

Electronic structure of silver (100)

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The electronic structure of silver (100) is calculated using the self-consistent local-orbital method. The work function is found to be 4.2 eV. A large density of surface states is obtained, comparable to that found for Ni(100), and larger than we found for Pd(100). \bar{k}_{\parallel} -selected densities of states (DOS) are given for \bar{k}_{\parallel} along the $\bar{\Gamma}-\bar{X}$ [110] and $\bar{\Gamma}-\bar{M}$ [100] directions. A strong variation with \bar{k}_{\parallel} is found. Results for states which are even with respect to mirror-plane reflection are very different from those for states which are odd. Peaks in \bar{k}_{\parallel} -selected DOS which are due to surface-state bands are identified.

I. INTRODUCTION

We have previously applied our self-consistent local orbital (SCLO) method¹ to compute the surface electronic structure of Cu(100),^{1,2} Ni(100),³ and Pd(100).⁴ For Cu(100) (Ref. 2) we found a large surface-state—surface-resonance density located near the top of the *d* band which we used to explain the large attenuation in photoemission signal near the top of the *d* band in chemisorption experiments on Cu(100).^{5,6} This density includes an unambiguous surface-state band which rises well clear of the bulk *d* bands at the \bar{M} point in the two-dimensional Brillouin zone. The presence of this band was subsequently observed experimentally.⁷ The high surface-state density is apparently the consequence of subtlety in the self-consistent Cu(100) potential since earlier non-self-consistent but otherwise sophisticated Cu(100) calculations⁸⁻¹⁰ predict no significant surface-state density at the top of the *d* band.

In the entirely analogous calculation on paramagnetic Ni(100) (Ref. 3) we found a significant number of surface states, but there were fewer than on Cu(100). Further, they were not concentrated in any energy interval. This led us to speculate³ that this difference might be due to the effect of the filled Cu(100) surface states themselves on the self-consistent potential which is absent in the Ni(100) potential.

For palladium (100) (Ref. 4) we found a substantial surface-state density which included a high-density region centered about 1 eV below the Fermi level. A similar region was found by Louie¹¹ for palladium (111). We analyzed our Pd(100) electronic structure in a new fashion by computing densities of states (DOS) arising from small regions of the two-dimensional Brillouin zone. These \bar{k}_{\parallel} -selected DOS varied rapidly with \bar{k}_{\parallel} and exhibited significant mirror plane symmetry effects. Further, peaks associated with surface-state bands can be clearly identified.

This will hopefully facilitate the location of these bands via angular photoemission.

It is of interest to treat another noble metal to determine to what extent its surface-state properties are similar to Cu(100) and compare them with those of the transition metals Ni(100) and Pd(100). To this end we have carried out an SCLO calculation for Ag(100) and report the results here.

In Sec. II we describe the application of the SCLO method to Ag(100) and present the surface electronic structure in the form of the two-dimensional band structure with surface states delineated, and planar and total densities of states. In Sec. III we provide \bar{k}_{\parallel} -selected DOS along [110] and [100] azimuths, and summarize results in Sec. IV.

II. Ag(100) ELECTRONIC STRUCTURE

The SCLO method, as applied to Cu(100), has been described in detail.¹ Ag is of course a 4*d* metal and therefore requires a larger number of more complex atomic orbitals than does the 3*d* metal copper. As for palladium, in fitting the atomic orbitals we used 13 *s*-type, 9 *p*-type, and 7 *d*-type Gaussian orbitals: two more at each angular momentum type than for copper. The 5*p*, 5*d*, and 6*s* orbitals were constructed exactly as the 4*p*, 4*d*, and 5*s* orbitals were for copper. The atomic potential fits used 16 instead of 14 Gaussians. In the atomic calculation upon which these fits were based we used a 4*d*¹⁰ 5*s*¹ configuration. The copper, nickel, palladium, and silver calculations are analogous in other respects. The same number of components are used in the Fourier transforms and the mesh size used in computing transforms of the charge density was again chosen to be $\frac{1}{10}$ of the lattice constant. The iteration to self-consistency was carried out using 6 \bar{k}_{\parallel} points in the irreducible part of the Brillouin zone.

