

Electronic structure of steps on the (001) surface of copper*

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Using the extended-Hückel parameters previously obtained for smooth Cu thin films, we have calculated the energy bands and local densities of states of a (001) Cu film alternately 13 and 11 layers thick with two-dimensional lattice vectors $(1/2, -1/2, 0)a$ and $(5, 5, 0)a$. We find no surface states but several surface resonances, one of which may be designated an edge resonance. The upper atom at a step has a charge deficit of $-0.037e$ (an order of magnitude smaller than that obtained with ordinary Hückel calculations for atoms on smooth surfaces) but the lower atom at the step has a charge surplus of $0.031e$ and the two surface planes have a net deficit of only $-0.008e$ per atom without the use of any surface-parameter shifts.

I. INTRODUCTION

Stepped surfaces consisting of (111) or (100) terraces of constant width linked by steps of monatomic height are easily obtained by cutting a crystal to expose a high-Miller-index plane.¹ They are of great interest because gasses which do not readily chemisorb on smooth surfaces do so on stepped surfaces and interactions between chemisorbed species are much stronger on stepped surfaces than on smooth.² As far as we know there is only one calculation³ of the electronic structure of a stepped transition-metal surface. That calculation was performed using the continued-fraction method⁴ and therefore yielded local density of states (LDS) but not individual electron eigenfunctions and eigenvalues. Furthermore, it was restricted to a basis set consisting of the five $5d$ platinum orbitals, whereas we have demonstrated⁵ that there are hybridized surface states which contribute strongly to the d -band surface LDS that are not obtained when the s and p orbitals are omitted. Although we have been able to include s and p basis functions in continued-fraction calculations,⁵ we have very recently demonstrated⁶ that the non-orthogonality of the s and p functions must be explicitly taken account of in an extended-Hückel calculation if one wishes to avoid huge sp -surface-charge deficits. (In principle, one could use generalized Wannier basis functions⁷ and avoid the surface-charge deficits but there is no way to

know how the Hamiltonian matrix elements involving generalized Wannier functions near the surface will vary from those involving only bulk Wannier functions.) The continued-fraction method cannot be applied to nonorthogonal orbitals. Therefore we here apply our standard two-dimensional (2D) \bar{k} -space techniques⁶ to a stepped surface of copper. We chose copper rather than the more interesting case of platinum both because the matrices we have to diagonalize are so large that we could not stand the additional complexity of spin-orbit coupling and because we wished to see if the same extended-Hückel parameters we used for smooth surfaces of copper would yield charge neutrality for rough surfaces.

In order to have a reflection plane through the middle of the film we have chosen the steps to alternate rather than to be monotonic. In Fig. 1(a) we show the irreducible $\frac{1}{4}$ unit cell for a film 13 layers thick with alternate strips, five surface atoms wide, removed. The 2D lattice vectors are $(\frac{1}{2}, -\frac{1}{2}, 0)a$ and $(5, 5, 0)a$, where a is the fcc cube edge length and the unit cell contains 120 atoms.⁸ The $\frac{1}{4}$ irreducible 2D Brillouin zone (2D BZ) is shown in Fig. 1(b). The dots represent the \bar{k} points sampled in the calculation. Because all such points lie along the $\bar{\Delta}$ or $\bar{\Gamma}$ lines, the $(1\bar{1}0)$ reflection is a member of the group of the wave vector allowing us to combine our basis functions in the symmetrized form

$$\begin{aligned} \psi_{\alpha q n j}(\bar{k}) = (4N)^{-1/2} \sum_p e^{i\bar{k} \cdot \bar{R}_p} \{ & [\phi_{\alpha}(\bar{r} - \bar{R}_p - \bar{Z}_n - \bar{\tau}_j) \pm \phi_{\alpha}(\bar{r} - \bar{R}_p + \bar{Z}_n - \bar{\tau}_j)] \\ & \times e^{i\bar{k} \cdot \bar{\tau}_j} \pm [\phi_{\alpha}(\bar{r} - \bar{R}_p - \bar{Z}_n + \bar{\tau}_j) \pm \phi_{\alpha}(\bar{r} - \bar{R}_p + \bar{Z}_n + \bar{\tau}_j)] e^{-i\bar{k} \cdot \bar{\tau}_j} \}, \end{aligned} \quad (1)$$

