PHYSICAL REVIEW B VOLUME 48, NUMBER 15 15 OCTOBER 1993-I

Structure of H-covered Be(0001)

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(Received 25 March 1993; revised manuscript received 19 April 1993)

In accord with the inverse bond-order–bond-length correlation expected for group-II elements, linearized augmented-plane-wave (LAPW) calculations show that a 1×1 monolayer of H, adsorbed on Be(0001), should cause the outer Be layers' separation to be close to ideal, i.e., to be contracted relative to the substantial expansion seen for clean Be(0001). However, the LAPW work functions, and also the H-induced surface-state and resonance positions calculated for 1×1 H overlayers, are in poor agreement with experiment. Based on the known accuracy of LAPW calculations, these disagreements indicate that at monolayer coverage, adsorbed H does not all reside above the outer Be layer.

I. INTRODUCTION

The atomic arrangements of clean and H-covered Be surfaces are interesting from both scientific and technological perspectives. Technological interest stems from the recognition that in many ways, Be is an ideal candidate for a "first wall" or "plasma-facing" material in a tokamak fusion reactor.[1] Be metal is attractive for this application not only because of its low Z, which means that Be atoms eroded into the plasma radiate relatively little energy, its high thermal conductivity, which allows a Be wall to conduct away heat deposited by impinging α particles, and its mechanical properties (e.g., its ductility), but also because Be interacts weakly with hydrogen, implying that relatively few T's (T=tritium) from the plasma will end up *in* the first wall, unavailable for fusion. This last consideration raises several important surface science issues. For example, even if T does not dissolve into bulk Be metal, does it reside within or below the first Be layer?[2] If there is dissolved or subsurface T, under what conditions does it emerge onto the surface, recombine, and desorb back into the plasma? Calculations of the energetics and measurements of the structure of T-covered single-crystal Be surfaces should help answer these important questions.

H adsorption on Be is scientifically interesting because Be is a group-II atom, whose ground-state $(2s)^2$ electronic configuration implies that a 2.7-eV s-to-p promotion energy must be expended before Be can form bonds to its neighbors.[3] The result is that Be does not obey the usual bond-order–bond-length correlation.[4,5] The nearest-neighbor distance in bulk, hcp Be, for example, is 10% shorter than the bond length of Be_2.[6] In detail, the reason for this unusual behavior is that in bulk Be the price of s-to-p promotion is repaid by the formation of 12 bonds, while in Be_2 the payback, from the formation of a single bond, is considerably less. Similar reasoning explains[5] why, experimentally, the outer layer separation at the Be(0001) surface is expanded 6% relative to bulk.[7] The surface atoms lack three nearest neighbors. This means that there is less energetic gain from s-to-p promotion in the surface layer than in the bulk. Accordingly the surface atoms' p-electron population is reduced and they bond less well to the layer immediately below.

The idea that the outer layer expansion of Be is related to its position in the Periodic Table can be tested directly by looking at other group-II metals. To this end, Sprunger, Pohl, Davis, and Plummer have performed a low-energy electron diffraction (LEED) study of Mg(0001), concluding that its outer layer separation is expanded by 1.9%.[8] In excellent agreement with this result, a first-principles, plane-wave pseudopotential (PWPP) calculation[9] predicts a 1.5% expansion. At the same time, the calculation reveals a reduced p-electron count on the surface Mg's, relative to the bulk.

The work reported here was undertaken as an additional test of the promotion-hybridization argument. In the presence of an overlayer of H atoms, surface-layer Be's have as many neighbors, 12 that is, as Be's in the interior of the metal. Thus a H overlayer should inhibit $2p$- to $2s$-electron demotion at the surface and should "heal" the outer layer expansion. The results presented below verify that a H overlayer causes the Be(0001) outer layer separation to relax back to something close to its "ideal" bulk value.

