The locally self-consistent real space multiple scattering technique has been applied to calculate the electronic structure and chemical binding for the c(2x2)O/Cu(001) system, as a function of $d_{O-Cu_1}$ – the height of oxygen above the fourfold hollow sites. It is found that the chemical binding between oxygen and copper has a mixed ionic-covalent character for all plausible values of $d_{O-Cu_1}$. Furthermore, the electron charge transfer from Cu to O depends strongly on $d_{O-Cu_1}$ and is traced to the variation of the long-range electrostatic part of the potential. A competition between the hybridization of Cu1-$d_{xz}$ with O-$p_x$, $p_y$ and Cu1-$d_{x^2-y^2}$ with O-$p_z$ states controls modification of the electronic structure when oxygen atoms approach the Cu(001) surface. The anisotropy of the oxygen valence electron charge density is found to be strongly and non-monotonically dependent on $d_{O-Cu_1}$.

I. INTRODUCTION

Oxygen adsorption on Cu(001) has been the subject of much discussion and debate in the past three decades mainly because of the illusive nature of the adsorption geometry. The history of the field is nicely summarized in a recent paper [1]. Here we mention some of the essential points. Unlike the case of Ni(001) in which a true $c(2 \times 2)$ phase is observed as the oxygen coverage approaches 0.5ML [2] in which the oxygen atoms occupy fourfold hollow sites at a distance about 0.8Å [3] above the top Ni layer, the stable surface structure for similar oxygen coverage on Cu(001) has the periodicity $(2\sqrt{2} \times \sqrt{2})R45^\circ$ [4] and involves missing rows of Cu atoms according to LEED [4] and surface X-ray diffraction...
measurements. This conclusion was agreed upon after much debate and analysis of data from several complimentary experimental techniques, some of which indicated the presence of a \(c(2 \times 2)\) structure on an unreconstructed Cu(001) [7–10]. Other experiments have indicated the presence of both of these phases [11,12] and still others have given evidences of disordered phases in the system [13]. A more recent scanning tunneling microscopic (STM) study has also affirmed the presence of \(c(2 \times 2)\) overlayer of adsorbed oxygen on Cu(001) at low coverage, but only in nanometer size domains and not large well-ordered domains [14].

Currently, based on the above findings, the following picture can be built. If the adsorbate coverage is low, oxygen atoms adsorb on Cu(001) forming \(c(2 \times 2)\) islands. Increase in the coverage leads to the ordering of the \(c(2 \times 2)\) domains, forming \(c(4 \times 6)\) pattern. When the coverage approaches a critical value of 34\% of monolayer, the \(2\sqrt{2} \times \sqrt{2}R45^\circ\) structure made by a missing row type reconstruction is formed.

The competition between the observed O/Cu(001) phases and the subsequent reconstruction of the surface with the \(2\sqrt{2} \times \sqrt{2}R45^\circ\) overlayer shows signs of a delicate balance in the surface electronic structure of the system which tilts in favor of one phase or the other depending on the coverage. A detailed description of the electronic states and chemical bonds formed when oxygen atoms adsorb on the Cu surface should thus provide much needed insight into the factors responsible for the observed variations in the surface structure.

