

## Electronic structure and properties of $\text{Cu}_2\text{O}$

Eliseo Ruiz and Santiago Alvarez

*Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

Pere Alemany

*Departament de Química Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

Robert A. Evarestov

*Department of Quantum Chemistry, St. Petersburg State University, St. Petersburg, Russia*

(Received 18 February 1997)

The structural and electronic properties of  $\text{Cu}_2\text{O}$  have been investigated using the periodic Hartree-Fock method and *a posteriori* density-functional corrections. The lattice parameter, bulk modulus, and elastic constants have been calculated. The electronic structure of and bonding in  $\text{Cu}_2\text{O}$  are analyzed and compared with x-ray photoelectron spectroscopy spectra, showing a good agreement for the valence-band states. To check the quality of the calculated electron density, static structure factors and Compton profiles have been calculated, showing a good agreement with the available experimental data. The effective electron and hole masses have been evaluated for  $\text{Cu}_2\text{O}$  at the center of the Brillouin zone. The calculated interaction energy between the two interpenetrated frameworks in the cuprite structure is estimated to be around  $-6.0$  kcal/mol per  $\text{Cu}_2\text{O}$  formula. The bonding between the two independent frameworks has been analyzed using a bimolecular model and the results indicate an important role of  $d^{10}$ - $d^{10}$  type interactions between copper atoms. [S0163-1829(97)01735-9]

### I. INTRODUCTION

The recent interest in basic aspects related to the electronic structure of the copper oxides can be attributed to the importance of the different oxidation states of copper atoms in the physical properties of the high- $T_c$  superconductors. Another attractive feature of the cuprous oxide,  $\text{Cu}_2\text{O}$ , is that it crystallizes in the cuprite structure,<sup>1</sup> formed by a bcc array of oxygen atoms with metal atoms inserted between two consecutive oxygen layers, in such a way that each oxygen atom is surrounded by a tetrahedron of copper atoms. Each metal atom is two-coordinate, forming lineal  $\text{CuO}_2$  units (Fig. 1). Alternatively, the structure can be described by two interpenetrating frameworks, each one equivalent to the  $\text{SiO}_2$  cristobalite structure (Fig. 2).<sup>2</sup>

There have been several theoretical works dedicated to the study of the electronic structure of  $\text{Cu}_2\text{O}$ , mainly due to the interest aroused by the measurements of its excitonic spectrum.<sup>3,4</sup> Earlier studies were performed by Kleinman and Mednick using the Hartree-Fock-Slater method,<sup>5</sup> by Dahl and Switendick with a non-self-consistent augmented plane

wave (APW) method<sup>6</sup> and by Robertson using a tight-binding approach.<sup>7</sup> The works of Ghijsen and co-workers<sup>8,9</sup> and Mariot<sup>10</sup> have been devoted to the study of the x-ray photoelectron spectroscopy (XPS) spectrum and its comparison with the calculated density of states. Marksteiner, Blaha, and Schwarz,<sup>11</sup> performing full-potential linearized augmented plane wave (FLAPW) calculations, analyzed the chemical bond in  $\text{Cu}_2\text{O}$ , focusing on the linear coordination of the copper atoms and discussing mainly the hybridization found for the copper orbitals. More recently, Ching, Xu, and Wong<sup>12</sup> reported a density-functional study of the ground state and optical properties of  $\text{Cu}_2\text{O}$ . Evarestov and Veryazov<sup>13</sup> have carried out large unit cell-complete neglect

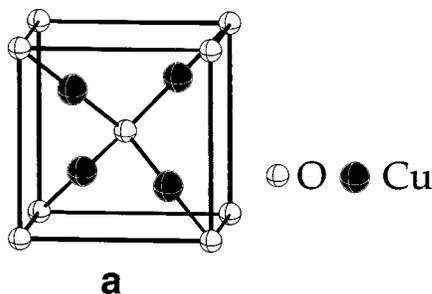


FIG. 1. Crystal structure of  $\text{Cu}_2\text{O}$ . Black balls represent copper atoms, white ones oxygen atoms.

