Self-consistent electronic structure of a Cu(100) monolayer

F. J. Arlinghaus, J. G. Gay, and J. R. Smith
Physics Department, General Motors Research Laboratories, Warren, Michigan 48090
(Received 20 November 1978)

The first fully self-consistent electronic structure calculation for a Cu(100) monolayer predicts no holes in $3d$ band, but does predict a state at the $\bar{M}$ point only 0.1 eV below the Fermi energy. This state is unique and lies 0.4 eV above the rest of the $3d$ band. The close proximity of this state to the Fermi energy, plus the demonstrated profound effects of going to self-consistency, suggests how some previous authors could have found d-band holes for a copper monolayer with a non-self-consistent calculation. The d-band edge falls further below the Fermi level as the film is thickened. The prediction of no band holes agrees with the results of Wang and Freeman.

I. Cu(100) MONOLAYER

The theoretical electronic structure of a copper monolayer has been the subject of much controversy[1–10] recently. The densities of states computed by various authors show substantial differences. For example, Cooper[1] reports the Fermi level for a Cu(100) monolayer to lie *below* the d-band edge (i.e., *holes* in the d band). At the other extreme, Abbati *et al.*[2] find for a Cu(111) monolayer it lies 3.7 eV *above* the d-band edge. Gurman,[3] for a Cu(100) monolayer, locates the Fermi level ~2 eV above the d-band edge.

Kar and Soven[4] commented that Cooper's result[1]—holes in the d band—seems very unlikely. Cooper[5] in turn argued that Kar and Soven's[4] results were very similar to his own and probably also exhibited d holes (the Kar and Soven paper is not detailed enough to be certain). Cooper suggested further that self-consistency should be important, and that to eliminate d holes at d-band metal surfaces the surface atoms might even have to move.

Wang and Freeman[10] have recently reported a calculation for a Cu(100) monolayer that is closer to self-consistency than any earlier calculations. In their calculation, the charge density is constrained to be a superposition of overlapping spherical charge densities. Within that approximation, only three numbers are iterated to self-consistency—the occupancies of the $3d$, $4s$, and $4p$ atomic orbitals in their basis set. They find that the Fermi level lies above the d-band edge so that their d bands are completely filled.

None of these monolayer calculations have been done fully self-consistently. We have previously demonstrated[11,12] the importance of self-consistency in surface electronic structure calculations. In an effort to clarify the present situation, we present in this paper the results of the first fully self-consistent calculation for a Cu(100) monolayer.

We use the self-consistent local orbital (SCLO) technique which is discussed in detail elsewhere.[11–14] It is an *ab initio* method, without pseudopotentials or other parametric forms. We use as basis functions all ground-state copper atomic orbitals as well as $4p$-, $4d$-, and $5s$-like excited-state orbitals. Charge densities are computed using 15 $k_{\parallel}$ points in the elemental $\frac{1}{8}$ of the surface Brillouin zone (SBZ), see Fig. 1. Full point-by-point self-consistency is obtained with final input and output potentials differing by <50 meV everywhere in the unit cell. We use 7800 (488 inequivalent) mesh points in our unit cell. Thus we iterate to self-consistency 488 different numerical values of the potential. The converged monolayer band structure is shown in Fig. 1. It agrees with respect to general features with all the work previously cited, but particularly with Painter[7] from which it cannot be distinguished at sight.

The highest state at $\bar{M}$ is about 0.4 eV above the highest state at $\bar{\Gamma}$, in agreement with earlier calculations. We plot the bands along three different symmetry directions. The very interesting and important

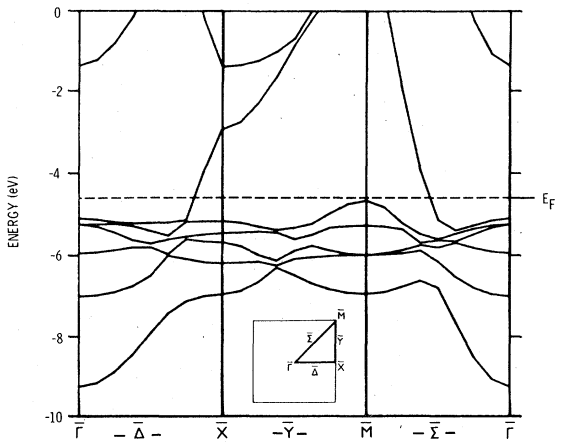

FIG. 1. Surface band structure.

fact is that $\bar{M}$ is unique. A glance at Fig. 1 suffices to see a well-defined top edge to the $3d$ band, except at $\bar{M}$, where the band rises 0.4 eV higher. This is still a $3d$ state, so the $3d$-band width is really 2.4 eV. This is to be compared with the 3.5 eV d-band width we obtained for a 9-layer thick Cu(100) film.[14] Furthermore, this state at $\bar{M}$ is only 0.1 eV below the Fermi energy. This small energy difference suggests an obvious explanation for the d-band holes[15] some authors find, a non-self-consistent result could easily misplace a level by considerably more than 0.1 eV.

The self-consistent density of states is shown in Fig. 2. For this plot, energy levels were computed at 45 $k_{\parallel}$ points in the elemental $\frac{1}{8}$ of the SBZ; the density-of-states curve itself was derived by a Monte Carlo procedure using 50 000 randomly chosen points in the SBZ and quadratic interpolation. The work function is 4.6 eV, as shown. This is within 0.1 eV of the value we obtained[14] for 3-, 5-, 7-, and 9-layer thick Cu(100) films. The interesting feature is that the d band appears to have a sharp edge at −5.0 eV with the Fermi level 0.5 eV above it. The $\bar{M}$ state 0.1 eV below the Fermi level can be seen only as a slight knee on the front edge of the d band. This is, of course, because its contribution to the DOS is quite small—it is prominent only on the band diagram.

