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## Theory of the Oxygen-Induced Restructuring of Cu(110) and Cu(100) Surfaces

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A model calculation based on the effective-medium theory of the oxygen-induced reconstruction of the (110) and (100) surfaces of Cu is presented. Equilibrium structures are calculated from a minimization of the total energy of the system. Missing-row-type reconstructions are found to be most stable in both cases, and an analysis is presented showing what the driving force is behind these reconstructions.

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It has become clear over the last few years that when atoms like oxygen, carbon, or nitrogen adsorb on metal surfaces they often induce a large restructuring of the metal surfaces. The exact nature of the different reconstructions is still under vigorous debate. Oxygen adsorption on Cu surfaces is among the most studied systems and still there are conflicting conclusions made based on various experimental techniques.<sup>1-16</sup> The solution of the structure problem therefore attracts a large amount of interest at present. An even more interesting question is why oxygen reconstructs these surfaces.

In the present Letter we present a model calculation based on the effective-medium theory of the chemisorption of oxygen on the (100) and (110) surfaces of Cu. We show that the model calculation indicates a strong tendency towards a missing-row-type reconstruction for half a monolayer of oxygen on both the (110) and (100) surfaces of Cu. These reconstructions involve the removal (or equivalently the addition) of rows of metal atoms. Because this involves the breaking of several nearest-neighbor metal-metal bonds these structures are found to be very unstable for the clean surfaces. The driving force behind the reconstructions is therefore related to a stronger metal-oxygen bond on the reconstructed surface. We find in general that the oxygen  $2p$  states hybridize more strongly with  $d$  states on metal atoms with a low metal coordination number.

Very briefly the experimental situation is the following. On the Cu(110) surface a  $(2 \times 1)$  structure has been observed after adsorption of half a monolayer of oxygen. Early low-energy ion-scattering experiments<sup>1</sup> suggested a missing-row model of the reconstructed surface, where every second of the Cu rows in the [001] direction were missing. Later high-energy ion-scattering experiments<sup>2</sup> have indicated a buckled-row model, where every second of the Cu rows in the [001] direction are shifted outwards. He diffraction,<sup>3</sup> alkali-ion scattering,<sup>4</sup> and surface extended x-ray-absorption fine-structure<sup>5</sup> experiments have been interpreted as giving evidence for the missing-row model. Photoemission experiments<sup>6</sup> and a recent scanning-tunneling-microscopy (STM) study<sup>7</sup> have indicated a buckled-row model. Most recently two STM studies clearly favor the missing-row model.<sup>8,9</sup> Early x-ray-scattering experiments<sup>10</sup> indicated a

buckled-row model, but again the most recent x-ray-scattering experiments<sup>11</sup> have shown the missing-row model to give the best agreement.

Oxygen on Cu(100) has for long been believed to be very similar to the unreconstructed O/Ni(100) system, but very recently it has been suggested<sup>12</sup> that the  $(\sqrt{2} \times 2\sqrt{2})$  structure observed for half a monolayer of oxygen involves a missing-row-type reconstruction like on the (110) surfaces.

In order to study these phenomena theoretically one must be able to calculate the total energy for the systems as a function of the nuclear coordinates and minimize the energy in order to calculate the equilibrium structure. To do this using "local-density *ab initio*" methods is computationally extremely demanding and has not been done yet. Our approach is to use an approximate theory to evaluate the total energy of the system. This makes the results less accurate, but makes the task of varying the many degrees of freedom of the system tractable. Moreover, it makes it easy afterwards to analyze the results.

