PHYSICAL REVIEW B VOLUME 50, NUMBER 23 15 DECEMBER 1994-I

Physics of the Be(0001) surface core-level spectrum

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(Received 1 August 1994)

First-principles calculations for slabs as many as 13 layers thick show that the three surface core-level features observed on Be(0001) correspond to core-electron ionizations in its three outermost atomic layers. The calculations also imply that the experimental peak identified with core ionization in the bulk is a composite; theoretical core-ionization potentials for the fourth and deeper layers differ by as much as 90 meV. The sign and surprisingly large magnitudes of the Be(0001) surface core-level shifts (SCLS's) are attributed to unusually large surface-state contributions to the three outer layers' local densities of states. Both initial- and final-state effects are substantial in the SCLS's, and their contributions are additive.

I. INTRODUCTION

A systematic effort to understand the electronic structure of metals, from the simple to the complex, might begin with the nearly-free-electron metals and progress to the transition series. Beryllium lies surprisingly far along this road. Accordingly, in this paper, we explain the unusual core-level spectrum of the Be(0001) surface[1] using ideas quite similar to those that underlie the trends seen in surface core-level shifts (SCLS's) across the transition series.[2]

Beryllium is of course *sp* bonded, but it is far from nearly-free-electron like. Many of its properties, both bulk and surface, are anomalous, and thus of scientific interest.[3] At the same time, Be is of considerable technological importance. The interior of the world's largest experimental tokamak, the Joint European Torus (JET), was, until recently, lined with Be, and a Be plasma-facing wall is planned for the new International Thermonuclear Experimental Reactor (ITER). Understanding how H-isotopes interact with a first wall is essential to simulating plasma behavior.[4] Be is also contemplated as a component of artificially-structured x-ray mirrors. Since x-ray mirror superlattices must have very flat interfaces, the ability to control epitaxial Be growth is vital.[5] These examples suggest a need to understand Be and its surface properties in detail.

Among the anomalous attributes of the Be(0001) surface is its core-level spectrum. In addition to a peak at an ionization potential (IP) of 112 eV, attributed to 1*s* core-level ionization in the bulk, three surface features are resolved via soft-x-ray-photoemission spectroscopy (SXPS),[1] at IP's lower by as much as 0.825 eV. To put this result in perspective, the close-packed surface of Al manifests no 2*p* core-level shift, to within experimental uncertainty, while the 2*p* surface core-level feature of Al(001) is poorly resolved and is shifted by only 96 meV relative to the bulk line.[6]

We interpret the surprising Be(0001) core-level spectrum following Plummer and Hannon's idea[3] that this surface has unusual properties because a large fraction of its electrons reside in surface states. Among the *d*-band metals, SCLS's are largely the result of electrostatic fields that adjust valence-band wave functions to maintain local charge neutrality in spite of band narrowing at the surface. In the case of Be(0001), electrostatic fields are again necessary to maintain local neutrality, but now *because surface states result in very different surface-layer and bulk local densities of states* (LDOS's). Final-state screening also contributes substantially to the Be(0001) SCLS's. This contrasts with what we know of the *d*-band metals, and is an additional surface-state effect; because Be(0001)'s surface states lie near the Fermi energy, E_F, screening is energetically cheaper at the surface than in the bulk.

Typically, electronic surface states are much less important in determining the behavior of metal than of semiconductor surfaces. The reason is that surface states necessarily lie in bulk band gaps. By definition, semiconductors have absolute band gaps while metals do not. Be is an exceptional metal, however. *In bulk, hcp Be, a wide band gap, encompassing E_F, covers almost all of the Brillouin zone.*[7,8] This implies a small bulk density of states at E_F and sets the stage for significant surface state effects. The layer-resolved LDOS plots of Fig. 1 (also see Ref. 8) show just how heavily surface bands are represented in the LDOS's of the first three layers of Be(0001). In the outermost layer, they account for roughly 80% of the LDOS at E_F. The integral of the surface band contributions remains substantial in the second layer and is non-negligible even in the third.