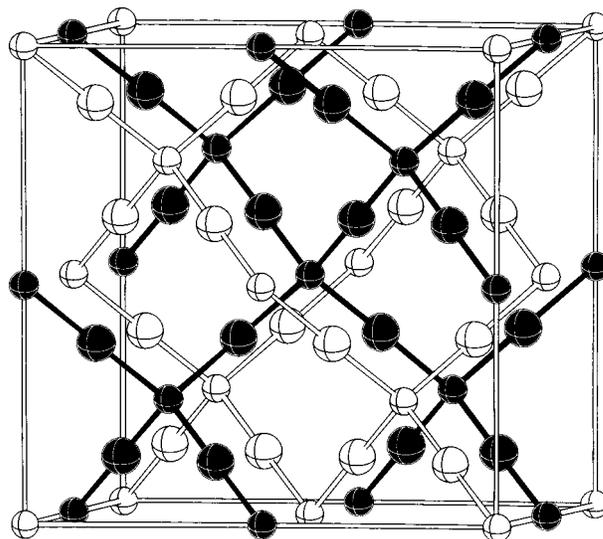


FIG. 2.  $\text{Cu}_2\text{O}$  ( $2 \times 2 \times 2$ ) supercell structure. Black and white balls represent the two independent frameworks, respectively.

of differential overlap (LUC-CNDO) calculations to review the electronic structure of different copper oxide crystalline compounds. From the point of view of cluster calculations, Nagel considers the chemical bonding in  $\text{Cu}_2\text{O}$  using the multiple scattering  $X$ -alpha ( $MSX_\alpha$ ) method,<sup>14</sup> indicating that it is unusual, with no strong covalent interactions but with significant deviations from the purely ionic picture. More recently, Goodman *et al.*<sup>15</sup> provided a comparison of the charge distribution in cluster models for different copper oxide compounds using a discrete variational Hartree-Fock-Slater method.

The work presented in this paper has two different aims. The first one is to report periodic Hartree-Fock-level calculations of selected electronic and structural properties of  $\text{Cu}_2\text{O}$  and to compare them with the previously published experimental and theoretical results. The second aim of our work is to look at the nature of the interactions between the two interpenetrating frameworks in the cuprite structure.

## II. METHODOLOGY

The calculations reported in the present work have been carried out using the CRYSTAL-92 (Ref. 16) and CRYSTAL-95 (Ref. 17) programs, which provide self-consistent solutions to the Hartree-Fock-Roothan equations subject to periodic boundary conditions. *A posteriori* density-functional corrections to the Hartree-Fock result for the total energy have been included, with the correlation functional proposed by Lee, Yang, and Parr (LYP). More details of the mathematical formulation of this method have been previously described<sup>18</sup> and will be omitted here.

The CRYSTAL programs employ a localized atomic-orbital basis set derived from Gaussian-type functions to construct the Bloch functions. As in the molecular Hartree-Fock calculations, the results can be quite sensitive to the choice of the basis set. The program can work at the all-electron level as well as with effective core pseudopotentials. The all-electron basis set used in our calculations has a triple- $\zeta$  quality. A more detailed description of the basis sets adopted is given in the Appendix.

Computational parameters controlling the truncation of both the Coulomb and exchange infinite series have been chosen to give a “good” level of accuracy defined in the sense of Pisani, Dovesi, and Roetti.<sup>18</sup> Integration of  $k$ -dependent magnitudes in the reciprocal space has been done using a mesh of ten  $k$  points in the irreducible wedge of the first Brillouin zone of the sample cubic lattice.

## III. RESULTS

### A. Crystal structure

Results of the geometrical optimization of the  $\text{Cu}_2\text{O}$  crystal structure with the all-electron basis set can be found in Table I. Comparison with other theoretical studies is not possible because no geometry optimization has been reported in the previous works devoted to  $\text{Cu}_2\text{O}$ . Our results for the lattice parameter show a well-known feature of the periodic Hartree-Fock (HF) method that results in an overestimation of the lattice size, mainly due to the neglect of electronic correlation.<sup>19,20</sup> The inclusion of the electronic correlation through density functional theory (DFT) corrections consid-

TABLE I. Calculated lattice constant, interatomic distances, bulk modulus, and elastic constants for  $\text{Cu}_2\text{O}$  using the Hartree-Fock method (HF) and Hartree-Fock plus *a posteriori* correlation energy correction using the Lee-Yang-Parr functional (HF+LYP). Available experimental data are reported for comparison.

