Spectroscopic determination of surface geometry:
Ti(0001)-H(1 × 1)

Peter J. Feibelman

Sandia Laboratories,* Albuquerque, New Mexico 87115

D. R. Hamann

Bell Laboratories, Murray Hill, New Jersey 07974

The electronic structure of a Ti(0001) film covered by a monolayer of H is shown to depend strongly on the location of the H atom in the surface unit cell. Best agreement with experiment is found with the H's in three-fold sites, 0.8 a.u. outside the outer Ti layer. In this geometry the H atoms "heal" the surface—the clean Ti(0001) surface state near the Fermi level is removed and the outer layer d-like local density of states (LDOS) is quite similar to that of the interior. Additionally, the calculated work function is 4.0 eV and an H-derived peak in the calculated LDOS appears 5 eV below E_F, in agreement with photoemission measurements.

Although there has been considerable progress in determining adsorption geometries via low-energy-electron diffraction[1] (LEED) and some progress using other types of scattering data,[2] at present it is still far from routine to determine the location of the atoms at a surface. This statement is particularly true for surface hydrogen atoms, since H is a weak electron scatterer. Accordingly it is important to learn the extent to which *spectroscopic* data are sensitive to surface atomic arrangement, and thus can be used to narrow down possible surface geometries.[3]

In this paper we consider the adsorption system Ti(0001)-H(1×1). The Ti-H system is important because Ti is a technologically important material and because H is a common impurity in it. It is also an interesting system to study because no previous calculation has been reported of adsorbate-induced changes in the surface electronic structure of a substrate of the left-hand side of the d-band transition series. We have calculated the self-consistent surface band structure for each of five different symmetry sites for H on the Ti surface, including the tetrahedral and octahedral sites between the outer and second Ti atomic layers, two threefold coordination sites outside the outer Ti layer at different distances outside it, and a onefold coordination site outside the surface (see Fig. 1). [We have restricted ourselves to sites which lie along symmetry lines of the Ti(0001) surface both for ease of calculation and because symmetry sites are intuitively plausible ones.] As is seen in Fig. 2 the calculated surface-layer local density of states (LDOS) is very sensitive to assumed surface geometry, not only in the region of the "H peak" which is present for all but the "atop" (onefold) site between 0.16 and 0.26 a.u. below E_F,

but also in the d-band region near E_F. This result contrasts somewhat with that of Louie[4] for Pd(111)-H(1×1), who found that the changes in the d bands of Pd(111) induced by the H layer were rather insensitive to the location of the H atoms while the position of the H peak was strongly dependent on it. The reason for this difference is that clean Ti(0001) (Fig. 2) has a strong d-like surface state coincident with E_F,[5] which clean Pd(111) does not.[6] The adsorption of H outside the outer Ti layer evidently has a strong effect on this surface state.

To date the only published photoemission data for Ti are the angle-integrated energy spectra of Eastman.[7] The specimens used in this work were evaporated polycrystalline Ti films, which, Eastman noted, were impossible to prepare free of H. The presence of H was easy to detect because, unlike Ni, for example, where the introduction of H simply leads to an overall increase in the d band emission,[8] H on Ti gives rise to a
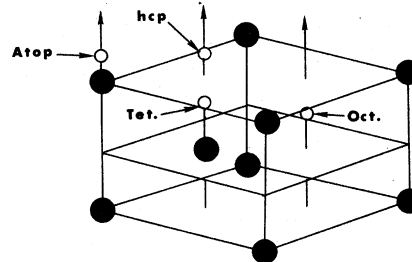

FIG. 1. Schematic of the unit cell of a basal-plane hcp film. The Ti atoms are represented by closed circles. The sites tried for the H adlayer are indicated, including the atop (onefold) site, a threefold "hcp" site, the tetrahedral underlayer site, and the octahedral site.
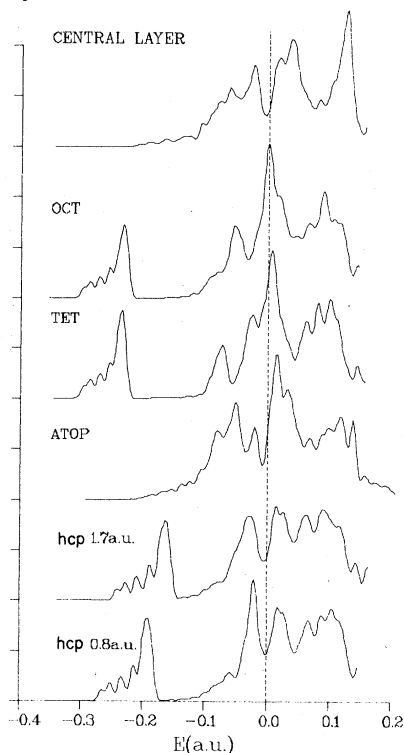
Layer 1 LDOS's vs H Site

