d holes and the electronic structure of transition- and noble-metal thin films and surfaces

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We point out that d holes are probably present in the non-self-consistent copper monolayer band structure of Kar and Soven. Contrary to the statement of Kar and Soven, this indicates that self-consistency probably has important qualitative effects on the copper monolayer band structure. This implies that self-consistency probably also has important qualitative effects on calculated surface behavior in transition and noble metals. We point out some features that are physically desirable to be included in a proper treatment of the thin-film electronic structure. Also we briefly discuss thin-film calculations for d-band metals by other workers.

There has been much recent interest[1-7] in calculations of electronic structure of thin films of d-band (noble and transition) metals. Much of this interest is based on the fact that the "healing length" for surface perturbations on d-band behavior is only a few layer thicknesses. Thus surface effects on rather thin films (say 15 or 20 layers) will accurately simulate those on bulk-metal surfaces. None of the existing techniques for calculations of this sort have been made self-consistent as yet.

One of the techniques developed to treat d-band thin-film electronic structure is that of Kar and Soven,[4] which is essentially identical to a technique developed independently by Kohn[5] and reported at the same time. This scheme is a direct generalization of the Korringa-Kohn-Rostoker (KKR)[8] formalism for band calculations of infinite systems and of Johnson's[9] scattered-wave formalism for molecular calculations. The potential is defined in three distinct regions of space: (I) the potential is spherically symmetric within each muffin-tin sphere within the film; (II) the potential is taken as constant in the interstitial region within the film; and (III) the potential is taken as depending only on the normal coordinate in the region of space outside the planes defining the film. The condition that the solution to the Schrödinger equation in the interstitial region smoothly connects the solutions in regions I and III yields the secular equation giving the electronic eigenstates.

The only numerical results reported[4] to date for the Kar-Soven technique have been for a non-self-consistent calculation for a monolayer film of copper. The potential was generated by superposing atomic potentials and charge densities using standard technique.[3,10,12] The boundary condition used is that the wave functions vanish at infinity.

In discussing their results Kar and Soven make the following statement about the Fermi level and potential for their calculation: "It is clear too,

that our guess at the potential is not very wrong, in that a reasonable filling of the band would place the Fermi level at roughly the correct place insofar as the work function of bulk copper is concerned. One would expect that self-consistency would make only quantitative changes in the band structure."

Also in their discussion, Kar and Soven remark on the fact that in my own calculations[1,2] for a monolayer of copper, there is a partial emptying of the d bands. They state that this is very unlikely; the implication being that this does not happen for their own[4] copper monolayer band structure.

In this note I first point out that in fact, Kar and Soven's bands are very similar to those for my $N = 1$ case [panel (b) of Figs. 1 and 2 of Ref. 1; panel (b) of Fig. 2 and right-hand panel of Fig. 3 in Ref. 2]; and therefore there are probably also d holes present in the Kar and Soven bands. I then discuss the implications of this for the question of the electronic structure of d-band thin films, particularly with regard to the importance of self-consistency. In particular, the statement by Kar and Soven that self-consistency would make only quantitative changes in the band structure is probably quite unjustified. Also, I make some remarks about the calculations of Kasowski[3] and of Gurman.[7]