	HF	HF+LYP	Expt.
$a$ (Å)	4.435	4.277	4.2696 <sup>a</sup>
Cu-O (Å)	1.920	1.852	1.849
Cu···Cu (Å)	3.136	3.025	3.012
$B$ (GPa)	100	93	112 <sup>b</sup>
$c_{11}$ (GPa)	118	103	116 <sup>b</sup> –126 <sup>c</sup>
$c_{12}$ (GPa)	90	88	105 <sup>b</sup> –108 <sup>c</sup>
$c_{44}$ (GPa)	59	65	11 <sup>b</sup> –13 <sup>c</sup>

<sup>a</sup>Reference 21.

<sup>b</sup>Reference 22.

<sup>c</sup>Reference 23.

erably improves the results of the geometry optimization. The experimental value of the Cu-O bond distance is 1.849 Å close to the HF+LYP value of 1.852 Å while the HF calculation bond distance is 1.920 Å.

The isotropic variation of the volume of the cubic unit cell employed in the determination of the lattice parameter can also be used to evaluate the bulk modulus. Results obtained for this property, its derivative with the pressure, and the three elastic constants are provided in Table I. The calculated bulk modulus is in good agreement with the available experimental data. The three independent components of the elastic tensor were derived numerically from the changes in energy obtained by applying adequate deformations to the unit cell. Good agreement has been obtained for the  $c_{11}$  and  $c_{12}$  elastic constants, while there is definite disagreement for  $c_{44}$ . The present disagreement is certainly to be attributed to the lack of precision of these methods of estimate small values of the elastic constants, as noted previously for cubic zirconia.<sup>24</sup> This observation is due to the fact that the elastic constants are related with the total energy through its second derivatives with respect to the strain components. Good quality calculations of the elastic constants would thus require a larger accuracy in contrast to those properties like the cell parameters.

### B. Band structure and density of states

The calculated band structure of  $\text{Cu}_2\text{O}$  is presented in Fig. 3. The labels corresponding<sup>25</sup> to the irreducible representation of the symmetry bands using Miller-Love indices<sup>26</sup> have been indicated for the lower conduction bands (the same analysis is shown afterwards for the valence bands). The representations of the individual atomic orbitals for the cuprite structure are indicated in Table II to allow comparison with the band structure. The results show the existence of a direct band gap of 9.7 eV at the center of the Brillouin zone ( $\Gamma$ ). The experimental value of 2.17 eV obtained by optical absorption<sup>27</sup> is in strong disagreement with the calculated one, reflecting the well-known overestimation of this property by the periodic Hartree-Fock method. This fact does not permit the use of this methodology for the interpretation of the excitonic spectrum of  $\text{Cu}_2\text{O}$ , because the band-gap en-

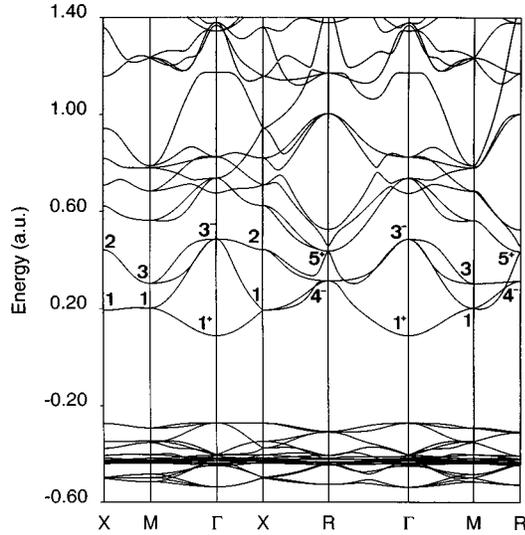


FIG. 3. Electronic band structure for Cu<sub>2</sub>O. The labels for the lower conduction bands indicate their irreducible representation in the space group  $Pn\bar{3}m$  ( $O_h^4$ ). The states located at energies below  $-0.20$  a.u. belong to the valence band.