The total-energy calculation used here is based on the effective-medium theory.<sup>16</sup> One makes the ansatz that the electron density of the system can be expressed as a superposition of electron densities from each of the atoms in the system. The atomic electron density for atom  $i$  is chosen as the density induced by the atom, when it is embedded in a homogeneous electron gas of a density given by the average  $\bar{n}_i$  of the density tails from the surrounding atoms in the vicinity of the atom in question. This ansatz takes into account the effect of the surrounding atoms in an average way. Effects like screening and charge transfer are thus included, but only approximately. Given this ansatz and a similar ansatz for the one-electron potentials the total energy of the system can be expressed approximately as<sup>16</sup>

$$E_{\text{tot}} = \sum_i E_{c,i}(\bar{n}_i) + E_{\text{AS}} + E_{\text{el}}, \quad (1)$$

where the sum is over all the atoms in the system. The cohesive function  $E_{c,i}(\bar{n}_i)$  is given from the embedding energy of atom  $i$  in a homogeneous electron gas of density  $\bar{n}_i$ . The second term, the atomic-sphere correction, is an electrostatic energy, and the last term is due to any

changes in the one-electron energies when atom  $i$  is taken from the homogeneous electron gas to the system of interest:<sup>16</sup>

$$E_{\text{el}} = \sum_i \left( \int_{-\infty}^{\epsilon_f} [\Delta n_i(\epsilon) - \Delta \bar{n}_i(\epsilon)] \epsilon d\epsilon \right). \quad (2)$$

$\Delta n_i(\epsilon)$  and  $\Delta \bar{n}_i(\epsilon)$  are the induced density of states of atom  $i$  in the real system and in the homogeneous electron gas, respectively. Because of the stationary property of the total-energy functional with respect to deviations of the electron density<sup>17</sup> or the one-electron potential<sup>16</sup> from the true ground state, the total-energy expression in Eq. (1) only has second-order errors due to the ansatz for the density and potential.

For a number of systems the last term is not important. These include simple metals and the noble metals, where the  $d$  bands are completely filled. It also includes simple chemisorption systems, where the coupling between the adsorbate levels and metal  $d$  levels are not important. The approach has been shown to give a good description of the cohesive properties of bulk metals, phonons, surface energies, surface relaxations and reconstructions, the chemisorption of hydrogen and potassium on copper, and finite-temperature properties of the bulk and surface of clean metals.<sup>18,19</sup> When only the first two terms are included, the energy expression is of the same functional form as used in the embedded-atom approach, which has proven useful in describing an additional long list of systems.<sup>20</sup>

For oxygen outside a Cu surface, the oxygen valence levels interact so strongly with the  $d$  bands of Cu that states can be shifted through the Fermi level. This makes the one-electron energy change important. In the calculations for these systems, we therefore treat the first two terms as usual, and the main new point is a model developed to include the main effect of the last term. The two terms and the densities are parametrized as described in detail in Refs. 16 and 21. A more detailed description of this, including the parameters used, will be published elsewhere.<sup>22,23</sup>

The one-electron energy difference Eq. (2) is not important for the clean Cu surfaces because the  $d$  bands of Cu are completely filled. The main contribution therefore involves the oxygen-induced changes in the density of states. To calculate the induced densities of states of oxygen outside the surface and in the homogeneous electron gas we have used a tight-binding-like (resonant level) model.<sup>21,24</sup>

The input into the calculation are the positions of the oxygen  $p$  and the metal  $d$  states, the width of the  $d$  band, and the coupling matrix elements. In a linear muffin-tin orbital description<sup>25</sup> the latter can be calculated directly from the oxygen and Cu  $d$ -wave functions as they are calculated in our reference system, the homogeneous electron gas. The local bandwidth  $W_{di}$  is, in a simple tight-binding model, proportional to the coordination number. We generalize this to make it proportional to

the metal electron density from the surroundings. Similarly, the local center of the  $d$  band  $C_{di}$  depends on the surroundings, and we take the position of the  $d$  band in bulk Cu from an independent bulk calculation and we include the variation of  $C_{di}$  with the surrounding density from the calculation in the homogeneous electron gas. The only parameter in the problem not determined independently is the adsorbate  $p$ -level position outside the surface. We take it to be at the position relative to the Fermi level found in the homogeneous electron gas except for a constant, which is fixed to give a good value for the bond length for oxygen adsorbed on Ni(100). A more detailed account of the model will be given elsewhere.<sup>22</sup>

