

Self-consistent electronic structure of tantalum (001): Evidence for the primary role of surface states in driving reconstructions on tungsten (001)

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The surface linearized augmented-plane-wave method is used to perform self-consistent scalar-relativistic local-density-functional calculations for the Ta(001) surface. Essentially, all of the surface states and resonances which were found on W(001) are also found on Ta(001), except that on Ta(001) most of these surface states are *unoccupied*; most differences between W and Ta can be described by rigid-band behavior. Unlike tungsten, where the Fermi energy falls in the center of a large surface-state peak in the surface-atom *d*-band projected density of states, this *same* peak in tantalum lies well above the Fermi energy. The sensitivity of surface states to the potential is demonstrated by the existence on Ta(001) of a highly localized and *occupied* Γ_1 surface state at the center of the Brillouin zone. This state is virtually identical, in all of its properties, to one found on the W(001) surface. On the basis of this calculation for Ta(001) and earlier W(001) calculations, it is concluded that surface states on W do indeed play a role in *destabilizing* W(001) against the observed reconstructions. The experimental observation that Ta(001) does not reconstruct is explained in this calculation by the fact that the relevant surface states are *unoccupied*. This is also evident in the absence of *d*-band "dangling bonds" in the contour plots of the Ta charge density near the surface. The theoretical work function for Ta(001) is 4.3 eV, in good agreement with the experimental value of 4.15 eV. The theoretical value for the surface core-level shift is 0.96 eV to greater binding energy, which is about 0.5 eV larger than the experimental value of van der Veen *et al.* obtained for Ta(111), but the sign of the shift agrees with experiment.

I. INTRODUCTION

I have used the surface linearized augmented-plane-wave (LAPW) method to perform the first self-consistent calculation for the Ta(001) surface. The principal motivation for this calculation is to examine differences in surface-state properties between Ta and W in order to clarify their role in the observed W(001) reconstructions. A recent paper by Titov and Moritz¹ reported the first low-energy electron diffraction (LEED) measurements that show that Ta(001), unlike W(001), does *not* reconstruct over the entire 150–600 K temperature range studied. They also found that low hydrogen coverage does not induce substrate reconstruction, again unlike the situation for W(001). Tantalum, of course, is tungsten's neighbor to the left in the Periodic Table, and it also has the bcc crystal structure. The focus of this investigation is not on the fine details of surface-state dispersion near the Fermi energy (nesting features, etc.), but on the more general features of these states [e.g., do they even exist on Ta(001), how do they contribute to the density of states at the Fermi energy, etc.].

Although the clean W(001) surface reconstruction is probably the most studied of any metal, and despite much experimental and theoretical work aimed at characterizing this transition, the interpretation of the phase transition still remains uncertain. LEED studies^{2–5} indicate that the W(001) surface undergoes a displacive phase transition on cooling, and LEED symmetry analysis^{4,5} suggests a displacive phase transition involving parallel shifts of the surface atoms. This is supported by a theoretical LEED

intensity analysis⁶ which indicates parallel shifts of the surface atoms with the shifts being about 0.15–0.30 Å. This interpretation has often centered on the possible formation and role of surface charge density waves^{7–14} (CDW) arising from Fermi-surface coupling of *d*-band-derived surface states.

It is not clear, however, whether or not the transition is an order-order or order-disorder transition. For example, using high-energy ion scattering at room temperature, Stensgaard *et al.*¹⁵ concluded that the proposed displacive transition model for the $c(2 \times 2)$ surface was not valid, since the proposed models call for all the surface atoms to be displaced, and the ion-scattering results indicated that about 50–70% of the atoms were displaced (already at room temperature). This experiment further suggested that the supposedly $p(1 \times 1)$ surface (as seen by LEED measurements) at room temperature could be characterized by *randomly* oriented displacements of the surface atoms, as would be expected in an order-disorder transition.

Other conflicting structural evidence comes from field ion measurements.^{16,17} For example, Melmed *et al.*¹⁷ found results which support a *perpendicular* shift model in the temperature range 15–460 K.

