

## Unoccupied surface states on clean and oxygen-covered Cu(110) and Cu(111)

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(Received 10 April 1989)

The experimentally observed surface states of the adsorbate systems Cu(110) $p(2\times 1)$ O and Cu(111)/O<sub>2</sub> can be simulated by a simple model using a planar-averaged surface barrier. The  $E(k_{\parallel})$  dispersion curves of the adsorbate case are obtained from those of the clean-surface case by a systematic downward shift in energy which is achieved, in this particular model, by an outward movement of the barrier by 1–2 a.u.

### I. INTRODUCTION

On inspecting the inverse photoemission data of Jacob *et al.*<sup>1</sup> on Cu(110) $p(2\times 1)$ O, we were struck by the resemblance of the  $E(k_{\parallel})$  dispersion curves for the oxygen-induced electronic states to those generated by a simple model which we had devised for clean surfaces.<sup>2</sup> In this paper, we explore this resemblance in numerical detail. We find that the  $E(k_{\parallel})$  relations for Cu(110) $p(2\times 1)$ O can be derived from those for clean Cu(110) by a systematic shift in energy. A similar result is obtained for the adsorption of oxygen on Cu(111). Our findings are relevant to a debate in the literature on the relative importance of planar-averaged electrostatic effects and local-orbital chemical-bonding effects.<sup>3</sup>

### II. SURFACE-STATE MODEL

#### A. Surface potential barrier

Following our previous work,<sup>2,4</sup> here we adopt the three-parameter model for a saturated image-potential barrier devised by Jones, Jennings, and Jepsen.<sup>5</sup>

$$V(z) = \begin{cases} -\frac{1}{2(z-z_0)}(1 - e^{-\lambda(z-z_0)}), & z > z_0 \\ \frac{U_0}{1 + Ae^{\beta(z-z_0)}}, & z < z_0 \end{cases} \quad (1)$$

The three disposable parameters are  $z_0$ , the distance of the image plane,  $U_0$ , the inner potential, and  $\lambda^{-1}$ , a characteristic distance over which the image potential saturation takes place. The two other parameters  $A$  and  $\beta$  are fixed by smooth continuity at  $z = z_0$ .

The ansatz of Eq. (1) reproduces very well the surface barrier for jellium obtained theoretically by Lang and Kohn<sup>6</sup> (see Ref. 7). It has been used successfully in the analysis of inverse-photoemission data on clean surfaces<sup>2,4</sup> and of preemergent fine structure in very-low-energy electron diffraction.<sup>5,7,8</sup>

#### B. Adsorbate simulation

Jennings and co-workers<sup>7-9</sup> have pointed out that in classical electrostatics the potential experienced by an

electron situated outside a metal with a dielectric layer on its surface may be written

$$V(z) \sim \frac{-1}{2|z - (z_0 + \delta)|} \left[ 1 - \frac{2\delta}{(\epsilon + 1)|z - (z_0 + \delta)|} \right], \quad (2)$$

where  $\delta$  is the thickness of the layer and  $\epsilon$  is its dielectric constant. The principal result is an outward shift of the effective image plane. Following the basic insight, we have tried to simulate the effects of adsorption by simply varying  $z_0$  in Eq. (1). This procedure has previously been found to work quite well in fitting the surface barrier for H chemisorbed on W(001) obtained from first-principles theoretical computations.<sup>7</sup>

It should be recognized that varying  $z_0$  is only one of the possible ways of simulating the adsorbed layer. As  $z_0$  moves away from the solid, the effect is to lower energies of all the surface states. The same effect can be achieved by increasing  $U_0$ , the depth of the inner potential well. Another way would be to introduce, near the outermost atomic layer, a thin sheet of attractive potential. Our derived numerical values for  $z_0$  should therefore not be taken literally. Our concern is to show how the surface states for the adsorbate case can evolve from those of the clean surface.

#### C. Procedure and terminology

We have used the multiple reflection model<sup>10</sup> in its elementary form<sup>11</sup> to generate the surface-state  $E(k_{\parallel})$  dispersion relations. The quantization condition is  $\phi_C + \phi_B = 2\pi n$ , where  $\phi_C$  and  $\phi_B$  are the phase changes on reflection at the crystal and surface barrier, respectively;  $\phi_C$  is obtained from a two-band nearly-free-electron model, and  $\phi_B$  is obtained for specific values of  $z_0$  by integrating Schrödinger's equation along the  $z$  axis.<sup>2,12</sup>

At  $\bar{\Gamma}$ , the surface states may be designated as  $S_n$ , with  $S_0$  being the usual Shockley state and  $S_1, S_2$ , etc. being the image state Rydberg series. For gaps centered at the boundary of the surface Brillouin zone, the quantization condition becomes  $\phi_C^{\pm} + \phi_B = 2\pi n$ , and the states may be designated  $S_n^{\pm}$ .  $S_0^-$  and  $S_0^+$  are odd and even Shockley states; the image states also alternate between odd and even symmetry.