On the other hand, the fact that one can perform calculations for a $H(1\times1)$ overlayer on Be(0001) does not mean that such an atomic arrangement is, or can be realized experimentally. In fact, both calculated work functions and H-induced surface-state positions for such overlayers agree poorly with experiment. The LAPW calculations yield H-induced work function changes between -1.6 and -2.3 eV for several plausible high-symmetry overlayer geometries, rather than the much smaller measured change, -0.4 eV, reported by Ray, Hannon, and Plummer (RHP).[10] For the best bound of these adsorption geometries, the calculated positions and widths of the H-induced surface bands are in poor agreement (discrepancies of the order of a couple of eV) with recent angle-resolved ultraviolet photoemission spectroscopy (ARUPS) measurements.[11] Finally, it is worth noting that preliminary LEED analysis suggests that the Be outer layer separation does not contract when a H monolayer is added.[11] While this is a plausible outcome if some of the H is subsurface, the calculations clearly imply that if all the H's are on top of the surface then the

0163-1829/93/48(15)/11270(7)/$06.00

outer layer separation should be virtually ideal.

The remainder of this paper is organized as follows. In Sec. II I describe the first-principles LAPW calculations of H-covered Be surfaces that confirm the promotion-hybridization picture of the Be surface relaxation. In Sec. II A, I review the calculation of the lattice parameters of bulk hcp Be. Section II B compares calculations for H overlayers in various symmetry sites, threefold hollows, and the twofold bridge. In Sec. II C, I discuss the results for H-induced relaxation of the outer Be layer spacing. Section II D is devoted to the question of why a H overlayer prefers a bridge geometry to the higher symmetry threefold hollows that H typically occupies on close-packed metal surfaces. In Sec. III I present theoretical results that cast doubt on the experimental reality of a H(1×1) overlayer on Be(0001). Work function results are discussed in Sec. III A, in comparison with experiment. In Sec. III B, I explain why the poor agreement between measured and computed work functions is unlikely to be improved by moving the H layer to a "tilted-bridge" overlayer geometry. Section III C is devoted to the comparison of the calculated, H-induced electron energy level dispersions and ARUPS data. Finally, in Sec. III D, I speculate on the possibility that at monolayer H coverage, a significant fraction of the adsorbed H lies subsurface.

II. CALCULATIONS FOR H(1×1)/Be(0001)

Results of first-principles calculations for H(1×1)/Be(0001) surfaces, based on the local density functional (LDF) approximation,[12] appear in this section. The calculations were done via the LAPW method,[13] using the computational scheme and computer code of Hamann.[14] In this approach, the one-electron potential is not subject to any shape approximation. Exchange and correlation effects are represented via the Wigner interpolation formula.[15] A slab rather than a supercell basis is used to compute surface properties.

A. Bulk lattice parameters of hcp Be

In order to compute atomic layer spacings near a crystal surface, one must decide how to fix the in-plane lattice parameter a. Since the relation between a and the calculated outer layer spacing roughly conserves the volume occupied by a surface atom, if one uses the experimental value of a, the computed surface geometry can differ substantially from what it would be using the LDF value. I use the LDF result $a=4.270$ bohr on grounds of consistency, which is actually in quite good agreement with the experimental value $a=4.29$ bohr. I also fix the layer spacings in the interior of the Be slabs at the LDF optimal bulk interlayer separation $c/2=3.389$ bohr, which is virtually indistinguishable from the experimental value.

The basis for the bulk Be calculations that lead to the LDF lattice parameters includes all LAPW's of plane-wave wave-vector square up to 10.0 bohr^{-2}. The irreducible $\frac{1}{24}$ of the Brillouin zone is sampled with 42 Bloch vectors, i.e., 14 equally spaced Bloch vectors in each of three equally spaced planes perpendicular to the c axis. I use plane waves of wave-vector square up to 100 bohr^{-2} in solving Poisson's equation, and allow for angular momenta up to $l=6$ in the muffin tins, both for wave functions and the charge density. I use a muffin-tin radius of 1.94 bohr; this is small enough that the muffin tins do not overlap for over a substantial range of crystal geometries.