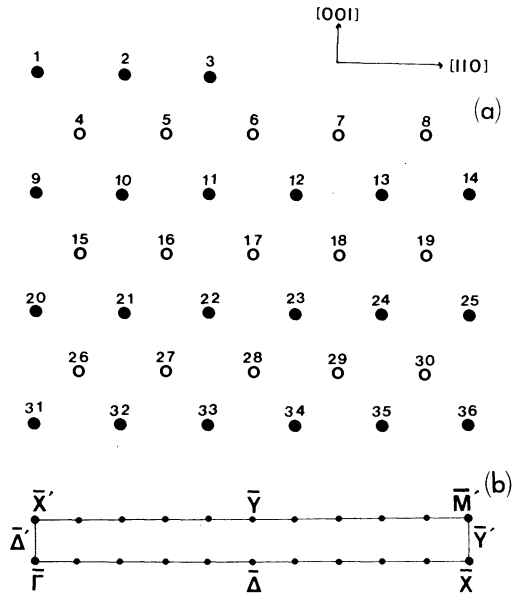


FIG. 1. (a) 36 atoms of the irreducible $\frac{1}{4}$ unit cell of a corrugated (001) copper film 13 layers thick. (b) The irreducible $\frac{1}{4}$ 2D BZ for the above film with the \bar{k} 's for which the calculations were made indicated by dots.

where q represents the symmetry under the $(1\bar{1}0)$ and (001) reflections, \bar{R}_p is a vector to the center of the p th unit cell, $\bar{\eta}_{jn} = \bar{\tau}_j + \bar{Z}_n$ is a vector from the center to the n th atom of the irreducible $\frac{1}{4}$ unit cell with $\bar{Z}_n = (0, 0, \frac{1}{2})na$ and α runs over the nine (one $4s$, three $4p$, and five $3d$) orbitals. The simplification of $\psi_{\alpha q n j}$ which occurs for atoms on the central plane ($n=0$) or at the center or edge of the 2D unit cell ($j=0$ or 10) is obvious. Although we have $9 \times 120 = 1080$ basis functions, this symmetry reduces our largest matrix to 287×287 . At the $\bar{\Gamma}, \bar{X}, \bar{X}'$ and \bar{M}' points in the 2D BZ the (110) reflection plane is also a member of the group of the wave vector, further reducing the matrix size.

II. RESULTS

In Fig. 2 we show the energy bands of the corrugated copper thin film of Fig. 1, calculated using the Hamiltonian and overlap parameters of Table III in Ref. 6. In Table I we display the character table for the symmetry points in the 2D BZ, $\Xi = \bar{\Gamma}, \bar{X}, \bar{M}'$ and \bar{X}' , and the compatibility relations between the symmetry lines and points. We see that $\bar{\Delta}'_2$ runs between $\bar{X}'_{2,3}$ and $\bar{\Gamma}_{2,3}$ and therefore forms a very narrow band. On other symmetry lines, however, states of each symmetry span the same energy range. There are two kinds of band degeneracies⁹ at the symmetry points. The $\Xi_{1,4}$ and $\Xi_{2,3}$ degeneracies are between bands even and odd under the (110) reflection. The wider the terraces, the more exact this degeneracy is. The $\Xi_{1,3}$ and $\Xi_{2,4}$ degeneracies are between states which differ only in an interchange of A and B planes of atoms (solid and open circles in Fig. 1) and since A and B planes are indistinguishable in the bulk, this degeneracy becomes practically exact for a moderately thick film. We note that there is only one gap in the 2D energy bands. It is a remnant of a larger gap which occurs for the smooth (001) film. In neither the smooth or corrugated film does this gap contain a surface state. Therefore the corrugated film has no surface states whatsoever.

There are, however, several surface resonances throughout the 2D BZ, the most extensive of which covers a region from¹⁰ $(0.3, 0)$ to $(1, 0)$ to $(0.7, 1)$ to $(0.2, 1)$. It runs from¹¹ -0.5956 Ry at $\bar{\Delta}'_1^+$ $(0.3, 0)$ to -0.5565 Ry at \bar{X}'_1^+ $(1, 0)$. The resonance is very sharp, containing only two states of opposite parity¹¹ at any \bar{k} which differ at most by 0.0016 Ry. Presumably for a thicker film the energy levels would be more closely packed and the resonance would contain several states at each \bar{k} . Other resonances do come close in energy; for instance, there is a resonance pair at $(0.3, 0)$ with energies

