Cluster studies of the electronic structure of Cu—O chains in high-temperature superconductors

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The electronic structure of Cu—O chains present in the crystal structure of high-temperature superconductors typified by $YBa_2Cu_3O_7$ is investigated by means of self-consistent local-spin-density calculations for a cluster of $Ba_4Cu_2O_7$ in different charge states. No magnetic moments are found on the Cu ions. The nature of the chemical bonding in the cluster is discussed on the basis of the calculated charge density.

This note reports a study of the electronic structure of the copper-oxygen chains present in structural models of the high-temperature superconductors typified by $YBa_2Cu_3O_{7-x}$. At the present time there are many competing theories of the origin of superconductivity in these materials. Although local-spin-density functional calculations cannot in any explicit way explain superconductivity, they can contribute through the determination of the spectrum of single-particle states and of the charge and spin densities in the system to the selection of an appropriate theory.

This note reports self-consistent spin-polarized calculations of the energy levels and charge and spin densities of a cluster representing the Cu—O chains believed important to the superconducting properties of the material. At this time, we are not able to make accurate calculations for a cluster large enough to represent the entire formula unit, and so have restricted our consideration to the Cu—O chain plus some neighboring atoms. The specific cluster considered is $Ba_4Cu_2O_7$. The geometry is shown in Fig. 1. The chemical formula $YBa_2Cu_3O_{7-x}$ leads to some uncertainty as to the valence of copper (2, 3, or possibly intermediate). If the valence of Cu were 3, a $Ba_4Cu_2O_7$ cluster would be expected to be electrically neutral; if the valence were 2, we would expect the cluster to be ionic. As a result, we considered both the neutral $Ba_4Cu_2O_7$ and the ionic $Ba_4Cu_2O_7{}^{2-}$ clusters. The results convinced us that a fully ionic picture is not appropriate, in accord with the actual metallic properties of $YBa_2Cu_3O_7$. Then we considered positively charged clusters: $Ba_4Cu_2O_7{}^+$ and $Ba_4Cu_2O_7{}^{2+}$, which allow for the possibility that the cluster could serve as an electron donor. Results will be presented below pertaining to the different charge states, and essentially, do not depend strongly on the charge state. Our present view, based on the position of the Fermi level, is that the 1+ state is most realistic.

Structural information for this calculation was taken from Beno *et al.*[1] Our calculation was made using a linear combination of Gaussian orbitals method. Contracted basis sets: $Ba(6s/4p/2d)$; $Cu(7s/5p/2d)$; $O(5s/3p/1d)$ were used. These sets were obtained from several sources.[2] Slightly different bases were used in the different change states. A variational charge fitting procedure was used in the evaluation of the matrix elements of the electrostatic potential, and a separate least-squares fitting procedure was used in regard to the exchange-correlation potential. Details of the calculational methods of our new, general cluster program will be published elsewhere. The Rajagopal, Singhal, and Kimball exchange correlation potential was employed.[3]

We will now discuss our results. Some of the theoretical models discussed in connection with high-temperature superconductivity imply or require the existence of antiferromagnetic coupling of electron spins, with moments being present on the Cu atoms.[4–5] In fact, antiferromagnetic order has been observed in La_2CuO_{4-y}, with a Néel temperature[6] of about 220 K. Paramagnetic resonance experiments show that at least some Cu atoms in $YBa_2Cu_3O_7$ are in the Cu^{2+} state and have moments.[7] It is not clear that all Cu atoms do. Our calculation shows no moment to be present in a $Ba_4Cu_2O_7$ cluster in any of the charge states studied (from 2+ to 2−). Our suggestion is that the Cu(2) atoms which have a square pyramidal oxygen coordination may have moments while the Cu(1) atoms in the chain do not. The calculation is begun with the assumption that there is a moment, but the
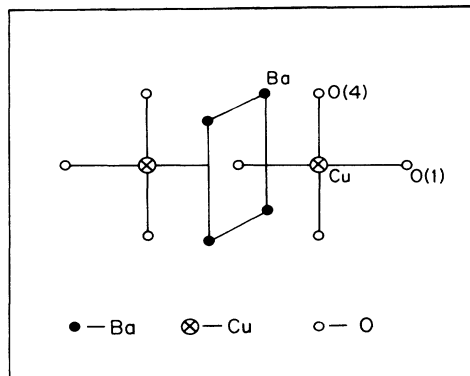

FIG. 1. Structure of the $Ba_4Cu_2O_7$ cluster, consisting of a Cu_2O_7 plane intersected by a Ba_4 plane perpendicularly in the middle.

moment disappears during the iterations leading to self-consistency.