There have been several calculations for the W(001) surface.^{18–25} A self-consistent LAPW calculation¹⁹ for a seven-layer W(001) slab by Posternak *et al.* provided a detailed mapping of the surface states and surface resonances along symmetry lines in the surface Brillouin zone. The results were in good general agreement with the angle-resolved photoemission-spectroscopy (ARPES) mea-

surements of Weng *et al.*²⁶ This was the first self-consistent calculation for the W(001) or, indeed, any other $5d$ -band metal surface. The importance of self-consistency in performing surface calculations was demonstrated, since this was the first calculation to account for the “Swanson-hump”²⁷ state which is located about 0.3 eV below the Fermi energy at the center of the two-dimensional (2D) Brillouin zone—the initial (non-self-consistent) starting potential does not yield this state. Self-consistency was also crucial, of course, for obtaining an accurate work function (4.5 eV) which was in excellent agreement with experiment.²⁸

In this LAPW calculation,¹⁹ a pair of surface states along the $\bar{\Sigma}$ direction were found to disperse upward in energy, cutting the Fermi energy midway along this symmetry direction at $q = (\frac{1}{2}, \frac{1}{2})\pi/a$. Theoretically there is significant Fermi-surface nesting of these surface states in the vicinity of this point, with nesting vector $q = (1, 1)\pi/a$.^{18,19} A calculation¹⁸ of $\chi(q)$ found a peak at this wave vector (just the wave vector of the displacement wave suggested to one to account for the observed LEED spots), and this supports suggestions that the reconstruction of the W(001) surface is, indeed, electronically driven via the CDW mechanism.

Others, however, have questioned this conclusion and have proposed a somewhat different role for these surface states. Inglesfield⁹ suggested that the ideal (001) surfaces of W and Mo are inherently unstable because of anharmonic surface-phonon effects. In his view, the surface states have the rather minor effect of selecting one of several possible incipient distortions. Terakura and co-workers^{13,14} also questioned the CDW mechanism, arguing instead in favor of a Jahn-Teller—type²⁹ effect. In their view, there would be a considerable energy lowering due to the elimination of a large peak in the surface density of states at the Fermi energy associated with the ideal surface distortion. Unlike the CDW mechanism, where gapping occurs only in a small region of the Brillouin zone, they suggested that surface states in large regions of the Brillouin zone would be affected.

The results of more recent ARPES measurements^{30,31} have also undermined the CDW interpretation. The measured surface-state dispersion curves near the Fermi energy were found to differ significantly from the LAPW¹⁹ surface-state bands. Besides obtaining different connectivities for these bands, these experiments show the bands crossing the Fermi energy with a larger q -wave vector, thus removing the nesting feature found in the LAPW calculation. [A similar LAPW calculation²⁰ was also performed for a seven-layer W(001) slab in which the surface-layer separation was contracted 6% relative to the bulk separation, but this produced only insignificant changes in the surface-state dispersions.]

These LAPW^{19,20} calculations included scalar-relativistic effects but neglected the spin-orbit interaction. Very recently, a similar calculation was reported for an unrelaxed seven-layer W(001) slab by Mattheiss and Hamann²² using an independently developed LAPW program. Their results were in good agreement with those in Ref. 19, and this calculation served as a useful “calibration check” for both programs. These authors then ex-

tended their results to a thicker 19-layer film and the fully relativistic²¹ limit by employing a tight-binding scheme combining fitting parameters derived from their LAPW bulk-band structure and their seven-layer results. The inclusion of spin orbit led to generally small effects on the band states. They found significant changes, however, in the surface-state dispersion along the critical Σ line of the surface Brillouin zone which tended to reduce the discrepancy with the ARPES measurements, the overall level of agreement being comparable to the differences in the two ARPES measurements.^{30,31}

Several possible sources for the remaining discrepancies between theory and experiment were considered in Ref. 22. These included the possible presence of geometric distortions on the W(001) surface at room temperature (suggested by the ion-scattering measurements¹⁵), whereas the calculations assumed an ideal $p(1 \times 1)$ termination of the bulk. Also considered were aspects of determining the tight-binding fit. Another possibility is that, strictly speaking, the ARPES measurements determine the single-particle excitations of the W(001) surface, and the local-density-functional band energies only approximate these. Since the surface states in question are derived from fairly localized $5d$ bands, this last possibility cannot easily be ruled out (especially since only small energy shifts are required to change the nesting features).