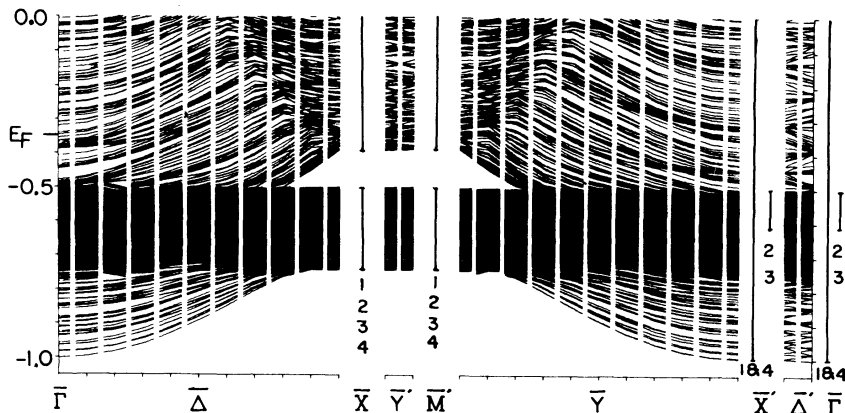


FIG. 2. Energy bands for the corrugated 13-layer Cu film.

TABLE I. Character table and compatibility relations for the four symmetry points $\Xi = \bar{\Gamma}, \bar{X}, \bar{M}',$ and \bar{X}' .

| | E | C_2 | $\sigma_{(\bar{1}10)}$ | $\sigma_{(110)}$ |
|--|-----|-------|------------------------|------------------|
| $\bar{\Gamma}_1$ | 1 | 1 | 1 | 1 |
| $\bar{\Gamma}_2$ | 1 | 1 | -1 | -1 |
| $\bar{\Gamma}_3$ | 1 | -1 | 1 | -1 |
| $\bar{\Gamma}_4$ | 1 | -1 | -1 | 1 |
| $\bar{\Delta}_1, \bar{Y}_1 \leftrightarrow \Xi_1, \Xi_3, \quad \bar{\Delta}_2, \bar{Y}_2 \leftrightarrow \Xi_2, \Xi_4$ | | | | |
| $\bar{Y}'_1, \bar{\Delta}'_1 \leftrightarrow \Xi_1, \Xi_4, \quad \bar{Y}'_2, \bar{\Delta}'_2 \leftrightarrow \Xi_2, \Xi_3$ | | | | |

$\bar{\Delta}_1^+ = 0.5966$ Ry and $\bar{\Delta}_1^- = 0.5961$ Ry. However there is a nonresonant $\bar{\Delta}_1^- (0.3, 0)$ at -0.5956 Ry which lies between this $\bar{\Delta}_1^-$ resonance and the $\bar{\Delta}_1^-$ level of the extended resonance at -0.5954 Ry indicating that these are two separate resonances. Another somewhat extended resonance runs from $\bar{\Gamma}_1$ at -0.7090 Ry to $\bar{\Delta}_1 (0.3, 0)$ at -0.6901 Ry. It barely extends to \bar{X}' where there is a \bar{X}'_1^+ resonance at -0.7115 Ry but no resonance of opposite parity. Altogether, at the 22 points sampled in the 2D BZ, we found 60 resonance pairs and 51 unpaired resonances covering the energy range from -0.7115 Ry up to positive energy. In Table II we display the electron density on each atom due to four representative surface resonances,

$$\rho_{ni}(l_q \bar{k}) = W_{ni}^{-1} \sum_{mj \in \alpha \beta} C_{\alpha q, ni}^{i \bar{k}} C_{\alpha q, mj}^{i \bar{k}} S_{ni, mj}^{\alpha q, \alpha q}(\bar{k}), \quad (2)$$

where $C_{\alpha q, ni}^{i \bar{k}}$ is the coefficient of the $\psi_{\alpha q ni}$ Bloch basis function [Eq. (1)] in the l_q th eigenfunction of q symmetry at \bar{k} , $S_{ni, mj}^{\alpha q, \beta q}(\bar{k})$ is the overlap of two Bloch basis functions and $W_{ni} = 1$ for corner atoms, 2 for edge atoms, and 4 for all other atoms in the irreducible $\frac{1}{4}$ unit cell.

