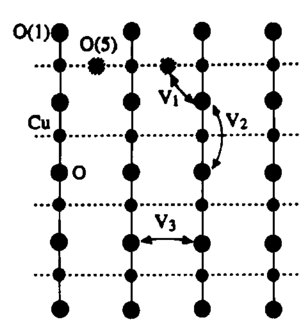

Figure 2. The two-body pair potentials, V_i.

Table I. Calculated Oxygen–Oxygen Pair Potentials (eV) for the Interplanar Region of the 1-2-3 Superconductor[a]

structure included[b]	V_1	V_2	V_4[c]
11,3, 2, 1, 10	0.028	–0.597	
11, 3, 2, 1, 12	0.062	–0.597	
11, 3, 2, 1, 16	0.062	–0.597	
11, 3, 2, 1, 16, 15	0.062	–0.597	–0.593
11, 3, 2, 1, 19	–0.087	–0.597	
11, 3, 8, 19, 16	–0.087	–0.448	
11, 3, 8, 19, 10	–0.087	–0.454	
Sterne and Wille[6]	0.094	–0.033	($V_3 = 0.015$)

[a] V_3 is computed to be positive but very close to zero in each case and is not reported here. [b] See Table II. [c] Only accessible via structure **15**.

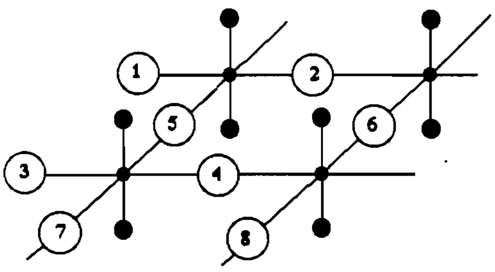

Figure 3. Unit cell used in the electronic structure calculations with some of the oxygen sites identified for use with Table II. Sites 1–4 are O(5) sites; 5–8, O(1) sites.

Table II. Structural Key for Use with Figure 3[a]

		site occupation[b]								pair potential coefficients (ξ_n)				
structure	oxygen stoichiometry	1	2	3	4	5	6	7	8	0	1	2	3	4
11	6.0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	6.5	0	0	0	0	0	1	1	0	2	0	0	0	0
2	6.5	0	0	0	0	1	0	1	0	2	4	0	0	0
8	6.5	0	0	0	0	1	1	0	0	2	0	0	4	0
19	6.5	0	0	0	1	0	0	1	0	2	0	1	0	0
1	7.0	0	0	0	0	1	1	1	1	4	8	0	8	0
10	7.0	0	0	0	1	0	1	1	1	4	4	5	2	0
12	7.25	0	1	0	0	1	1	1	1	5	8	8	2	0
16	7.5	0	1	0	1	1	1	1	1	6	8	16	2	0
15	7.5	1	1	0	0	1	1	1	1	6	8	16	2	4

[a] This is not an exclusive set of structures. Others with vacancies on the O(4) sites were used in the second part of the paper to look at pair potentials involving O(4). [b] 0 = empty site; 1 = occupied site.

calculated, is though, a non-trivial consideration, and a topic we will discuss later.

Of interest to us here is the energetic description of the mobile oxygen atoms in the interplanar region of $YBa_2Cu_3O_{7-\delta}$ by the use of a small set of parameters. The lowest energy structure when $\delta = 0$ is one where all of the O(1) sites are occupied (Figure 1), leading to rows of CuO_3 chains with copper atoms in square planar four-coordination (the Ortho I structure). For $\delta = 0.5$, half of the O(1) sites are occupied in such a way that CuO_3 rows alternate with CuO_2 rows of linear, two-coordinate copper. Occupation of the O(5) sites which lie between the chains probably lie higher energetically. In terms of the crystal chemistry we are interested in the two parts to this problem. First there is the question of the stable ordering patterns associated with a given oxygen stoichiometry, namely what controls the ordering of the oxygen atoms over the various O(1) and O(5) sites in this region? Second there is the question of the factors which control the oxygen stoichiometry itself. The first process leads to no change in the d electron count of the solid, but the second leads to a two-electron reduction every time an oxygen atom is removed from the material ($O^{2-} \rightarrow O + 2e^-$).