FIG. 2. Comparison of the outer-layer LDOS's for various locations of the H atoms. Also shown is the central layer LDOS, which is virtually independent of the H location. The labels "TET," "OCT," and "ATOP" correspond to the sites shown in Fig. 1. The atop site was chosen such that the Ti–H bond length was 3.6 a.u., the Ti–H separation in TiH_2. The two "hcp" sites correspond to "H" of Fig. 1 with different Ti–H spacings. The hcp 1.7-a.u. site has the H's 1.7 a.u. from the outer Ti layer, resulting in a Ti–H bond length equal to that in bulk TiH_2, 3.6 a.u. The hcp 0.8-a.u. site has the H's 0.8 a.u. outside the outer Ti layer, resulting in a Ti–H bond length of 3.3 a.u., equal to the Ti metallic radius plus 0.6 a.u.

large peak 5 eV (0.184 a.u.) below E_F. Eastman verified that the 5 eV peak seen on the cleanest Ti surface was due to H by observing it to rise as the surface was deliberately exposed to H_2.

There is some experimental reason to believe that the H responsible for Eastman's 5-eV peak resides outside the outer Ti layer, specifically the fact that CO adsorption removes the 5 eV feature and replaces it with peaks at 5.7 and 3.6 eV. It seems likely that the CO is adsorbed outside the outer Ti layer. If the H responsible for the 5-eV peak were below the surface we might expect to see some evidence for its continued existence even after CO is chemisorbed. But we do not. The idea that H adsorbs outside the outer Ti

layer is strongly supported by our calculations, as is evident from Figs. 1 and 2, and as we discuss further below.

In comparing calculations for a Ti(0001)-H(1×1) film to Eastman's early ultraviolet-photoemission (UPS) data we are implicitly assuming that his evaporated films were largely (0001) in their surface orientation, and that the H responsible for his UPS data corresponds to monolayer adsorption or perhaps to 1×1 islands. Our success at reproducing the experimental spectra not only in the region of the H peak but also near E_F is strongly suggestive of the validity of these assumptions, but is not conclusive. Current angle-resolved UPS experiments on a Ti(0001) single crystal should clarify the situation.[9]

In what follows we briefly review the method which underlies our calculations. We discuss and compare the geometries of the various H sites we have investigated and we discuss and compare the LDOS's, and detailed band structures to which they lead. The comparison to Eastman's data suggests that the H atoms reside in threefold sites outside the outer Ti layer under the site where the next Ti atoms would be if the crystal continued. The distance of the H's outside the surface corresponds to assuming a radius for them of ~0.6 a.u., the same as that found by Louie for H on Pd(111). In this geometry the H atoms are relatively hydridic as expected,[10] having a charge of about 1.2 electrons.

The self-consistent linear-combination-of-atomic-orbitals (SC-LCAO) method used in our calculations has been described in detail elsewhere.[5,11] The only physical approximation in the calculation is that of a local exchange-correlation potential, which we choose to be of the Wigner interpolation form.[12] The fact that this approximation provides a quantitative description of the spectra of metal-hydrogen systems is well documented.[13] The main numerical approximation in our procedure is the representation of both the solutions to the Schrödinger equation *and* the self-consistent charge and potential[14] in terms of necessarily incomplete bases of Gaussians. Neither the Gaussian basis for the wave functions nor that for the charge and potential is confined to Gaussians centered on atom sites. In order to permit charge to flow into bonding regions and to flatten out in the surface region[15] we include a considerable number of relatively long-range Gaussians in our charge and potential basis, centered at interstitial sites and at sites outside the outer atomic layer (as described in detail in our paper[5] on clean Ti). In order to permit our wave functions to describe the spillover of electronic charge into the vacuum, we include in our wave-function basis

s- and p-like "floating" Gaussians at a site just above the outer Ti atoms[5] (except in the case of H adsorption atop the Ti's, for which these supplementary Gaussians are superfluous).