Note that the \bar{M}_1^+ resonance is very highly peaked about atoms 1 and 2 in the middle of the upper terrace. The \bar{Y}_2^- resonance is peaked on atom 3 and has a moderate amplitude on atoms 5, 6, 7, 8, and 11; this should probably be called an edge resonance. The \bar{X}_1^+ resonance is very sharply peaked on atoms 1 and 3 having an order of magnitude more density on each of those two atoms than on any other atom. The $\bar{\Delta}_1^+$ resonance is much smoother with appreciable density on the first four planes of atoms. None of these resonances appear to decay beyond the fifth plane (the \bar{M}_1^+ and \bar{X}_1^+ do not decay beyond the second plane) so that they would not be appreciably changed in a much thicker film except that they would extend through the entire film and therefore require an overall renormalization.

We next calculate the local density of states (LDS) on each atom,

$$\mathcal{N}_{ni}(E) = \frac{1}{20} \sum_{q i_q \bar{k}} W(\bar{k}) \rho_{ni}(l_q \bar{k}) \delta(E - E_{i_q \bar{k}}), \quad (3)$$

where the factor $\frac{1}{20}$ is 2 (for spin) divided by the number of points sampled in the 2D BZ and $W(\bar{k})$ is the number of times each point in the irreducible 2D BZ occurs in the 2D BZ. The LDS for 17 of the 36 atoms together with the total density of states (TDS) is shown¹² in Fig. 3. In spite of the fact that such a large fraction of the atoms in this corrugated 13 layer film are close to the surface, the TDS looks very similar to that for the 40 layer smooth film.⁶ Although we cannot ascribe any of the features of the LDS's to surface resonances

TABLE II. Electron density on each atom due to four surface resonances: \bar{M}_1^+ at -0.4832 Ry, $\bar{Y}_2^- (0.5, 1)$ at -0.5725 Ry, \bar{X}_1^+ at -0.5565 Ry and $\bar{\Delta}_1^+ (0.3, 0)$ at -0.5956 Ry, and the total net charge on each atom (defined as the number of electrons on the atom minus eleven).

| Atom | \bar{M}_1^+ | $\bar{Y}_2^- (0.5, 1)$ | \bar{X}_1^+ | $\bar{\Delta}_1^+ (0.3, 0)$ | Net charge |
|------|---------------|------------------------|---------------|-----------------------------|------------|
| 1 | 0.1380 | 0.0101 | 0.1203 | 0.0272 | -0.0074 |
| 2 | 0.0999 | 0.0079 | 0.0140 | 0.0311 | -0.0123 |
| 3 | 0.0301 | 0.0768 | 0.1339 | 0.0190 | -0.0368 |
| 4 | 0.0009 | 0.0090 | 0.0013 | 0.0175 | -0.0139 |
| 5 | 0.0047 | 0.0129 | 0.0015 | 0.0065 | -0.0267 |
| 6 | 0.0032 | 0.0160 | 0.0066 | 0.0131 | +0.0312 |
| 7 | 0.0000 | 0.0113 | 0.0006 | 0.0043 | +0.0005 |
| 8 | 0.0002 | 0.0156 | 0.0001 | 0.0223 | +0.0021 |
| 9 | 0.0004 | 0.0061 | 0.0054 | 0.0190 | +0.0047 |
| 10 | 0.0028 | 0.0071 | 0.0020 | 0.0023 | +0.0034 |
| 11 | 0.0064 | 0.0158 | 0.0048 | 0.0062 | -0.0005 |
| 12 | 0.0051 | 0.0014 | 0.0011 | 0.0038 | +0.0003 |
| 13 | 0.0007 | 0.0016 | 0.0001 | 0.0109 | -0.0096 |
| 14 | 0.0002 | 0.0015 | 0.0001 | 0.0131 | -0.0078 |
| 15 | 0.0004 | 0.0084 | 0.0003 | 0.0065 | +0.0003 |
| 16 | 0.0017 | 0.0046 | 0.0017 | 0.0055 | +0.0015 |
| 17 | 0.0013 | 0.0063 | 0.0004 | 0.0146 | +0.0062 |
| 18 | 0.0003 | 0.0033 | 0.0008 | 0.0065 | +0.0085 |
| 19 | 0.0003 | 0.0011 | 0.0001 | 0.0087 | +0.0067 |
| 20 | 0.0010 | 0.0042 | 0.0005 | 0.0013 | +0.0015 |
| 21 | 0.0020 | 0.0038 | 0.0004 | 0.0022 | +0.0023 |
| 22 | 0.0045 | 0.0033 | 0.0045 | 0.0027 | +0.0057 |
| 23 | 0.0051 | 0.0046 | 0.0017 | 0.0027 | +0.0061 |
| 24 | 0.0024 | 0.0018 | 0.0006 | 0.0049 | +0.0063 |
| 25 | 0.0003 | 0.0025 | 0.0019 | 0.0043 | +0.0048 |
| 26 | 0.0002 | 0.0052 | 0.0002 | 0.0039 | +0.0006 |
| 27 | 0.0002 | 0.0043 | 0.0022 | 0.0066 | +0.0019 |
| 28 | 0.0003 | 0.0041 | 0.0025 | 0.0037 | +0.0035 |
| 29 | 0.0003 | 0.0039 | 0.0004 | 0.0039 | +0.0057 |
| 30 | 0.0001 | 0.0005 | 0.0001 | 0.0007 | +0.0047 |
| 31 | 0.0013 | 0.0057 | 0.0042 | 0.0056 | -0.0024 |
| 32 | 0.0017 | 0.0048 | 0.0010 | 0.0047 | +0.0006 |
| 33 | 0.0036 | 0.0015 | 0.0009 | 0.0018 | +0.0008 |
| 34 | 0.0052 | 0.0035 | 0.0031 | 0.0019 | +0.0017 |
| 35 | 0.0029 | 0.0008 | 0.0000 | 0.0028 | +0.0039 |
| 36 | 0.0000 | 0.0007 | 0.0022 | 0.0016 | +0.0047 |