The pair potentials which have been used most frequently in dynamical simulations of the 1-2-3 problem are those which were calculated by Sterne and Wille.[6] For $YBa_2Cu_3O_{7-\delta}$ they calculated the energies of five systems, differing in geometry and sometimes stoichiometry ($\delta = -0.5, 0, 0.5, 1.0$). The calculations naturally took into account the change of oxidation state of the copper atoms demanded by the change in oxygen stoichiometry. The resutls from these five calculations lead to five parameters. One is simply the energy of the 6.0 material, the second is the energy associated with insertion of an O(1) or O(5) atom, V_0, and three are the pair potentials shown in Figure 2, which describe the interactions between the oxygen atoms in the interplanar region. Thus the sum of eq 1 has been truncated at the two-atom level, the V_i ($i \neq 0$) just the two-atom potentials used in place of the $\Phi_n(r)$, i.e.

$$E_i = V_0 + \sum\nolimits_n V_n \xi_{ni} \tag{3}$$

Calculations on a set of five different structures will lead to five energies (E_i) which through knowledge of the ξ_{ni} will lead to values for the V_n. The values reported by Sterne and Wille are listed on the last line of Table I. We have calculated similar pair potentials using tight-binding theory which employed the extended Hückel ansatz. (The geometrical and electronic parameters are those used in ref 13 for the $YBa_2Cu_3O_7$ compound.) For simplicity these calculations only included the atoms in the interplanar region (the chains of square planar coordinated copper) of stoichiometry CuO_3. Figure 3 shows the unit cell used in the calculations (with a total of 64K points in the irreducible wedge of the Brillouin zone) and Table II the key to the collection of structures and their contributions (ξ_n) to the pair potentials of Figure 2 we chose

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(13) Burdett, J. K.; Kulkarni, G. V. *Phys. Rev.* **1989**, *B40*, 8908.

for the calculations. These include both hypothetical arrangements for $\delta = -0.5, 0, 0.5$, and the observed structures for the $\delta = 0$ (Ortho I), 0.5 (Ortho II), and 1.0 stoichiometries. The average electron count at the metal varies as $d^{8+2\delta}$. The average stoichiometry of the materials used in the set of calculations is variable, and the assumption is made that it is possible to describe the energetics of these materials with wide-ranging stoichiometries with the same set of parameters. V_3 is always rather small and repulsive from our calculations (and not reported in Table I), but larger in the Sterne–Wille computations. This is probably exclusively due to rather small O–O overlaps which result from our choice of oxygen wavefunction exponents. The fact that V_3 is always calculated to be positive, i.e., repulsive, is readily understandable in terms of the repulsions of closed shells of electrons. The sign of this parameter has some striking structural consequences. Although phase separation occurs in many of these cuprates, an interesting observation is the lack of *macroscopic* phase separation in the 1-2-3 compound. The positive value for V_3 from these calculations (or indeed simple Madelung considerations) show that chains where the O(1) site is completely occupied avoid being adjacent to each other. The Ortho II structure (at the 6.5 stoichiometry) with its alternate occupancy of chains is ideal, here there are none. However the macroscopic alternative is (7.0 + 6.0)/2 which has those adjacent chains in the 7.0. Such repulsions may be the reason behind the instability of the 7.0 with respect to the 6.0 plus O_2, although one should be careful here. This model, of course does not address any change in potential parameters on moving across the phase diagram from 6.0 to 7.0, neither does it take into account the energetics associated with the *c*-axis anomaly which occurs close to the 6.3 stoichiometry.

One of the structures (**15**) allows access to an O(5)–O(5) pair potential (V_4). It is calculated to be slightly smaller in this structure than V_2, a result in accord with the longer O–O distance in this direction. Of more particular interest, however, is the variation in the sign and magnitude of the pair potentials, V_1, V_2, which connect chemically bonded atoms, as a function of the identity of the structures included in the set. We are not as concerned about the difference in the magnitudes of the potentials, as the difference in sign for V_1. The results suggest that it is not possible to generate a self-consistent set of parameters by this route for compounds with such wide-ranging stoichiometries. Sensitivity of the computed parameters to the choice of structure set was found[14] too in the earlier computations.

