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Electronic Properties of Ultrathin *d*-Band Metal Films with Simple Metal or Vacuum Interfaces

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The Green's-function method has been used to study the changes in electronic structure of fcc *d*-band metals on going to ultrathin films. Varying the boundary where the electronic wave functions vanish allows an accurate treatment both for a *d*-band metal film embedded in a simple metal and for a *d*-band metal film in vacuum. Calculations for a copper monolayer predict striking changes from bulk behavior, in agreement with photoemission experiments.

I have reformulated the Green's-function [Korringa-Kohn-Rostoker (KKR)] method[1] for film geometry in order to study the changes in electronic structure of fcc transition and noble metals on going from bulk samples to ultrathin (oligatomic) films. *The observation, making detailed, high-quality calculations of the electronic structure for the film practical, is that the film problem with a vanishing wave-function boundary condition has electronic eigenstates which, within the film boundaries, are identical to those of an appropriately defined three-dimensional periodic tetragonal complex lattice.* The boundary where the wave functions are constrained to vanish can lie outside the physical boundary limiting the region where the potential corresponds to the *d*-band metal, and can vary with energy. This has enabled us to allow for electron leakage from the film and simulate either the situation of a *d*-band metal film suspended in vacuum or the more experimentally realizable situation of an ultrathin film of a *d*-band metal with interfaces with a simple metal. Calculations for a monolayer of copper predict striking changes from the bulk[2,3] density of states, as observed in photoemission experiments[4] for Cu deposited on Ag (results available subsequent to the calculations).

There are basically two changes from a bulk muffin-tin potential in going to ultrathin film geometry. First is the geometrical effect: The electrons, instead of being scattered by an infinite, periodic lattice of identical spherical potentials, are scattered by a lattice that is quite thin in one dimension. The other effect is that the spherically symmetric localized atomiclike potential will change on approaching the surface. The present work deals with the first effect, the change in electronic properties brought about by the termination of a lattice of identical spherically symmetric potentials at sharp boundaries. As shown below, this effect brings about large qualitative changes in the electronic behavior from that in the bulk,[2,3] in agreement with experiment.[4] (One could incorporate the surface-potential change into the calculations, since the atomiclike spherical potential in each layer can differ in the calculations. The difficulty would be in choosing the potential, ideally self-consistent, to use at the surface.)

We consider a slice $\mathcal{N}_d$ layers thick of an fcc lattice having a muffin-tin potential appropriate to a *d*-band metal, with the constant value V_0 between muffin-tin spheres; while for $(\mathcal{N}_d+\sqrt{2}-1)a/4 \leqslant |z| \leqslant Na/4$ (z measured from the film center, parallel to the film normal) with $N \geqslant \mathcal{N}_d+\sqrt{2}-1$, the potential has the constant value V_0. At $z=\pm Na/4$ the wave function is constrained to vanish. *(N is not required to be an integer and can vary with energy.)*

For the Schrödinger equation in integral form,[1] the Green's function for this potential lattice and these boundary conditions is

$$G(\vec{r},\vec{r}\,')=\frac{-16}{Na^3}\sum_p\sum_n\frac{\sin[(2p\pi/Na)z+p\pi/2]\sin[(2p\pi/Na)z'+p\pi/2]\exp[i(\vec{K}_{n\parallel}+\vec{k}_\parallel)\cdot(\vec{r}-\vec{r}\,')]}{|\vec{K}_p+\vec{K}_{n\parallel}+\vec{k}_\parallel|^2-\epsilon}, \qquad (1)$$

with p summed over all positive integers, and n summed over reciprocal-lattice vectors ($\vec{K}_n$) for the two-dimensional lattice corresponding to the slice taken of the fcc lattice. Equation (1) is equivalent to

$$G(\vec{r},\vec{r}\,')=\frac{-1}{Na^3}\sum_{p,n}\frac{\exp[i(\vec{K}_p+\vec{K}_{n\parallel}+\vec{k}_\parallel)\cdot(\vec{r}-\vec{r}\,')]}{|\vec{K}_p+\vec{K}_{n\parallel}+\vec{k}_\parallel|^2-\epsilon}, \qquad (2)$$

where

$$\vec{K}_p = (2p\pi/Na)\hat{z}. \qquad (3)$$

Here ϵ is the energy, a the fcc lattice parameter, and $\hat{z}$ a unit vector along the film normal. In (2) p is summed over all positive and negative integers and zero. Thus (2) formally defines a three-dimensional tetragonal reciprocal lattice, and thus formally defines a three-dimensional tetragonal lattice in real space. (The lattice is complex with $\mathfrak{N}_d$ sites in the unit cell.)