A possible theoretical explanation follows from effective medium theory [15] which predicts a reconstructed stable state for the substrate. These researchers find that the O valence levels interact very strongly with the Cu \(d\)-bands such that the states can be shifted through the Fermi level. The difference in the total energy of the reconstructed and the unreconstructed Cu surface arises from dependence of the energetic location of the antibonding levels, derived from the O 2\(p\) – Cu 3\(d\) hybridization, on coordination. A missing row can force this level up, thereby pushing up the hybridized antibonding level which can straggle the Fermi level, leading to a reduced occupation and thus stronger net bonding. In the case of a Ni substrate the 3\(d\) band straggles the Fermi level, and so its position is largely pinned by the need for charge neutrality.
The rationale for a reconstructed Cu surface with O as adsorbate has also been related to the instability of the unreconstructed surface due to the large charge transfer to the adsorbate \[^{16,17}\]. Calculations performed for oxygen on small clusters of Cu (2–25 atoms \[^{18}\] and 5 atoms \[^{17}\]) find a strong electronic charge transfer from the metal atoms to oxygen in the amount of 1.2e \[^{18}\] or 1.5e \[^{17}\]. These two factors (the degree of the pO – dCu hybridization and amount of the effective charge on O) have thus far been proposed as the driving forces for the phase instability of the c(2 × 2) structure. The *ab initio* cluster calculations has also found the O–Cu bond to be mostly ionic with some participation of the d-electrons of Cu \[^{17}\]. It should be borne in mind, however that models like the effective medium theory are at best semi-empirical. Further none of the theoretical methods as far employed take into account the contribution of the Madelung potential for these two overlayer structures, which may significantly change the subband energetic positions and charge distribution. If indeed an appreciable charge transfer and details of pO – dCu hybridization are responsible for the stability of a superstructure on Cu(001), a systematic calculation of these quantities is warranted. Such a calculation must also provide a comprehensive description of the relationship between the electronic and geometric structures of the system, including the contribution of the Madelung potentials. This paper is an effort in this direction.

We have carried out detailed calculations of the electronic structure of the O/Cu(001) system using a reliable method and by varying the separation between the oxygen overlayer and the Cu(001) surface. As we shall see, there continues to be a debate also on the height of the oxygen atoms above the Cu surface. Our calculational strategy allows us to compare the local charge redistribution, modifications of hybridization of various electronic states and variations of the local and long-range contributions to the potentials, as a function of the height of the oxygen overlayer above the surface. It is through such systematic studies and, in conjunction with experimental observations, that we expect to gain insights into the nature of the chemical binding between the O and Cu atoms and establish rationale for the formation of a particular overlayer. Since, both c(2 × 2) and \((2\sqrt{2} \times \sqrt{2})R45^\circ\) phases have been shown to exist \[^{1,14}\], our focus in this paper is on the former. At a later stage we will...
undertake a study of the missing row reconstructed surface with the large surface unit cell to represent the \((2\sqrt{2} \times \sqrt{2})R45^\circ\), which would require a much larger computational effort than the present one. It should be mentioned that Wiell et al. \[19\] have used a realistic full-potential LMTO method to examine the hybridization of orbitals of the N overlayer on Cu(001). These authors have also touched upon the O/Cu(001) system, but no details of the O – Cu electronic state hybridization or the charge transfer have been provided.

The structural studies of the \(c(2 \times 2)\) O/Cu(001) system performed with different techniques provide quite different results as the interlayer O–Cu spacing \(d_{O-Cu1}\) ranges from 0 to 1.5Å. However, a majority of results \[1][9][12\] gives \(d_{O-Cu1}\) value in the range 0.4 – 0.8Å. The SEXAFS measurements \[12\] suggest three different configurations. In one of them the O atoms are located at the fourfold hollow (FFH) sites with \(d_{O-Cu1} = 0.5\)Å. Two other configurations represent the distorted FFH geometries with \(d_{O-Cu1} = 0.8\)Å. The authors of recent photo-electron diffraction studies also propose a two-side model involving the O atoms at FFH positions with \(d_{O-Cu1} = 0.41\) and 0.7Å \[1\]. They associate these two values with the edge and center positions in small \(c(2 \times 2)\) domains, respectively. Our calculations are performed for the exact FFH geometry for a set of \(d_{O-Cu1}\) including the values obtained from the different experiments. We use a computational method based on the theory of multiple scattering in real space. This allows us to explicitly obtain the local electronic structure of atoms with different locations. Our results show a general picture of the electronic state modification when oxygen atoms approach the Cu(001) surface and reveal the factors controlling charge transfer and chemical bond formation.