ergy is included in all exciton series. The topology and the main features of the band structure agree well with previous calculations<sup>5,7,11,12</sup> except for the aforementioned gap value. The calculated width of the valence band is 7.7 eV, in good agreement with the experimental estimation around 8 eV obtained from the ultraviolet photoelectron spectroscopy (UPS) experiments reported by Ghijsen *et al.*<sup>8</sup>

The calculated total density of states and its orbital-projected contributions are displayed in Fig. 4. The valence band is dominated by the Cu 3*d* states, while the contribution of the Cu 4*p* states is practically zero. However, the 4*s* Cu states show a small contribution to the valence band, in good agreement with the Orgel model<sup>28</sup> that proposes an *s-d* hybridization at the metal atoms to explain the linear coordination of Cu<sup>+</sup>. The energy corresponding to the maximum of intensity of the Cu 3*d* band in the x-ray emission spectra for the Cu 3*d* states has been reported at 2.5 (Ref. 10) and 3.1 eV (Ref. 8) (taking the origin at the upper edge of the valence band), in good agreement with our calculated value of 3.1 eV.

The only contribution from the O atoms to the valence band comes from the 2*p* states, while those of the *s* states and *d* polarization functions are negligible. For the O 2*p* band, both experimental and calculated results yield two

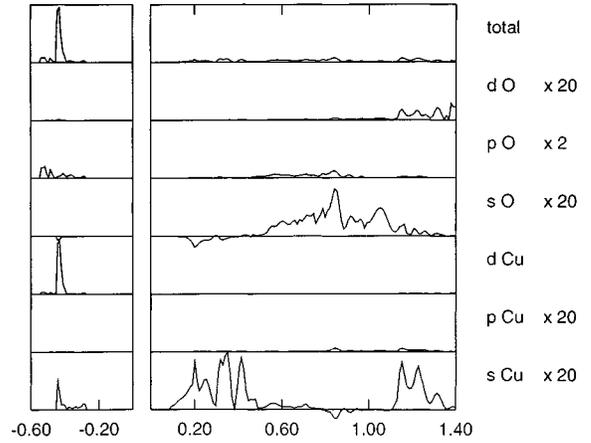


FIG. 4. Atomic orbital projections of the density of states obtained for Cu<sub>2</sub>O. The scale corresponding to the conduction bands has been augmented five times in comparison with the valence bands. The atomic orbital contributions have been obtained using a Mulliken partition scheme.

peaks: the calculated values of 5.7 and 7.1 eV are in excellent agreement with the experimental values<sup>8</sup> of 5.93 and 7.3 eV.

The conduction band was studied by Ghijsen *et al.*<sup>8</sup> using bremsstrahlung isochromat spectroscopy (BIS). The three peaks of the spectra were assigned using the results of a calculation performed by the augmented spherical wave (ASW) method. According to their assignment, the peak at 3.1 eV corresponds to Cu 3*d* and O 2*p* states, the peak at 8.1 eV is due to the Cu 4*s* states, and the peak at 13.4 eV comes from Cu 4*p* states with some O 2*p* admixture. In our calculated density of states, however, the main contribution in the lower region of the conduction band corresponds to the Cu 4*s* states and practically all the other contributions are negligible.

### C. Electron density

Electron density maps were calculated for Cu<sub>2</sub>O in the (110) plane. Figure 5(a) displays the total electron density, while Fig. 5(b) shows the difference between the crystalline charge density and the superposition of the spherical atomic densities. The total electron density presents a practically spherical distribution around both atoms, with only the oxygen atoms showing a very slight distortion. The calculated difference map presents a shape for the contour lines similar

TABLE II. Band representations of the space group  $Pn\bar{3}m$  ( $O_h^4$ ).