III. Two-Atom Pair Potentials

The striking results shown in Table I for the potential parameters connecting pairs of oxygen atoms bound to the same copper atom encourage us to explore other ways of thinking about pair potentials, particularly those which do not allow any choice concerning the structures which are to be included in the calculations. As we will show, our deliberations lead to rather fundamental questions concerning how the energies of the various structures are compared.

There are two rather simple ways of defining atom–atom pair potentials. The first, from surface chemistry, tells us that the pair potential between X and Y, Φ_{XY}, is just the energy difference between the two calculations of Figure 4a. If there is an increase in energy on bringing together X and Y, then the pair potential is repulsive; if a decrease in energy, then the pair potential is attractive. In the second viewpoint, if the bond energy of atom X with respect to fragment A (BE_0) and the bond energy of atom X with respect to fragment AY (BE_1) are different then there is a non-zero pair potential between X and Y. If this difference is positive, then X and Y effectively repel each other. The pair potential may be obtained from the values of the two energies BE_0 and BE_1 in the following way. Since

$$BE_0 = E(AX) - E(A+X) \\ = E(AX) - E(A) - E(X) \qquad (4)$$

and

$$BE_1 = E(AYX) - E(AY+X) \\ = E(AYX) - E(AY) - E(X) \qquad (5)$$

the pair potential, $\Phi_{XY}(n)$, between X and Y is

$$\Phi_{XY}(n) = BE_1 - BE_0 \\ = [E(AYX) - E(AY) - E(X)] - [E(AX) - E(A) - E(X)] \\ = [E(AYX) + E(A)] - [E(AX) + E(AY)] \qquad (6)$$

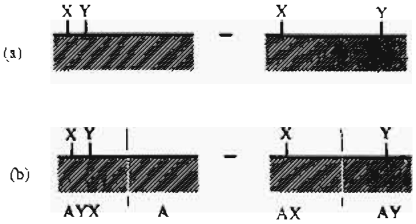

Figure 4. (a) Pair potential from surface studies. (b) Diagram showing how the four densities of states of eq 6 are related to (a).

$\Phi_{XY}(n)$ has been written as a function of *n*, some electron counting label. In contrast to the determination of the V_i of Table I, there is no choice allowed us concerning the stoichiometry or geometry of the four systems A, AY, AX, and AYX. (If X and Y are chemically equivalent, then the number of structures needed is only three.) It is clear though in all of these calculations that the geometries used in the computations are the unrelaxed AYX geometry. Thus, even if the $YBa_2Cu_3O_{6.0}$ and $YBa_2Cu_3O_{6.25}$ stoichiometries are used to derive pair potentials for $YBa_2Cu_3O_{6.5}$, the geometry for the $YBa_2Cu_3O_{6.5}$ stoichiometry is used throughout. Notice that eq 5 describes an isodesmotic process. If the pair potential is not only repulsive, but is large in addition, then, as we have suggested elsewhere,[12,15,16] one of the atoms might be ejected from the structure. Thus between 8 and 9 electrons for main group compounds and between 18 and 19 electrons for transition metal complexes, the pair potential changes from being close to zero to being large and positive, a result in accord[12] with the electronic underpinnings of the 8- and 18-electron rules. Thus stable structures have pair potentials which are small, but unstable ones, much larger potentials.