II. COMPUTATIONAL METHOD

The calculations are based on the density functional theory within the local density approximation (LDA) \[20\] and multiple scattering theory. Our approach embodies the local self-consistent multiple scattering method \[21\], in which a compound is divided into overlapping clusters called local interaction zones (LIZs) centered around atoms in different local
environments. For each LIZ, a system of equations for the $T-$ scattering matrix in the
lattice site – angular moment representation for the muffin-tin (MT) potential \[22\] is solved
self-consistently. The solutions are used to determine the cluster Green’s functions and
subsequently the local and total electronic densities of states and valence charge densities.
An application of this method to materials related to the work here (copper oxides) has
demonstrated its high efficiency and reliability \[23,24\].

In our model system, apart from the oxygen overlayer, the top four Cu layers (Cu1 –
Cu4) were considered to be different from the bulk Cu. The fifth and lower Cu layers were
supposed to have bulk properties. LIZ’s were built around nonequivalent atoms belonging to
the five different layers and contained 71 to 79 atoms depending on the local configuration.
The sizes of the LIZ’s were taken such that the calculated characteristics of the bulk system
closely matched those obtained from other reliable methods.

At each iteration of the self-consistent process a new potential is built by solving the
Poisson’s equation with the charge density obtained at the previous iteration. To take into
account surface effects we follow the approach developed in Ref. \[25\] where the MT potential
at the $\alpha$th atom belonging to the $i$th layer is given by

$$V(r_{i\alpha}) = \frac{-2Z_{i\alpha}}{r_{i\alpha}} + 8\pi \left[ \frac{1}{r_{i\alpha}} \int_{0}^{r_{i\alpha}} \rho_{i\alpha}(x)x^2 dx + \int_{r_{i\alpha}}^{R_{i\alpha}} \rho_{i\alpha}(x)x dx \right]$$

$$+ V^{xc}[\rho(r_{i\alpha})] - V^{EC} - V^{xc}(\rho_0^i) - 4\pi \rho_0^i + V_{i\alpha}^{Mad}$$

The nuclear and the MT electronic charge density contributions to the potential (the first
term and the terms in square brackets in (1), respectively) are of the same form as in the
bulk calculations \[26,27\]. The electrostatic ($V^{EC}$) and exchange-correlation ($V^{xc}(\rho_0^i)$) parts
of the MT constant are taken from the bulk. The last two terms in the above expression
represent the distant part of the MT potential:

$$V_D = -4\pi \rho_0^i + V_{i\alpha}^{Mad}$$

This part contains explicit information about the surface. The interstitial charge density
$\rho_0^i$ is supposed to be layer-dependent reflecting the asymmetry of the system. In such an
approach the space in the vicinity of the surface is divided by layers belonging to different atomic planes parallel to the surface. In the present calculations we keep the thickness of the oxygen layer independent of the interlayer O–Cu1 spacing such that the radius of the corresponding Wigner-Seitz sphere is equal to the O-II ionic radius $R_O = 1.24\text{Å}$. The thickness of the Cu2 and next Cu layers corresponds to the bulk lattice parameter. The Cu1 layer takes the rest of the space between the O and Cu2 layers. The $\rho_i^0$ values are obtained by averaging the interstitial charges. The latter are differences between Wigner-Seitz ($Q_{i\alpha}^{WS}$) and MT ($q_{i\alpha}^{MT}$) charges, which are calculated by integration of the electronic charge density over Wigner-Seitz and MT spheres, respectively. The $Q_{i\alpha}^{WS}$ values are multiplied by a coefficient to meet charge neutrality condition for the region disturbed by the surface. This coefficient approaches unity, with charge convergence. The Madelung potential includes monopole $M_{i\alpha,j\beta}^{00}$, dipole $M_{i\alpha,j\beta}^{10}$ and interstitial $V_{ij}[\rho_j]$ terms:

$$V_{i\alpha}^{Mad} = \sum_{j,\beta} \left( q_{j\beta} M_{i\alpha,j\beta}^{00} + d_{j\beta} M_{i\alpha,j\beta}^{10} + V_{ij}[\rho_j] \right),$$