The crystal must be chosen to be sufficiently thick

so that the electronic structure is well representative of experimental samples. For Cu(100) and Ni(100) we used a nine-plane slab to ensure a slab sufficiently thick to study surface states. However, comparison of seven- and nine-plane results for Cu(100) has convinced us that seven planes give essentially the same surface states as nine planes. We have therefore chosen to limit the Ag(100) slab to seven planes in the interests of economy. The Pd(100) crystal was also taken to be seven planes thick for the same reason.

We initiated the seven-plane calculation by carrying out a three-plane calculation. The self-consistent charge density for this calculation was used, as described in Ref. 1, to generate a starting charge density for the seven-plane slab which was then iterated to self-consistency.

After the self-consistent solution has been determined, the electronic structure of the slab is computed at 45 uniformly spaced points in the elementary $\frac{1}{8}$ of the surface Brillouin zone. These solutions are used to compute electronic densities of states and to display the energy bands of the slab.

Figure 1 exhibits the density of states (DOS) results for Ag(100). The top panel contains the DOS result for the entire film. It contains both bulk and surface contributions. The panel beneath it shows the bulk results of Morruzzi, Janak, and Williams.¹² The third panel has the projected density of states (PDOS) for the central plane of the crystal. Because of short screening lengths in metals, it has been our experience that all but the outermost atomic layer of the films are quite bulklike. A comparison of the bulk results and our central plane projection shows that they are very similar indeed. The surface PDOS in the next panel down is very different, however. It is much narrower than that for the central plane. This is to be expected because there are only $\frac{2}{3}$ as many near neighbors for a surface atom as for a bulk atom. Further, its shape is more triangular than square, very different from that of the central plane. This is reminiscent¹ of the surface PDOS for Cu(100). For Cu(100) we found a large peak at the upper *d*-band edge which was due primarily to surface states.

For the seven-layer film, we define a surface state on Ag(100) as one which has at least 80% of its charge density in the surface layer and the next layer beneath it. A substantially equivalent criterion may be defined for thicker films.⁴ This criterion was used to determine surface states in the nine-plane Cu and Ni calculations which are compared with the seven-plane Pd and Ag calculations below. One can make planar projections of that part of the total DOS which is due to surface states, and these are shown in Fig. 2. As in Cu(100), there is a large density of surface states at the upper *d*-band edge in Ag(100), which appears as the largest peak in Fig. 2. This is a source

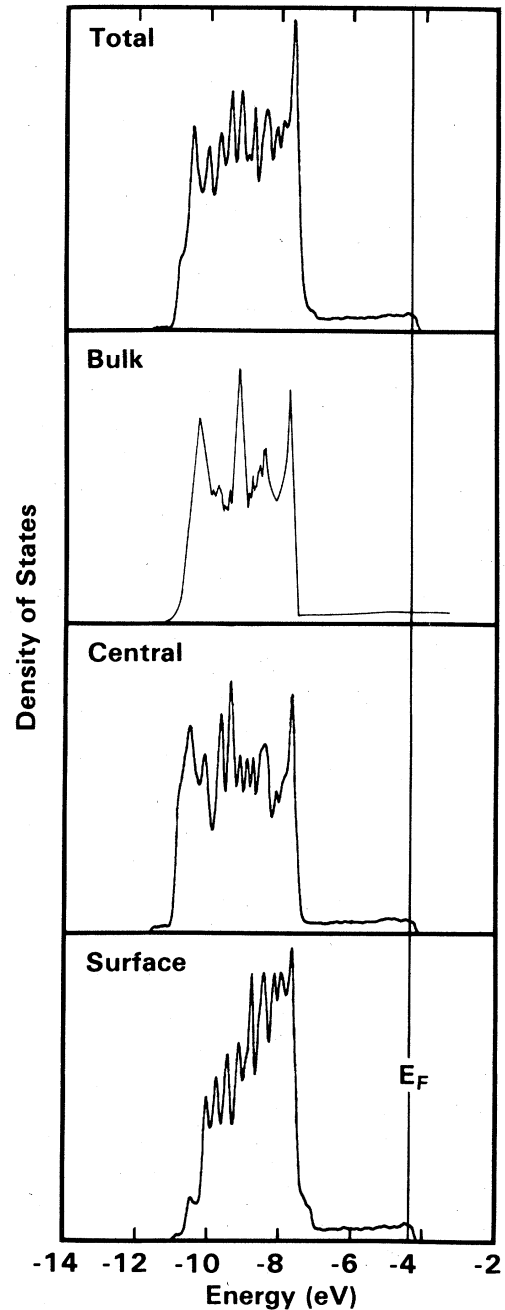


FIG. 1. Density-of-states curves for the seven-plane Ag(100) film. The bulk density of states was taken from Ref. 12.