What we actually mean by the symbols of eq 6 leads to further debate concerning the derivation of these pair potentials. What, for example, is the proper electron count appropriate for the calculations. Should the oxygen atoms X, Y be removed as O atoms or O^{2-} ions? In the calculations of Sterne and Wille noted above, and in our calculations designed to mimic them, the structures for each of the computations for the 7.0, 6.5, and 6.0 stoichiometries are regarded as being neutral, implying that the oxygens are removed as atoms. In terms of the chemistry of eq 6, the computed pair potential then describes the tendency for the loss of oxygen atoms. Relative to the AYX structure, A has four, and AX and AY two more d electrons. Figure 5 shows computed atomic pair potentials for some pairs of oxygen atoms in $YBa_2Cu_3O_{7.0}$ in the interplanar region using the four electronic energies with appropriate electron counts for the relevant structures. Because of the electron count restriction the plot has an upper limit of a d^9 average electron count. Figure 6 shows similar plots for the pair potential in terms of oxygen *ion* loss.

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(15) Burdett, J. K.; Chung, J. T.; Pourian, M. R. *New. J. Chem.* **1991**, *15*, 853.

(16) Burdett, J. K.; Chung, J. T. *Surf. Sci.* **1990**, *236*, L353.

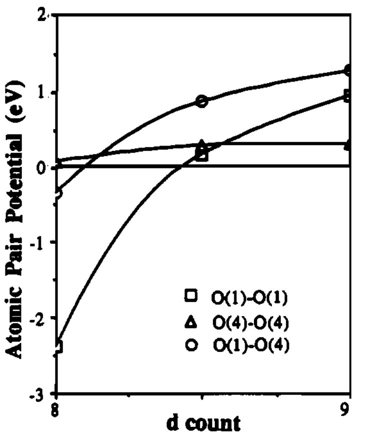

Figure 5. Computed atomic pair potentials for the $\mathrm{YBa_2Cu_3O_7}$ compound.

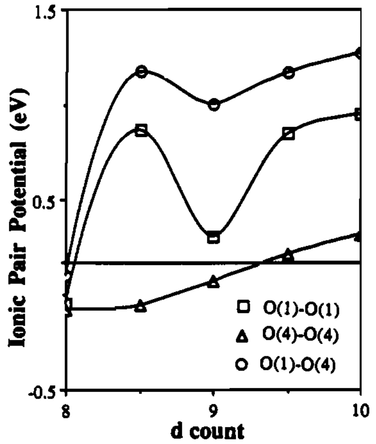

Figure 6. Computed ionic pair potentials for the $\mathrm{YBa_2Cu_3O_7}$ compound.

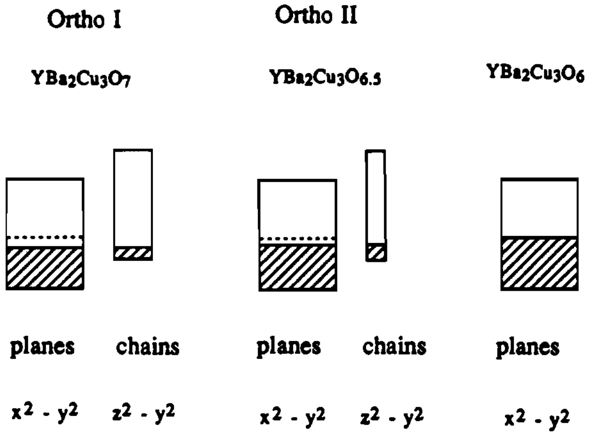

Figure 7. Schematic electronic structure for the 1-2-3 compound using a band model. Note the overlap of the $x^2 - y^2$ band of the planes and the $z^2 - y^2$ band of the chains leading to plane-to-chain electron transfer.

Here the oxygens are removed as $\mathrm{O^{2-}}$ and the d electron count of each of the four structures of eq 6 are the same. There is no restriction on the d count range and that from d^8 to d^{10} is shown. Notice that the two pair potentials are not the same and depend on the nature of the ejected particle, although there are some similarities in their behavior with d count which we will discuss below. From eq 6 the average stoichiometry of both calculations is one atom less than the system under consideration.