B. H(1×1) overlayers in various registries on Be(0001)

Although H typically resides in high coordination sites on close-packed metal surfaces, the vibration spectroscopy measurements of RHP and the PWPP calculations of Yu and Lam[16] (YL) suggest that H/Be(0001) behaves otherwise. YL compare the energy of H monolayers in various registries on a four-layer Be(0001) slab, whose in-plane lattice constant a and interlayer separations $c/2$ are set to the experimental values for bulk Be. They find that the twofold bridge site is preferred by 0.09 eV relative to the second-best symmetry site, which is the fcc threefold hollow. RHP find that at H coverages from 0 to about 0.4 ML, H occupies a single high-symmetry site, but that from 0.4 to 1.0 ML the adsorption geometry has a lower symmetry. The evidence is the appearance of several dipole-active vibration modes, as opposed to only one in the lower coverage regime. The low-coverage adsorption geometry is identified as bridge site adsorption on the basis of (a) good agreement of the frequency of the dipole-active mode (185 meV) with YL's prediction for bridge adsorption (178 meV), and (b) the shift to lower frequency vibrations at higher coverage. Since lower frequency stretch modes typically correspond to higher coordination adsorption sites, the shift to lower frequency implies that the low-coverage site has a relatively low coordination. Onefold adsorption is excluded by YL's calculation, which says that H in an atop geometry is disfavored by 0.72 eV relative to the bridge. This means that the relatively low coordination site that gives rise to the observed high frequency vibration is likely to be a twofold bridge. RHP suggest that the adsorption site for higher coverages is a "tilted bridge site," i.e., a site somewhere between a bridge and one of the threefold positions.

The present calculations differ in several respects from YL's, but agree with the conclusion that, for a 1×1 H overlayer, the bridge site is preferred to either of the threefold symmetric bonding geometries. In the present case, the Wigner exchange-correlation potential[15] is used rather than the Hedin-Lundqvist potential[17] employed by YL. The LAPW calculation scheme is based on a frozen-core approximation, while YL represent core potentials via Hamann *et al.* pseudopotentials,[18] starting from a $2s^{1}2p^{1}$ valence configuration for Be. They use a plane-wave cutoff of 20.0 bohr^{-2}. As noted above, I set the in-plane lattice parameter a to its LDF optimum value for bulk Be, rather than the experimental value that YL use. Finally, in order to permit the optimization of the outer Be layer separation, the Be substrate is represented here as a seven- rather than a four-layer slab.

The basis set once again includes all LAPW's of plane-wave wave-vector square up to 10.0 bohr^{-2}. This cutoff provides adequate convergence, if one is interested in H bonding geometries, and the corresponding work functions and electron energy levels. It is too small to yield absolute H binding energies more accurately than within a few tenths of an eV, given the 0.60-bohr muffin-tin radius used for the H atoms. This small radius was used to allow calculations over a wide range of adsorption geometries. With a muffin-tin radius of 0.90 bohr, as it turned out, appreciably better converged binding energies could have been computed at no additional computer cost.

For adsorption in threefold sites, where the rotation symmetry of the H-covered slab is C_{3v}, I sample the irreducible 1/12 of the surface Brillouin zone (SBZ) with 14 equally spaced Bloch vectors. In the case of Bridge adsorption the slab symmetry is lowered to C_{2v}, because the unit cell contains three equivalent bridge sites, of which only one is occupied by a H atom at monolayer coverage. In this case I sample the irreducible 1/4 of the SBZ with 42 equally spaced Bloch vectors. In all adsorption geometries, I use plane waves of the wave-vector square up to 100 bohr^{-2} in solving Poisson's equation, and allow for angular momenta up to $l=6$ in the muffin tins. To determine the optimal geometries of the H-covered seven-layer films, I perform a least-squares fit of the most general cubic polynomial (containing ten terms) to the energies calculated for 13 or more sets of Z_{H} and Z_{Be}, the distances of the hydrogen and the outer-Be layers from the central Be layer. Because the relaxation of the outer Be layer is small for the threefold and twofold H-adsorption geometries, I fix the positions of the interior Be layers at their bulk LDF values. The results of the geometry optimization are presented in Table I.

Table I shows that as in YL's calculations, the bridge site is favored energetically relative to the second-best high-symmetry adsorption site, the fcc threefold hollow. In the present calculations, the energetic preference is 0.15 eV per H adatom rather than YL's value of only 0.09 eV—a difference of this magnitude is reasonable considering the various differences in the calculations. The preference for the fcc as against the hcp threefold hollow is 0.07 eV as compared to YL's value of 0.09 eV. The energy differences calculated here for the various geometries are affected only very slightly (i.e., by less than 0.01 eV) by the fact that the Be outer layer has been allowed to relax, since the optimal relaxations of the outer Be interlayer spacing are of the order of a percent or less.