Considering the consequences of an "excess" density of states leads to a straightforward qualitative explanation of the sign and magnitude of the SCLS's observed by Johansson *et al.*[1] in recent SXPS experiments. The basic idea is similar to the usual explanation for the SCLS trend in the transition-metal series, from large positive shifts on the left side of the periodic table to large negative ones on the right. In that case, one argues[2] that because a surface atom has fewer neighbors than a bulk atom, the LDOS in the surface layer is narrower. Since the Fermi level is the same in all layers, and since strong electrostatic forces impose layerwise charge neutrality, the surface-layer LDOS must shift. If E_F lies higher than

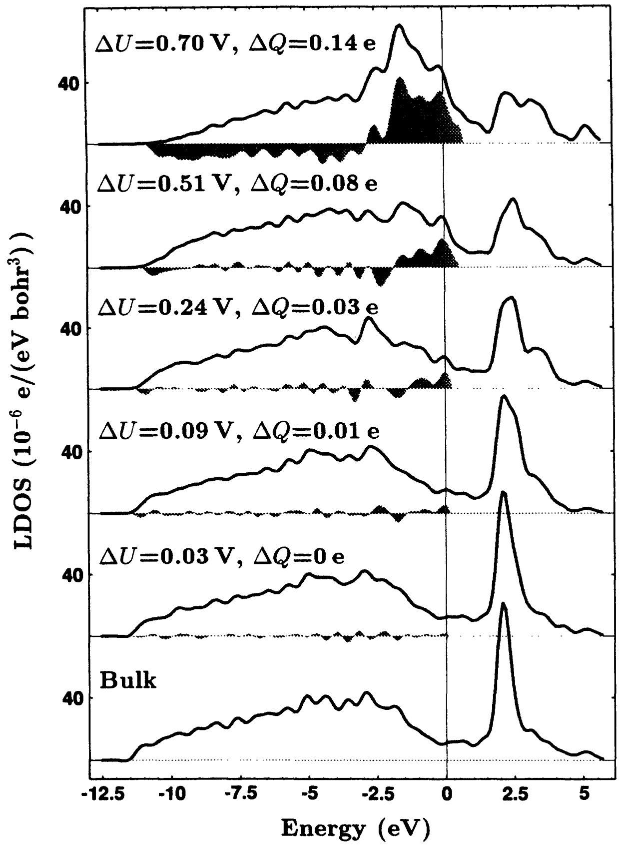

FIG. 1. Layerwise, local densities of states (solid lines) for a fully relaxed 11-layer Be(0001) slab, as computed using the supercell method. Details of the computation are explained in the main text (see Sec. IV). The uppermost panel corresponds to the outermost atomic layer. Each successively lower panel corresponds to the next deeper layer. The sixth layer is labeled "bulk." Shaded regions indicate surface contributions. For the *n*th layer, the shaded area is computed by shifting the occupied portion of the "bulk" LDOS by $\Delta U(n)$ and then subtracting it from layer *n*'s LDOS. $\Delta U(n)$ is layer *n*'s total initial-state shift. (This quantity is the sum of the ES and XC shifts for that layer, as reported in Sec. III, Table II.) The ΔQ value quoted for each layer represents the excess charge that layer would have, per atom, if there were no initial state shift. The ΔQ's equal the integrals of each layer's shaded region.

midband, the narrower LDOS must shift to lower binding energy so that it will not be overpopulated. On the contrary, if E_F lies below midband, then the surface LDOS shifts to higher binding energy so that the surface layer will not be underpopulated by electrons. The electrostatic fields that shift the surface layer LDOS's, and thus enforce local charge neutrality, are also sensed by the core electrons. Accordingly, the core-electron eigenvalue, for each layer, shifts in parallel with its LDOS, and the requirement of charge neutrality thus accounts for the observed SCLS trend across the transition metal series.

It is important to recognize that even if band narrowing, based on a reduced nearest-neighbor count, were the concept that explains the SCLS of Be(0001)'s outermost layer, this concept would not be much use in explaining shifts associated with layers 2, 3, and so on. Their atoms are fully coordinated. Thus, there is little or no second- or third-layer band narrowing. On the other hand, a glance at Fig. 1 reveals that surface contributions to the LDOS's of the first three layers of Be(0001) are substantial. Thus a different, if related, explanation of the Be(0001) core-level spectrum is necessary.

In bulk Be, the LDOS within about 1 eV of E_F is quite low (see the lowest panels of Fig. 1). Near the surface, however, the bulk LDOS is supplemented by the contributions of surface bands. If these "supplemented" LDOS's were not shifted to lower binding energies, in proportion to the "excess" integrated densities of states, then charge neutrality would be violated at the surface. Accordingly, (see Fig. 1) there is a large shift in the first-layer Be(0001) LDOS to lower binding energy, a smaller shift in the second layer, and still smaller ones in the deeper layers. As mentioned above, the fields that bring these shifts about also shift the core-electron eigenvalues by close to the same amounts. Thus, "initial-state shifts" of the bands at the surface can at least qualitatively explain the core-level spectrum of this non-*d*-band metal surface.