The use of these supplementary wave functions complicates the assignment of charge and local density of states to the surface Ti's and H's. That is, we cannot distinguish unambiguously how much amplitude in the supplementary wave functions belongs to which partial wave of which surface atom. Accordingly in our LDOS plots, "Layer 1" always refers to the sum of contributions from the outer Ti atoms plus that of the H's plus that of the floating wave functions, while "Layer 2" results refer to the second Ti layer alone.

Results from our earlier calculation of a *clean* 11-layer Ti(0001) film are compared to Eastman's angle-integrated UPS spectrum in the upper portion of Fig. 3. We see that the data disagree with the theoretical outer layer LDOS, not only by the presence of the H-induced peak at –5 eV (–0.184 a.u.) relative to E_F, but also apparently by the
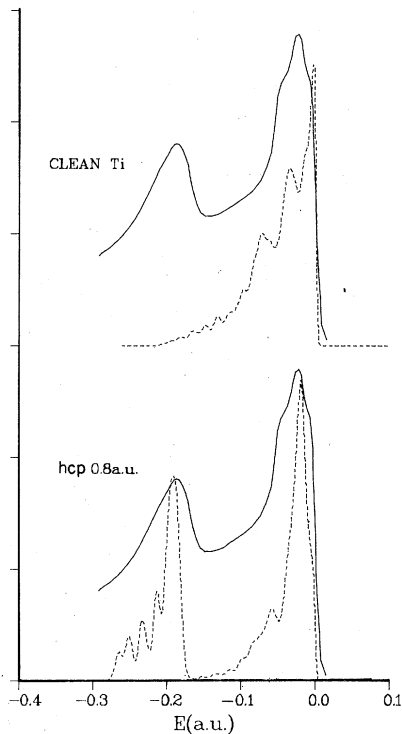
Layer 1 LDOS's vs UPS Data

FIG. 3. Comparison of Eastman's UPS spectrum (solid lines) for a Ti film (Ref. 7) with the outer layer occupied LDOS's of clean Ti(0001) (upper dashed curve) and Ti(0001)-H(1×1) with the H's in the hcp 0.8-a.u. site (lower dashed curve). The energy zero in these curves is at the Fermi energy.

absence of a peak at E_F. It is possible that theoretical peak at E_F corresponds to the highest energy shoulder in the UPS data, not quite resolved from the experimental peak, which by virtue of the low (21.2-eV) photon energy used[7] should largely be due to the bulk Ti d bands. (In this regard it is satisfying that the peak in the "Central layer" spectrum of Fig. 2 agrees in position with the peak in the UPS data.) Pursuing this argument, one is tempted to conclude that the presence of the high-energy shoulder in the data is evidence for clean regions on a 1×1 "islanded" surface. However it would be prudent to await single-crystal UPS data taken over a wider range of photon energies before drawing such a conclusion definitively.

The peak at E_F in the theoretical LDOS corresponds to the existence of bands of surface states which occupy large gaps in the projected bulk Ti band structure, in the outer region of the surface Brillouin zone (SBZ).[5] This fact can be seen in Fig. 4 which shows the dispersion of the even-parity states[16] of the clean Ti film. The heavy lines in this figure indicate states whose amplitude is found (via a Mulliken-like population analysis)[5,17] to be largely in the surface, and thus are surface states or resonances.[18] Note that in the neighborhood of $E_F = -0.139$ a.u., there is a surface state at K which lies in a large (~0.1 a.u.) symmetry gap at that point. (The surface state is of P_1-P_2 symmetry while the bulk band it overlays is of P_3 symmetry.[5]) Proceeding along K-T'-M this state mixes with the bulk band (since the symmetry of the K point is broken along T'), becoming a surface resonance. After the bulk band has dispersed upward somewhat, the surface state reemerges from the band and exists everywhere in the large gap about M in the projected bulk band structure above the second group of d bands.[19]

In addition to the disagreement between the clean Ti film outer layer LDOS and the UPS data, the calculated Ti work function is only 3.8 eV (0.139 a.u.) compared to measured values of ~4.3 eV (0.158 a.u.).[20] Consequently, in attempting to locate the H contaminant on the Ti(0001) surface, we set out to find a geometry such that (i) the H peak in the LDOS lies at –0.184 a.u. relative to E_F, (ii) the surface state peak at E_F disappears, and (iii) the work function increases by ~0.1 to 0.02 a.u. (i.e., a few tenths of an eV).