The calculations have been made for four different systems. The (110) and (100) surfaces of Cu with half a monolayer of oxygen have been treated, and for each of these both the unreconstructed and a missing-row-type structures have been investigated. For each of the systems the coordinates for the oxygen atoms and the metal atoms in the first three layers have been varied to find the optimum structure. The optimization has been performed using the direction set method.<sup>26</sup> It is relatively efficient and does not only seek out the nearest minimum like, for instance, the steepest-descent method. The search for the global minimum did, for instance, include the buckled-row model suggested in the literature.<sup>2</sup> Several starting configurations were tried in an attempt not to bias the optimization routine to a particular geometry. We are thus rather confident that the results presented in the following represent the global minimum for the present model potential, but we cannot completely rule out the existence of even lower minima for the systems studied or that other structures exist with lower energy.

The results for the four systems studied are summarized in Table I and in Fig. 1. Table I shows the calculated equilibrium properties of the four systems and Fig. 1 shows the lowest-energy structures for the two surfaces. Two observations can be made from Table I. The model calculation clearly favors the missing-row-type reconstruction in both cases, and for the reconstructed surfaces the agreement with experiment is quite good for bond lengths and vibrational frequencies.

From Fig. 1 it can be seen that on Cu(110) we find the oxygen atoms to occupy the long bridge sites as observed experimentally. We find the oxygen to be slightly subsurface, but a tiny error in our bond length could change this. We therefore cannot put any emphasis on this.

On the Cu(100) surface we also find the oxygen atoms to go underneath the first layer which is then shifted out by 0.3–0.5 Å. At the same time there is a pairing of the Cu atoms over the missing row.

We now turn to the question why oxygen induces such reconstructions. The clean surfaces show no tendency to reconstruct like this at all. The cost in energy to make

TABLE I. Calculated equilibrium chemisorption energies  $\Delta E$  (relative to atomic oxygen and a clean unreconstructed surface), oxygen-copper bond lengths  $d_{\text{O-Cu}}$ , and perpendicular vibrational frequencies  $\omega$  compared to experiment. The calculated values are shown for both the missing-row (MR) and the unreconstructed (Unrec.) structures. The experimental values are shown for the most probable structure. The vibrational frequency for the Cu(100) MR structure is so low that interactions with the Cu phonons are bound to change it (up in frequency) considerably.

		$\Delta E$ (eV)	$d_{\text{O-Cu}}$ (Å)		$\omega$ (meV)	
			Theory	Expt.	Theory	Expt.
Cu(110)	MR	−10.57	1.88,2.00	1.84,2.00 <sup>a</sup>	48	49 <sup>b</sup>
	Unrec.	−10.13	1.86,2.12		35	
Cu(100)	MR	−10.50	1.90–1.95	1.94 <sup>c</sup>	(30)	37 <sup>d</sup>
	Unrec.	−9.38	1.96		52	

<sup>a</sup>From Ref. 5.

<sup>b</sup>From Ref. 13.

<sup>c</sup>From Ref. 14.

<sup>d</sup>From Ref. 15.

the reconstruction is 0.30 eV on both the (110) and the (100) surfaces (for both surfaces the value refers to two primitive unit cells of the unreconstructed surface). The driving force must therefore be due to a larger oxygen binding energy on the reconstructed than on the unreconstructed surface. In fact, the bond energy is 0.74 eV larger on the reconstructed (110) surface and 1.42 eV larger on the (100) surface giving a net energy gain due to reconstruction of 0.44 and 1.12 eV for the two surfaces.

The remaining question is then the origin of the larger binding of oxygen to the reconstructed than to the unreconstructed surface. Figure 2 indicates the reason for Cu(110). The picture is the same for the other surface.