These considerations indicate the shortcomings of comparing only theoretical and experimental surface-state dispersions on the W(001) surface. In this paper self-consistent LAPW calculations of the surface state and related properties on the Ta(001) are reported which provide evidence for the primary role of surface states in driving the observed reconstructions of W(001).

In the next section the LAPW method is briefly reviewed. Section III presents a discussion of the results obtained, and the primary conclusions are summarized in Sec. IV.

II. METHODOLOGY

The self-consistent LAPW film method^{19,32} is used with the Hedin-Lundqvist exchange-correlation potential.³³ In the LAPW method, the variational band states are treated scalar-relativistically (spin-orbit effects are neglected), and the core electron states are treated fully-relativistically using an atomiclike treatment. All electron states are calculated self-consistently.

In the interstitial and vacuum regions, the full potential without any shape approximation is determined self-consistently and included in the computations while non-spherical terms are neglected inside the muffin-tin spheres. The Coulomb potential is obtained by an accurate solution of Poisson’s equation¹⁹ permitting a very precise determination of the potential near the surface region, thus giving a good description of the surface states and surface electronic properties.

Calculations were performed for an ideal (e.g., no relaxation) five-layer Ta(100) slab. As found for the W(001) surface,^{19,20} the electronic structure (e.g., surface states) is not expected to be very sensitive to small (5%) relaxations of the surface atoms. Therefore, the approximation of using the bulk bond distances for the surface atoms also is

believed to be a good one in the present calculations. For the systems under consideration, the basis size is about 55 LAPW's per atom resulting in eigenvalues which are converged to better than about 3 mRy. Ten special k points in the irreducible wedge of the 2D Brillouin zone are used to generate the charge density during the self-consistent iterations. A uniform 15 k -point set is used to generate the final densities of states. Self-consistency is considered achieved when the rms difference between input and output potential is less than 10 mRy.

III. RESULTS AND DISCUSSION

A. Charge densities, dangling bonds, and work functions

Figure 1 shows the total valence charge density in a vertical (110) plane for the upper half of the five-layer Ta(001) slab. For comparison, contour plots for the upper half of a seven-layer W(001) slab¹⁹ are also shown. The contours are labeled in units of electrons per bulk unit cell. The charge density is seen to fall off smoothly as one progresses outward to the vacuum and to rapidly "heal" to bulklike character on going away from the surface into the solid. The vacuum charge density on Ta is very simi-

lar to that on W. The rapid falloff of charge density into vacuum is associated with the formation of the surface dipole layer which sensitively determines the work function. The work function for the Ta(001) slab is 4.3 eV and the experimental value³⁴ is 4.15 eV. Similar agreement¹⁹ was found for the W(001) surface [the work function for the W(001) seven-layer slab¹⁹ was 4.5 eV, the experimental value²⁸ for W is 4.63 eV].

The bonding characteristics of these roughly half-filled d -band metals are also evident in Fig. 1. In the interior atoms, the bonding $xy, xz, yz (t_{2g})$ d orbitals form fairly localized lobes pointing along the body diagonals to the nearest-neighbor atoms. There is a rather uniform metallic-bonding-type charge density in the interstitial regions. These features persist up to the second layer from the surface. Aside from a rigid-band reduction in the magnitude of the Ta contours relative to the W contours, the charge-density features are virtually identical in the interior of the Ta and W slabs.