Our success in fulfilling these requirements is shown in Figs. 2 and 3 and in Table I. The very convincing LEED analysis of Shih *et al.*[21] which showed that a monolayer of N on Ti(0001) occupies the octahedral sites between the outermost and second Ti layers, with a slight expansion of the inter-Ti-layer separation, suggested that we try
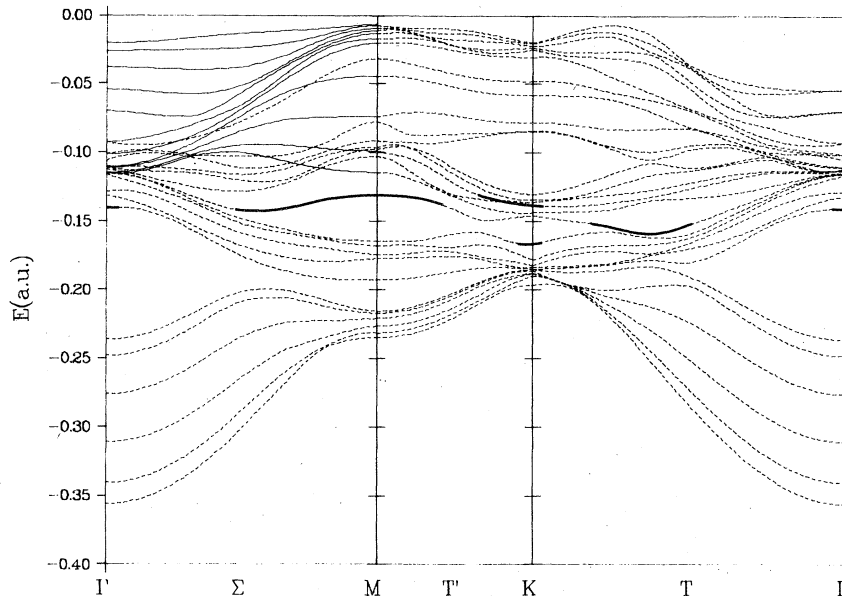
FIG. 4. Even-parity energy-band structure of a clean 11-layer Ti(0001) film. The low-lying surface states and res-
onances are shown as heavy lines. Solid and dashed lines along Γ-Σ-M correspond to states of odd and even parity un-
der reflection across the (0001) surface mirror plane.

placing the H atoms under the Ti surface layer.[22]
However, as is seen in Fig. 2, placing the H's at
the octahedral underlayer site (with no expansion
of the Ti interlayer spacing) has no effect on the
surface state at E_F. In addition it introduces an
H peak at -0.232 a.u., about 0.05 a.u. (1.4 eV) too
low compared to Eastman's data, and (cf. Table I).
(On the other hand it does increase the work func-
tion slightly, into reasonable agreement with mea-
surements.)

Moving the H's to the tetrahedral site directly
above a second layer Ti atom shifts the surface
state up, so that the predicted peak at E_F for this
geometry is weaker than for the clean Ti(0001)
case, but still there. Moreover the H peak is still
0.05 a.u. too deep compared to Eastman's results.
On the other hand the work function for the tetra-
hedral site is 0.16 a.u., in very good agreement
with experiment. This increase in work function
presumably reflects the fact that we have moved
the quite negatively charged H's further out into
the dipole region.

The poor agreement between outer layer LDOS's
and experiment for underlayer sites suggests that
one should try putting the H's outside the outer Ti
layer. However, as is seen in Fig. 1, of the sym-
metry sites outside the film the "atop" site (3.6
a.u. above a surface Ti)[23] is a poor choice. In this
case the H-derived level below the Ti s bands dis-
appears entirely. At the same time, despite the
fact that the H's have an excess charge of ~-0.2|e|
as against -0.5|e| for the tetrahedral underlayer

sites, the work function for the atop site is 0.21
a.u., significantly larger than the measured value,
due to the fact that the negative H's are now quite
far into the vacuum region, appreciably increasing
the surface dipole. The one aspect of the outer
layer LDOS for the atop site that is in improved
agreement with experiment is the absence of the
surface state at E_F.