of the triangular shape of the surface PDOS of Fig. 1. Because of the similarities with copper, this suggests that a high concentration of surface states there may indeed be a common feature of the (100) surfaces of noble metals.

Figure 3 shows the two-dimensional band structure

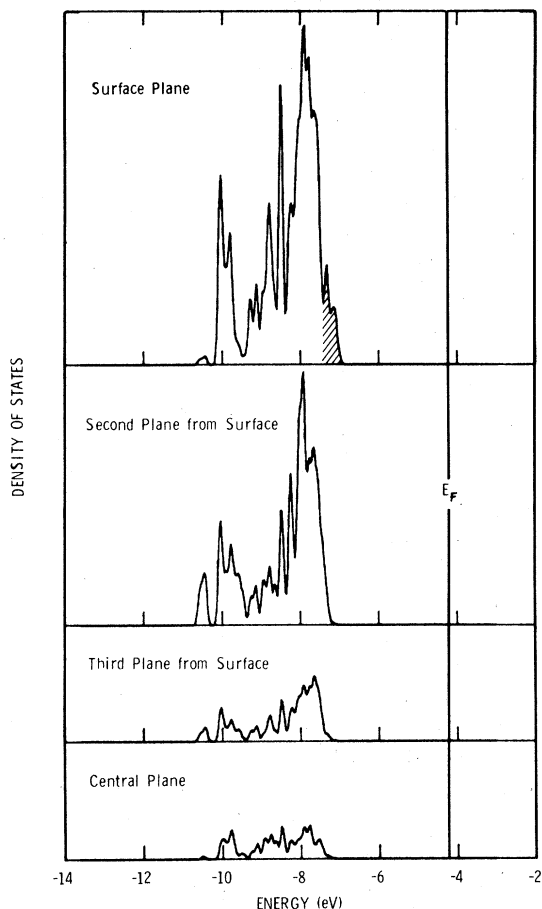


FIG. 2. Calculated surface-state densities of states for the seven-plane Ag(100) film.

of the slab along high-symmetry directions in the Brillouin zone. Surface states and resonances are indicated by open circles. There is a definite concentration of these states at the top of the d band as for Cu(100). The concentration at the upper d -band edge was notably absent in Ni(100) (Ref. 3) and Pd(100) (Ref. 4). The surface states contribute 22% to the charge density in the surface plane. Thus silver occupies a position between palladium and copper. In order of descending surface-state contribution to the surface-plane charge density we have copper (36%), nickel (23%), silver (22%), and palladium (19%).

A well-separated surface-state band in the sd gap at \bar{M} which we first observed in Cu(100) (Refs. 1 and 2) is present also for Ag(100). It is not as well separated for Ag(100) as it was for Cu(100), but it is otherwise remarkably similar. This band and the less-well-separated band just below it in Fig. 3 produce a distinct feature in the DOS of the surface states. Planar projections of this DOS are presented