The absolute binding energies that I find for H in the various adsorption sites are about 1 eV smaller than those reported by YL. Of this discrepancy, 0.57 eV is due to the fact that YL reference their binding energies to -13.03 eV per isolated H, their LDF value, rather than the experimental value of -13.6 eV. The remainder results from using a cutoff of only 10.0 bohr^{-2} for the LAPW basis set. With a 15.0 bohr^{-2} cutoff, tests show, the remaining discrepancy is reduced to roughly 0.05 eV, while bonding geometries, work functions, and electron energy levels are only slightly modified.

C. Outer Be layer relaxation, with H present

The initial reason for the present calculations was to see whether the presence of a H overlayer would cause a contraction of the outer layer separation of the Be(0001) surface back toward its "ideal" bulk value, from its expanded value on the clean surface. Table I shows that this is exactly what happens. In the optimal bridge adsorption geometry, the outer Be layers' separation is very close to ideal, perhaps a small fraction of a percent contracted. In the fcc and hcp adsorption sites, H leaves the outer layer separation expanded somewhat relative to ideal, 1.4% in the former case and 0.4% in the latter, but considerably contracted relative to the 4.4% expansion found theoretically for a clean seven-layer Be(0001) slab.[5]

Table II shows that with the H layer present, in all three adsorption geometries, the population of p_σ electrons in the outer Be muffin tins is much closer to the populations in the interior muffin tins, than for clean Be(0001), where the p_σ-population in the outer muffin tins is greatly depleted. (σ and π are defined relative to the surface normal through an outer layer Be nucleus.) This is true whether one compares to the relaxed or to the ideal, clean surface. These results confirm the picture that the absence of neighbors above the outer Be's, in the case of clean Be(0001), leads to a demotion of p electrons which in turn leads to the outer layer expansion. With the overlayer of H's present, the demotion is much less or is replaced by an enhancement, and the outer layer separation is nearly ideal.

TABLE I. For three H-binding geometries, the total valence electron energy per unit cell, in Ry, of the seven-layer Be slab, covered on both sides with H(1×1) overlayers, the binding energy per adsorbed H atoms, in eV, referenced to the seven-layer Be(0001) calculations of Ref. 5 and 13.6 eV per isolated H atom, the separation of the H layer from the outer Be layer, $d_{\text{H-Be}}$, the separation of the outermost and next deeper Be layer, d_{12}, the percentage relaxation in d_{12} relative to 3.389 bohr the spacing of (0001) planes in bulk (LDF) Be, and the calculated work function Φ in eV. The H binding energies would be roughly 0.4 eV higher had the LAPW calculations been done with a 15.0-bohr^{-2} basis-set cutoff instead of 10.0 bohr^{-2}.

H site	Energy (Ry)	B.E./ atom (eV)	$d_{\text{H-Be}}$ (bohr)	d_{12} (bohr)	$\Delta d_{12}/3.38$ 3.38 bohr (%)	Φ (eV)
twofold bridge	-18.2718	1.38	1.87	3.38	-0.3	3.24
threefold fcc	-18.2500	1.23	1.75	3.43	$+1.4$	3.89
threefold hcp	-18.2396	1.16	1.82	3.40	$+0.4$	3.45

TABLE II. For H in three registries on a seven-layer Be(0001) slab, and for ideal and relaxed nine-layer Be(0001) slabs, the percentage difference of angular-momentum resolved electron numbers in the outer Be muffin tins, relative to the average of the same number among the three central layer Be muffin tins. Here σ and π are defined relative to a surface normal through a Be nucleus.