The electronic description of the 1-2-3 compound itself[13] is shown in Figure 7. There is overlap between the $x^2 - y^2$ bands of the planes with the z^2 band of the chains, except in the 6.0 stoichiometry. This means that because of plane-to-chain charge transfer the d electron count in the planes is smaller than d^9. In fact, if we assume that there are 0.15 holes in the planes in 1-2-3 by analogy with the optimal doping level in 2-1-4, then the chain d count is around 8.3 in $\mathrm{YBa_2Cu_3O_{7.0}}$ and its average over the two different copper atoms in the Ortho II structure is probably around 9.07 in $\mathrm{YBa_2Cu_3O_{6.5}}$. (The two-coordinate species are d^{10} and the single chain $d^{8.15}$ from Figure 7.) Such electron transfer is extremely important in determining the electronic properties of the material, at least in generating a less than half-filled band, and hence a metal (see ref 17). As we will see this electron transfer crucially affects the sizes of the pair potentials.

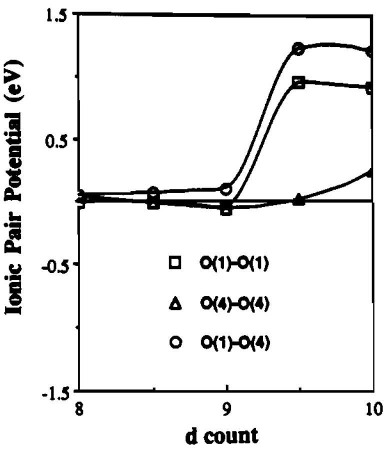

Figure 8. Computed ionic pair potentials for the Ortho II $\mathrm{YBa_2Cu_3O_{6.5}}$ compound.

The plots for the Ortho I and II 7.0 and 6.5 stoichiometries are quite instructive. Figure 8 shows the ionic pair potential plot for the latter. They are similar in many ways and reflect the weak computed interactions between the chains. So notice that the behavior of the ionic curves from d^8–d^9 ($\mathrm{YBa_2Cu_3O_7}$) of Figure 6 is similar to that from d^9–d^{10} of Figure 8 for $\mathrm{YBa_2Cu_3O_{6.5}}$. (Similar results are found (but not shown) for the atomic pair potentials in $\mathrm{YBa_2Cu_3O_{6.5}}$.) From these figures it is interesting to note that both the ionic O(1)–O(1) and O(1)–O(4) potentials increase as the d count increases from 8 to 8.3 (in $\mathrm{YBa_2Cu_3O_{7.0}}$) and from 9 to 9.07 (in $\mathrm{YBa_2Cu_3O_{6.5}}$). The results suggest that the tendency for O(1) ion loss should increase with d count. The O(4)–O(4) interaction potential remains negative. Notice in the atomic pair potential plots of Figure 5 for the $\mathrm{YBa_2Cu_3O_{7.0}}$ material that the O(1)–O(1) and O(1)–O(4) potentials within a given chain become repulsive too as the d count increases past about 8. Again, using the ideas described earlier this leads to a tendency for oxygen loss, a key feature of the chemistry of this material. Each O(4) atom is connected to one other O(4) via an O(4)–O(4) interaction, and to two O(1) atoms via an O(1)–O(4) interaction. Each O(1) atom, however, is connected to two other O(1) atoms via an O(1)–O(1) interaction and four O(4) atoms via an O(1)–O(4) interaction. By weighing the size of the relevant pair potentials it is clear that the O(1) atom is involved in the stronger repulsions and should be the atom lost from the structure. This is indeed the case. There is little evidence for O(4) loss. It implies too that oxygen should not be lost from structures containing the $\mathrm{CuO_3}$ chain when the d count is 8. It is the increased d count which leads to this result via the overlap of the two metal bands shown in Figure 7, discussed in more detail elsewhere,[13] which leads to the oxygen nonstoichiometry in this compound. It is interesting to compare the chemistry implied by positive ionic or atomic pair potentials. Since atomic potentials measure the tendency for loss of oxygen atoms, the eventual product is $\mathrm{O_2}$. Ionic potentials which lead to loss of $\mathrm{O^{2-}}$ describe movement of the particle out of the chain region into another part of the solid without any change in oxidation state of the chain atoms. Probably both processes are important when considering the change in stoichiometry.