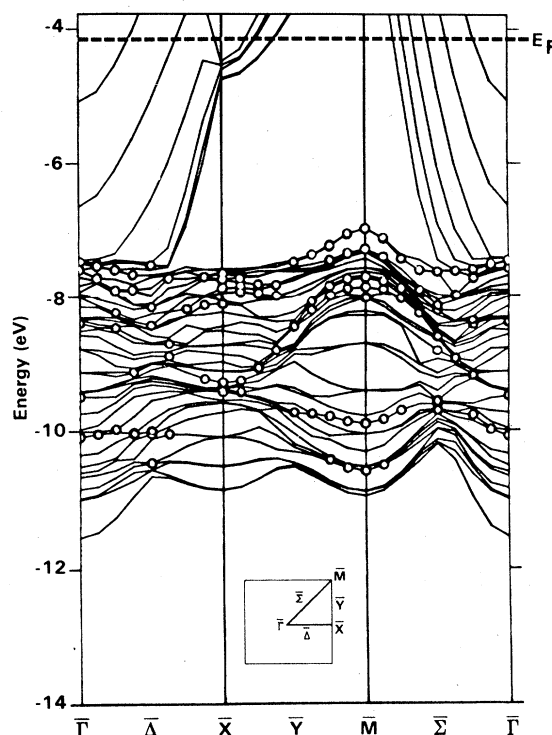


FIG. 3. Surface band structure along high-symmetry directions for the seven-plane Ag(100) slab. The open circles represent states on the 45 $k_{||}$ -point mesh (see text) which are highly localized in the surface plane of the slab.

in Fig. 2. The shaded area at the top of the d bands in the surface plane is contributed by these bands. One may prove that states at \bar{M} containing $d_{x^2-y^2}$ orbitals can only have amplitude on alternate planes. The $d_{x^2-y^2}$ orbitals are referred to the coordinate system with x and y axes along the nearest-neighbor bond direction (surface unit cell, Fig. 2). If the axes are taken along the edges of the bulk (cubic) unit cell, the orbitals would be labeled d_{xy} . This alternate plane property is a consequence of a peculiar symmetry effect whereby at \bar{M} the $d_{x^2-y^2}$ orbital is completely decoupled from orbitals of other symmetry, and in addition, $d_{x^2-y^2}$ orbitals on adjacent planes are completely decoupled from one another. The effect has been discussed by Caruthers *et al.*¹³ The appearance of the shaded region on the surface plane and the small shoulder at the top of the d band for the third plane from the surface when none appears for the second plane from the surface is a consequence of this effect. Surface states in the sd gap have now been predicted for Cu(100) (Refs. 1 and 2) and here for Ag(100), and observed for Cu(100) (Ref. 7) and Au(100),¹⁴ indicating that they are a universal feature

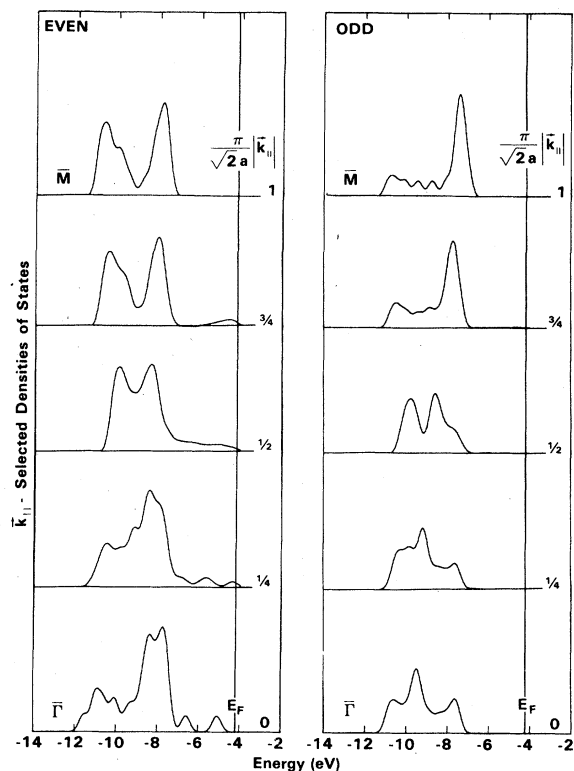


FIG. 4. \vec{k}_{\parallel} -selected densities of states for Ag(100), [100] azimuth.

of the (100) noble metal surfaces. There are interesting orbital symmetry variations ($d_{xy}, d_{x^2-y^2}$, etc.) of the surface-state densities among the metals we have considered. Our results for the (100) surfaces of Cu, Ni, Pd, Ag, and Rh will be compared in a forthcoming publication.¹⁵

Our calculation yields a value of 4.2 eV for the work function of Ag(100). The only experimental values to our knowledge for this surface are 4.64 eV obtained by Dweydari and Mee¹⁶ and 4.2 eV as indicated by the cutoffs of the photoemission energy distribution curves of Hansson and Flodström.¹⁷ We note that a value of 4.0 eV has been reported¹⁸ for evaporated polycrystalline films. The agreement between theory and experiment is satisfactory. We note that relativistic corrections are significant¹⁹ in Ag and could act to increase the work function.

