Self-Consistent Calculation of Work Function, Charge Densities, and Local Densities of States for Cu(100)†

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A fully self-consistent calculation of electron charge densities, work function, and local densities of states is reported for an unsupported three-layer copper thin film with (100) surfaces. The work function agrees well with experiment. The electronic charge density contours are bulklike for the central plane. There is a marked variation of the local density of states in the surface region. Comparison is made with photoemission spectra and bulk calculations.

We would like to report the first *ab initio* self-consistent surface-electronic-structure calculation for a d-band metal. The metal is an unsupported three-layer film of copper with (100) surfaces. No pseudopotentials or other parametric forms are used.

Following the very early and classic work of Bardeen[1] and Smoluchowski,[2] the first fully self-consistent metal-surface calculations were due to Smith[3] who used a jellium model and a parametric form for the electron density. Lang and Kohn[4] then solved the Kohn-Sham[5] equations self-consistently for the jellium model. Appelbaum and Hamann[6] reported self-consistent pseudopotential surface calculations for Na(100) and Si(111) using plane-wave bases; and this was followed[7] by a number of other self-consistent pseudopotential calculations on crystalline semiconductors and simple metals.

There is great interest in, and a wealth of experimental data on, d-band metal surfaces. However, calculations on these surfaces are more difficult primarily because of the localized nature of the valence d orbitals. The only previous self-consistent calculation was done for Nb(100).[8] It was not *ab initio* as is the one reported here, but was based on a pseudopotential obtained by fitting the spectroscopic term values of a (gaseous) Nb^{+4} ion. Good agreement is obtained with experiment for the work function (0.4-V error). Because of the absence of further experimental data on Nb(100), the validity of such a potential in a solid-surface calculation cannot be further assessed at present.

There have been a number[9,10] of non-self-consistent calculations for the surface bands of copper recently with some rather interesting results. There are as yet no computations of electron work functions or surface charge densities for the crystalline noble metals because those quantities can only be predicted with accuracy by self-consistent calculations.

Because of the contracted nature of the d orbital, an atomic-orbital basis lends itself quite naturally to the problem. Rath and Callaway[11] have shown that an atomic-orbital basis yields accurate band structures for bulk d-band metals. We have shown[12] that one can obtain very accurate wave functions in surfaces using simple, localized, nonorthogonal (Gaussian) basis functions. Thus we have used as basis functions the ground-state copper atomic orbitals: $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, and $4s$ computed with the Herman-Skillman[13] atomic structure program. These are fitted to Gaussians in order to facilitate the subsequent Hamiltonian matrix-element computations.

The potential includes the usual electrostatic term and the Kohn-Sham[5] ($X\alpha$ with $\alpha = \frac{2}{3}$), exchange potential. The Schrödinger equation is solved to numerical accuracy within the atomic-orbital basis set. That is, no spherical symmetrization, muffin tin, or other potential constraints were employed. As many neighboring lattice sites in the film as necessary were kept in the computation in order to assure that no Hamiltonian matrix elements between atomic orbitals $\geqslant 10^{-5}$ H were omitted. This amounted to, e.g., nine inequivalent neighbors for the $4s$-$4s$ matrix elements.

Periodicity parallel to the surface made use of Fourier-transform[14] techniques and group theory very profitable in the computation of Hamiltonian matrix elements. An odd number (three) of atomic layers also assured inversion symmetry about the film center.

The potential from overlapping atomic[13] charge densities was used to start the iteration. An important saving in the computational time for the starting potential was had by breaking it up into a sum of overlapping spherically symmetric atomic potentials plus the rest (the rest coming from the nonlinearity of the exchange potential). Matrix elements of the former can be easily dealt with through analytic three-center direct-space integrals. Matrix elements of the rest were found using Fourier-transform[14] techniques. A number of other computational techniques were developed in order to minimize the total computer time. These will be discussed in a subsequent publication.

Changes in the matrix elements accompanying the iterative solution of the matrix eigenvalue problem were again determined using Fourier transforms. The total potential ultimately converged (was self-consistent) to better than 50 meV everywhere in the film.

A thin-film configuration was chosen in this calculation for computational convenience. In the following, a comparison of our results will be made with experimental data taken on much thicker crystals and with bulk calculations.

The results for the electron work function that we obtained for the film is 5.6 eV. This agrees well with the value of 5.16 eV obtained experimentally[15] for Cu(100). This accurate value is a direct result of achieving self-consistency (the value using the starting potential is 3 eV) since the work function depends directly on the dipole barrier which builds up during the approach to self-consistency. While this kind of accuracy is as good as one might expect to obtain in the local density approximation,[16] some of the disagreement could be due to the thin-film configuration. Schulte,[17] who computed the work function of a jellium film as a function of film thickness, shows variations of the order of $\frac{1}{2}$ eV for films of the thickness of a three-layer Cu film.

