

Beryllium-hydrogen ultrathin films. I. Metallic behavior of the BeH₂ monolayer

J. Z. Wu and S. B. Trickey

Quantum Theory Project, Department of Physics and Department of Chemistry, University of Florida, Gainesville, Florida 32611

J. C. Boettger

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Equilibrium lattice parameters, total energies, the in-plane energy second derivative, and Kohn-Sham energy bands for the BeH₂ 1-layer are determined by all-electron, full-potential, local-density-functional calculations. The BeH₂ 1-layer is predicted to be metallic, in contrast with a previous Hartree-Fock calculation which predicted large-gap insulating behavior. By direct calculation, this disparity is traced to basis-set restrictions in the Hartree-Fock calculation that drive the highly localized Be surface state into the conduction band. The minimum-energy lattice constant a , (i.e., the square edge that is twice the Be-H distance) for the BeH₂ 1-layer is 5.51 a.u. The calculated H-H distance is 3.90 a.u., lower than Switendick's empirical criterion (3.97 a.u.) for stable metal hydrides but still well above the 3.40 a.u. involved in Overhauser's conjecture about superconductivity in LiBeH₃.

I. BACKGROUND AND MOTIVATION

Recently Overhauser¹ directed attention to hydrides of low- Z metals, e.g., LiBeH₃, as a possible approach to the design of high- T_c superconductors. The key physics is to obtain metallic-atomic-hydrogen-like behavior by contriving a crystal with both high atomic and electron density. From appraisal of x-ray powder diffraction data, Overhauser proposed a modified perovskite structure for LiBeH₃ with a lattice parameter of 9.62 a.u. This conjecture corresponds to a H-H distance of 3.40 a.u., substantially below Switendick's long-standing empirical criterion for stable metal hydrides, namely, that all of them have H-H distances greater than 3.97 a.u.²

Overhauser's suggestion motivated an unrestricted Hartree-Fock (HF) embedded-cluster calculation³ for several possible LiBeH₃ structures. The resulting equilibrium lattice parameters (i.e., cube edge length), 10.56→11.48 a.u., are somewhat larger than Overhauser's proposal. Reference 3 also made a detailed investigation of the charge distribution and electronic structure via embedded-cluster (to as many as 27 atoms), local-spin-density-approximation (LSDA) calculations. As is appropriate with the extrapolation of cluster eigenvalues to predict crystalline band structures, those authors were cautious about the metallic character, if any, of bulk LiBeH₃. From both the directional bonding seen in the density and from the relatively featureless (but nonzero) density of states at the Fermi level, they concluded that bulk LiBeH₃ "does not have as much metallic character as previously expected." They remarked, however, that the total density of states "resembles strongly those found in ... high- T_c materials" and discussed features in the density and bonding which produce corridors for electron conduction. There is at least the suggestion in the cluster results, therefore, that both LiBeH₃ and its BeH₂ planes might be a peculiar metal.

A pseudopotential LSDA calculation⁴ of the total energy of LiBeH₃ in two ordinary cubic perovskite structures, Be centered and Li centered, found the Be-centered version to be energetically favored by 0.77 eV/atom. That Be-centered phase is predicted to be a semiconductor, however, with a band gap of 0.8 eV. Furthermore, its predicted lattice constant is 6.01 a.u. much larger than the ordinary cubic perovskite lattice constant, 4.81 a.u., which seems to correspond most simply to the structure Overhauser proposed. Almost concurrently,⁵ Martins reported pseudopotential, total-energy LSDA calculations on several candidate structures for LiBeH₃. In summary he found the solid to be an ionic insulator with an energetically favored pseudocubic silicate structure whose band gap is 1.9 eV at an equilibrium density about half that suggested by Overhauser. Allowing for differences in LSDA models, the modified perovskite band structures reported by Yu and Lam⁴ and by Martins⁵ are identical with a bit less than 1 eV band gap. [An earlier LDA calculation⁶ in the $X\alpha$ approximation (at $\alpha=1$ to attempt at least rough compensation for known problems of gap compression in Kohn-Sham one-electron energies) and with the cubic perovskite lattice constant fixed straightforwardly at 4.81 a.u., had found semiconducting behavior with a 0.21 eV indirect band gap.]