Bridge site	Outer Be layer	Subsurface Be layer
$\rho(s)/\bar{\rho}_{\mathrm{ctrl}}(s)$	−0.9%	0.03%
$\rho(p_\pi)/\bar{\rho}_{\mathrm{ctrl}}(p_\pi)$	−0.02%	−1.6%
$\rho(p_\sigma)/\bar{\rho}_{\mathrm{ctrl}}(p_\sigma)$	+7.8%	+2.9%
fcc site	Outer Be layer	Subsurface Be layer
$\rho(s)/\bar{\rho}_{\mathrm{ctrl}}(s)$	+4.7%	+4.0%
$\rho(p_\pi)/\bar{\rho}_{\mathrm{ctrl}}(p_\pi)$	+2.1%	−3.5%
$\rho(p_\sigma)/\bar{\rho}_{\mathrm{ctrl}}(p_\sigma)$	−2.2%	7.2%
hcp site	Outer Be layer	Subsurface Be layer
$\rho(s)/\bar{\rho}_{\mathrm{ctrl}}(s)$	−3.4%	−1.5%
$\rho(p_\pi)/\bar{\rho}_{\mathrm{ctrl}}(p_\pi)$	−2.8%	−1.6%
$\rho(p_\sigma)/\bar{\rho}_{\mathrm{ctrl}}(p_\sigma)$	+1.4%	−1.0%
clean, ideal, nine-layer Be(0001)	Outer Be layer	Subsurface Be layer
$\rho(s)/\bar{\rho}_{\mathrm{ctrl}}(s)$	+0.4%	+3.1%
$\rho(p_\pi)/\bar{\rho}_{\mathrm{ctrl}}(p_\pi)$	−5.6%	−2.4%
$\rho(p_\sigma)/\bar{\rho}_{\mathrm{ctrl}}(p_\sigma)$	−34.6%	−1.7%
clean, relaxed, nine-layer Be(0001)	Outer Be layer	Subsurface Be layer
$\rho(s)/\bar{\rho}_{\mathrm{ctrl}}(s)$	+0.05%	+1.4%
$\rho(p_\pi)/\bar{\rho}_{\mathrm{ctrl}}(p_\pi)$	−5.8%	−3.3%
$\rho(p_\sigma)/\bar{\rho}_{\mathrm{ctrl}}(p_\sigma)$	−39.6%	−7.8%

D. Why the bridge site is preferred

YL attribute the H adatoms' preference for bridge adsorption to the substantial strength of the pseudopotential for p electrons in Be. Though this may be true, such an argument does not provide a *physical* understanding of the unusual site preference. The pseudopotential, after all, is not a physical entity but a mathematical construct. A more satisfying interpretation of the energetic advantage of the bridge site follows when one asks why the Be outer layer separation is somewhat expanded for the threefold sites while it is slightly contracted for the bridge, and why at the same time, for H in *either* threefold site, there are substantially fewer p_σ electrons in the outer Be muffin tins than for H adsorbed at the bridge.

The answer is that "healing" the Be(0001) surface means enabling the p_σ electrons of the outer Be's to participate in additional bonds. Each Be atom has six inplane Be neighbors whether at the surface or in the interior. The addition of a H-overlayer thus adds little bonding capability to what is already available for the p_x and p_y electrons of the outer Be's. What these atoms lack, relative to those in the interior of the metal, is three of the Be neighbors that can form bonds with their p_σ orbitals. From this point of view, the important difference between the threefold and bridge adsorption sites is the larger lateral displacement, in the threefold case, of H nuclei from surface normals through outer layer Be's. This reduces the overlap of the H(1s) orbitals with the p_σ orbitals of the surface Be's. Thus in the threefold adsorption geometries, the p_σ occupation of the outer Be muffin tins is less well restored by the presence of H adatoms, the healing of the outer-layer separation back to ideal is somewhat less and the H binding energy is reduced, relative to the bridge site.[19]

The preference for the bridge, where the H is twofold coordinated relative to the onefold atop site is surely determined by H's preference for higher coordination geometries, while the choice between the twofold and threefold geometries, as explained in the preceding paragraph, is determined by the bonding requirements of the outer Be atoms. This underlines the fact that the optimization that determines an adsorbate's bonding geometry involves a balance between the requirements of the adatom *and* of the surface in question. A similar conclusion was drawn in a recent study of H adsorption on Al(331).[20]

III. DO H(1×1)/Be(0001) OVERLAYERS REALLY EXIST?

Although the foregoing results for H(1×1) overlayers on Be(0001) provide a lesson concerning bonding energetics, the low-energy electron loss spectroscopy (LEELS) measurements of RHP make it clear that a monolayer of H does not reside in a high-symmetry site on the Be(0001) surface. A comparison of the calculated and measured work functions for H/Be(0001) makes it doubtful that one can ever realize a H overlayer comprising one H atom per surface Be. This result is consistent with the low, calculated binding energies reported in Table I.