Final state, or screening effects in the surface layer of a metal are typically not expected to be appreciably different from those in its bulk.[9] Again, however, Be(0001) is exceptional. To understand why, recall that screening improves the binding of a core-ionized atom, and thus reduces the corresponding core-electron IP. Screening effects in each layer of a metal are roughly proportional to the corresponding E_F LDOS, because the E_F LDOS determines the ease with which electrons can polarize from filled to unfilled levels. Since the E_F LDOS's of the outer layers of Be(0001) are drastically larger than those of the bulk, screening near the surface will lead to still larger SCLS's to lower IP, supplementing the initial-state effects discussed above.

In Sec. II of this paper, we outline the calculations that establish these ideas. In Sec. III, we present and discuss our numerical results, comparing to Johansson *et al.*'s observations,[1] and documenting the dominant role of surface-state-related initial-state shifts. In Sec. IV, we speculate on the differences between the SCLS's that we obtain and those reported in Ref. 1. We suggest that one would find better correspondence between theory and SXPS experiment if the feature identified by Johansson *et al.* as a single "bulk" peak[1] were refit under the assumption that it is actually a composite of lines at slightly different energies, corresponding to core ionizations in the fourth and deeper layers.

II. NUMERICAL CALCULATIONS

In the first of the following subsections, we review the formal aspects of our SCLS calculations. Then we discuss how one may assess their systematic error and convergence levels. Finally, we specify the numerical details of our various computations. Results and their comparison to experiment are subjects of the following section (Sec. III).

A. Equivalent core formalism

To compute SCLS's from first principles, including both initial- and final-state contributions, we use the "equivalent core" or "$Z+1$ approximation."[10] This means representing a core-ionized Be atom as a substitutional "B impurity." At a core-ionization threshold, whether for a surface or an interior Be, a 1s electron is excited to the Fermi level. But E_F is the same everywhere in a crystal. Therefore, core-level IP shifts correspond directly to the energies gained by substituting "B atoms" into different crystal layers. In a layer where "B atom" substitution is more favorable, the core IP is lower.

The core-level shift for the nth layer of the crystal is defined as

$$\Delta E_C(n) \equiv I(n) - I(b) \ , \tag{1}$$

where $I(n)$ and $I(b)$ are the energies required to ionize core electrons in the nth crystal layer and in the bulk ("b"). Equation (1) establishes a sign convention: A surface core-level shift is negative if the core-ionization potential for a surface atom is lower. Modeling semi-infinite Be(0001) as a finite thickness slab, we identify "bulk" with the slab's central layer, c. The surface core-level shift for layer n is accordingly,

$$\Delta E_C(n) \equiv \Delta H(c,B,\mathrm{Be}) - \Delta H(n,B,\mathrm{Be}) \ , \tag{2}$$

where $\Delta H(n,B,\mathrm{Be})$ is the energy cost of removing a Be from layer n to infinity and replacing it with a B brought in from infinity. $\Delta H(c,B,\mathrm{Be})$ is the corresponding energy for the central layer. We allow no lattice relaxation around the substitutional B atoms, in calculating the ΔH's. This is consistent with the short time scale of a core-ionization event compared to an inverse phonon frequency.

B. Systematic errors and convergence

Two earlier theoretical efforts failed to account accurately for measured values of the Be(0001) SCLS's.[11,12] To improve on this situation, it is important to learn what theoretical approximations were at fault, or otherwise, to prove that the measured core-level spectrum was in some way "extrinsic."

In the augmented-spherical-wave[13] (ASW), Green's-function calculation of the Be(0001) core-level spectrum, by Alden, Skriver, and Johansson the one-electron potential is necessarily of the muffin-tin form, and the outer-layer separations are required to be "ideal." Reference 11 reports four SCLS's corresponding to ionization of core electrons in the outer four-crystal layers. However, no subset of the calculated shifts agrees especially well with the three surface features in Johannson *et al.*'s[1] spectra.

In a recent paper, Aldén *et al.*[14] have attempted to reduce the systematic error inherent in the ASW potential-shape approximation. This does lead to improved SCLS predictions.[14] But discrepancies of almost 0.2 eV remain between theory and experiment. Below (see Sec. III), we show that the Be(0001) SCLS's are quite insensitive to outer layer relaxation. Thus, it is likely that residual potential-shape approximation effects in Ref. 14 are responsible for the remaining discrepancy with Johansson *et al.*'s[1] SCLS's.