III. \vec{k}_{\parallel} -SELECTED DENSITIES OF STATES

The DOS in Figs. 1 and 2 result from averaging over all of \vec{k}_{\parallel} space. As such one runs the risk of having averaged away a good deal of interesting information. In fact angular photoemission results in-

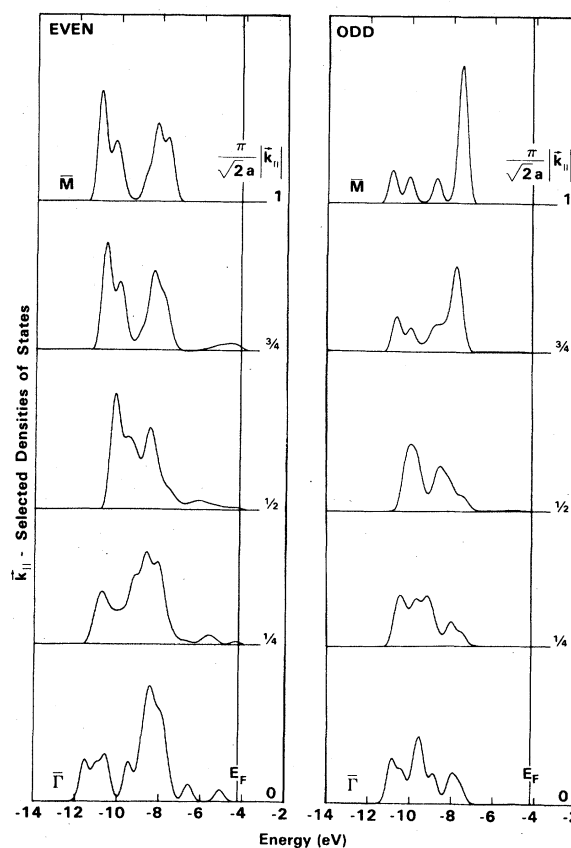


FIG. 5. \vec{k}_{\parallel} -selected densities of states for Ag(100) central plane, [100] azimuth.

dicate that there is a great deal of information to be had. We therefore have devised a procedure for computing \vec{k}_{\parallel} -selected DOS. This is described at some length in Ref. 4. For \vec{k}_{\parallel} vectors along mirror plane directions, the wave functions are either even or odd with respect to mirror plane reflection. We compute DOS for each symmetry because they can be separated experimentally using polarized light in angular photoemission. Perhaps more importantly, we can determine projections of \vec{k}_{\parallel} -selected DOS on atomic planes. This allows one to identify peaks associated with surface-state bands. Surface states are difficult to find experimentally on metals because there is no bulk band gap. Locating surface-state peaks in \vec{k}_{\parallel} -selected DOS may facilitate their location in angular photoemission spectra. The validity of the identification of a peak in a photoemission spectrum as being due to a surface-state band can then be checked by varying the photon energy and making sure the peak does not shift in energy. This applies equally well to the identification of adsorbate bands.

The \vec{k}_{\parallel} -selected DOS along the [100] azimuth ($\bar{\Gamma} - \bar{M}$) are shown in Fig. 4 for both even and odd mirror plane symmetries. We show plots at $\bar{\Gamma}$, and

$\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and all the way to \bar{M} . Two results are immediately obvious from a glance at these plots.

First, these DOS vary rapidly with \bar{k}_{\parallel} . Secondly, the even and odd symmetry states have very different DOS. The first result suggests that averaging over \bar{k}_{\parallel} space does indeed conceal information. The second result suggests that the use of polarized light in angular photoemission experiments is important since without it one obtains some weighted average of even and odd results. This is not to suggest that angular photoemission spectra should be identical to \bar{k}_{\parallel} -selected DOS. There are many complications such as energy-dependent cross sections and direct-transition (k_{\perp} -conservation) requirements. However, one might hope to separate out surface-state bands, since for them k_{\perp} of the electron does not have to be conserved in the photoemission process. This provides the motivation for projecting the \bar{k}_{\parallel} -selected DOS on the central and surface atomic planes. These are shown for the [100] azimuth in Figs. 5 and 6,