In the surface layer, however, there is a marked difference between these two metals. On the W surface, there is a well-defined d -band dangling bond pointing out towards the missing nearest neighbor in the vacuum. This feature is clearly absent on the Ta(001) surface. Similar unsatisfied dangling bonds on semiconductor surfaces have been associated with a tendency for the surface to reconstruct,⁷ and it is possible that the clean surface reconstruction of the W(001) surface would reduce the energy of this dangling bond. The nonreconstruction of the Ta(001) surface strengthens this argument, of course.

B. Surface core-level shifts

Energy shifts of surface-atom core-level states with respect to the same core level on an interior atom are also sensitive to the changes in bonding that occur at the surface. The $4f - \frac{7}{2}$ core-state energies (with respect to the Fermi energy) are given in Table I. The theoretical value for the surface core-level shift (0.96 eV to greater binding energy) is about 0.5 eV larger than the value measured by van der Veen *et al.*³⁵ for the Ta(111) surface, but the sign of the shift agrees with experiment. It is possible that the neglected nonspherical components of the potential in the muffin-tin spheres in this calculation could account for some of this discrepancy.

Qualitatively, the surface core-level shift is related to the reduced coordination of an atom at the surface (somewhat disparate models of the core-level shift have been

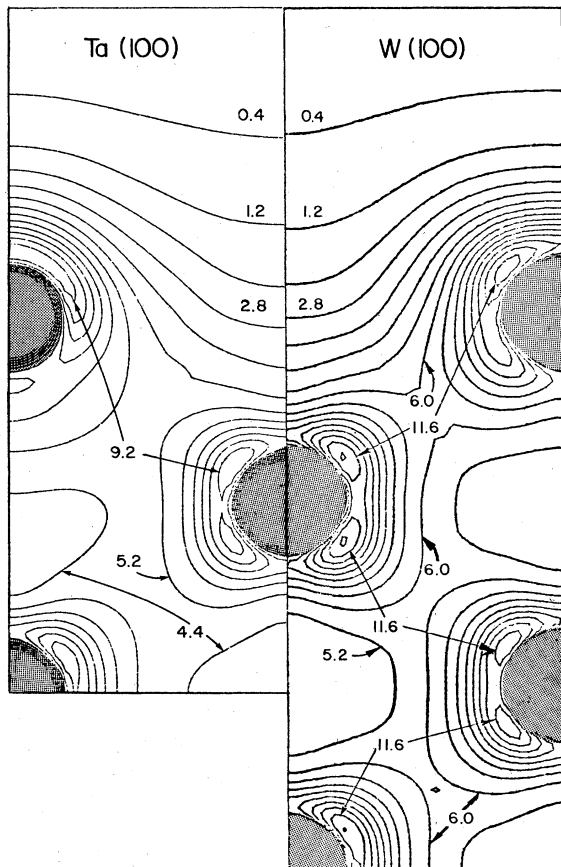


FIG. 1. Contour plot of the charge density for the Ta(001) five-layer slab and the W(001) seven-layer slab for a (110) plane which is normal to the surface. Successive contours are separated by 0.8 in units of electrons per bulk unit cell. The W contour plot is taken from Ref. 19.

TABLE I. $4f - \frac{7}{2}$ core-level eigenvalues and core-level shifts for the Ta(001) slab for the surface, subsurface, and central atoms. All energies are in eV.

Layer	$E_F - \epsilon_{\text{core}}$	Surface-central
Surface Center (S)	19.18	0.96
$S - 1$	18.22	0.00
Central	18.22	0.00
Experimental (Ref. 35) Ta(111) surface core-level shift:		0.40

discussed by Feibelman³⁶ and the consequent narrowing of the surface d -band density of states. For less than half-filled d bands, this leads to a shift to greater binding energy because layer-wise neutrality is favored energetically.³⁶ Since the bcc (111) surface is less dense than the (100) surface [and hence the coordination of an atom on the (111) surface is less than on the (100) surface], the d band experiences more narrowing on the (111) surface, and the experimental core-level shift for the Ta(100) surface may turn out to be even less than that for the Ta(111) surface.