In Feibelman's study,[12] only the core-level shifts of layers 1 and 2 of a Be(0001) slab were found to be large enough to have been resolved in the SXPS experiment. On the basis of this result, Feibelman speculated that a plentiful surface defect of some kind might be responsible for the observation of a third line. Whether the observed core-level spectrum is intrinsic or not is an important question. We began the present work in the hope of settling it. As shown in Sec. III, we have done so. The two surface-line spectrum of Ref. 12 is an artifact of too coarse a surface Brillouin-zone (SBZ) sample. To obtain results representative of semi-infinite Be(0001), it is also important to use a thicker model slab.

In a self-consistent, local-density approximation (LDA) electronic structure calculation,[15] one seeks a variational energy minimum by iterative improvement of the electron number density,

$$\rho(\mathbf{r}) = A_{\mathrm{SBZ}}^{-1} \Sigma_s \int_{\mathrm{SBZ}} d^2k f_s(\mathbf{k}) |\Psi_s(\mathbf{r};\mathbf{k})|^2 \ . \tag{3}$$

Here $\Psi_s(\mathbf{r};\mathbf{k})$ is the one-electron, Kohn-Sham wave function[15] for band s, A_{SBZ} is the area of the SBZ, and $f_s(\mathbf{k})$ is the Fermi function. To evaluate Eq. (3)'s k-space average numerically, one approximates it as a sum over a discrete grid of k vectors, thus "sampling" the variation of $f_s(\mathbf{k})|\Psi_s(\mathbf{r};\mathbf{k})|^2$ across the SBZ. To the extent that this integrand varies rapidly with $\mathbf{k}$ an accurate determination of $\rho(\mathbf{r})$ demands a correspondingly fine k-space grid.

The surface band-structure calculations of Refs. 7 and 8 make it plain why the SBZ grid must be finer for Be(0001) than is generally the case—surface states near E_f only occur in a small portion of the SBZ. In fact, much of the large LDOS surface-state peak encompassing E_f (cf. the upper panel of Fig. 1) corresponds to surface-state contributions from the neighborhood of the point $\bar{K}$ in the SBZ, where the surface bands are rather flat. If an equal-spaced SBZ mesh has too little representation near this symmetry point, then the magnitude of the surface-state contributions to $\rho(\mathbf{r})$ will not be faithfully represented.

C. Supercell, iterative-diagonalization calculations

In order to study basis-set, SBZ-sample, and slab-thickness convergence systematically, we have performed supercell calculations using a very efficient[16] plane-wave, pseudopotential,[17,18] Car-Parrinello-type[19] implementation of the LDA.[15] The unit cell is relatively small in these calculations. It contains four atoms per crystal layer, and corresponds to a rectangular $2\times\sqrt{3}$ superlattice. (We investigate the consequences of this approximation by comparing to Green's-function calculations, as described in subsection E, below.)

To compute a value of $\Delta H(n,B,\mathrm{Be})$, we determine the total-energy change upon substituting a $2\times\sqrt{3}$ array of B atoms for Be atoms in layers n and $N+1-n$ in an N-layer Be(0001) slab. To study convergence with slab thickness, we perform calculations for $N=9$, 11, and 13. In each case, the substitution preserves reflection symmetry in the slab's central plane. This reduces the number of iterations required to achieve self-consistency of the electron density, but produces somewhat doubtful results for B substitution in the layers immediately adjacent to the films' central layers, since in that case there are two B-substituted layers separated by only one pure Be layer.

The $2\times\sqrt{3}$ unit cell has a single mirror plane perpendicular to the surface. Thus, if the in-plane Be lattice parameter is a, then the irreducible part of the SBZ (the ISBZ) is rectangle of area $\pi^2/2\sqrt{3}a^2$. To analyze k-space convergence, we compare calculations that sample the ISBZ with nine equally spaced points to corresponding calculations with 36 (cf. Sec. III, Table III).

For pure Be slabs, we use a plane-wave cutoff of 20 Ry. This cutoff yields surface energies accurate to 0.01 eV and outer-layer relaxations accurate to 0.003 bohr, or 0.1%. Since B has a stronger pseudopotential, we use a 30-Ry cutoff for total-energy calculations with B's substituted for Be atoms. Good agreement with our Gaussian-orbital-based calculations (see subsection II D) further confirms the adequacy of our choices of plane-wave cutoffs.

Since it costs little, in the Car-Parrinello approach, to optimize lattice geometry at the same time as one iterates the electron density to self-consistency, we reoptimize the outer-layer geometry for each slab thickness and k-vector sample. This results in differences in the outer-layer relaxations of the various model slabs, of the order of a few tenths of a percent, at most. Comparison with calculations for "ideal" slabs (cf. Sec. III, Table IV), however, in which all layer separations are fixed at the optimal bulk values, makes it clear that the computed SCLS's are hardly affected by relaxation changes of this order. The biggest effect is on the second-layer ionization potential and amounts to only 0.04 eV.