The form of (2) allows one to calculate the bands for the film problem in exactly the same way as that of a conventional three-dimensional lattice, where, however, k is restricted to lying in the plane of the film.

Our first calculations have been for a ⟨100⟩ monolayer ($\mathfrak{N}_d = 1$) of copper (using the Chodorow[5] potential). Monolayer calculations have been done for three cases: $N=1$ (wave functions allowed to be nonvanishing only over a region the thickness of a layer in the bulk crystal), $N=4$ (corresponding to embedding the monolayer in a simple metal), and $N=$ an energy-dependent value such that the conduction-electron charge leakage equals that for the work function of a clean copper surface (corresponding to a copper monolayer in vacuum). The $N=1$ case shown in Fig. 1(b) is instructive for purposes of comparison with the two physical cases shown in Figs. 1(a) and 1(c). To get good quality, ultrathin films will probably involve metal-on-metal deposition. Thus the metal interface case, represented here by the $N=4$ case, is more likely to be experimentally relevant than the vacuum interface case. ($N=4$ is sufficient to show the effects of interfacing with a bulk metal since the significant effect of having more conduction electrons is the change in hybridization with the d electrons, and these are quite localized.)

Figure 1 shows band energy versus $\vec{k}$ along the symmetry lines of the two-dimensional Brillouin zone for a ⟨100⟩ plane of an fcc lattice. The two-dimensional Brillouin zone is a square: The center is[6] $\bar{\Gamma}$, the corner is $\bar{M}$, and the center of side is $\bar{X}$.

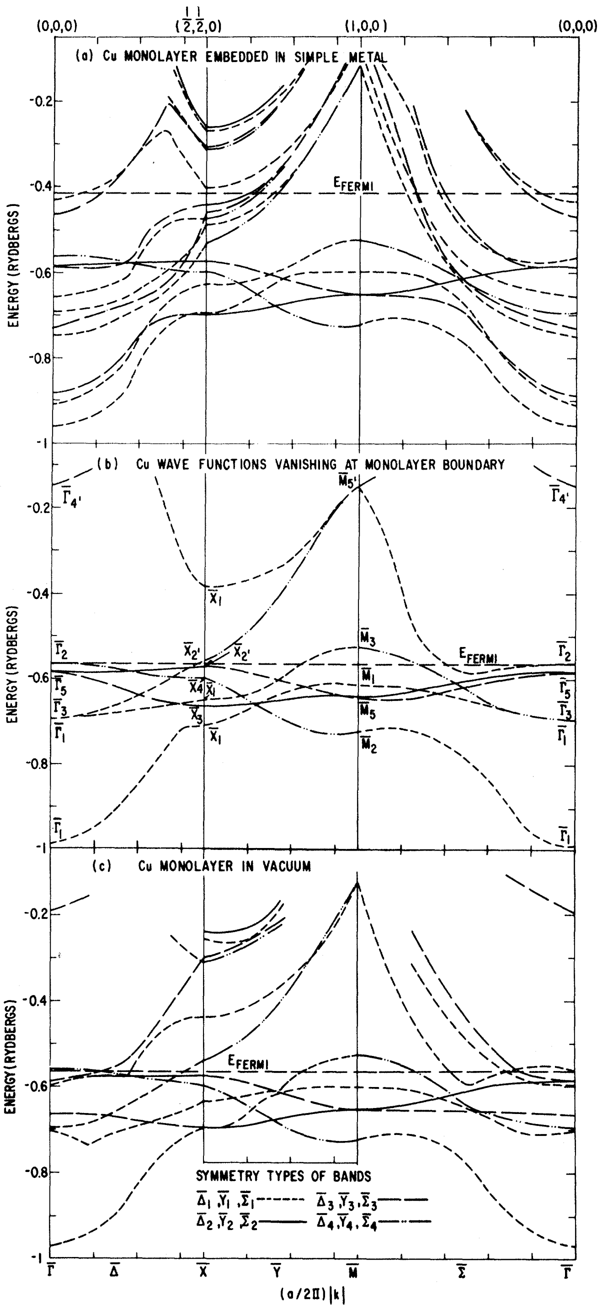

FIG. 1. Energy bands for a monolayer of copper, with symmetries labeled as in Ref. 6. Boundary conditions are described in the text. The bands in (a) are for a simple metal–copper–simple metal slab with an overall width $= 2a$. [The various kinds of lines (solid, dashed, etc.) indicate the band symmetry types.]