To emphasize the importance of self-consistency, we show in Fig. 3 the density of states derived from our starting potential. This starting density of states is very different from the final self-consistent density of states. The d band is sufficiently higher relative to the s-p band that holes appear in it. While other non-self-consistent potentials may be more accurate than this starting potential they will of necessity contain certain arbitrary features whose consequences are not foreseeable, and which may, in particular, lead to unfilled d bands.

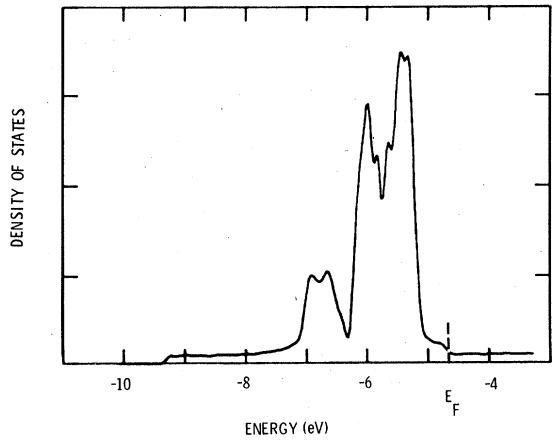

FIG. 2. Self-consistent density of states.

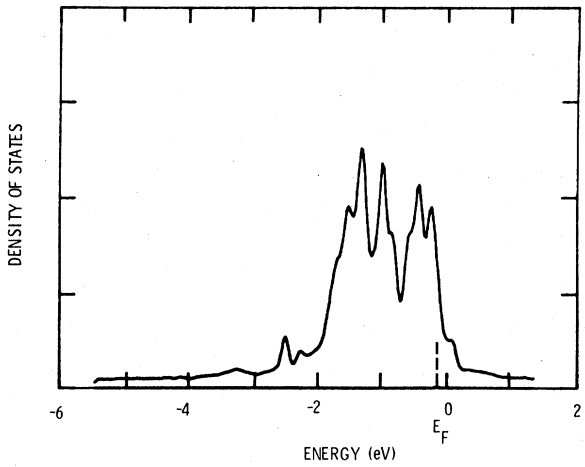

FIG. 3. Density of states from starting potential.

The partially self-consistent calculation of Ref. 10 has completely filled d bands in agreement with our findings but the published density of states is quite different from the fully self-consistent result of Fig. 2.

After submitting this manuscript for publication we received a private communication from the authors of Ref. 10. Upon seeing our results as shown in Figs. 1 and 2, they refined their procedure for calculating the density of states. A new calculation using 45 points in the elemental $\frac{1}{8}$ of the surface Brillouin zone yields a density of states in very close agreement with our Fig. 2. This suggests, at least for this particular monolayer film, that their charge-density constraints are not too severe.

Finally, we note that Abatti *et al.*[2] find from a non-self-consistent calculation that the Fermi level gets closer to the d-band edge as the film thickens. On the contrary, we have found that for a 3-layer Cu(100) film, the Fermi level is 1.4 eV above the d-band edge, which is considerably larger than the corresponding displacement for one layer. For a 9-layer film it is 1.5 eV above.[14] The bulk value is 1.5 eV.[16]

To sum up, we find that a self-consistent Cu(100) monolayer calculation finds no holes in the d band, but does find a state at M only 0.1 eV below the Fermi energy. This state has popped up above the bulk of the d band by 0.4 eV; this peculiar and unique situation is one facet of the explanation of why several authors actually predict d-band holes from non-self-consistent calculations. The other facet is the profound change found on going to self-consistency. Self-consistency is always important, but especially so in borderline situations like this one.

[1]Bernard R. Cooper, Phys. Rev. Lett. 30, 1316 (1973).
[2]I. Abbati, L. Braicovich, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. Lett. 40, 469 (1978); see also C. M. Bertoni, O. Bisi, C. Calandra, and F. Manghi, Thin Solid Films 93, 251 (1977).
[3]S. J. Gurman, J. Phys. F 5, L194 (1975).
[4]Nikhiles Kar and Paul Soven, Phys. Rev. B 11, 3761 (1975).
[5]Bernard R. Cooper, Phys. Rev. B 16, 5595 (1977).
[6]R. V. Kasowski, Phys. Rev. Lett. 33, 83 (1974).
[7]G. S. Painter, Phys. Rev. B 17, 3848 (1978).
[8]G. S. Painter, Phys. Rev. B 18, 955 (1978).
[9]O. Jepsen, J. Madsen, and O. K. Andersen, Phys. Rev. B 18, 605 (1978).
[10]C. S. Wang and A. J. Freeman, Phys. Rev. B 18, 1714 (1978).
[11]J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 10, 561 (1977).
[12]J. R. Smith, F. J. Arlinghaus, and J. G. Gay, Solid State Commun. 24, 279 (1977). See especially Fig. 4.
[13]J. R. Smith, F. J. Arlinghaus, and J. G. Gay, *Proceedings of the International Conference on Transition Metals,* Inst. Phys. Conf. Ser. No. 39 (Institute of Physics and Physical Society, London, 1978), Chap. 5.
[14]J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 42, 332 (1979).
[15]A "*d* band" will of course have some orbital character other than *d*, but the *d* character will predominate. The issue here is not this, but rather whether any predominantly *d*-like band rises above the Fermi energy.
[16]J. F. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B 6, 4367 (1972).