A. Calculated work functions for H/Be(0001) overlayers

As reported in Table I, the work functions for the bridge, fcc, and hcp threefold hollow geometries are, respectively, 3.24, 3.89, and 3.45 eV, compared to my previously calculated work function of 5.5 eV for clean Be(0001).[5] [YL do not mention the values of their calculated work functions for H/Be, although they expound at length on the results for the clean surface. They obtain 5.1 eV for the clean, ideal four-layer Be(0001) slab.] Thus the calculated work function change for a monolayer of H on Be(0001) for the optimal bridge geometry is -2.3 eV. This is a very substantial work function change in itself. However, the important concern is that the measured value, reported by RHP, is only -0.4 eV for 1 ML of H. LDF calculations are far from perfect, but not that far. Modern work function measurements, in which surface defects and impurity concentrations are carefully monitored, are also reliable to much better than 2 eV.

To understand the reason for the discrepancy, I therefore return to the fact RHP only see a single, high-symmetry form of adsorbed H at coverages up to 0.4 ML, at which point the induced work function change is roughly -0.6 eV. If one ignores the interaction of the dipoles of the adsorbed H's, on the ground that the measured work function change is linear up to that coverage, then one estimates the work function that one would calculate for 0.4-ML H in bridge sites as 0.4×-2.3 eV $=-0.9$ eV. Although this is not exactly the measured -0.6 eV, it is within the range of typical LDF vs experimental discrepancies. I next assume that the new adsorption site observed in the RHP LEELS experiment above 0.4 ML corresponds to a very different dipole moment per ad-H than bridging H. According to RHP's estimate, the moment per H ("tilted bridge") must be $\frac{1}{4}$ that per H (bridge). The question is what the adsorption site may be. For example, is it a "tilted-bridge" site, as RHP suggest?

B. Other adsorption sites and the work function discrepancy

As shown in Table I, the work function changes corresponding to the threefold-symmetric adsorption geometries and the bridge are *all* large compared to the measured 0.4-eV decrease for 1 ML. At the same time, any "tilted-bridge" site is close to a short line joining a threefold site and a bridge. Thus, unless the work function versus position is a very rapidly varying function, H in a tilted-bridge site is unlikely to yield a work function change that agrees any better with experiment than in one of the symmetric adsorption geometries.

C. Photoemission spectra for H/Be(0001)

Ray, Pan, and Plummer (RPP) have recently reported measurements of angle-resolved photoemission spectra for H/Be(0001).[11] The data correspond to a coverage of 0.4 ML, such that only one site, assumed to be a bridge, is occupied. In this regime, RPP observe a 1×1 LEED pattern and find H-induced surface bands and resonances split off the clean Be band edges, that disperse roughly parabolically. Both the coverage dependence of the H-induced work function change, which is linear up to 0.4 ML, and of the surface-state spectra, which appear to be sums of spectra from clean and H-covered Be regions, suggest to RPP that H islands form at low coverages. The fact that the LEED pattern remains 1×1 suggests that the islands are domains of bridging ad-H's in nearest-neighbor surface unit cells.

On the other hand, there is both experimental and theoretical reason to disbelieve the formation of 1×1 islands. Experimentally, taking RPP's coverage measurements at face value,[21] the clean Be surface states disappear not at 1 ML coverage but at 0.4 ML. Since 60% of the surface must be uncovered at a 0.4-ML coverage of islands, one should still see the clean surface's surface states. But one does not. Theoretically, if ad-H corresponds to a large work function change, then rather large dipole moments of neighboring H's must repel each other strongly. In this case, the ad-H's should not form 1×1 islands at low coverages, but rather should spread as far from each other as possible. This means that the observed 1×1 LEED pattern should correspond to a *disordered* arrangement of ad-H's. One then wonders why the H-induced bands should disperse smoothly, i.e., why crystal momentum should remain a good quantum number. Presumably the answer is that the H-induced bands are not "H(1*s*) derived," but rather are Be bands, perturbed by a "mean field" whose strength is determined by the average areal density of H's.