The calculated core-level shifts in Table I are "chemical shifts," since they are determined from the single-particle core-state eigenvalues. They do not include final-state relaxation effects.^{36,37} A recent calculation³⁷ of the relaxation shift for the $3s$ level of Cu(001) found a relaxation shift which was comparable in magnitude and of the opposite sign as the chemical shift, leading to a reduction of the chemical shift. If similar behavior occurred for Ta(001), this would tend to bring the theoretical shift in Table I into better agreement with the measured value. In the Cu(001) calculation³⁷ the screening of the final-state core hole was treated by a self-consistent band-structure calculation in which every atom in a given layer (surface or interior layer) had a core "hole." This was done in order to retain the two-dimensional periodicity required by such band-structure calculations. As a result, it has been argued³⁸ that the Cu(001) calculation³⁷ presents only weak evidence for the importance of relaxation contributions to the core-level shifts, since a "sheet" of such core holes can develop a dipole (or higher multipole) moment providing a mechanism for interaction between neighboring core holes.

C. Density of states

The dangling bond feature on the W(001) surface in Fig. 1 is due to a high density of occupied surface states on this surface,¹⁹ and these states are unoccupied on the Ta(001) surface. This can be seen in Fig. 2 which presents the local density of states (DOS) for each layer of the slab. The surface-layer d -band DOS shows the narrowing due to the reduced coordination of the surface atoms. For the central and subsurface layers, the Fermi energy is seen to fall between two peaks in the DOS due, respectively, to the occupied bonding $5d$ orbitals and the unoccupied antibonding $5d$ orbitals. The bonding and antibonding orbitals are separated by what is almost a gap in the DOS. The most significant difference in the surface-layer DOS is the large peak just above the Fermi energy, in an energy range corresponding to the gaplike region of the interior or bulk DOS. This large peak is due to a high density of surface states and surface-resonance states which are quite localized in the surface layer. The same general features can be seen in the layer-projected DOS of W(001) in Ref. 19, except that on W(001) the Fermi energy falls in the middle of the surface-state peak in the surface-layer DOS.

Indeed, the differences between the Ta(001) DOS and that of W(001) are well described by rigid-band behavior and the fact that Ta has one less $5d$ electron than W. On the W(001) surface, the high density of *occupied* surface states in what is otherwise a gaplike region in the bulk

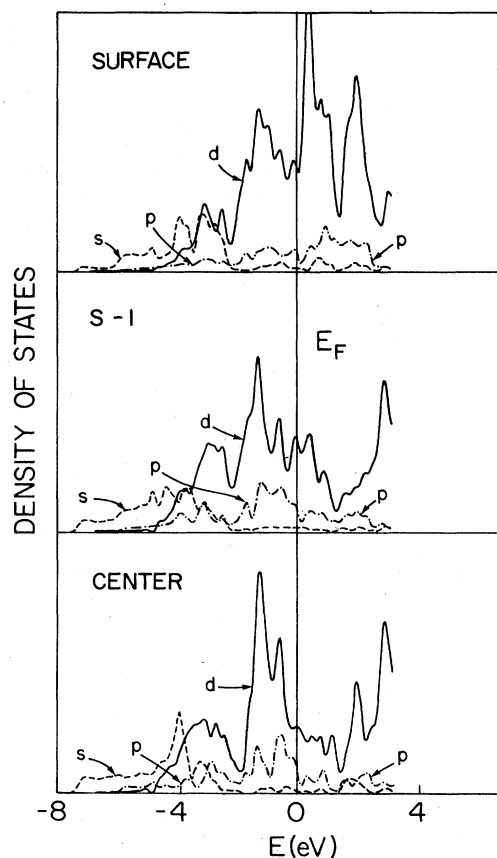


FIG. 2. Layer-projected density of states for the five-layer Ta(001) slab. The top, middle, and bottom panels are for the surface, subsurface, and central layers, respectively.