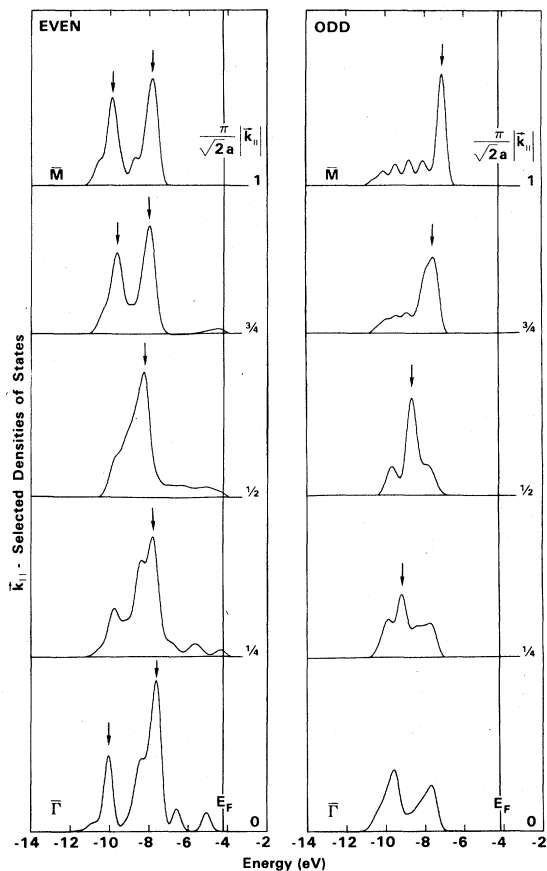


FIG. 6. \bar{k}_{\parallel} -selected densities of states for Ag(100) surface plane, [100] azimuth. The arrows indicate peaks which either do not exist in the central (bulk) plane, or are much smaller there.

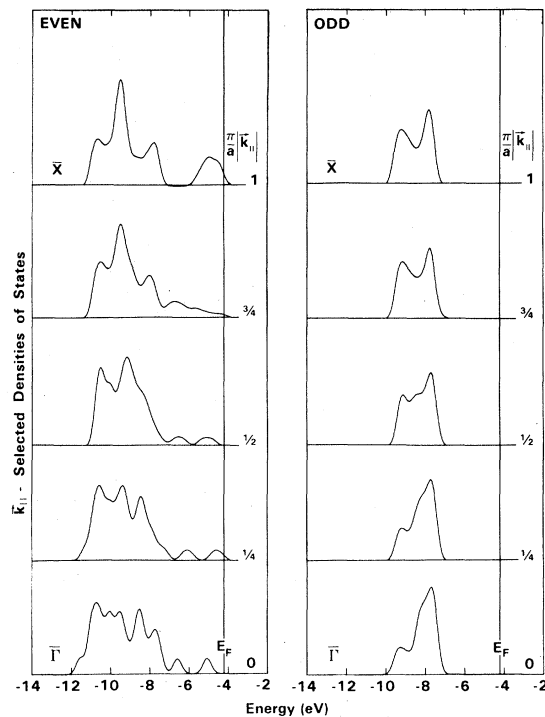


FIG. 7. \bar{k}_{\parallel} -selected densities of states for Ag(100), [110] azimuth.

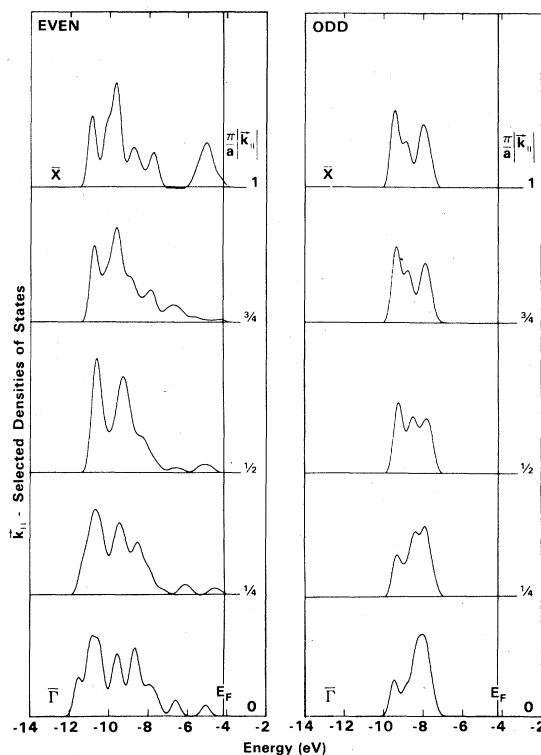


FIG. 8. \bar{k}_{\parallel} -selected densities of states for Ag(100) central plane, [110] azimuth.