			$\Gamma$	$R$	$M$	$X$	
Cu ( $D_{3d}$ )	$s$	$a_{1g}$	$1^+5^+$	$1^+5^+$	1 3	1 4	
	$4b$	$p_x, p_y$	$e_u$	$3^-4^-5^-$	$3^-4^-5^-$	1 2 3 4	1 2 3 4
		$p_z$	$a_{2u}$	$2^-4^-$	$2^-4^-$	1 4	1 3
		$d_{z^2}$	$a_{1g}$	$1^+5^+$	$1^+5^+$	1 3	1 4
		$d_{x^2-y^2}, d_{xy}$	$e_g$	$3^+4^+5^+$	$3^+4^+5^+$	1 2 3 4	1 2 3 4
		$d_{xz}, d_{yz}$	$e_g$	$3^+4^+5^+$	$3^+4^+5^+$	1 2 3 4	1 2 3 4
O ( $T_d$ )	$s$	$a_1$	$1^+2^-$	$1^+2^-$	1	1	
	$2a$	$p_x, p_y, p_z$	$t_2$	$4^-5^+$	$4^-5^+$	1 3 4	1 3 4

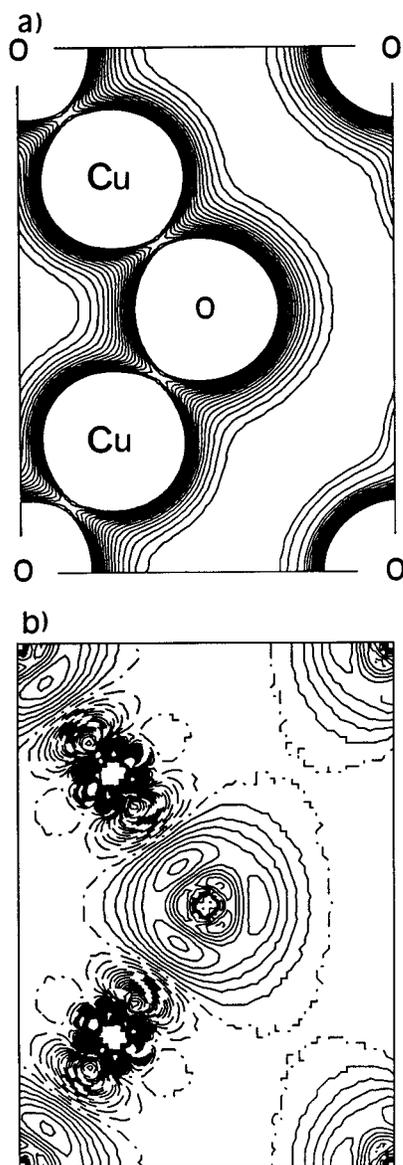


FIG. 5. Electron density maps obtained for  $\text{Cu}_2\text{O}$  on a (110) plane. (a) Total electron density. (b) Density difference maps, bulk minus neutral atom superposition. Values corresponding to neighboring isodensity lines differ by  $0.01 e/\text{bohr}^3$ . The full and broken curves in (b) indicate density increase and decrease, respectively.

to the experimental map obtained by Restori and Schwarzenbach.<sup>29</sup> The electron density decreases in the region close to the copper atom in the Cu-O bond direction, while an increase of the electron density appears at the O atom.

The Mulliken population analysis gives values of +0.79 and  $-1.58$  for the charges of the copper and oxygen atoms, respectively. Previous theoretical results for these values are contradictory. The FLAPW band-structure calculations done by Marksteiner, Blaha, and Schwarz<sup>11</sup> give a very large interstitial electron density, reflecting the usual problems of the muffin-tin approaches to determine atomic populations. Ching, Xu, and Wong,<sup>12</sup> with a density-functional method using a basis set of Gaussian functions, obtained a quasineutral description of  $\text{Cu}_2\text{O}$  with a small negative charge of  $-0.07$  on the copper atoms. The LUC-CNDO method used by

TABLE III. Static structure factors for  $\text{Cu}_2\text{O}$  calculated with the periodic Hartree-Fock method. Experimental values are those obtained with the x-ray data using the LAZY PULVERIX program (Ref. 30) and the diffraction module of the Cerius 2 package.

$hkl$	$F^{\text{calc}}$	$F^{\text{expt}}$
110	13.52	12.42
111	94.78	93.70
200	79.48	78.98
211	9.10	8.53
220	84.34	82.52
222	61.07	59.40
310	6.94	6.56
311	69.22	67.49
330	4.63	4.71
331	55.57	53.78
332	4.39	4.24
333	46.86	45.42
400	65.05	63.09
411	4.80	4.71
420	49.72	48.06
422	53.90	52.18

Evarestov and Veryazov<sup>13</sup> gave a strongly ionic picture with a charge of +0.97 for the copper atoms. On the other hand, cluster calculations done by Nagel<sup>14</sup> using the  $MSX_\alpha$  method yield a value of +0.43 for the copper atom, whereas the calculations of Goodman *et al.*<sup>15</sup> using the Hartree-Fock-Slater method yield a value of +0.65. Restori and Schwarzenbach<sup>29</sup> have done an orbital fitting of the experimental x-ray electron density showing for  $\text{Cu}_2\text{O}$  a situation close to a fully ionic picture.