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(17) Burdett, J. K. *Adv. Chem. Phys.* **1993**, *83*, 207.

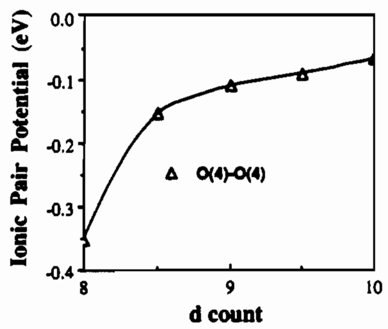

Figure 9. Computed ionic pair potentials for the $YBa_2Cu_3O_6$ compound.

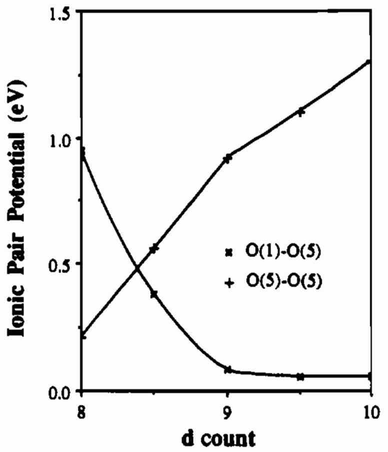

Figure 10. Computed ionic pair potentials for the hypothetical $YBa_2Cu_3O_{7.5}$ compound.

At one end of the compositional spectrum lies the $YBa_2Cu_3O_6$ system, an insulator, which has all O(1) sites unoccupied leading to CuO_2 dumbbells. Figure 9 shows the computed ionic O(4)–O(4) pair potentials for this stoichiometry. Note that here the pair potential connecting oxygen atoms bound to the same copper atom is negative at d^{10}, a result in accord with the lack of O(4) loss from the dumbbell sites at this stoichiometry. Notice that the shape of the ionic O(4)–O(4) pair potential, defined in the 6, 6.5, and 7.0 stoichiometries, varies with the system under consideration and is not transferable, although the differences are not enormous.

Some ionic pair potentials for the hypothetical $YBa_2Cu_3O_{7.5}$ material are shown in Figure 10. (The actual compound undergoes a phase transformation if attempt is made to increase oxygen content past the 7.0 stoichiometry.) The structure consists of alternating square planes and octahedra. At this oxygen stoichiometry, an important point to note is that the O(5) sites, completely unoccupied in $YBa_2Cu_3O_{7.0}$, become partially occupied. This stoichiometry needs to be used in order to calculate the O(5)–O(5) pair potential. Note that for these O(5) pair potential plots there is a strong repulsion between it and all other atoms at d^8. This will lead on the model to ion loss from these sites and the generation of the d^8 $YBa_2Cu_3O_{7.0}$ system. One could regard the instability of oxygen in these O(5) sites as arising from the Jahn–Teller instability of the octahedron at these electron counts. The atomic pair potentials show a different picture (Figure 11). Here addition of extra oxygen to the $YBa_2Cu_3O_{7.0}$ compound leads to an average d count of 7. The stability of octahedral d^6 and square planar d^8 coordination shows up as a strong negative pair potential at the average d^7 electron count. Such a result though does not accommodate the energetic penalty associated with the generation of d^6 Cu^V.

There is another factor here which is perhaps difficult to estimate quantitatively. We know, empirically, that certain geometrical arrangements are frequently associated with certain d counts. Specifically in $YBa_2Cu_3O_7$, the interplanar copper is in square planar coordination, a geometry typically found for the low spin $d^8(Cu^{III})$ configuration. In $YBa_2Cu_3O_6$, this copper is in a linear, two-coordinate environment, a geometry typically seen for $d^{10}(Cu^I)$ configurations. The octahedral d^6 and square planar d^8 coordinations, although not found in copper chemistry, are found together in the well-known platinum mixed valence compounds. Interestingly, all of these observations show up as zero or negative pair potentials between the oxygen atoms for the relevant structure at the proper d count. Chemists have very little understanding concerning the electronic factors underpinning the frequently made statement "geometry Q is "stable" for a given metal M in its *v*th oxidation state". Almost certainly our calculations do not include all of the electronic ingredients which control such effects; however it is interesting that the stabilities just referred to are indeed mimicked by the form of the pair potentials.