In Fig. 1(a) is shown the total density of states (TDS) for bulk copper as calculated by Mueller[18] [who fit to Burdick's[19] augmented-plane-wave (APW) bands]. In Fig. 1(b) is our TDS for the thin film computed using 45 $\vec{k}_{\parallel}$ points in the one-eighth irreducible wedge of the surface Brillouin zone. Monte Carlo averaging and smoothing techniques were used. Note that there is *detailed* agreement between our TDS and the bulk TDS. The d bands have the same width, the same principal peaks, and are located at the same place relative to the Fermi level.[20] This is a remarkable result because it suggests, barring monumental coincidence, that a three-layer Cu film looks very much like bulk Cu. Secondly, our atomic-orbital calculation and an APW calculation—using entirely different methods—lead to similar results. We now put forward a suggestion as to why TDS has the same d-band width as the bulk TDS. This may be due to the fact that the central-plane atoms have the same number of nearest neighbors as in bulk Cu, coupled with the fact that because the d functions are localized, the off-site d-d matrix elements which control the d-band width are dominated by nearest neighbor terms. Also it will be seen that the charge contours in the central plane have a shape similar to the bulk.

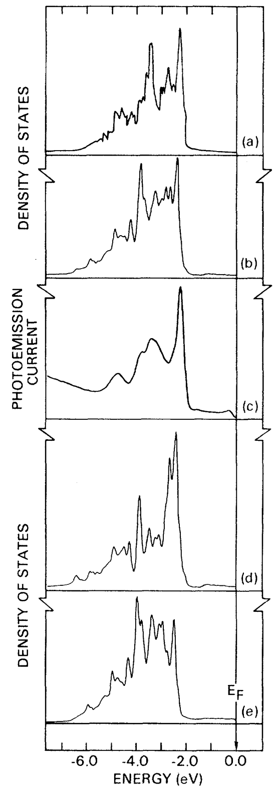

FIG. 1. (a) Bulk copper density of states as calculated by Mueller (Ref. 18) who fitted to Burdick's (Ref. 19) bands. (b) TDS for thin film. (c) 21.2-eV photocurrent from Ref. 20. (d) Central plane LDS. (e) Surface plane LDS.

The solid curve in Fig. 1(c) is the experimental photoemission spectrum for 21.1-eV photons incident on Cu(100) as taken by Burkstrand *et al.*[21] Note that it has essentially the same d-band width and energy interval between the Fermi level and the d-band edge as in Fig. 1(b).

Now the peaks in the photoemission spectrum come primarily from electrons which have not suffered inelastic collisions. For copper in the 20–40-eV kinetic energy range, the electron mean free path is approximately[22] 6 Å. The distance between planes is 1.81 Å. Thus, it is of interest to compute the local density of states (LDS). These can be computed for each plane by weighting the TDS at each energy by the sum of the squares of the coefficients of each basis function on that plane. The result for the central plane, the second plane from the surface, is shown in Fig. 1(d). That for the surface plane is in Fig. 1(e). Now the second moment of the central-plane LDS is larger (by a factor of 2) than that for the surface plane. This is expected because of the larger number of neighbors for the central plane. In this connection, note that the central-plane atoms have the same number (12) of nearest neighbors as a bulk Cu atom The most important conclusion one can draw from the comparison of Figs. 1(d) and 1(e) is that the LDS varies quite markedly between the first and second plane from the surface. Such a marked variation has been seen[23] for alkali and alkaline-earth metals, at rather short mean free paths. It also is suggested in the angular-dependent photoemission data from Cu(100) of Wagner, Hassain, and Fadley.[24]

There is a qualitative agreement in the overall shape of our Figs. 1(b), 1(d), and 1(e), and that of the corresponding figures of Ref. 9. The quantitative disagreements are presumably due to one or more of the following. Reference 9 was not a self-consistent calculation, and only third neighbors were included in the matrix elements. On the other hand, a much thicker film was treated. It should be pointed out that our central-plane LDS is different in detail from the TDS. This is a result of having only three layers in the film.

Finally, in Fig. 2 we show the self-consistent electronic charge density for the conduction band. Note that by the central plane, the charge contours are nearly spherical. This shape is very much like what one finds in bulk copper (see, e.g., Fig. 10 of Fong, Walter, and Cohen[25]). In the surface plane, the charge spreads into the vacuum and smooths parallel to the surface, as originally postulated by Smoluchowski.[2] It is this spreading and smoothing which leads to the surface dipole barrier.