(3)

where $d_{j\beta}$ is a dipole moment of the MT charge density and

$$q_{j\beta} = Z_{j\beta} - q_{j\beta}^{MT} + \frac{4\pi}{3} \rho_j R_j^{3\beta}$$

The $M_{i\alpha,j\beta}^{00}$ and $M_{i\alpha,j\beta}^{10}$ terms in (3) are calculated by an Ewald-like plane-wise summation, and explicit solution of one-dimensional (normal to the surface) Poisson’s equation, using the technique described in Ref. [25].

The exchange and correlation parts of the potential are determined within LDA using the technique described in Ref. [28].

To test the applicability of the method to surface problems, we have calculated the electronic structure of the clean Cu(001) surface and compared our results with ones obtained by means of TB-LMTO method [29], screened KKR Green’s function method [30] and self-consistent localized KKR scheme developed for the surface calculations [25]. As we shall see in the next section, our projected densities of electronic states calculated for the $c(2 \times 2)$ O/Cu(001) system are in good agreement with those obtained by full potential LMTO method [19].
III. RESULTS AND DISCUSSION

We have calculated the electronic structure of the O/Cu(001) surface with the c(2x2) symmetry for selected values of the O-Cu1 interlayer spacing $d_{O-Cu1}$. As already discussed, there is some discrepancy in the values of $d_{O-Cu1}$ obtained from different experiments. However a majority of experiments have found $d_{O-Cu1}$ to lie between 0.4Å and 0.8Å ($0.11a - 0.22a$, where $a$ is the lattice parameter of bulk fcc copper). With this in mind we have varied $d_{O-Cu1}$ from 0.15a to 0.3a in our calculations and examined its effect on the surface electronic structure. The local densities $N^\alpha_l(E)$ of electronic states, their projection $N^\alpha_{lm}(E)$ on the cubic harmonics, and the valence electron density $\rho(r)$ have been calculated for the oxygen overlayer and the four top Cu layers, for selected values of $d_{O-Cu1}$.

The densities of the $pO$- and $dCu$-electronic states of the system are plotted in Fig. 1 for the longest and shortest interlayer spacings considered. As seen in Fig. 1, the $N^Cu_l(E)$ calculated for the Cu3 and Cu4 atoms (third and fourth layer) are hardly affected by the choice of $d_{O-Cu1}$ and differ slightly from the bulk values whereas the $dCu2$-states are noticeably disturbed. The $dCu1$ and $pO$ state densities are found to have a rich structure and for both values of $d_{O-Cu1}$ the spectra show a clear signature of the $pO - dCu1$ hybridization. Note the position of the peaks marked "$a$" and "$b$" for $d_{O-Cu1} = 0.3a$ and "$a'$" and "$b'$" for $d_{O-Cu1} = 0.15a$ in Fig. 1. When the oxygen overlayer approaches the Cu(001) surface ($d_{O-Cu1} = 0.15a$), the splitting (the distance between $a'$ - $b'$ peaks in the figure) increases reflecting an enhancement of the hybridization, which even involves the second copper layer.