If there were actually 1×1 islands of bridging H, then one would expect three domains of adsorbed H to be present on the surface. In each, the local symmetry is C_{2v}, because, as noted above, the occupation of a single bridge site per unit cell lowers the symmetry of the surface. As a consequence, the usual plots of energy dispersions along the symmetry directions appropriate to C_{3v} symmetry, i.e., $\bar{\Gamma}$ to $\bar{K}$, $\bar{\Gamma}$ to $\bar{M}$, and $\bar{K}$ to $\bar{M}$ are inappropriate. *In the C_{2v} irreducible surface Brillouin zone there are two inequivalent $\bar{\Gamma}$ to $\bar{M}$ and two inequivalent $\bar{\Gamma}$ to $\bar{K}$ directions, as shown in the inset to Fig. 1.*

For a H(1×1) overlayer in the optimal bridge geometry, Fig. 1 shows the calculated bands for the two different $\bar{\Gamma}$ to $\bar{M}$ and $\bar{\Gamma}$ to $\bar{K}$ lines in the SBZ and also RPP's data. Assuming that all three H-adsorption domains were present simultaneously during the ARUPS measurements, the data taken for the "$\bar{\Gamma}$ to $\bar{M}$ direction" should be a sum of contributions from the two inequivalent $\bar{\Gamma}$ to $\bar{M}$ directions, and similarly for the $\bar{\Gamma}$ to $\bar{K}$ data. For this reason, I have plotted RPP's experimental results for $\bar{\Gamma}$ to $\bar{M}$ in both $\bar{\Gamma}$ to $\bar{M}$ panels of Fig. 1, and similarly for $\bar{\Gamma}$ to $\bar{K}$. Notice that only one of the inequivalent $\bar{\Gamma}$ to $\bar{M}$ and $\bar{\Gamma}$ to $\bar{K}$ directions reveals a high-lying H-induced state. On the other hand, the low-lying H-induced band lies at virtually the same position along the inequivalent $\bar{\Gamma}$ to $\bar{M}$ lines and similarly for two different $\bar{\Gamma}$ to $\bar{K}$ lines. Had this not been true, RPP should have seen *two* low-lying H-induced bands.

There are several obvious, major discrepancies between the computed bands of Fig. 1 and those measured by

RPP. One is that the calculated low-lying band is a "surface state." It lies almost 1 eV below the bottom of the projected Be bulk bands. By contrast the measured low-lying H-induced state is a surface *resonance* over the entire $\bar{\Gamma}$ to $\bar{M}$ line and most of the way from $\bar{\Gamma}$ to $\bar{K}$. The energetic discrepancy between the calculated and measured low-lying bands is almost 2 eV at $\bar{\Gamma}$, and substantial elsewhere. Another glaring discrepancy is the absence, in the calculation, of a high-lying H-induced band centered at $\bar{\Gamma}$. Such a band is clearly present in the experimental data.

Although bands that emerge from LDF calculations should not agree exactly with photoemission spectra, typically the two do agree quite well for wide bands, provided that one has done the LDF calculation for the correct arrangement of surface atoms. [Consider, for example, the excellent agreement between calculated and measured surface-state bands of clean Be(0001),[5] of H/Ti(0001),[22] and of H/Pd(111).[23]] The fact that the bands in the present case are 4 to 5 eV wide thus implies that the calculation corresponds to an incorrect H-adsorption geometry. This is hardly a surprise, since as noted above, the ad-H's should repel each other and therefore they should not form islands at the 0.4-ML coverage where the measurements were done.

D. Speculations on the monolayer adsorption geometry

In their early theoretical paper, YL discuss the possibility that H occupies subsurface sites. They find that the barrier to penetrating the outer Be layer is rather high, and that the binding energy of the H in the most open interstitial site, the octahedral site, is not large. Indeed it is something like 1.5 eV less than in the bridges above the surface. However, as YL point out, these calculations are for 1×1 monolayers and do not allow for local relaxations of the Be about the subsurface H. They also note that mutual repulsion of ad-H's at higher coverages may provide the driving force for subsurface occupation.

This reasoning is consistent with the work function results discussed in Sec. III A above. Neighboring ad-H dipoles mutually repel. Dipole-dipole repulsion is a mechanism that has been proposed to explain how oxidation begins, and possibly is at work in driving H's adsorbed on Be(0001) to move subsurface. The presence of inverted dipoles, or simply the presence of numerous ad-H's that