My own copper monolayer calculation[1,2] with the boundary condition forcing the wave functions to vanish at the monolayer boundary ($N = 1$ case of Refs. 1 and 2) yielded a band structure with approximately 0.6 d holes per Cu atom. For the energy-dependent boundary condition case labeled "Cu monolayer in vacuum" this d-hole feature is carried over [see panel (c) in Figs. 1 and 2 of Ref. 1] with the number of d holes increasing to approximately 1.3. Now as shown in Fig. 1 of this paper, my $N = 1$ band structure is quite similar to the Kar and Soven[4] band structure for $\vec{k}$ along the diagonal of the two-dimensional Brillouin zone. The absolute value of energy in Fig. 1 is not significant, and the agreement would be even better
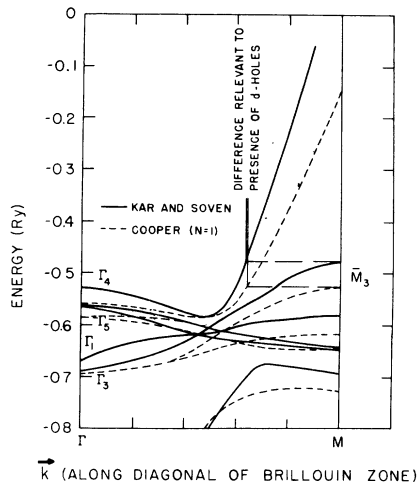
FIG. 1. Band structure along diagonal of Brillouin zone for a copper monolayer film corresponding to a {100} plane of the fcc lattice. Bands for the $N=1$ case of Cooper (Refs. 1 and 2) are superimposed on Fig. 3 of Kar and Soven (Ref. 4), giving their band structure.

with an overall upward shift of the $N=1$ band structure relative to that of Kar and Soven. Kar and Soven did not show their band structure for the $\overline{\Gamma X}$ and $\overline{XM}$ lines (see Fig. 1 of Ref. 2 for the two-dimensional Brillouin zone). However, it is a reasonable expectation that the similarity persists for those directions.

For whatever reason, the similarity between the $N=1$ and the Kar and Soven copper monolayer band structures exists, once a band structure is given, the placing of the Fermi energy, and therefore the presence or absence of d holes, follows from a straight-forward counting of states (i.e., it is irrelevant whether or not the similarity of the band structures is coincidental.) Most of the d holes for the $N=1$ band structure come from the part of the two-dimensional Brillouin zone about $\overline{M}$, the corner of the two-dimensional square Brillouin zone for a {100} plane of an fcc lattice, while some come from around $\overline{\Gamma}$, the center of the Brillouin zone. Therefore, a good measure of the number of d holes is the value of $\vec{k}$ for which the free-electron-like band has the same energy as the top most d state, $\overline{M}_3$. As shown in Fig. 1, this value of $\vec{k}$ is almost the same for the two calculations. *This indicates that the Kar and Soven copper monolayer band structure quite likely yields some d holes.*

Upon inquiry, Soven has informed me that Kar and Soven had not actually calculated the Fermi energy. They had simply assumed that the Fermi energy would fall at some reasonable value with no d holes.

The probable presence of d holes in the Kar and Soven monolayer band structure, as well as in my

two calculations,[1,2] shows that the presence of d holes is certainly not some simple artifact associated with the particular choice of boundary condition, but indeed occurs for physically reasonable non-self-consistent potentials for various boundary conditions. This indicates the importance of self-consistency for obtaining a physically correct description of the electronic structure. (This central importance of self-consistency at d-band metal surfaces has also been discussed by Caruthers and Kleinman[6] in connection with their work on iron, indicating that qualitative changes in surface-state behavior are dependent on the details of the potential.)

There are two possibilities. Either the occurrence of d holes is a true physical phenomenon associated with extreme thinness; or, perhaps more likely, the d holes will vanish for a physically correct self-consistent potential. (The non-self-consistent potential in my calculations[1,2] and those of Kar and Soven[4] correspond to having all d states filled.) While the copper monolayer in vacuum may be an academic case so far as experimental realization is concerned, the presence of d holes in the non-self-consistent calculations makes it an important test case for the inclusion, through self-consistency, of physically important effects in the potential. Also we can expect effects related to any anomaly for the charge density distribution of the monolayer to appear for the surface of a bulk solid.