To examine the charge transfer in the vicinity of the surface we have calculated the Wigner-Seitz charges that allowed us to obtain the amount of charge deviation ($\Delta Q_i$) from electric neutrality per 2D–unit cells belonging to the different layers. The results are shown in Fig. 2. One can see a strong charge transfer from the Cu1 layer to the O overlayer coupled with some increase in the electron charge in the Cu2 layer. The effect is significantly enhanced when the oxygen atoms approach the Cu1 layer. From this result one would conclude that the O – Cu1 chemical binding has an essentially ionic character and that the
ionicity increases as oxygen atoms approach the Cu(001) surface. In Table 1, we present the amount of charge transfer for the five different heights of the oxygen overlayer that we considered. At the shortest O–Cu1 distance, the two Cu atoms in the unit cell of the first layer have a deficit of about one electron each, with 1.5 electron going to the O atom and 0.25 electron for each of the 2 atoms of the second layer. The amount of charge provided to the O atom drops to 1 electron when it’s height above Cu1 is doubled to 0.3a. The charge deviation $\Delta Q_O$ of the O layer and the distant part $V_D$ of the potential in Eq. (2) at the O site are plotted versus $d_{O-Cu1}$ in the lower panel of Fig. 2. A clear correlation between $\Delta Q_O$ and $V_D$ seen in the figure suggests that the long-range electrostatic interaction is a driving force for the charge transfer in the system.

In the system under consideration, each oxygen atom and its four nearest Cu1 neighbors form a pyramid. Such an atomic configuration is expected to cause a strong anisotropy in the electronic structure. Therefore an analysis of the $N_{ln}^a(E)$ distributions for O and Cu1 is very useful for understanding the nature of the chemical bonds formed when oxygen adsorbs on the Cu surface. A simple symmetry consideration shows that only the O-$p_x$, $p_y$–Cu1-$d_{xz}$ and O-$p_z$ – Cu1-$d_{x^2-y^2}$ hybridization can be significant in the O – Cu1 subsystem. Therefore our focus is mainly on these electronic states. In Fig. 3, the densities of the O-$p_z$ and Cu1-$d_{x^2-y^2}$ states are plotted for the values of $d_{O-Cu1}$ as labeled. Both projected densities are considerably modified with the decrease in $d_{O-Cu1}$. The band broadens and distinct new peaks appear as $d_{O-Cu1}$ takes the values 0.2a and 0.15a. An energetic alignment of the O-$p_z$ and Cu1-$d_{x^2-y^2}$ peaks in the $a$, $b$ and $c$ regions is a signature of hybridization of these states. An increase in the peak amplitudes and an extra splitting with the decrease in $d_{O-Cu1}$ reflect a strong enhancement of the hybridization as the oxygen atoms approach the surface. In contrast, the splitting of the O-$p_x$, $p_y$ and Cu1-$d_{xz}$ states is almost independent of the $d_{O-Cu1}$ value (see Fig. 4). This means that the hybridization of these states is not changed noticeably, when $d_{O-Cu1}$ is varied within the range that we considered. Such a difference in the response of the electronic states to variation of the O-Cu1 interlayer spacing can be explained on the basis of a simple geometric analysis. When the oxygen atoms approach the
Cu1 layer, the O – Cu1 bond length decreases and the symmetry of the O-p_z and Cu1-d_{x^2−y^2} cubic harmonics is such that their overlap increases enhancing the hybridization. On the other hand, the symmetry of the O-p_x, p_y and Cu1-d_{xz} states is such that the overlap of their cubic harmonics is diminished with decrease in d_{O–Cu1} that compensates the effect of the O – Cu1 bond length reduction.

Thus, according to these results, a noticeable covalence pO – dCu1 binding takes place in the system along with the strong ionic binding. If the O – Cu1 interlayer spacing is long enough (d_{O–Cu1} = 0.3a), the covalence component of chemical binding is mostly determined by the O-p_x, p_y – Cu1-d_{xz} hybridization. When d_{O–Cu1} is smaller, the O-p_z – Cu1-d_{x^2−y^2} contribution to the covalence bond increases. This competition mostly controls modification of the electronic states when the oxygen atoms approach the surface.