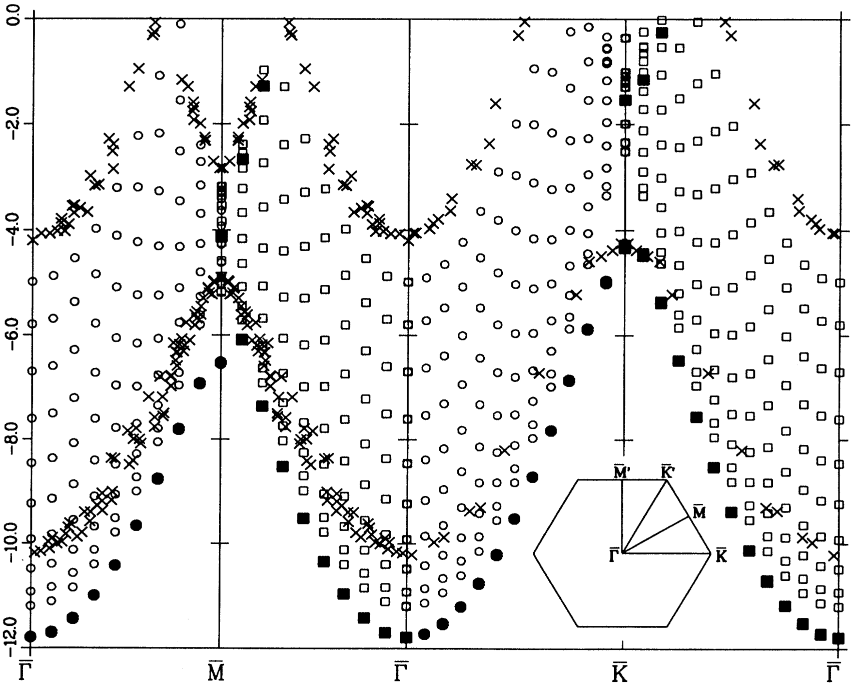

FIG. 1. Electron energy levels vs wave vector for 1 ML of H adsorbed in the optimal bridge on each side of a seven-layer Be(0001) slab, with the Fermi level at 0.0 eV. Inset: Schematic of the surface Brillouin zone. With no H's present, the irreducible part of the zone (the ISBZ) is bounded by $\bar{\Gamma}\bar{K}\bar{M}\bar{\Gamma}$. With the H adatoms in bridge sites, the ISBZ is bounded by $\bar{\Gamma}\bar{K}\bar{K}'\bar{M}'\bar{\Gamma}$. In the calculation, the projection of the H-Be bonds in the surface plane is along the x axis, i.e., the $\bar{\Gamma}$ to $\bar{K}$ direction, the leftmost panel corresponds to $\bar{\Gamma}\bar{M}$, the next panel to $\bar{M}'\bar{\Gamma}$, the third to $\bar{\Gamma}\bar{K}$, and the fourth to $\bar{K}'\bar{\Gamma}$. The experimental positions of H-induced surface features, from Ref. 17, are represented by ×'s. The experimental data plotted in the first panel are the same as that plotted in the second, and similarly for the data in the right two panels. This is because in the experiment, where all three H-adsorption domains were certainly present on the surface, data from $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{M}'$, and similarly from $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{K}'$, were collected simultaneously and indistinguishably. The solid dots and squares represent calculated states that are heavily weighted on the outer two layers of Be atoms and the H's. The dots belong to the segments $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{K}$, while the squares correspond to $\bar{M}'\bar{\Gamma}$ and $\bar{K}'\bar{\Gamma}$. The remaining calculated states are represented by open circles.

contribute nothing to the work function change, would help explain the large discrepancy between the measured work function change and that computed for monolayer adsorption above the surface.

It is also worth wondering about the meaning of RPP's remark that preliminary LEED measurements for H/Be indicate that the absorbed H does not heal the outer layer expansion of clean Be(0001). One way to reconcile this result with the calculations of Sec. III A is to assume that some of the adsorbed H is subsurface. In this case, the Be outer layer separation might have to remain large to accommodate the H underlayer.

IV. CONCLUSION

There is ample reason to pursue the issue of the atomic arrangement of H on Be(0001), both from the scientific and technological perspectives. We may learn that Be is not as ideal a first-wall material as has been hoped, or that we may have to tailor the plasma-facing surface in such a way as to inhibit H penetration. We may also expand our knowledge of the principles that govern adsorption geometries.

ACKNOWLEDGMENTS

I am grateful to E. W. Plummer and D. R. Hamann for helpful discussions, to K. B. Ray for measured H/Be(0001) surface-state dispersions in digital form, and to J. S. Nelson for performing plane-wave pseudopotential calculations that helped resolve basis convergence issues. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

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