Finally, in our Car-Parrinello-type calculations, we use the Ceperley-Alder[20] version of the exchange-correlation potential. As noted below, this choice represents another difference between our plane-wave and matrix Green's-function calculations (cf. subsection II E) that seems to have virtually no effect.

D. Calculations of layerwise local densities of states

As discussed in Sec. I, the LDOS's of Fig. 1 are persuasive evidence that the Be(0001) SCLS's are largely a consequence of a surface-potential shift that depopulates an "excess" density of states near the surface. These LDOS's are computed as follows: First the slab is divided into bins by planes parallel to the atomic layers, such that each bin contains two valence electrons per Be atom.[21] The contribution of each eigenfunction, Ψ, to the lth bin is then taken to be the integral of $|\Psi|^2$ between the planes that define that layer. Each state is smeared out in energy using the first-order Methfessel-Paxton scheme,[22] with a smearing width of 0.4 eV. The LDOS's of Fig. 1 emerge from our supercell calculation for an 11-layer Be(0001) slab, using a 36 k-vector sample in the irreducible SBZ for the four atom unit cell corresponding to a $2\times\sqrt{3}$ superlattice.

E. Gaussian-orbital-based matrix Green's function calculations

Because (cf. Sec. III) initial-state contributions dominate the calculated SCLS's for Be(0001),[23] and because we use the same $\frac{1}{4}$ monolayer arrangement of "B atoms" in each layer for which we calculate a substitution energy, it is likely that the error attributable to the small size of our supercell is relatively small. Nevertheless, we directly test convergence with respect to supercell size, and simultaneously further test basis-set and SBZ-sample convergence by performing Gaussian-orbital-based matrix Green's-function scattering theory calculations,[9,24] in which *only one Be atom* of an infinitely extended Be(0001) slab is replaced by a B.

Apart from using initial-state Be slabs with the same number of atomic layers, our Green's function and plane-wave calculations are quite different in their particulars. Thus, comparing the results of the two approaches provides a particularly meaningful test. In the Green's-function calculations, the basis set is comprised of contracted Gaussian orbitals centered at each nucleus, plus floating orbitals in the vacuum region (see Ref. 12 for details of the basis).

For the Green's-function calculation, the initial state is a 1×1 nine-layer Be(0001) slab. Its ISBZ is $\frac{1}{12}$ of the SBZ and has an area of $2\pi^2/3\sqrt{3}a^2$, i.e., $\frac{4}{3}$ the area of the ISBZ corresponding to the $2\times\sqrt{3}$ unit cell. We sample this somewhat larger region of k space with a honeycomb lattice of 35 special k points.[25] Since our Car-Parrinello calculations show little sensitivity of the calculated core-level shifts to outer-layer relaxation, we leave the relaxation in the Green's-function calculation as was found optimal in Ref. 7. Finally, consistent with the Green's-function calculations of Ref. 12, we use the Wigner form[26] of the exchange-correlation potential in the present Green's-function work.

As detailed below, in Sec. III, the agreement between Gaussian Green's-function and plane-wave supercell results, for the nine-layer Be(0001) films is at the level of 0.02 eV, for the three SCLS's corresponding to the outer three crystal layers. This excellent comparison provides confidence that the basis sets used are adequate, that the k-vector sampling is converged, and that the use of the Ceperley-Alder as against the Wigner exchange-correlation potential does not represent a significant choice.

III. NUMERICAL RESULTS, ERROR ANALYSIS, AND COMPARISON TO EXPERIMENT

In this section, we report Be(0001) SCLS's, computed in the $Z+1$ approximation. The theoretical and experimental shifts are in excellent agreement, if one accepts the assumption that Johansson *et al.*'s SXPS "bulk" line[1] is a composite, whose peak corresponds to core ionization in the 4th and deeper crystal layers. We dwell at

TABLE I. Comparison of theoretical core-level shifts for a nine-layer Be(0001) slab, to each other, and to the experimental observations of Ref. 1. All results are in eV. The first column gives SCLS's from Ref. 1. The second and third columns report SCLS's calculated as substitution energies [cf. Eq. (2)] using the supercell and Green's-function methods. Columns 4–6 give the electrostatic, exchange-correlation, and total initial-state contributions to the supercell SCLS's. The last column gives the final-state screening contribution. It is just the difference between the "total" and "initial" supercell contributions.