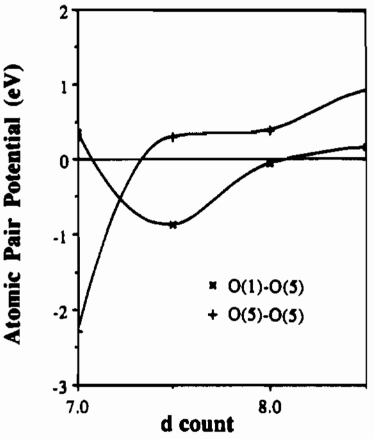

Figure 11. Computed atomic pair potentials for the hypothetical $YBa_2Cu_3O_{7.5}$ compound.

We return now to the view of the pair potential from surface chemistry, and how it is connected to the picture we have just used. We can rewrite the way the calculations of Figure 4a are performed as in Figure 4b, a result which highlights the comparison with the bracketed terms of eq 4. At first sight this looks very similar to the way pair potentials were calculated before, but there is a difference. The densities of states of AYX and A are merged to give $[E(AYX) + E(A)]$, and those of AX and AY merged to give $[E(AX) + E(AY)]$. Thus the evaluation of the pair potential here reduces to the energy difference between two calculations via the use of two merged densities of states. In the present situation this type of pair potential is therefore the one which is best suited to understanding the ordering patterns of the oxygen atoms in the interplanar region without a change in stoichiometry. The average stoichiometry of the calculation is, just as before, one atom less than the system under consideration. Figure 12 shows some computed results for the $YBa_2Cu_3O_{6.5}$ stoichiometry and shows an attractive O(1)–O(1) potential at $d^{9.07}$. Thus the oxygen atoms want to order in such a way so as to form chains. Contrast this with the atomic and ionic pair potentials which are measures of particle ejection from the chain region. The negative O(1)–O(1) potential here and the positive potentials found earlier are quite consistent with their definitions.

IV. Conclusions

This study has shown that the representation of the energetics of solids by means of a set of pairwise interaction potentials is not a straightforward matter. The form of the interaction potentials depends very much on what one means when defining such parameters. All of these simple two-atom pair potentials certainly include higher order terms of the most general expansion, a result highlighted by the results of Table I, where the magnitude of the V_i and the sign of V_1 change with the identity of the structures included in the determination. In terms of the most stable

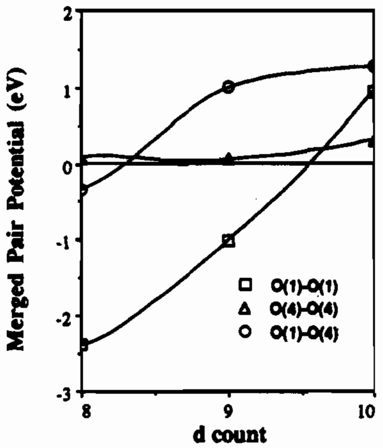

Figure 12. Computed merged pair potentials for the $YBa_2Cu_3O_{6.5}$ compound.

structure *for a given stoichiometry*, the merged pair potentials are useful. Probably too the energetic penalties of putting an oxygen ion in an O(5) site are well-represented by the size of the ionic pair potentials around the d^8 electron count. Certainly the calculated energy difference between structures **1** and **10** (Table II) of ~0.5 eV at the d^8 electron count indicates the energy cost of removing an atom from a chain O(1) site and placing it in an interchain O(5) site. The behavior of the both the atomic and ionic pair potentials for the $\delta = 0, 0.5$, and 1.0 structures are very consistent with their chemistry, but as we have discussed, the atomic pair potentials for the $\delta = -0.5$ stoichiometry do not reflect the instability of this material.

In a more general way, although the discussion here has centered around the cuprate superconductor, the meaning and derivation of the various types of pair potentials have been interesting in their own right.

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