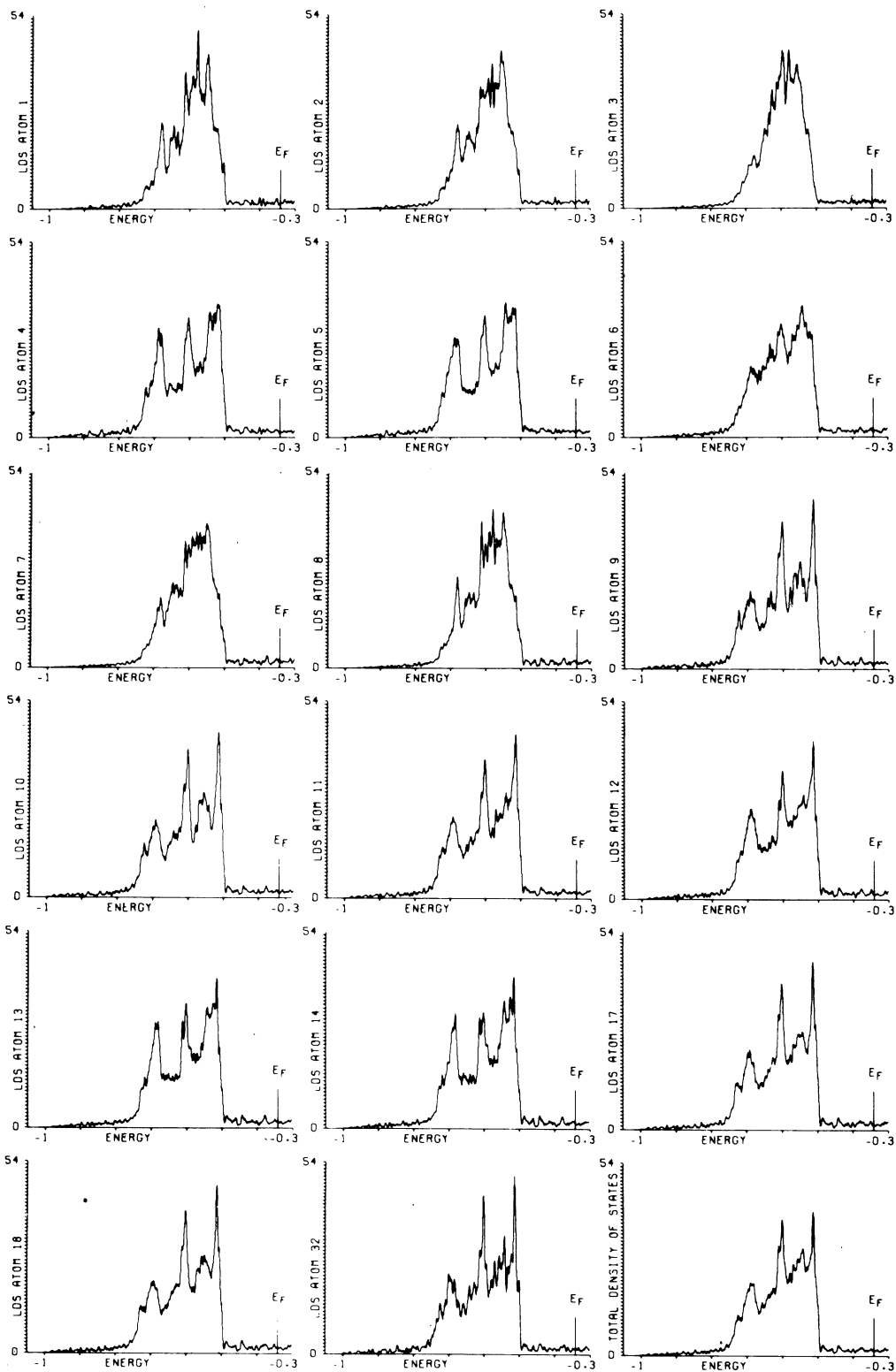


FIG. 3. Local density of states for 17 of the 36 atoms in the $\frac{1}{4}$ unit cell and the total density of states for the film. When multiplied by two for spin, the units are electrons per atom per Ry.

(which account for only 1% of the total number of eigenfunctions calculated), we can find many features which atoms in particular positions have in common. For instance the LDS of atoms 1 and 8, both of which are surface atoms far from an edge, are very similar to each other and to the LDS for an atom on a smooth Cu (001) surface.⁶ Similarly atoms 4 and 14 have LDS's similar to each other and to that of an atom one layer in from a smooth Cu (001) surface. On the other hand the LDS's for the edge atoms 3 and 6 are much different from each other and from any other LDS. The general rule that atoms with more neighbors have wider LDS's than atoms with less is seen to be true.

The Fermi energy, defined as that energy below which the TDS contains 11 electrons was found¹³ to be $E_F = -0.3417$ Ry. The net charge on each atom was found by integrating the LDS up to E_F and subtracting eleven. This is listed in the last column of Table II. The average charge on the first two planes (atoms 1–8) is -0.008 electrons, compared with the $-0.009e$ one would get if one assumed atoms 1–3 had the excess charge of atoms on the smooth (001) surface and atoms 4–8 had that of atoms one plane in from the smooth surface.

The relatively large deficit of $-0.037e$ and surplus of $0.031e$ on the edge atoms are still an order of magnitude smaller than the deficits found on smooth copper surfaces with ordinary Hückel calculations.