For $N=1$ the d-band structure narrows from that in the bulk, giving a d-band peak in the density of states [Fig. 2(b)] about 1.3 eV wide. The main effect of easing the constraint on the vanishing of the wave functions as shown in Figs. 1(a) and 1(c) is to introduce more free-electron-like states (many more of these in the simple metal interface case than in the vacuum interface case) causing an increase in s-d hybridization. This increased hybridization modifies the density of states as shown in Figs. 2(a) and 2(c), but the basic appearance of the structure due to the localized d electrons, as shown in Fig. 2(b),

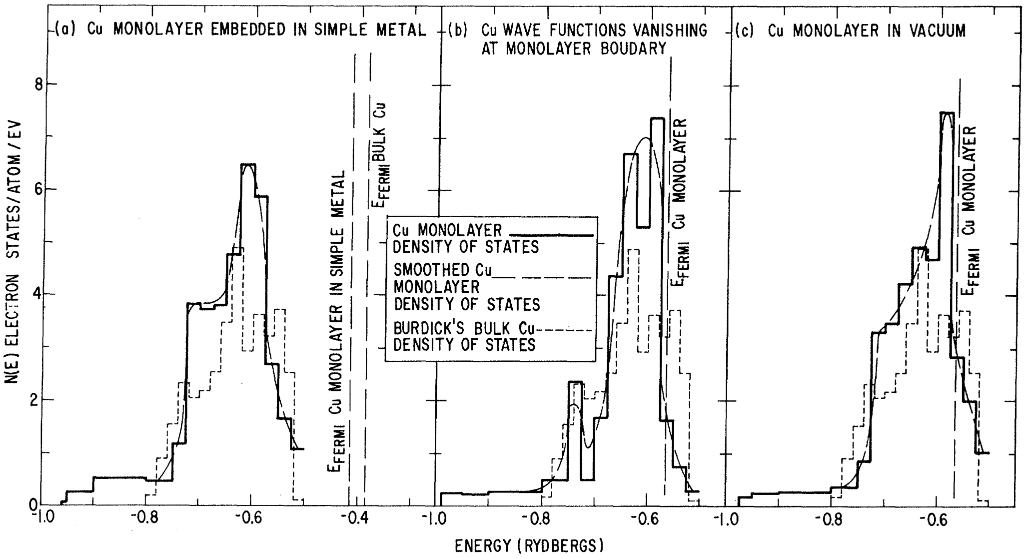

FIG. 2. Density of states for the three cases of Fig. 1 and of bulk Cu (Ref. 3).

is preserved. [For the monolayer in a simple metal the s-d hybridization effects broaden out the low-energy satellite peak and the main peak in Fig. 2(b) so as to give a distinct shoulder about 1 eV wide next to a peak of equal width.] This is because of the great localization of the d states to the region encompassed by the atom-like potential associated with a given lattice site, whether or not artificially constrained to vanish beyond that region. (Only 0.17 out of 10 d electrons for the free atom fall outside the volume associated with a Cu atom in the solid state.[5])

For monolayer geometry there are relatively more free-electron-like states at low energy than in the bulk. For the Cu monolayer in vacuum this causes the Fermi energy (E_F) to drop so there are about 1.3 d holes per atom. The presence of d holes has possibly important implications for magnetic behavior. (There are no d holes for the monolayer embedded in simple metal, since E_F is that of the simple metal.) Just as in non-self-consistent bulk band calculations for metals, such as Ni or Pd, having a significant number of d holes, the presence of the d holes for the vacuum interface case might imply a significant change in the potential. This effect would be included in a self-consistent calculation of the potential.