### III. NUMERICAL RESULTS AND DISCUSSION

#### A. Clean Cu(110)

The results of the model for clean Cu(110) are compared with the inverse-photoemission data of Jacob *et al.*<sup>13</sup> and the photoemission data of Kevan<sup>14</sup> in Fig. 1. Inverse-photoemission data on this surface have also been reported by Reihl and Frank<sup>15</sup> and by Bartynski *et al.*<sup>16</sup> In the gap centered at  $\bar{Y}$  (associated with the bulk  $L_2, L_1$  gap), three surface states are seen: the odd and even Shockley states  $S_0^-$  and  $S_0^+$ , and the first image state  $S_1^-$ . A feature labeled  $B_1$  is also seen in inverse photoemission. This may be associated with the  $S_0^-$  state but it overlaps in energy with a bulk direct transition<sup>13</sup> and so its identification is ambiguous. In the gap centered at  $\bar{X}$  (associated with the  $X_4, X_1$  gap), only the  $S_0^+$  state is clearly seen; the  $S_0^-$  state, if present, is obscured by the bulk direct transition  $B_2$ .

The theoretical curves of Fig. 1 were generated with a Jones-Jennings-Jepsen barrier having  $z_0=1.7$  a.u.,  $U_0=1.06$  Ry, and  $\lambda=1.01$  a.u. The overall match to the data is good, with the exception of the  $S_0^+$  state at  $\bar{Y}$  where the theoretical curve lies too high. This discrepancy appears to run consistently through the fcc metals which have been studied<sup>4</sup> and is not understood. Within the limitations of the multiple reflection model, there appears to be no nonpathological pair of  $(\phi_C, \phi_B)$  curves which can simultaneously reproduce the  $S_0^-, S_0^+$ , and  $S_1^-$  states of the  $\bar{Y}$  gap. Some physical phenomenon beyond the scope of the model, such as contraction of the outermost atomic layer,<sup>17</sup> may be responsible.

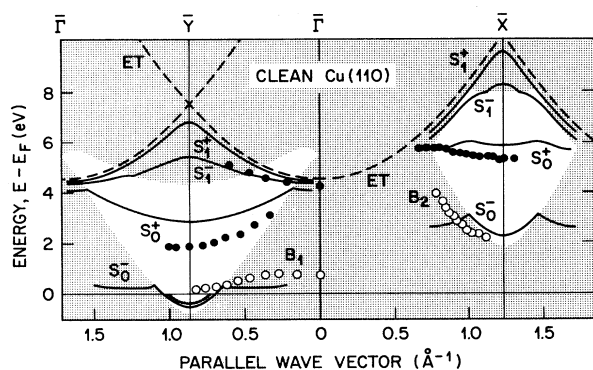


FIG. 1.  $E(k_{\parallel})$  dispersion of the surface states of clean Cu(110) along the two principal azimuths  $\bar{\Gamma}\bar{Y}$  and  $\bar{\Gamma}\bar{X}$ . The large solid circles are the inverse-photoemission data of Ref. 13. The photoemission data of Ref. 14 below  $E_F$  and  $\bar{Y}$  are also indicated. Open circles labeled  $B_1$  and  $B_2$  are attributable to bulk direct transitions. Solid curves are the dispersion relations generated by the simple phase accumulation model with an image-plane distance  $z_0=1.7$  a.u.  $S_0^-$  and  $S_0^+$  denote odd and even Shockley states.  $S_1^-$  and  $S_1^+$  are the first members of an image-state Rydberg series converging on the escape threshold (ET) indicated by the dashed curves. The toned area represents the projection of the bulk band structure.