I would like to point out two features that are physically desirable for a proper treatment of the thin film or surface electronic structure for d-band metals. First, it is desirable to have a simple representation of the wave functions in the interstitial region (region II in the labeling in the second paragraph of this note) so that one can treat non-muffin-tin effects. Second, as discussed below, the presence, or absence, of d holes for the copper monolayer may depend strongly on the variation of potential in the direction parallel to the surface. Thus it is important to include this parallel variation of potential both within, and just outside, the monolayer. I also anticipate that such parallel variation may be important for the properties of bulk d-band metal surfaces. A linear combination of muffin-tin-orbitals type treatment (LCMTO)[12-15] can capture these desirable features, as well as having other advantages.[15]

Next, I would like to briefly discuss why the presence of d holes may depend strongly on the variation of potential in the direction parallel to the surface. The d holes arise from having "too many" free-electron-like states at low energy, so that the Fermi energy falls until it starts to cut the topmost d bands. It is possible that the prob-

lem of having too many free-electron-like states is associated with the potential in the interstitial region (region II) within the plane of the mono-layer. There is no atom "on top" or below (as there is in the bulk because of the *ABAB* stacking pattern for {100} fcc layers) to restrict the electron motion. A charge redistribution within the plane of the surface, or immediately outside, to restrict the motion of electrons in the interstitial region may be necessary to eliminate the *d* holes. To include this possibility in a self-consistent potential, we want to be able to vary the external potential in the direction parallel to the plane. Indeed to eliminate *d* holes at *d*-band metal surfaces, it may even be necessary to have movement of the surface atoms to give some sort of clamping restricting free-electron-like motion, in effect compensating for the effect of the missing plane above or below.

Finally, I would like to comment briefly on the calculations of Kasowski[3] and of Gurman.[7] Kar and Soven[4] have already pointed out that there is a peculiar disparity between Kasowski's copper monolayer energy levels at $\bar{\Gamma}$ and their own. The same disparity holds between Kasowski's energy levels and mine[1,2] for the $N=1$ case.[16,17]

There is a peculiar feature to Gurman's results[7] for the copper monolayer using his "reflection coefficient method" when compared to the results for my $N=1$ case.[1,2] In particular, in Gurman's results there is a gap in the density of states from about $E - E_F = -2$ eV to about -1.3 eV. This gap arises from the fact that in Gurman's band structure,[18] the free-electron-like band lies completely above the *d* bands with an energy gap between. Gurman takes the film as bounded by two plane potential barriers, taken as potential steps placed at half-layer intervals from the centers of the end atoms. The only difference between Gurman's potential and my $N=1$ potential is that Gurman places a finite step in the potential at the film boundary, and I have an infinite step. Within the film boundaries, both calculations use the Chodorow potential with phase shifts parametrized according to the scheme of Cooper *et al.*[19] The $N=1$ calculation[1,2] is essentially an exact numerical solution for that case. The only change Gurman's monolayer potential could yield would be to *lower* the free-electron-like band relative to the *d* bands, because of relaxing the constraint at the boundary relative to the infinite potential step for the $N=1$ case. This, in fact, is opposite to what Gurman's calculation yields. In his copper monolayer calculation the free-electron-like band is *raised* relative to the $N=1$ case[1,2] behavior. Thus there is either some unrecognized technical (i.e., numerical) error or there appears to be a fundamental question about Gurman's technique.

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[16]Recently, a paper giving a further description of Kasowski's technique has appeared [R. V. Kasowski, Phys. Rev. B 14, 3398 (1976)]. This description has enabled Krakauer and Cooper (Ref. 15) to discuss a possible reason for this disparity.

[17]From a conversation with R. V. Kasowski, it seems that the technical procedures Kasowski used to obtain his "monolayer" results make it difficult to attach significance to this discrepancy. This is because Kasowski's "monolayer" calculations were apparently done as a subcase of calculations for thicker films in such a way as not really to correspond to a monolayer (private communication).

[18]I am indebted to Dr. S. J. Gurman for providing me with a figure showing his copper monolayer bands and for some comments. Only the density of states appears in Ref. 7.

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