In order to appreciate in more detail the differ-
ence between adsorbing the H's in the tetrahedral
and atop sites, it is useful to compare the surface
band structures calculated for the two cases,
shown in Figs. 5(a) and 5(b). In Fig. 5(a) we see
that for the tetrahedral site we have in the d-band
region a situation not very different from that of
the clean surface, cf. Fig. 4. The surface state
split off the top of the second d-band pair has been
pushed somewhat higher into the gap about M and
consequently is slightly more dispersive. The
surface state at K (of symmetry P_1-P_2, overlap-
ping a bulk band of symmetry P_3)[5] now extends all
the way across K-T'-M, becoming a second sur-
face state in the large gap about M, having ap-
preciable H character. (The lower surface state
at M has little amplitude on the H's.) We also
find surface-localized bands near the center of
the SBZ. The lowest of these bands is split off
the bottom of the lowest d band at Γ into the s-d
hybridization gap. The corresponding wave func-
tions have appreciable amplitude on the H atoms.
Higher up at Γ is a doubly degenerate surface
state, of appreciable p_x-p_y amplitude on the H's,

TABLE I. Work function Φ and charge q_H on the H atom (via a population analysis) for various H sites on Ti(0001). The measured Ti work function is ~0.15 to 0.16 a.u.

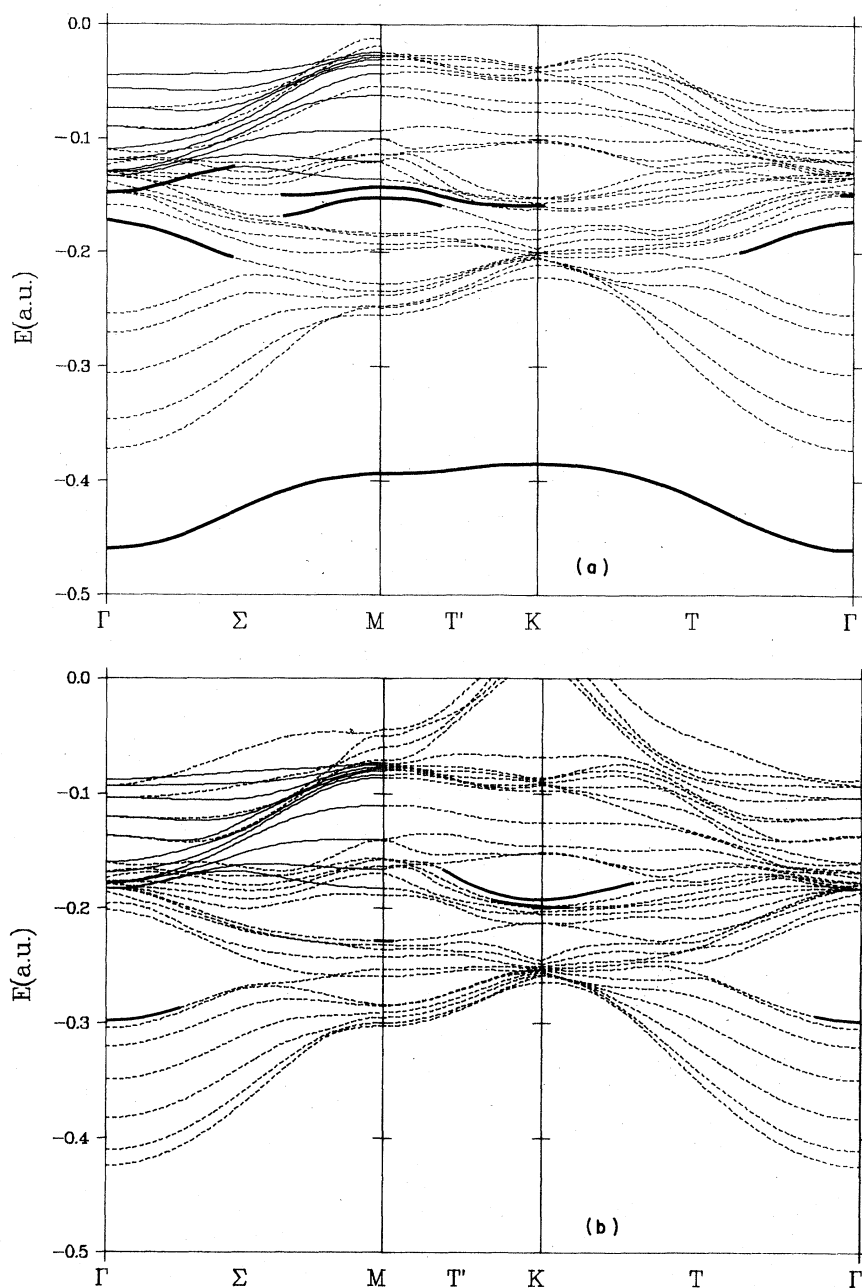|	Clean	Oct.	Tet.	Atop	hcp 1.7 a.u.	hcp 0.8 a.u.
Φ (a.u.)	0.14	0.15	0.16	0.21	0.16	0.15
q_H		1.4	1.5	1.2	1.2	1.3