#### B. Cu(110)p(2×1)O

The results of the model are compared in Fig. 2 with the inverse-photoemission data of Ref. 1 on the adsorbate system Cu(110)p(2×1)O. The symbols  $A_{1-6}$  denote the data. For the  $\bar{\Gamma}\bar{X}$  azimuth, dashed curves indicate the zone folding (or surface-umklapp effect) associated with the  $p(2\times 1)$  superlattice. The theoretical curves themselves were obtained by setting  $z_0=3.6$  a.u. while keeping the values of  $U_0$  and  $\lambda$  the same as for the clean Cu(110) case discussed above. The effect of the larger value of  $z_0$  is to force the  $E(k_{\parallel})$  curves downwards in energy. In the phase accumulation model, the surface-state quantization condition is, of course, cyclical in nature; we could easily have arrived at a satisfactory match by a smaller upwards shift of the clean Cu(110) solutions. We choose a downward shift for two reasons. Firstly, it is more physically plausible; the adsorbed oxygen atoms are electronegative, a situation which, if simulated by a thin sheet of attractive potential, would pull the energies down. Secondly, a downward shift is consistent with our treatment of oxygen on Cu(111) presented below.

Near  $\bar{Y}$ , we may identify the observed features  $A_4, A_3$ , and  $A_1$  with the states  $S_0^+, S_1^-$ , and  $S_1^+$ , respectively. On moving from  $\bar{Y}$  to  $\bar{\Gamma}(k_{\parallel}=0)$ , the  $A_1$  identification is less clear, although this may be a resolution limitation in which the  $S_1^-$  and  $S_1^+$  states are not fully resolved. Near  $\bar{X}$ , we may identify the observed features  $A_5$  and  $A_6$  with the states  $S_0^+$  and  $S_1^-$ , respectively. Near  $\bar{\Gamma}$ , we may identify  $A_1$  and  $A_2$  with the states  $S_0^+$  and  $S_1^-$  near  $\bar{X}$  which have been translated by surface umklapp through a reciprocal-lattice vector of the  $p(2\times 1)$  superlattice. Thus, all the observed features  $A_{1-6}$  are susceptible to interpretation as surface states by a straightforward elaboration of the phase accumulation model.

Our interpretation differs in an important respect from the one offered in Ref. 1. That paper distinguishes be-

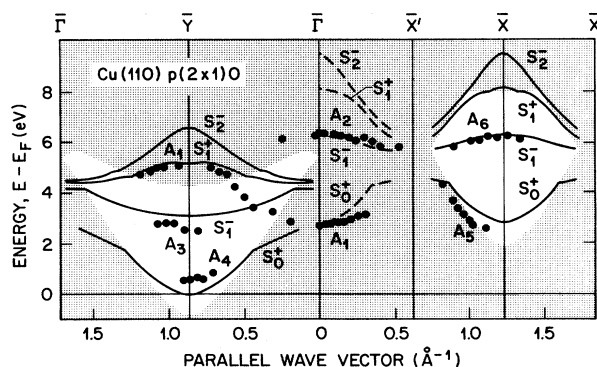


FIG. 2.  $E(k_{\parallel})$  dispersion of the surface states of the adsorbate system Cu(110)p(2×1)O. Solid circles labeled  $A_{1-6}$  are the inverse-photoemission data of Ref. 1. Solid curves labeled  $S_n^{\pm}$  are the dispersion curves generated by the phase accumulation model with  $z_0=3.6$  a.u. The dashed curves near  $\bar{\Gamma}$  in the  $\bar{\Gamma}\bar{X}$  azimuth are generated from those near  $\bar{X}$  by "surface umklapp," i.e., translation through a reciprocal-lattice vector of the  $p(2\times 1)$  superlattice.

tween features derived from the clean Cu(110) states (identified as  $A_3$ ,  $A_4$ , and  $A_5$ ) and those which are not (identified as  $A_1$ ,  $A_2$ , and  $A_6$ ). It is then suggested that one of the latter is the antibonding component of the metal-adsorbate covalent bond. This possibility is plausible, but, as our analysis shows, the distinction may not be necessary.

### C. Cu(111)/O<sub>2</sub>

Jacob *et al.*<sup>1</sup> also report inverse-photoemission data for oxygen adsorbed on Cu(111). One adsorbate-induced feature is seen, and its  $E(k_{\parallel})$  dispersion is shown in Fig. 3 as solid circles. We identify this feature as the  $S_1$  image state shifted downwards in energy from its clean surface position. The photoemission<sup>18</sup> and inverse-photoemission<sup>19</sup> data for clean Cu(111) are shown in Fig. 3 for comparison.

Figure 3 also compares the data with the results of our model. The clean Cu(111) and Cu(111)/O<sub>2</sub> cases are simulated quite well with image distances  $z_0=2.3$  and  $3.7$  a.u., respectively. (The values for  $U_0$  and  $\lambda$  are 1.10 Ry and 1.17 a.u. in each case.) Note that adsorbate case could not be derived from a *small* upwards shift of the clean surface case, reinforcing our choice of downwards shifts in energy as mentioned in Sec. III B.