The energy level structure of both the neutral and the ionic clusters are quite similar (except for a small shift of the Fermi level). We calculate a density of states from the cluster levels by broadening the levels with a Gaussian of width 0.74 eV. We compare this density of states directly with photoemission measurements. This should be adequate as far as the basic structure (location of peaks) is concerned, although it would be preferable to include matrix element effects on orbital-dependent photoemission cross sections). Likewise, we neglect electronic relaxation. Our results for the neutral cluster are compared with the ultraviolet resonant photoemission measurements of Kurtz et al.,[8] in Fig. 2. Results for the ionic clusters are quite similar except for a shift of the Fermi energy. There is a substantial degree of agreement. In our calculation the low-energy peak A (31.3 eV) is associated with barium $5s$ states; peak B (20.6 eV) with the oxygen $2s$ states; peak C (16.8 eV) with the barium $5p$ states. The unoccupied states of peak F were found to have a mixture of copper $4s$ and oxygen s states.

The states in the neighborhood of the Fermi energy are a mixture of copper d states and oxygen p states. There are two peaks in the density of states; D (3.4 eV below E_F), and E (1.0 eV). In the neighborhood of D, Cu d states predominate (about 60% Cu d and 40% O p), while near E, oxygen p states dominate (about 88%).

This picture is not inconsistent with the results of two band calculations[9,10] except that the oxygen p copper d states seem to be distributed over a somewhat wider range of energies here (about 15 eV in comparison with 10 eV) than in the band calculations cited. A third set of results for the energy bands[11] differs more substantially (insofar as one can judge from graphical data) in that these authors find a substantially higher contribution from copper states to the first peak below E_F in the density of states.

Our work is in rather good agreement with the band calculations of Ching et al.,[12] and Krakauer and Pickett.[13] Ching et al., find that the copper atoms are predominately in the Cu$^+$ state. Krakauer and Pickett
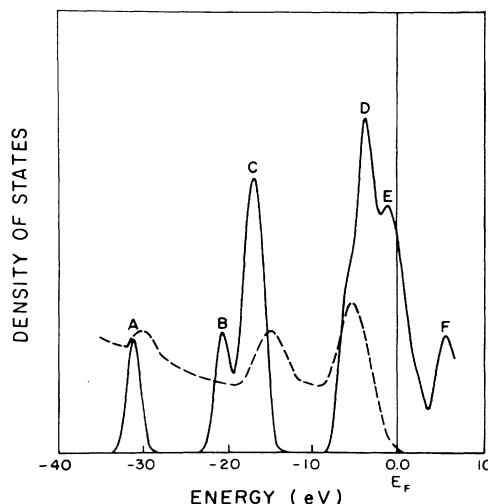
FIG. 2. The calculated total density of states of $Ba_4Cu_2O_7$ neutral cluster (solid line) as compared with experimental photoemission data (dashed line) of Ref. 8.

separate the contributions to the density of states from Cu(1) and Cu(2) atoms. Most of the Cu (1) density is in states well below the Fermi level, inhibiting the formation of moments.