DOS suggests that the reconstruction of W(001) might lower the energy of the surface by removing this peak at the Fermi energy via gapping introduced by new Brillouin-zone boundaries.^{18,19} By contrast, this large peak of surface states is *unoccupied* on Ta(001), and this is consistent with the nonreconstruction of Ta(001).¹

D. Surface band energy dispersions

A more detailed look at the surface states and surface resonances is given in Figs. 3 and 4. States with $\bar{\Delta}_1-\bar{\Gamma}_1-\bar{\Sigma}_1$ symmetry (these are symmetric with respect to mirror planes which are perpendicular to the slab) are shown in Fig. 3 and states with $\bar{\Delta}_2-\bar{\Gamma}_2-\bar{\Sigma}_2$ symmetry (these are antisymmetric with respect to the mirror planes corresponding to the given symmetry line) are shown in Fig. 4. At the symmetry points, only states whose symmetry is compatible with these are shown. States which are localized in the surface layer are indicated by the closed circles (these typically have more than 70% of their weight in the surface layer). The only bands which cross in these figures are bands of opposite z -reflection symmetry.

Essentially all the surface states and resonances which were found on W(001) (Ref. 19) are also in Figs. 3 and 4, except that on Ta(001) most of these surface states are *unoccupied*. This is the origin of the rigid-band behavior

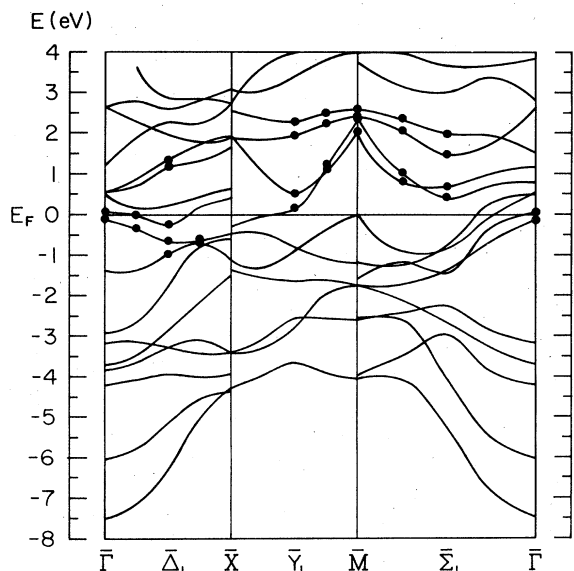


FIG. 3. Energy bands of the five-layer Ta(001) slab, showing states of $\bar{\Delta}_1-\bar{\Gamma}_1-\bar{\Sigma}_1$ symmetry. At the symmetry points, only states whose symmetry is compatible with these are shown. States which are localized in the surface layer are indicated by the filled circles.

already noted in discussing differences between the Ta- and W-layer projected DOS.

On W(001) the $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ surface bands cross the Fermi energy about midway between the $\bar{\Gamma}$ point and the \bar{M} point.¹⁹ The nesting vector which spans the two-dimensional Fermi surface of these states is $q=(1,1)\pi/a$, and this results in a peak in the generalized susceptibility¹⁸ at this wave vector. This is precisely the wave vector of the displacement wave used to describe the Debe and King³⁻⁵ parallel-shift model of the clean-surface reconstruction of W(001). The charge density of these surface states is also responsible for the dangling-bond feature on