The densities of O-p_x, p_y and O-p_z electronic states have also been calculated for O/Cu(001) by means of the full-potential LMTO method [19], which is considered to be one of the best approaches for electronic structure calculations. These authors considered an oxygen overlayer with a c(2×2) structure with the oxygen atom occupying an FFH and a quasi-FFH sites. In Fig. 5 we have compared our results obtained for d_{O–Cu1} = 0.15a (0.514Å) with the results of Ref. [19] at the FFH site at a height of 0.5Å, for O-p_z and O-p_{x,y}. Both the splitting and peak amplitudes are in very good agreement attesting to the reliability of the method used here. We note from Fig. 5 that a shift the height between 0.15a and 0.2a produces a shift of about 1eV of the spectrum, again in good agreement with the results in Ref. [19].

We have calculated the radial dependence of the valence electron charge density around the O and Cu1 – Cu4 atoms along some symmetrical directions. The plot of the oxygen charge density in Fig. 6 displays it to be essentially anisotropic. We have also found that the anisotropy increases when d_{O–Cu1} is reduced from 0.3a to 0.2a whereas further d_{O–Cu1} reduction leads to a decrease in the anisotropy. This effect is illustrated in Fig. 7, in which the radial dependence of the difference between the densities along the (001) and (100) directions is plotted for systems with different values of d_{O–Cu1}. Such a non-monotonic
behavior can be explained by the hybridization competition mentioned above. The change in the anisotropy of the oxygen charge density occurs because different amounts of charge flow to the O-\(p_x\) and O-\(p_z\) states, as \(d_{O-Cu_1}\) decreases. The stronger covalence binding, the larger an increase in the electron-electron repulsion caused by an extra electronic charge in the bond region. Therefore the charge tends to come to the states less involved in hybridization, which are the O-\(p_z\) states when \(d_{O-Cu_1}\) is large. This leads to an increase in the anisotropy. The tendency is changed at short interlayer distances, when the hybridization of the O-\(p_z\) and Cu1-\(d_{x^2−y^2}\) is enhanced significantly that can make preferable an occupation of the O-\(p_x,p_y\) states.

We now turn to the implication of the results presented here to a simple model proposed for the adsorption of oxygen on Cu(001). To describe this phenomenon, the authors of Ref. [12] use a model isotropic potential based on the local part of the Madelung potential. At the same time they assume that not only the O and Cu1 layers are involved in charge transfer, but also deeper ones. Our results confirm the latter assumption (see Fig. 2) and imply that an accurate model potential should be based on the long range Coulomb interaction rather than on the local one. Furthermore, using the experimental data obtained for the \(c(2 \times 2)\) and \((2\sqrt{2} \times \sqrt{2})R45^\circ\) phases the authors of Ref. [12] build the isotropic potential, which appears to have step-like dependence on the O – Cu1 bond length. To obtain this, these authors attribute a step-like behavior to the effective atomic charges. They assume that such a behavior can be induced by an increase in covalence, as the O – Cu1 bond length is reduced. Our results do not support these assumptions. We have found that the charges and covalence of the bonds are smooth functions of the interatomic distance. The \(c(2 \times 2)\) and \((2\sqrt{2} \times \sqrt{2})R45^\circ\) phases are different in the symmetry of the oxygen local surrounding rather than in the interatomic distances. This suggests that the phase transition can be properly described only by means of an anisotropic potential. Moreover, a noticeable covalence of the O – Cu1 binding (even for relatively long bond lengths) and its anisotropy obtained in our study allows us to propose that an accurate modelling of the \(c(2 \times 2)\) phase itself requires an anisotropic potential.
IV. CONCLUSIONS

The electronic structure has been calculated for the O/Cu(001) system in the $c(2\times2)$ with five different O – Cu1 interlayer spacings. We find that the oxygen and copper atoms form a mixed ionic-covalence chemical binding in the O/Cu(001) system for the whole range of the considered O – Cu1 interlayer spacings. The oxygen atom gains an extra charge varying between 1 and 1.5 electron when its height is varied between 0.3a and 0.15a. This charge comes solely from the atoms at the top layer of the substrate with a small enhancement of the second layer electronic charge. We also find that this charge transfer is controlled by variation of the long-range electrostatic interaction. The detailed analysis of the properties of the local electronic structure reveals that the electronic structure of the O/Cu(001) system is governed by a competition between the hybridization of Cu1-$d_{xz}$ – O-$p_x$, $p_y$ and Cu1-$d_{xz-\gamma z}$ – O-$p_z$ states, which depends on O – Cu1 spacing. The anisotropy of the oxygen valence electron charge density is found to be strongly and non-monotonically dependent on the interlayer spacing.