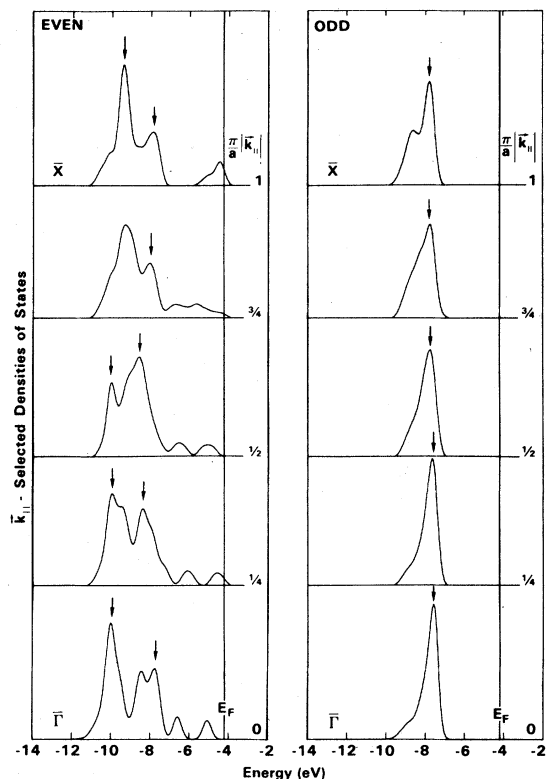


FIG. 9. \bar{k}_{\parallel} -selected densities of states for Ag(100) surface plane, [110] azimuth. The arrows indicate peaks which either do not exist in the central (bulk) plane, or are much smaller there.

respectively. One can see that while there are definite similarities between the central (bulklike) projections and those of the surface, there are a number of peaks which belong to the surface. That is, they either do not exist in the bulk or are much smaller there. Such peaks are denoted by the arrows in Fig. 6. For example, the peak associated with the surface-state band at \bar{M} is the large one in the odd

projection in Fig. 6 (at the upper d -band edge).

Similar comments can be made about the \bar{k}_{\parallel} -selected DOS along the [110] azimuth ($\bar{\Gamma} - \bar{X}$), shown in Figs. 7–9. The surface-state peaks can be identified by comparing Figs. 8 and 9 and are indicated by the arrows in Fig. 9. These peaks correspond to the open circles in Fig. 3, as they should. Note the rather striking differences between the odd \bar{k}_{\parallel} -selected DOS in Fig. 8 and those in Fig. 9.

There are results from several angular photoemission experiments on Ag(100) in the literature.^{17, 20, 21} None of these investigations unambiguously identified surface-state bands. One can perhaps understand that through either Fig. 3 or Figs. 5, 6, 8, and 9. Those figures show that the surface states are either in the midst of the energy range of the bulk d band, and hence obscured, or are split off from it for only a small range of \bar{k}_{\parallel} . For example, the surface band which is split off above the bulk d band around \bar{M} could easily be missed as one stepped through angles of collection, unless one took rather small increments [as was done successfully for Cu(100) (Ref. 7) and Au(100) (Ref. 14)].

IV. SUMMARY

We found that 22% of the electrons in the surface layer of Ag(100) are in surface states or resonances. There is in fact a lot of similarity between many of the surface-state bands of Cu(100) and Ag(100). These results, together with our results on Pd(100) and Ni(100), suggest that from now on surface states will have to be considered in analyzing physical and chemical processes at surfaces.

The \bar{k}_{\parallel} -selected densities of states exhibit the surface-state features on comparison of surface and central-plane projections. This will hopefully facilitate the location of these surface states via angular photoemission. We also found a significant dependence on mirror plane symmetry properties, suggesting the potential importance of using polarized light in angular photoemission experiments.

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