FIG. 5. Even-parity energy-band structure of Ti(0001)-H(1×1) films having 11 Ti layers plus a monolayer of H on each surface. (a) H's in the tetrahedral sites. (b) H's in the atop sites. The low-lying surface states and resonances are shown as heavy lines. Solid and dashed curves along Γ-Σ-M indicate states of odd and even parity, respectively, under reflection in the surface mirror plane.

at the energy of the lowest state which is odd under reflection in the (0001) surface's mirror plane. (The second of the degenerate functions is even under this reflection.) Along Γ-Σ-M the odd state disperses upward parallel to the band of odd states from which it is weakly split off. The even state quickly merges into the band of bulk states which it overlaps, and loses its surface character. Along Γ-T-K one of the degenerate pair [shown as a heavy solid line in Fig. 5(a)] quickly loses its surface character by mixing with bulk bands. The other acts as a surface resonance. Moving along Γ-T-K we find the surface localized state moving up among the dispersion curves without causing one curve to split away from the rest. This behavior is difficult to represent by a heavy solid line, and accordingly is not. These three bands of surface-localized states are rather strongly dispersive and, as noted, neither is highly surface localized. Accordingly they do not distort the surface layer LDOS much.

The most significant perturbation of the clean Ti(0001) film band structure due to the tetrahedral site H's is obviously that a state, which contains virtually all the H $1s$ amplitude, is split off the lowest Ti bands all the way across the SBZ. That this state is split off the Ti bands, and is not a new state introduced by the presence of the H's, is clear when one counts bands in Figs. 4 and 5(a).[18] This result is in fact not surprising—it is identical to what is found by Switendick[24] for a wide variety of bulk metal hydrides, including TiH_2.

The band picture for the atop site, shown in Fig. 5(b), is very different from that for the tetrahedral. In this case, instead of splitting a state off the bottom of the Ti bands which has a large s amplitude on the H's, the proton potential splits a state off the bottom of the lowest d band, near the SBZ center and moves it all the way across the s-d hybridization gap. This state is strongly surface localized near Γ. It has considerable amplitude on the H sites, but unlike the tetrahedral case the neighboring "bulk" states do also. Proceeding along Γ-Σ-M or Γ-T-K, the state loses its surface character as it disperses upwards and mixes with the bulk band. Close to M it reemerges from the lowest bulk states and becomes surface localized once again (though weakly) continuing so along M-T'-K.

In the gap about M a state of (weakly) surface character is split off the bottom of the third d band. No state analogous to that split up from the second d band in the clean and tetrahedral-H cases is found. At K the usual surface state of P_1-P_2 symmetry is found overlaying the P_3 bulk band near the Fermi energy.[5] In addition a surface localized state is weakly split off the top of

this P_3 symmetry band into the second gap about K.

The fact that the most important surface state in the atop case is found near Γ is presumably related to the direction of the Ti–H bond in this case. By rotation symmetry the states near Γ must be strongly $3z^2$–r^2 rather than (xz, yz) or $(x^2$–$z^2, xy)$ in character. Since the Ti–H bond lies along the z axis $3z^2$–r^2 is favorable for accommodating bond charge. The fact that the surface states in the atop case are split off the opposite sides of the bulk Ti bank from what is found in the tetrahedral-H and clean film cases suggests that the potential induced by atop H is of the opposite sign to that in the other cases.

We turn finally to two threefold sites outside the outermost Ti layer, the latter of which yields the excellent agreement with UPS data shown in Fig. 2. Both sites lie along a line parallel to the c axis directly above a second layer Ti atom and directly below the site where the next Ti atom would be were the hcp lattice continued beyond the surface plane. The two sites correspond to placing the H's respectively 1.7 a.u. and 0.8 a.u. outside the outer Ti layer, positions which correspond respectively to the Ti–H bond length in TiH_2 and to a bond length equal to the metallic radius of Ti plus an H radius, $r_{cov}(H) \approx 0.6$ a.u., the value found by Louie[9] to give good agreement with UPS data for Pd(111)-H(1×1).