	Expt	*G-fn*	Supercell				
Layer	Ref. 1	Total	Total	ES	XC	Initial	Final
1	−0.825	−0.84	−0.85	−0.57	−0.04	−0.61	−0.24
2	−0.570	−0.58	−0.60	−0.43	−0.01	−0.44	−0.16
3	−0.265	−0.24	−0.23	−0.16	−0.00	−0.16	−0.07
4		−0.06	0.01	−0.03	0.00	−0.03	0.04

some length on systematic and convergence error levels in the calculated SCLS's. We show that they are low by comparing results for different slab thicknesses, k-vector samples, basis sets and substitutional B arrangements. Finally, to permit interpretation of the Be(0001) core-level spectrum, we report electrostatic and exchange-correlation initial-state contributions to the SCLS's, as well as the remaining contribution from screening in the final state. The latter accounts for about $\frac{1}{4}$th of the shift for the outermost Be layer.

To begin, in Table I, we compare the results of Green's function, and supercell nine-layer slab calculations to each other and to the experimental results of Ref. 1. The "bulk" reference for the calculated core-level shifts in the table is the fifth or central layer of the model slab. The remarkable agreement between the two different calculations, and between either and experiment, lends support to the idea that the calculations are converged and represent a good model of reality. In particular, recall that the two theoretical approaches use different basis sets, k-vector samples, surface-layer relaxations, and exchange-correlation potentials. Nevertheless the predicted SCLS's agree to 0.02 eV.

We attribute the one notable disagreement between the two calculations, namely, their fourth layer SCLS's, to the fact that in the supercell calculation, we always substitute B atoms for Be's symmetrically in layers above and below the model slab's central layer, since film-symmetry speeds convergence. Thus to compute the supercell "fourth-layer" core-level shift, we place B's in the fourth *and the sixth* slab layers. Since they are only separated by the central Be layer, and since the low Fermi level LDOS in bulk Be implies weak bulk screening, the B's in layers 4 and 6 interact. The +0.01-eV fourth layer shift in the fourth column of Table I is an artifact of this interaction.

In the right-hand columns of Table I, we report initial-state contributions to the supercell SCLS's of the various film layers, both from the perfect Be(0001) surface's electrostatic field and its exchange-correlation potential. We compute these contributions via zeroth-order perturbation theory, as expectation values of one-electron potential components in the core-electron wave function. To deal with the fact that the spatial variation of this wave function is rapid for the equal spaced numerical integration mesh of the Car-Parrinello calculation, we extrapolate a series of results computed for smoothed approximations to it.[27]

The screening contributions to the SCLS's in the last column are obtained by subtracting the initial-state numbers from the total shifts. Notice that while the calculated shifts are dominated by the initial-state electrostatic contribution, the screening effect in the final state is far from negligible, accounting for almost $\frac{1}{3}$ of the first-layer shift.

In Table II, we compare supercell results for 9- and 11-layer slabs. As before, the SCLS's for the nine-layer slab are referred to its central, or fifth layer. However, for the 11-layer slab, the results are referred to *its* central layer, i.e., its *sixth* layer. Notice that SCLS's of the 11-layer slab are shifted by −0.06 to −0.09 eV, into generally worse agreement with experiment than was the case using the nine-layer model.

This effect is almost entirely associated with the electrostatic, initial-state shift. Evidently, screening in bulk Be is sufficiently poor that size effects on the slab electrostatic field are nonzero, even for a thickness of nine layers. This result presents two problems. The first is whether even 11 layers are enough to obtain theoretical SCLS's that are converged with respect to slab thickness. The other is how to interpret what now appears to be *disagreement* between the theoretical SCLS's and the observations of Ref. 1.

To deal with the first issue, we wish to compare results for 11- and 13-layer model slabs. Since the 13-layer calculations are quite time consuming if performed at the same level of convergence as those for thinner slabs, we first compare 11-layer initial-state electrostatic shifts using fine (36 k point) and coarser (nine point) k samples.

TABLE II. Comparison of supercell core-level shifts for 9- and 11-layer Be(0001) slabs, to each other and to the observations of Ref. 1. Theoretical SCLS's, and their electrostatic and exchange-correlation, initial-state contributions are shown. All results are in eV.

	Expt.	Total SCLS		ES		XC	
Layer	Ref. 1	9 layer	11 layer	9 layer	11 layer	9 layer	11 layer
1	−0.825	−0.85	−0.94	−0.57	−0.66	−0.04	−0.04
2	−0.570	−0.60	−0.67	−0.43	−0.50	−0.01	−0.01
3	−0.265	−0.23	−0.29	−0.16	−0.23		
4		0.01	−0.09	−0.03	−0.09		

TABLE III. Comparison of initial-state electrostatic contributions to the SCLS's of 9-, 11-, and 13-layer Be(0001) films for fine (36 *k* vectors) and coarse (nine vectors) surface Brillouin-Zone samples. The calculations were done using the supercell method. All results are in eV.