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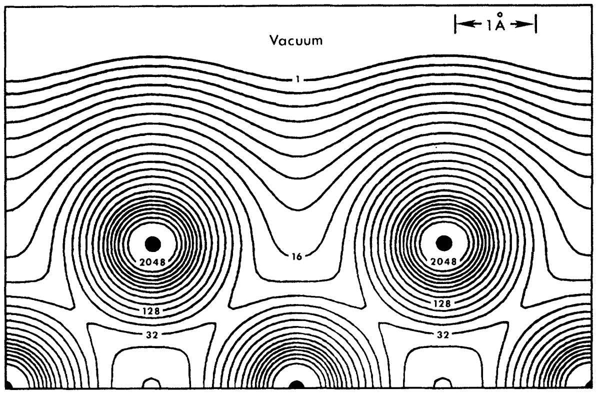

FIG. 2. Electronic charge density at a copper (100) surface plotted on a plane perpendicular to the surface and passing through a line connecting a surface atom with one of its nearest neighbors in the second plane of atoms. The units of charge density are 1.15×10^{-3} a.u. Charge densities on successive contours are in the ratio $\sqrt{2}$. The range of contours shown is 1 to 2048.

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Correlation between d-Band Occupancy and Crystal Structure in the Rare Earths

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The rare-earth crystal structure sequence hcp→Sm-type→double-hcp→fcc observed for decreasing atomic number and increasing pressure is quantitatively correlated with the d-band occupancy through the d-band energy contribution to the total energy. Self-consistent calculations show that the number of d electrons is very sensitive to the relative size of the ion core. The theory thus accounts for La's anomalous double-hcp structure and the apparent deviations from the electron-per-atom rules exhibited by certain rare-earth Laves phases.

In a recent paper Johansson and Rosengren[1] found an empirical correlation between the crystal structure of the rare-earth metals and the fraction of the atomic volume occupied by the ion core. In particular, increasing the relative volume of the ion core leads to the crystal-structure sequence hcp→Sm-type→double-hcp→fcc which is observed both for increasing pressure and for decreasing atomic number from right to left across the trivalent rare-earth series.[2-5] However, their attempt to understand this correlation in terms of pseudopotential theory failed. We will show in this Letter that the relative volume of the ion core is in fact a measure of the occupancy of the d band and that it is the d-band contribution to the total energy which drives the lattice through the observed crystal-structure sequence as the number of d electrons changes from about $1\frac{1}{2}$ to $2\frac{1}{2}$. The theory will be shown to account for Lanthanum's anomalous[6] double-hcp (dhcp) structure and for the apparent deviations from the electron-per-atom rules which certain rare-earth Laves phases exhibit.[7,8]

Figure 1 shows the self-consistent energy bands of La in the fcc structure as a function of the atomic volume. They were calculated using Pettifor's[9] development of the atomic sphere approximation[10] in which the main approximation[11] is the neglect of hybridization between the nearly free-electron s band and the tight-binding d band. The bands display the expected behavior as the atoms are brought together to form the solid. The bottom of the conduction band B_s starts out at very

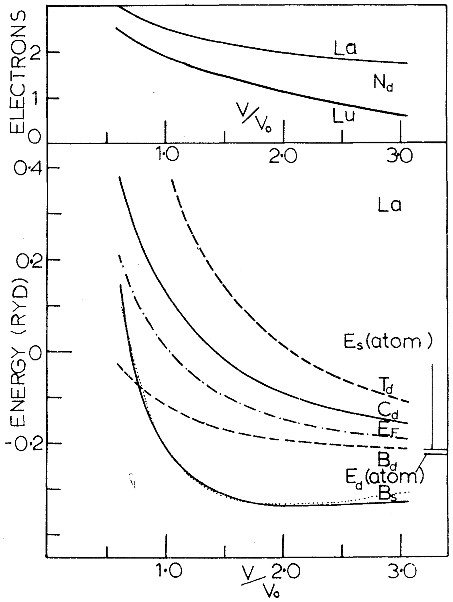

FIG. 1. The energy bands of La about the equilibrium atomic volume V_0 and the corresponding change in the d-band occupancy N_d of La and Lu. T_d, C_d, and B_d are the top, center, and bottom of the d band, respectively, and E_F is the Fermi level. The dotted curve gives the Bardeen-Fröhlich fit [Eq. (1)] to the bottom of the s band B_s.