⁶ Self-consistency would reduce these charges but because they are a short range fluctuation, it will not eliminate them. One could take partial account of self consistency effects by raising the zeroth-neighbor parameters on atoms with electron surplusses and lowering it on atoms with deficits by an amount which would reduce the surplusses and deficits to about half of their initial values. That shift can easily be estimated from the LDS; however, this correction is small compared with uncertainties due to surface atom relaxation and we have not included it. The power of the extended-Hückel method is that it reduces the needed surface parameter shifts (whose uncertainties are a large fraction of their value, especially for complicated surfaces like this) to a very small fraction of what is needed in a Hückel calculation. If the edge dipole persists after surface relaxation is correctly included, it could play an important role in the interactions between chemisorbed species.

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⁸There are 25 atoms inside the $\frac{1}{4}$ irreducible unit cell which occur four times in the full unit cell, nine edge

atoms which occur twice, and two corner atoms which occur once.

⁹By band degeneracy we mean that two bands of different symmetry span essentially the same energy range, not that two individual eigenstates are degenerate.

¹⁰Where $(\alpha, \beta) \equiv \pi(\alpha/a_1, \beta/a_2)$ and \bar{a}_1 and \bar{a}_2 are the 2D lattice vectors, and $a_2 = 10a_1$.

¹¹The superscript (\pm) refers to the symmetry of the state under a (001) reflection.

¹²The smoothing procedure used in Ref. 6 and described in K. S. Sohn, D. G. Dempsey, L. Kleinman, and E. Caruthers [Phys. Rev. B **13**, 1515 (1976)] is used here. We show the LDS over a somewhat smaller energy range here in order to display the details of the narrow d bands more clearly.

¹³We have included the same -0.018 -Ry shift of the energy bands that we made in Ref. 6 in order to obtain a Fermi energy for the smooth (001) film of -0.3423 Ry.