	36 *k* vectors		9 *k* vectors	
Layer	9 layer	11 layer	11 layer	13 layer
1	−0.57	−0.66	−0.68	−0.68
2	−0.43	−0.50	−0.47	−0.48
3	−0.16	−0.23	−0.19	−0.20
4	−0.03	−0.09	−0.08	−0.08
5		−0.03	−0.02	−0.02

The duration of the supercell calculations scales linearly with the number of *k* points. The second and third columns of Table III show that results for the coarser *k*-space mesh differ by at most 0.04 eV from those for the finer one. This justifies using the coarser *k*-space mesh to study convergence with respect to slab thickness. Accordingly, we now compare electrostatic potential shifts between 11- and 13-layer films, based on coarse *k*-space samples. The results in the third and fourth columns of Table III imply that at a thickness of 11 layers, the calculated SCLS's are converged to 0.01 eV.

The question that remains is why the 11-layer results seem to disagree with Johansson *et al.*'s experiment,[1] while the nine-layer theoretical results agreed to within 0.03 eV. A reasonable guess is that the "bulk" feature in Ref. 1 is a composite of electrons emerging from core ionizations in the fourth and deeper layers. The position of the "bulk" peak thus represents an average of the ionization potentials corresponding to layers 4, 5, 6, etc. Were the experiment redone using higher-energy incident x-rays, our results imply, the bulk peak would appear to shift downward. If it shifted down by −0.07 eV, at the highest energies, then the experimental results would once again agree reasonably well with those which we calculate for the 11-layer film[28]

A final note concerns the question of the sensitivity of the SCLS's to geometry optimization. Returning to Table I, note that the Green's function and supercell SCLS's for the nine-layer slab are in excellent agreement despite the fact that the outer-layer relaxations in the two calculations are not identical. In the Green's-function case, we used the results Ref. 7, 3.9%, and 2.2% expansions of the outer-two-layer separations, while in the supercell computation we used 2.6% and 0.8%. This suggests that the Be(0001) SCLS's are simply not sensitive to outer-layer relaxations at the level of a few percent.

On the other hand, attempting to rationalize the discrepancy between the observed Be(0001) core-level spectrum, and their ASW calculation Aldén, Skriver, and Johansson[11] suggest that their use of the ideal rather than the relaxed outer-layer geometry may be at fault. We address this conflict of ideas, by comparing SCLS's calculated for relaxed and ideal 9- and 11-layer slabs.

In Table IV, we give results from full $Z+1$ approximation calculations for the outer-two-layers' shifts. Since the geometric-relaxation dependence of the final-state effect is already quite small in layers 1 and 2, and since the exchange-correlation (XC) initial-state contributions to the SCLS's is negligible below layer 2, we only look at the electrostatic initial-state effect for layers 3 and deeper. Notice that the biggest effect of optimizing the outer-layer geometry is the SCLS's of the second-crystal layer, and even there it only amounts to 0.04 eV. This makes it clear why the Green's function and supercell results do not disagree despite different outer-layer positions, and also shows that the trouble in the ASW calculations lies elsewhere, presumably in the potential shape approximation intrinsic to that electronic structure method.

IV. DISCUSSION

Johannson *et al.*[1] report three surface core-level IP's shifted by −0.825, −0.570, and −0.265 eV relative to the IP for a "bulk" atom. Our most accurate calculation, for an 11-layer slab, implies core-level shifts of −0.94, −0.67, −0.29, and −0.09 eV for layers 1–4, and −0.03 eV for the fifth layer, if one assumes that the screening shifts for the fifth layer are negligible. These results are all referenced to the IP of the sixth, or central slab layer. If, instead, we referenced to an IP that is an average of those of the fourth and fifth slab layers, say at −0.07 eV,

TABLE IV. Comparison of supercell core-level shifts for 9- and 11-layer Be(0001) films of relaxed as against unrelaxed outer-layer separations. Full SCLS's are given for the outer two layers. Initial-state electrostatic (ES) contributions are given for all layers. The ES contributions for the inner layers are on the order of only 0.01 eV. A similar magnitude can be expected for the full SCLS's in the Be interior. The largest effect of geometric relaxation, 0.04 eV, is on the second-layer shift. All results are in eV.