We do not expect any significant difference in behavior for the copper monolayer being on one surface of a bulk simple metal rather than being embedded in that metal. This is because the simple metal serves basically only as a reservoir of conduction electrons to increase hybridization effects and determine E_F.

The behavior in Fig. 2(a) is in close agreement with that in photoemission[4] for Cu deposited on Ag. (The photoemission experiments show nondirect transitions for monolayer thickness; and thus the photoemitted electron energy distribution is directly proportional to the density of states.) The photoemitted electron energy distribution for a Cu monolayer has a peak 1 eV wide, 2.4 eV below E_F; and at energies below the peak there is enhanced emission indicative of the presence of a shoulder in the density of states.

Since the top of the d bands for Ag is about 2 eV further below E_F than that of bulk Cu, it is reasonable that the behavior of the copper monolayer on silver corresponds closely to that of the copper interfacing a simple metal. The lower 1 eV of the bulk Cu d bands overlap the upper d bands of Ag, and one could develop a more complex model to investigate the question of any influence of the Ag d bands on the local density of states at the surface of AgCu. Probably the best way to obtain a definitive comparison of theory and experiment would be to perform experiments with a simple metal substrate, specifically aluminum. Ag deposited on Al should be[7] a particularly favorable situation for obtaining high-qualtiy ultrathin films.

We are presently extending our studies to thicknesses greater than the monolayer to see the approach to bulk behavior. The photoemission experiments[4] indicate bulk behavior for $\mathcal{N}_d \approx 5$. We anticipate no great difficulty in directly extending the calculations to this thickness. For a film $\mathcal{N}_d$ layers thick, the $\mathcal{N}_d$ sites of the formally equivalent complex tetragonal lattice lie in a regular array corresponding to a slice for an fcc crystal. Thus there are only $\mathcal{N}_d - 1$ independent off-diagonal structure coefficients instead of the $\mathcal{N}_d(\mathcal{N}_d - 1)/2$ for a general complex lattice with $\mathcal{N}_d$ sites per unit cell. This implies a computational time roughly $\mathcal{N}_d$ times that for the monolayer.

It will be interesting to see the repercussions of the changes in electronic structure with film thickness on the characteristic properties of d-band metals, especially magnetic, superconducting, and catalytic behavior. In looking for these various effects it should be remembered that on going from a bulk d-band metal to an ultrathin film deposited on a bulk substrate of a different metal, one changes the d-band electronic behavior in two ways. The first is the change in d-band density of states with thinness; and second is the setting of the Fermi energy by the substrate metal.

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Observation of $\log\sigma \sim T^{-1/2}$ in Three-Dimensional Energy-Band Tails*

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Detailed measurements of the conductivity in controlled-occupancy energy-band tails of isotropic bulk material at low temperatutes (< 20 K) are found to be accurately described by the relation $\log\sigma \sim T^{-1/2}$. The only theory that predicts such a relation applies to one-dimensional conduction, not three. It is suggested that these results may reflect the filamentary character of electron transport in random potentials.

A key relation in the behavior of electronic conduction in disordered, nonmetallic materials is the prediction by Mott[1] that the conductivity σ should depend on temperature as $\log\sigma \sim -(T_0/T)^{1/4}$ for hopping among localized states at low temperatures. The same conclusion was reached in more detailed treatments of the problem in the framework of percolation theories.[2,3] The common features of all of these is the assumption that phonon-assisted tunneling (i.e., hopping) is the dominant transport process; then if the density of states is not strongly energy dependent at the Fermi energy, the $T^{-1/4}$ dependence of $\log\sigma$ results. It should be noted that the 4 in the exponent is a consequence of the three-dimensionality of the available conduction space. Thus, disordered layerlike materials should exhibit a dependence like $T^{-1/3}$ and in one-dimensional materials (e.g., polymers) $\log\sigma$ should vary[4] as $T^{-1/2}$. There is extensive controversy, however, concerning the success of the numerous attempts to confirm these relations experimentally. This paper reports a new experimental test of these theories in energy-band tails of disordered semiconductors having three important advantages over any previously used materials: (i) The band tails are describable by quite widely accepted theories, (ii) the Fermi level in the band tails can be controlled, and (iii) the experiments can be done at the very low temperatures required for