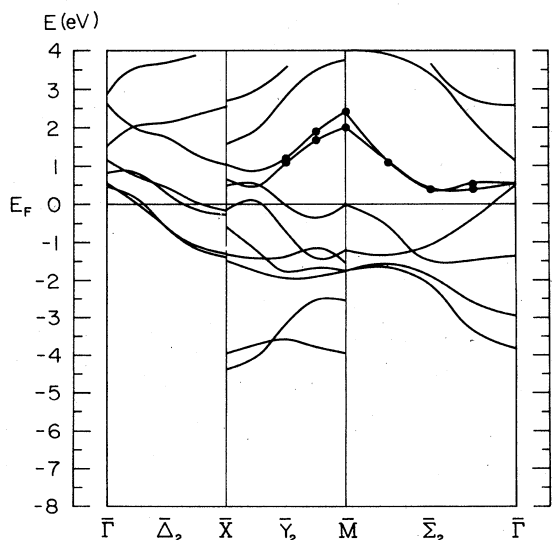


FIG. 4. Energy bands of the five-layer Ta(001) slab, showing states of $\bar{\Delta}_2-\bar{\Gamma}_2-\bar{\Sigma}_2$ symmetry.

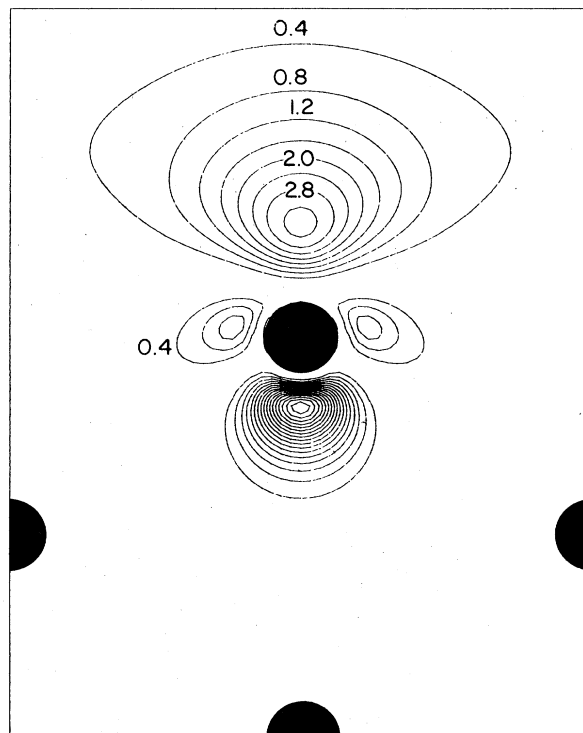


FIG. 5. Charge-density contour plot for the very localized $\bar{\Gamma}_1$ surface state just below the Fermi energy in Fig. 3.

W(001) in Fig. 1.

The energy dispersion of these states on Ta(001) is virtually identical to those on W(001) except that the Ta states are completely unoccupied. This is an important new result; although rigid-band behavior is not a complete surprise in going from tungsten to tantalum, the occurrence of surface states and their properties is well known to be sensitive to the details of the near-surface potential. Thus these results for Ta strongly implicate the surface states on W(001) in driving the clean-surface reconstruction and the low-hydrogen-coverage substrate reconstruction.²⁻¹⁴

The sensitivity of surface states to the potential on Ta(001) is demonstrated by the existence of a highly localized and *occupied* $\bar{\Gamma}_1$ surface state at the center of the Brillouin zone in Fig. 3. This state is virtually identical in all its properties to one found on the W(001) surface. The existence of this state is a notable exception to the rigid-band behavior obtained for the other surface states. This state is predicted to lie just below the Fermi energy just as in W(001) (the Swanson's-hump state²⁷). There is some indication that this state may have been observed in ARPES measurements.³⁹ Figure 5 presents a contour plot of the charge density of this surface state. This figure is virtually identical to that of the W(001) $\bar{\Gamma}_1$ surface state in Ref. 19. To further emphasize that this is indeed the *same* surface state, Fig. 6 displays *all* the slab eigenvalues at $\bar{\Gamma}$ as though they were derived from the projection of the three-dimensional crystal band structure along $\Gamma-H$ in the bulk bcc Brillouin zone (open circles are even and closed circles are odd with respect to z reflection). The