Given the important discrepancy reflected in the calculated atomic charges, it is imperative to evaluate the quality of the electron density determined above. For that reason, we have calculated the structure factors associated with 16 low index reflections (Table III), and will compare them with the experimental values. These calculations do not include vibrational effects on the structure factors while the experimental values obtained by Restori and Schwarzenbach<sup>29</sup> have been measured at 100 K. To allow comparison with our calculated results we have used the program LAZY PULVERIX<sup>30</sup> and the diffraction module of the Cerius 2 package to obtain the structure factors extrapolated at 0 K using the experimental data. The agreement coefficient defined as

$$R = \frac{\sum_i |F_i^{\text{expt}} - F_i^{\text{calc}}|}{\sum_i F_i^{\text{expt}}}$$

obtained by comparing the calculated structure factors with those obtained from the experimental data at 0 K is 0.024, indicating a good agreement between the calculated and experimental electron densities.

#### D. Compton profiles

One of the more stringent tests to check the accuracy of the electron density is the evaluation of the Compton profiles.<sup>31</sup> To compare with the experimental polycrystalline data, a weighted average of the directional Compton profile



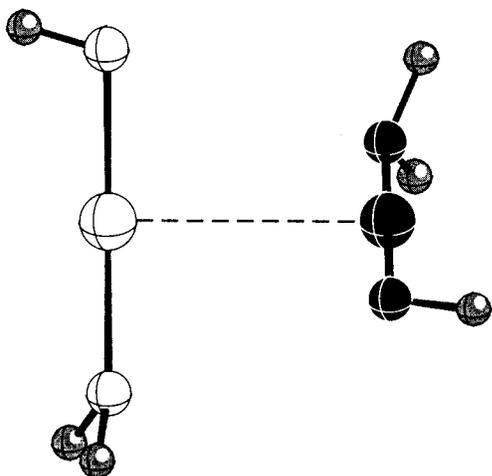


FIG. 8. Bimolecular model used to analyze the  $d^{10}$ - $d^{10}$  interaction.

types for very hard materials. Afterwards, Valerio *et al.*,<sup>38</sup> using a periodic Hartree-Fock method, have shown that these structures should be unstable. They found that the bulk modulus of both interpenetrated frameworks is practically equal to the sum of the bulk moduli of the independent frameworks. Usually, the hardness of a material can be assimilated to its bulk modulus.

We have carried out periodic Hartree-Fock calculations to estimate the interaction energy between both frameworks without correcting our values for the basis set superposition error (BSSE). The calculated interaction energy at the HF+LYP level for Cu<sub>2</sub>O is  $-6.1$  kcal/mol per Cu<sub>2</sub>O formula unit, while the HF result is only  $-0.6$  kcal/mol. This kind of interaction energies can be partitioned in different terms,<sup>39</sup>

$$E_{\text{int}} = E_{\text{Coulomb}} + E_{\text{induction}} + E_{\text{dispersion}} + E_{\text{repulsion}},$$

where the dispersion and repulsion terms are normally grouped together as a generic van der Waals term. The induction energy, being a second-order term, is usually less important than the van der Waals or Coulomb terms. The previous results reflect the importance of the dispersion term for the description of these kinds of interactions. This term is included by means of correlation energy through the LYP functional, but is neglected at the HF level.