The results for the two cases are quite similar, as can be seen in the LDOS plots of Figs. 2 and 6. At the site corresponding to the TiH_2 bond length, the split-off H peak lies at –0.161 a.u. relative to E_F, somewhat too weakly bound. At the "hcp 0.8-a.u." site the H-peak lies at –0.188 a.u., in virtually perfect agreement with Eastman's data. In both cases the surface state at E_F has been removed, and as is seen in Table I, the work function is in good agreement with measurements. In the case of the hcp 1.7-a.u. site the d-band peak just below E_F lies at –0.028 a.u. relative to E_F, while in the hcp 0.8-a.u. case it is somewhat sharper, and lies at –0.020 a.u. In Eastman's experiment this peak lies at –0.026 a.u., which does not disagree with either of the theoretical results, given the accuracy of the calculation.

An interesting question is why the H level is shallower for the hcp site in which the H atom lies farther outside the surface, particularly in view of the facts that the work function is greater and the negative charge on the H is less for this site. The answer is that when the H atom is farther outside the surface, removing an electron from it requires passage through less of the surface dipole layer. This greater proximity to the vacuum is a dominant effect in determining where the H level lies. This argument also helps explain
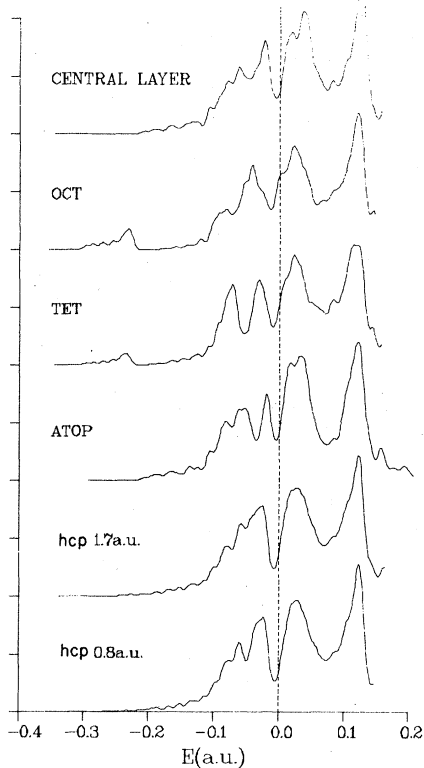
Layer 2 LDOS's vs H Site

FIG. 6. Second layer LDOS's for various H sites in Ti(0001)-H(1×1) films.

why the H level disappears up into the d bands when the H is placed in the atop site, still farther out into the vacuum than the two hcp sites we have considered.[25]

Another interesting question is why, when we place the H atoms along the line through the next hcp site outside the surface, the outer layer LDOS in the d-band region now bears such a strong resemblance to the DOS in the interior of the metal (cf. Fig. 2). This fact can be appreciated as well in the band structure plots for the hcp sites, e.g., that of the "0.8-a.u. site" in Fig. 7. Note that apart from the deep H-induced level the only strongly surface localized states are in a band emanating from the surface state of P_1-P_2 symmetry at K. Since this band disperses upward and only occupies a small part of the SBZ it affects the surface LDOS little, and the occupied part not at all ($E_F = -0.147$ a.u. in this case).

An argument that accounts for this "healing" of the Ti(0001) surface by H's at the hcp sites is the following: (a) a monolayer of H's provides exactly the right number of electrons per unit cell, namely one, to satisfy the bonding requirements of the outer Ti layer, and (b) in the threefold sites the geometry of the Ti–H bonds is a good approximation to the geometry of the bonds that would be present if the Ti crystal continued. Accordingly at the hcp sites the H(1×1) layer provides the ideal termination of the Ti(0001) film for making the outer layer Ti's behave as though the crystal con-