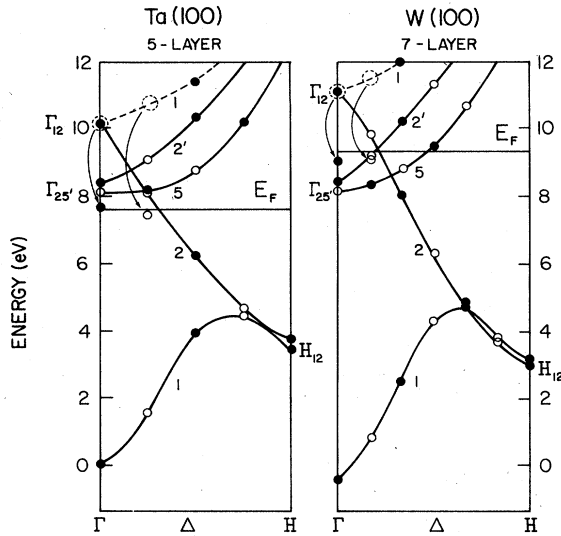


FIG. 6. Slab-derived "bulk" energy bands along Γ - H , showing the origin of the very localized surface state depicted in Fig. 5. The W(001) results are taken from Ref. 19.

right-hand panel depicting the W(001) states is taken from Ref. 19. (There are five slab states per Ta "bulk" band, since they are derived from a five-layer slab calculation.) This figure shows that two states from the upper Δ_1 band are shifted downwards into a Δ_1 symmetry gap, giving rise to the pair of surface states (odd and even with respect to z reflection). The Ta states are pulled down by a greater amount than the corresponding states on the W surface. It is possible that the absence of the "dangling-bond" feature on Ta(001) lowers the Coulomb repulsion experienced by this state, stabilizing it to below the Fermi energy.

IV. CONCLUSIONS

I have presented results of all-electron self-consistent scalar-relativistic local-density-functional calculations of the Ta(001) surface. This study was carried out in order to examine differences in surface-state properties between Ta and W in order to clarify their role in the observed W(001) reconstructions. Essentially all the surface states and resonances which were found on W(001) (Ref. 19) are

also found on Ta(001), except that on Ta(001) most of these surface states are *unoccupied*; most differences between W and Ta can be described by rigid-band behavior. Unlike tungsten, where the Fermi energy falls in the center of a large surface-state peak in the surface-atom d -band projected density of states, this *same* peak in tantalum lies well above the Fermi energy. Although rigid-band behavior is not a complete surprise in going from tungsten to tantalum, the occurrence of surface states and their properties is well known to be sensitive to the details of the near-surface potential. The sensitivity of surface states to the potential is demonstrated by the existence on Ta(001) of a highly localized and *occupied* $\bar{\Gamma}_1$ surface state at the center of the Brillouin zone in Fig. 3. This state is virtually identical in all its properties to one found on the W(001) surface. The existence of this state is a notable exception to the rigid-band behavior obtained for the other surface states. This state is predicted to lie just below the Fermi energy just as in W(001) (the Swanson's-hump state²⁷). There is some indication that this state may have been observed in ARPES measurements.³⁹

On the basis of this calculation for Ta(001) and earlier W(001) calculations, it is concluded that surface states on W do indeed play a role in *destabilizing* W(001) against the observed reconstructions. The observation¹ that Ta(001) does not reconstruct is explained in this calculation by the fact that the relevant surface states are *unoccupied*. This is also evident in the absence of d -band dangling bonds in the contour plots of the Ta charge density near the surface.

The theoretical work function for Ta(001) is 4.3 eV in good agreement with the experimental value,³⁴ 4.15 eV. The theoretical value for the surface core-level shift is 0.96 eV to greater binding energy, which is about 0.5 eV larger than the experimental value³⁵ obtained for Ta(111), but the sign of the shift agrees with experiment. Since the bcc (111) surface is less dense than the (001) surface, the discrepancy may even be somewhat larger for the (001) surface. This may indicate that final-state relaxation shifts are different on a surface atom compared to an interior atom, as has been reported by Smith *et al.*³⁷

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