A detailed analysis of the geometrical structure shows that each copper atom is surrounded by six other copper atoms at a distance of  $3.012$  Å belonging to the other framework ( $3.025$  Å in the calculated structure at the HF+LYP level). It is well known that the interaction between  $d^{10}$  closed shell ions provides a non-negligible stabilization energy.<sup>40-42</sup> To check the importance of these interactions in our case, we have performed calculations using a bimolecular model of the solid isolating a pair of CuO<sub>2</sub> units including hydrogen atoms to preserve the neutrality of the system (see Fig. 8). We have carried out calculations at Hartree-Fock and second-order Moller-Plesset perturbations<sup>43</sup> (MP2) levels using the GAUSSIAN-94 code<sup>44</sup> with the same basis set as in the periodic calculations and correcting the BSSE through a counterpoise scheme.<sup>45</sup>

The calculated interaction energies at the distance corresponding to the optimized structure are shown in Table V.

These results show an attractive interaction between both fragments in all cases. The inclusion of the electronic correlation results in an increase of the interaction energy because more attractive contributions are included in the van der Waals terms. However, the BSSE-corrected energy values present a considerable reduction due to the lack of diffuse Gaussian functions in the basis sets used for the periodic calculations. It should be borne in mind, though, that the BSSE is less important in the periodic calculation than in the bimolecular model. The interaction energy including electron correlation calculated at the BSSE-corrected MP2 and HF+LYP level are  $-2.8$  and  $-5.0$  kcal/mol, respectively, as we have indicated previously. Although the interaction energy has no additive character, its calculated value (HF+LYP level) is  $-1.0$  kcal/mol per each independent Cu $\cdots$ Cu contact in the periodic structure. For each copper atom in the crystalline structure there are six Cu $\cdots$ Cu contacts, thus logically each Cu $\cdots$ Cu contact will be stronger in the bimolecular model than in the periodic structure, as found in our calculations. The bimolecular model used might introduce an artifact, since the hydrogen atoms placed to saturate the bonds of the structure might form hydrogen bonds, thus artificially increasing the interaction energy. In order to eliminate this problem, we have rotated the two fragments to reach a value of  $90^\circ$  for the O-Cu $\cdots$ Cu-O torsion angle (the experimental value is  $70.5^\circ$ ). In this case the interaction energy at the HF+LYP level is  $-3.3$  ( $-0.5$  BSSE corrected) kcal/mol, showing an important decrease in comparison with the non-rotated structure. This value is closer to that found for the periodic system. It can be concluded that  $d^{10}$ - $d^{10}$  interactions are responsible for an important contribution to the interaction energy between the two sublattices and amount roughly to  $-1.0$  kcal/mol per each Cu $\cdots$ Cu contact.

We have also performed calculations for the analogous Ag<sub>2</sub>O structure. The optimized lattice parameter at the HF+LYP level is  $4.860$  Å (cf., the experimental value of  $4.718$  Å). The calculated interaction energies between the two sublattices are shown in Table V. For the bimolecular model, we obtain an interaction energy of  $-3.4$  ( $-1.7$  BSSE corrected) kcal/mol for the rotated conformation (O-Cu $\cdots$ Cu-O= $90^\circ$ ) to avoid the interactions between hydrogen and oxygen atoms. Comparing these BSSE-corrected values for the bimolecular model or those obtained for the periodic system, one can see that the Ag $\cdots$ Ag contact is stronger than the Cu $\cdots$ Cu contact. These results show that the  $d^{10}$ - $d^{10}$  interactions are stronger when the orbitals are more diffuse.

The difference in stability between Cu<sub>2</sub>O and the hypothetical compounds BeF<sub>2</sub> $\cdots$ SiO<sub>2</sub> and BeF<sub>2</sub> $\cdots$ GeO<sub>2</sub> is probably due to the different size of the independent frameworks in the latter structures. In this case, an additional repulsive energy term should be included to take into account the distortion of both frameworks and this term might become larger than the stabilization provided by the Coulomb and van der Waals terms. In the case of Cu<sub>2</sub>O and Ag<sub>2</sub>O, the two frameworks have the same size and therefore no distortion of any of the independent lattices is needed, while the presence of the  $d^{10}$ - $d^{10}$  interactions favor the existence of the interpenetrated frameworks. This result suggests that two chemically different networks can only form interpenetrated lattices if both have similar cell sizes.