It is apparent from Fig. 2 that the peak structure near E_F in the calculated density of states is shifted to higher energy with respect to the peak in photoemission spectrum by about 2 eV. A similar result has been reported by Redinger, Freeman, Yu, and Massida,[14] and attributed by them to the lack of metallic screening for the Cu d holes. We are now investigating the effect of electronic relaxation through transition-state calculations. Preliminary results indicate an effective Hubbard U of 5 eV in reasonable agreement Fujimori, Takayama-Muromachi, Uchida, and Okai.[15] This was obtained from the difference of eigenvalues of a copper d state in which the occupancies were fixed as $\frac{3}{2}$ and $\frac{1}{2}$. Note that this U is of the order of
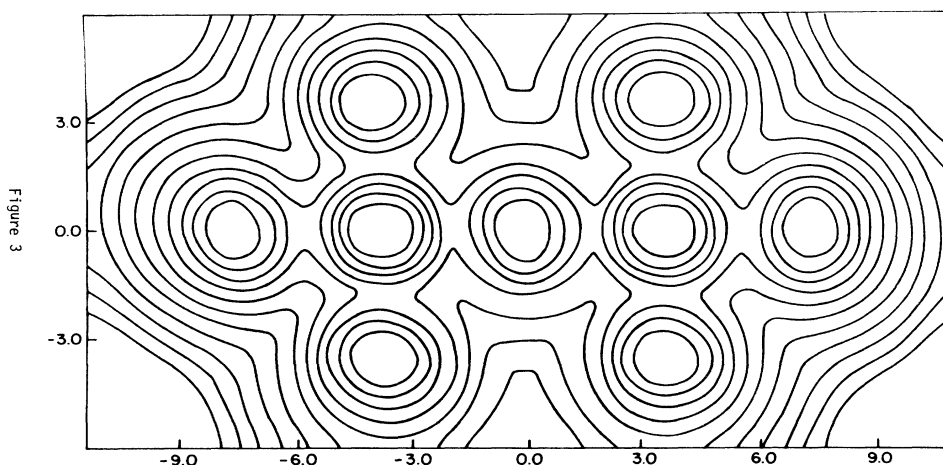
FIG. 3. Contour plot of valence charge density in Cu—O plane. The adjacent contours differ by a factor of 2, with initial value $=0.0002$ (the outermost contour).

TABLE I. Valence population analysis for each atom.

	Mulliken population						Numerical integration			
	Ba s	Cu s	Cu p	Cu d	O s	O p	Ba	Cu	O(1)	O(4)
$Ba_4Cu_2O_7^{2+}$	0.15	0.25	0.34	9.32	0.13	4.92	0.12	9.56	2.82	3.02
$Ba_4Cu_2O_7^{+}$	0.22	0.24	0.32	9.30	0.12	5.05	0.13	9.57	2.90	2.99
$Ba_4Cu_2O_7$	0.32	0.55	0.39	9.19	0.06	5.13	0.14	9.66	2.92	2.99
$Ba_4Cu_2O_7^{2-}$	0.67	1.03	0.42	9.18	0.02	5.25	0.21	9.66	2.92	2.98

the bandwidth. The system is not in the limit in which U is much greater than the bandwidth.

The charge distribution resulting from our calculations is shown in a contour plot in Fig. 3. We infer from this graph that the Cu—O subsystem is not strongly ionic. The population of atomic states (in terms of s, p, d, etc.) has been estimated in two different ways: (1) the traditional Mulliken population analysis (which is only valid for qualitative understanding) and (2) by numerical integration through a sphere around each atom. For this purpose, covalent radii were chosen (Ba, 2.47 a.u.; Cu, 2.21 a.u., and O, 1.38 a.u.). The use of covalent radii for this case is justified by the contours of Fig. 2. The results of these two analyses are in fairly good agreement. In the case of oxygen, the small results obtained by numerical integration indicate that the oxygen charge distribution is quite diffuse. Numerical values are given in Table I. We conclude that the cluster is not as strongly ionic as might have been anticipated. Most of the oxygen is present as O⁻. From this and from the density of states, we expect the dominant conduction. process to involve holes mainly of O $2p$ character, as proposed by Emery.[16] There is no appreciable difference between the population of O (1)

and O (4) sites: in other words, the hole distribution is reasonably uniform over the oxygen sites. There is little difference in the electron density on copper between the different charge states. The copper atoms may fluctuate between Cu^+ and Cu^{2+} states, although Cu^+ should be dominant. However, there is no indication of the presence of Cu^{3+}. There are no permanent magnetic moments on the Cu sites, although instantaneous moments could arise due to fluctuations.

Recently Callaway, Kanhere, and Misra[17] proposed a model Hamiltonian which may describe motion of holes along a Cu–O chain. The present calculation is consistent with their model in that a range of model parameters can be found which describes a nearly uniform distribution of holes on the oxygen sites. Addition of a copper-oxygen repulsion and a polarization interaction as described in Ref. 13 then leads to the formation of a strongly correlated state.

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