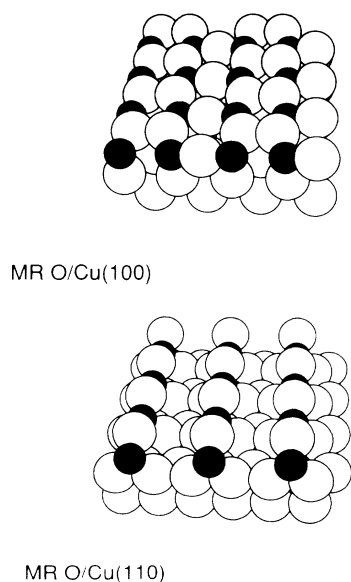


FIG. 1. The equilibrium structure for the missing-row structures of Cu(110) and Cu(100) with half a monolayer of oxygen adsorbed. The Cu and O atoms are shown as open and solid circles, respectively.

The interaction between the oxygen  $p$  states and the metal  $d$  states gives rise to a bonding down-shift of the  $p$  states and to antibonding states that are partly shifted up above the  $d$  bands. This gives rise to a net energy contribution through the one-electron energy term Eq. (2), which depends crucially on how many of the antibonding

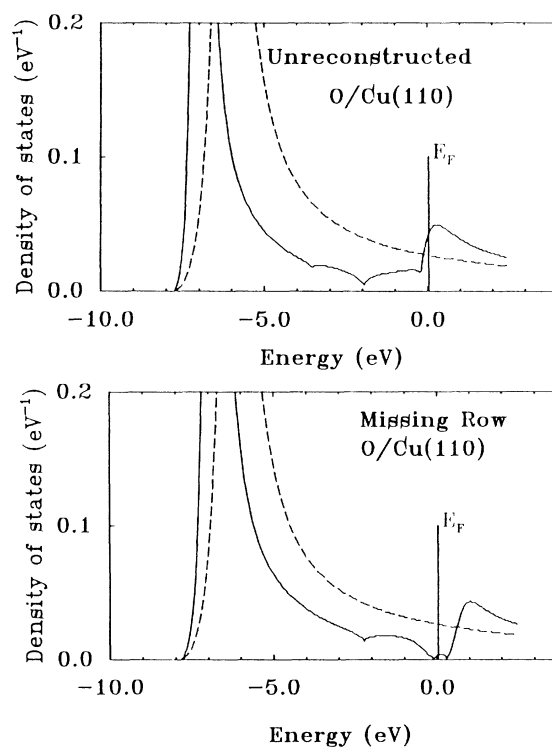


FIG. 2. The local density of states on the oxygen atoms at the equilibrium position at the unreconstructed and the reconstructed Cu(110) surfaces. The local density of states in the homogeneous electron gas is shown for comparison. On the reconstructed surface the antibonding states formed by hybridization between the oxygen  $p$  state and the metal  $d$  states are less occupied and therefore this structure is more stable than the unreconstructed one.

states are above the Fermi level and thus are empty. The figure shows how the antibonding states are less occupied for oxygen on the reconstructed Cu(110) surface than on the unreconstructed one.

The smaller occupancy of the antibonding states for the reconstructed surface is related to the fact that the  $d$  states of the surface atoms lie higher in energy on this surface. Metal atoms with a low coordination number have  $d$  states that are shifted up in energy relative to states for atoms with a high coordination number. This can be observed for self-consistent calculations of the  $d$  density of states for surface layers compared to bulk atoms.<sup>27</sup> Similarly, we find in our calculations for Cu (and other transition-metal) atoms embedded in the homogeneous electron gas that the  $d$  resonance shifts up in energy relative to the Fermi level as the electron-gas density goes down. The up-shift in the  $d$ -resonance position is a consequence of an up-shift in the effective one-electron potential as the density decreases. It is this shift that makes the low-coordination-number Cu atoms bind oxygen more strongly, and if it is not included in the model, the oxygen-induced reconstructions are not stable at all.

In conclusion, we have shown that model calculations for the oxygen-covered Cu surfaces support missing-row-type reconstructions of Cu(110) and Cu(100). We have identified the main factor driving the reconstruction. The reconstructed surfaces have low-coordination-number metal atoms with high-lying  $d$  states, which interact more strongly with the oxygen  $p$  states.

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