### D. Closing comments

What we have shown in the numerical exercises of this paper is that almost the entire manifold of unoccupied adsorbate-induced surface states on Cu(110) $p(2\times 1)$ O and Cu(111)/O<sub>2</sub> can be derived from the states of the clean surfaces by a simple modification of the surface barrier. In the interpretive model we have used, the surface states are essentially the standing-wave resonances of the effective cavity between the crystal and surface barrier. Lindgren and Walldén<sup>20</sup> have reported similar success in explaining the surface states for layers of alkali metal on various metal substrates. Lenac *et al.*<sup>21</sup> have used a similar approach in the study of hydrogen-covered Pd surfaces. These effects may therefore be of some generality. We conclude that such planar-averaged "cavity-resonance" possibilities need to be considered before adsorbate-induced features in inverse-photoemission spectra can confidently be assigned to local orbital configurations of a substrate-adsorbate bond.

In the specific case of Cu(110) $p(2\times 1)$ O, we find that our simple model explains immediately the observed adsorbate-induced features  $A_3$ ,  $A_4$ ,  $A_6$  and the feature  $A_1$  near  $\bar{Y}$ . In our analysis, we are obliged to separate  $A_1$  into two features: an  $A_1$ -near- $\bar{Y}$  feature attributable to the expected  $S_1^+$  image state, and an  $A_1$ -near- $\bar{\Gamma}$  feature. The latter and also the  $A_2$  feature are explained less directly as the  $S_0^+$  and  $S_1^-$  states near  $\bar{X}$  translated by

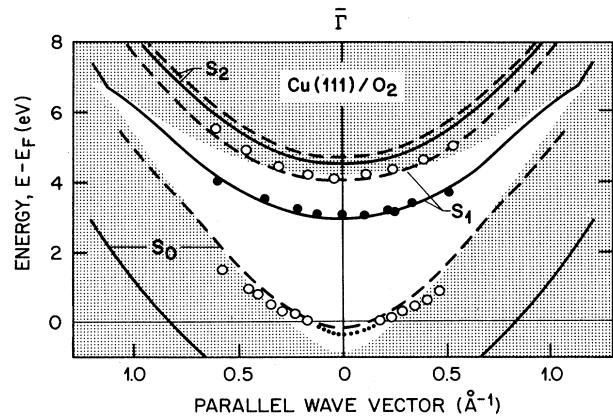


FIG. 3.  $E(k_{\parallel})$  dispersion relations for clean Cu(111) and the adsorbate system Cu(111)/O<sub>2</sub>. Open circles are the inverse-photoemission data of Ref. 18 on clean Cu(111); the photoemission data of Ref. 17 on clean Cu(111) are shown as the dots near  $\bar{\Gamma}$ . Solid circles are the inverse-photoemission data of Ref. 1 for Cu(111)/O<sub>2</sub>. The clean and adsorbate cases have been simulated with the phase accumulation model with image-plane distances  $z_0=2.3$  and  $3.7$  a.u. shown, respectively, as the dashed and solid curves.

surface umklapp to the region near  $\bar{\Gamma}$ . Inspection of Fig. 2 shows that this works well for  $A_2$ , but is less satisfactory for  $A_1$ -near- $\bar{\Gamma}$ .

Angle-resolved photoemission experiments on Cu(110) $p(2\times 1)$ O by Didio *et al.*<sup>22</sup> reveal an oxygen-induced peak within 1 eV of the top of the Cu  $d$  band, which is attributed to the antibonding surface-molecule state in accordance with first-principles calculations on such systems.<sup>23</sup> This work has been refined in some detail by Courths *et al.*,<sup>24</sup> who find that of the three anticipated antibonding states, one is missing. It is suggested that the missing state is either buried within the Cu  $d$ -band manifold or is pushed up above  $E_F$  to be identified with the  $A_1$  inverse-photoemission feature as advocated in Ref. 1. Tight-binding simulations<sup>24</sup> indicate that the latter hypothesis requires a large arbitrary shift of the Cu  $d$ -state center of gravity to 3 eV above  $E_F$ , as opposed to the 2 eV below  $E_F$  which works well for the occupied adsorbate-induced states.

A first-principles calculation would be most welcome to distinguish between the competing possibilities. Such a calculation would need to be done for the  $(2\times 1)$  supercell in order to test for the proposed surface-umklapp effects. It would also need to incorporate the image-potential asymptotic form for the surface barrier, since this is crucial to the existence of the  $S_1^-$  and  $S_1^+$  states and higher members of the image state Rydberg series.

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