TABLE V. Calculated interaction energies (in kcal/mol) for Cu<sub>2</sub>O and Ag<sub>2</sub>O using the Hartree-Fock method (HF) and Hartree-Fock plus *a posteriori* correlation energy correction using the Lee-Yang-Parr functional (HF+LYP). For the bimolecular model (see Fig. 8), MP2 molecular calculations have also been performed. The values in parentheses correspond to the BSSE-corrected energy.

	HF	HF+LYP	MP2
Cu <sub>2</sub> O			
Periodic system	-0.1	-1.0	
Bimolecular model	-6.2 (-3.8)	-7.8 (-5.0)	-7.3 (-2.8)
Ag <sub>2</sub> O			
Periodic system	-0.7	-3.2	
Bimolecular model	-4.9 (-3.4)	-7.1 (-5.4)	-5.9 (-3.9)

#### IV. CONCLUSIONS

The periodic Hartree-Fock method has been applied to investigate structural and electronic properties of Cu<sub>2</sub>O. The calculated values of the lattice parameter, bulk modulus, and elastic constants show a good agreement with the available experimental data. The lack of electronic correlation in the Hartree-Fock method is reflected in the larger calculated value for the unit cell volume, as can be seen in the optimized geometry using the HF+LYP method. The accuracy provided by the methodology employed is not enough to reproduce small values of second derivatives of the total energies (elastic constants smaller than 50 GPa), as shown by the result obtained for the  $c_{44}$  elastic constant.

The electronic structure, analyzed by means of the band structure and the density of states, shows that the main contributions to the valence band come from the Cu 3*d* and O 2*p* states. The size and the shape of the bands are in good agreement with those obtained from XPS experiments and previous theoretical results. The electron charges obtained for the oxygen and the copper atoms indicate a highly ionic nature with some covalent character for the Cu-O bond, which is also confirmed by the electron density maps. In order to check the quality of the calculated electron density, the static structure factors and the Compton profile have been calculated. These magnitudes are in good agreement with the reported experimental data.

The calculated values for the effective hole and electron masses reflect an anisotropic character for the hole masses while for the electrons, the mass is practically direction independent. The comparison between our data and the experimental results shows a good agreement for the hole values. However, the calculated electron mass is significantly smaller than the experimental value. This fact is also present in previous theoretical works and is probably related to an inaccurate description of the conduction band in these methodologies.

An energy of -6.0 kcal/mol (per Cu<sub>2</sub>O formula unit) has been obtained for the interaction between the two interpenetrated frameworks in the cuprite structure calculated at the HF+LYP level. The very small interaction energy calculated at the HF level shows that the main role in these interactions is played by the dispersion term included by the electronic

correlation. The analysis of the  $d^{10}$ - $d^{10}$  bonds between copper atoms using a bimolecular model shows that these interactions can play a fundamental role in the stability of these compounds. The stability of the interpenetrated networks appears to depend also strongly on an adequate size match between the two independent frameworks. Thus a new interpenetrated material with two chemically different sublattices should only be stable if the sizes of both frameworks are very similar.

#### ACKNOWLEDGMENTS

The authors are grateful to C. Pisani, R. Dovesi, and C. Roetti for providing them a copy of the CRYSTAL-92 code. The kind help of R. Dronskowski with the experimental structure factors is also acknowledged. We thank D. Proserpio for providing us with a copy of his manuscript devoted to the interpenetrated frameworks prior to publication. The stay of R.A.E. in Barcelona was made possible by a bilateral cooperation program between both universities. The computing resources at Centre de Supercomputació de Catalunya (CESCA) were generously made available through a grant of Fundació Catalana per a la Recerca. Financial support of this work was provided by DGYCIT and CIRIT through Grant Nos. PB95-0848-C02-01 and 1995SGR-00421, respectively.

#### APPENDIX

The contraction patterns that have been employed are (632111/33111/311) and (841/41/1) for Cu and O, respectively. The oxygen basis set has been previously used in periodic calculations<sup>46</sup> while the copper basis set is a modified molecular basis set. For silver, we have used a modified all-electron basis set proposed by Godbout *et al.*<sup>47</sup> The modifications consist in a reoptimization of the exponents for the most diffuse functions using the experimental crystal structure. The contraction pattern for the silver basis set is (633311/53211/531). The most diffuse exponents for the *sp* functions are 0.5996 and 0.2071, while for the *d* functions it is 0.2579.

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