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FIG. 1. The density of \( p \)-electronic states of the oxygen overlayer and \( d \)-electronic states of the four top Cu layers for O/Cu(001) for O–Cu1 interlayer spacings of 0.3\( a \) (dashed line) and 0.15\( a \) (solid line).

FIG. 2. Upper panel: the layer charges per 2D-unit cell. The layer \# 0 corresponds to the oxygen overlayer. Lower panel: charge deviation for the oxygen overlayer and the distant part of the MT potential plotted versus the O–Cu1 interlayer spacing.

FIG. 3. The densities of the O-\( p_z \) (dashed line) and Cu1-\( d_{x^2-y^2} \) (solid line) electronic states for \( c(2 \times 2) \) O/Cu(001) with different O–Cu1 interlayer spacings.

FIG. 4. The densities of the O-\( p_{x,y} \) (dashed line) and Cu1-\( d_{xz} \) (solid line) electronic states for \( c(2 \times 2) \) O/Cu(001) with different O–Cu1 interlayer spacings.

FIG. 5. The densities of the O-\( p_{x,y} \) and O-\( p_z \) electronic states calculated in the present work for two O heights (solid line 0.541 Å) and (long-dash dotted line 0.722 Å) compared with those in Ref. 18 (dashed line) for \( c(2 \times 2) \) O/Cu(001) at 0.5 Å. A convolution with a lorentzian with 0.7 eV full width at its half maximum is used.

FIG. 6. The oxygen valence electron charge densities plotted along the (001) (dashed line) and (100) (solid line) directions for O/Cu(001) with two different O–Cu1 interlayer spacings.

FIG. 7. The radial dependence of the difference between the oxygen valence electron charge densities calculated along the (001) and (100) directions for O/Cu(001) with three different O–Cu1 interlayer spacings.

TABLE I. Valence electronic charge variation \( \Delta Q(e) \) for different O-Cu1 interlayer spacing. The percentage change is given in parentheses

| Layer | 0.15a        | 0.17a        | 0.20a        | 0.25a        | 0.30a        |
|-------|--------------|--------------|--------------|--------------|--------------|
| O     | 1.493 (37.3%)| 1.429 (35.7%)| 1.329 (33.2%)| 1.144 (28.6%)| 0.983 (24.6%)|
| Cu1   | -2.108 (−9.6%)| -1.986 (−9.0%)| -1.800 (−8.2%)| -1.484 (−6.8%)| -1.211 (−5.5%)|
| Element | Cu2 | Cu3 | Cu4 |
|---------|-----|-----|-----|
|        | 0.575 (2.6%) | 0.519 (2.4%) | 0.430 (2.0%) | 0.313 (1.4%) | 0.207 (0.9%) |
|        | 0.040 (0.2%)  | 0.039 (0.2%)  | 0.041 (0.2%)  | 0.027 (0.1%)  | 0.021 (0.1%)  |
|        | 0.000 (0.0%)  | 0.000 (0.0%)  | 0.000 (0.0%)  | 0.000 (0.0%)  | 0.000 (0.0%)  |
$O_{P_{xy}}$

$O_{P_z}$

$N(E)$ (arb. units)

$E(eV)$
0.0 0.4 0.8 1.2

r(A)

0 0.4 0.8 1.2

r(A)

\rho(r)(A^3)

\rho(r)(A^3)

\text{d_{O-Cu1}=0.3a}

\text{d_{O-Cu1}=0.15}