	9 layer, relaxed		9 layer, ideal		11 layer, relaxed		11 layer, ideal	
Layer	Full	ES	Full	ES	Full	ES	Full	ES
1	−0.85	−0.57	−0.85	−0.57	−0.94	−0.66	−0.92	−0.65
2	−0.60	−0.43	−0.64	−0.46	−0.67	−0.50	−0.69	−0.53
3		−0.16		−0.17		−0.23		−0.24
4		−0.03		−0.04		−0.09		−0.09
5						−0.03		−0.02

then we would find SCLS's of −0.87 eV, −0.60 eV, and −0.22 eV, not in perfect agreement with Ref. 1, but not far off. Moreover, if the data of Ref. 1 were refit, assuming that the "bulk" line is a composite of two or more features, it is possible that the new "best fit" surface IP's would change somewhat, perhaps yielding still better agreement between theory and experiment. Such a refit is warranted in any case, to try to place experimental limits on the core-level IP differences for layers 4, 5, and 6.

ACKNOWLEDGMENTS

We are pleased to acknowledge many useful discussions with J. B. Hannon and E. W. Plummer. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000. The work of R. Stumpf is also supported by NEDO, The New Energy and Industrial Technology Development Organization of Japan.

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[21] The dividing planes are symmetric with respect to reflection in the film's central plane. However, they are not precisely equally spaced, even in the slab interior, mainly because of the long screening length in bulk Be. Relative to $c/2$, the spacing between bulk Be layers, the spacings of the dividing planes are $0.981c/2$, $0.990c/2$, $0.995c/2$, $1.002c/2$, and $1.013c/2$, for layers 6, 5, 4, 3, and 2. The first-layer bin is defined by the plane between the first and second layer of Be nuclei on one side, and a plane at infinity on the other.

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[28] Since curve fitting is an essential part of extracting SCLS's from the experimental data, assuming more than four lines will in itself lead to somewhat different values of the observed SCLS's.

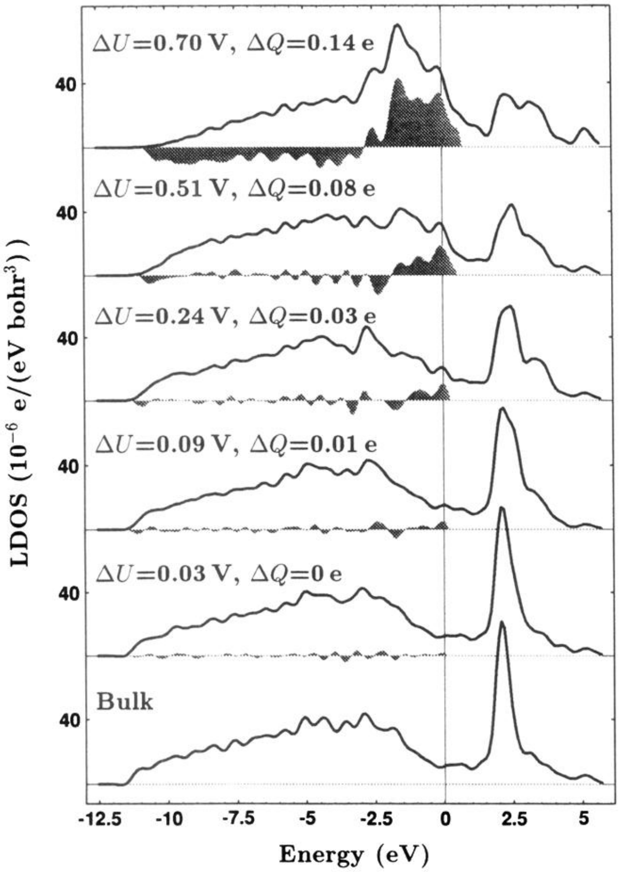

FIG. 1. Layerwise, local densities of states (solid lines) for a fully relaxed 11-layer Be(0001) slab, as computed using the supercell method. Details of the computation are explained in the main text (see Sec. IV). The uppermost panel corresponds to the outermost atomic layer. Each successively lower panel corresponds to the next deeper layer. The sixth layer is labeled "bulk." Shaded regions indicate surface contributions. For the *n*th layer, the shaded area is computed by shifting the occupied portion of the "bulk" LDOS by $\Delta U(n)$ and then subtracting it from layer *n*'s LDOS. $\Delta U(n)$ is layer *n*'s total initial-state shift. (This quantity is the sum of the ES and XC shifts for that layer, as reported in Sec. III, Table II.) The ΔQ value quoted for each layer represents the excess charge that layer would have, per atom, if there were no initial state shift. The ΔQ's equal the integrals of each layer's shaded region.