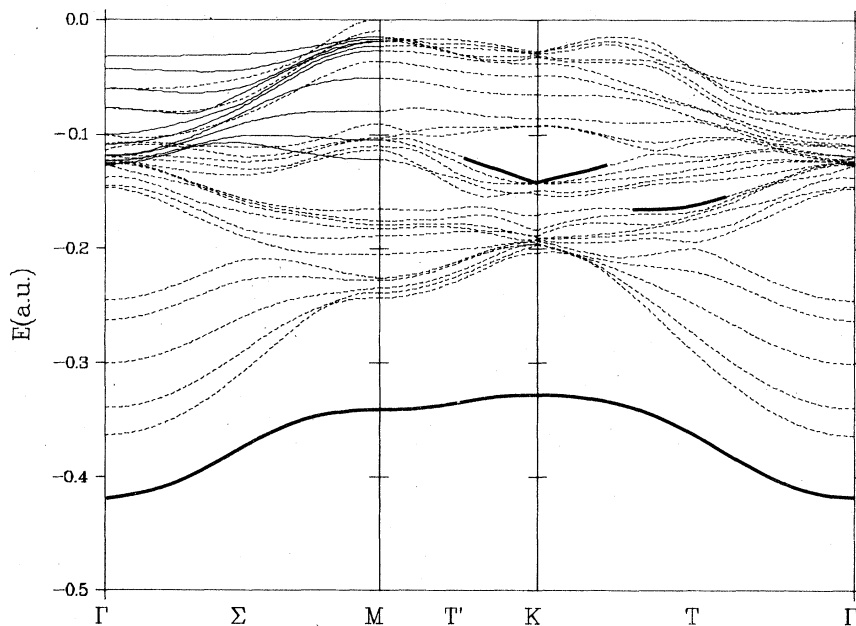

FIG. 7. Even-parity band structure for Ti(0001)-H(1×1) with the H's in the hcp 0.8-a.u. sites.

tinued. An elaboration of this argument and a test involving the Sc(0001)-H(1×1) system will be reported elsewhere.[26]

Incidentally it should be noted that the "healing" of the spectrum of the outer Ti layer by hcp-situated H's occurs not only in the d-band region, but also in the core spectrum. In clean Ti(0001) we found[5] that core electron binding energies are ~0.25 eV deeper in the surface Ti's than in the interior layer atoms, due to surface charge redistribution. To within the accuracy of our calculations the corresponding core binding energy shift is zero for the Ti(0001)-H(1×1) surface with the H's at the hcp 0.8-a.u. sites.

One final issue that must be discussed is whether we can distinguish H's sitting in the hcp sites from H's which reside in the inequivalent threefold sites that lie along the line which passes through the octahedral sites of the film (cf. Fig. 1). A glance at Fig. 6 suggests that we cannot. Despite the strong H level in the two hcp sites in the Layer 1 LDOS's there is no perturbation at the corresponding energies in the second layer. Consequently, the results for H's in the two inequivalent threefold sites outside the surface which differ only in their coordination to the second Ti layer are likely to be indistinguishable. This picture is in agreement

with the results of Louie[4] for Pd(111)-H(1×1).

Figure 6, incidentally, merits some attention in itself. Note that in the octahedral position the H-level perturbs the LDOS in the second Ti layer more than in the tetrahedral site. This result is due to the increased coordination to second layer Ti's in the octahedral case. In the tetrahedral site the weaker perturbation of the second layer Ti's causes a strong distortion of the lowest d bands rather than a larger peak at the position of the H level.

In summary, to the extent that calculations for Ti(0001)-H(1×1) may be compared to Eastman's data for polycrystalline evaporated Ti films[7] we have found a location for the H atoms which yields good agreement with the UPS spectra and a reasonable work function. These results combined with those of Louie for Pd(111)-H(1×1) suggest a bright future for the determination of surface atomic arrangement via spectroscopic calculations and measurements.

ACKNOWLEDGMENT

*A U. S. Department of Energy facility.

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[16]Since the hcp film is symmetric under reflection in its central plane, the wave functions have good parity with respect to $z \rightarrow -z$. In the H-adsorption calculations, an H monolayer was assumed to be on both film surfaces, maintaining this symmetry.

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[18]As the surface bands merge into the bulk bands it becomes difficult to distinguish a surface state from a resonance, in an 11-layer film calculation.

[19]In the bulk band structure of an hcp crystal each state of the constituent atoms broadens into a pair of bands, since there are two atoms per unit cell. Similarly, in an N-layer hcp (0001) film each atomic state broadens into N bands, because there are N atoms per unit cell. In the 11-layer case we thus expect 11 states per band of which six will be of even (odd) parity and five will be of odd (even) parity under reflection in the central plane. This argument explains the number of states in the groups of bands seen, e.g., in Fig. 4 and also permits the use of band counting to determine the bulk band from which a surface state is split off.

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[22]In our underlayer calculations we left the separation between the first and second Ti layers at its bulk value of 4.42 a.u.

[23]3.6 a.u. is the Ti–H bond length in TiH$_2$.

[24]A. C. Switendick, J. Less Common Met. **49**, 283 (1976), and references therein.

[25]Of course this argument only makes sense if the H and Ti atoms are in chemical contact. If the overlap between the H and Ti orbitals is essentially zero, the use of a local exchange-correlation potential no longer provides a valid description of the Ti–H system.

[26]P. J. Feibelman and D. R. Hamann, Solid State Commun. (in press).