Seel *et al.*⁷ have calculated the equilibrium lattice constants and one-electron energies of LiBeH₃ in the HF approximation for the ordinary cubic perovskite crystal and for a 27 atom cluster corresponding to that cubic perovskite using the unrestricted HF approximation plus correlation corrections. Again, the calculated lattice constant, 6.24 a.u., is significantly larger than the conjectured 4.81 a.u. and the system is found to be a large (indirect) band-gap insulator, even after allowing for usually substantial correlation corrections to the HF gap (50% or more). Because of the importance of the BeH₂ planes in Overhauser's scheme, Seel *et al.* also calculated the HF

equilibrium lattice constant and one-electron energies for a BeH_2 square monolayer (1L hereafter). The equilibrium lattice constant, 5.86 a.u., is decreased from the value for LiBeH_3 . However, they find that the 1L one-electron energies are good replicas of the two lower (of three) valence bands of the LiBeH_3 crystal and the large-band-gap insulator behavior remains in the HF treatment of the BeH_2 1L.

Except for Seel *et al.*,⁷ the formation of the BeH_2 1L is unexamined. In particular, no LDA study existed prior to the present work to provide interconnection among the previous studies. This omission is important since there is at least the possibility of contradictory predictions^{3,7} about whether the BeH_2 planes are conducting, an issue critical to the problem of LiBeH_3 behavior. It also appears that a surface-state precursor, which we had previously shown to cross the Fermi level in the Be, 1L, 2L, and 3L,⁸ lies above the band gap in the calculation of Seel *et al.* The positioning of that highly localized Be surface state is critical to the understanding of conductivity (or its absence) in the BeH_2 1L. To explore these and related issues we report here an all-electron, full-potential, LDA determination of the equilibrium lattice parameters, total energies, the intraplanar uniaxial energy second derivative, Kohn-Sham eigenvalues, and Fermi energy for the BeH_2 1L. (In Paper II (Ref. 9) we report complementary results for the three distinct registered heterogeneous 2L's comprised of one hexagonal Be 1L and one hexagonal H 1L apiece).

II. SYSTEM AND CALCULATIONAL PROCEDURE

The BeH_2 1L structure corresponding to a plane in cubic perovskite LiBeH_3 is shown in Fig. 1. The square-cell lattice constant and nearest-neighbor distance will be denoted a_s and a_{NN} , respectively ($a_s = 2a_{\text{NN}}$). Various neighbor spacings will be indicated by obvious species subscripting, e.g., a_{BeH} .

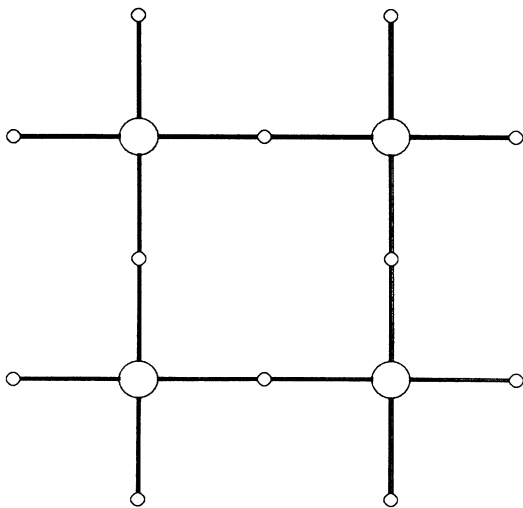


FIG. 1. Portion of the square BeH_2 monolayer showing relative orientations of Be and H as viewed normal to the film. Large circles are Be, small circles are H.

The Hedin-Lundqvist LDA for the exchange-correlation energy density was used throughout. In this context, the calculations are entirely first principles in that they are fully self-consistent, include all electrons (no pseudopotentials are used), and make no assumptions about the shape of the potential. The Kohn-Sham equations are solved using linear combination of Gaussian-type orbitals fitting function techniques¹⁰ embodied in the program FILMS.^{10(b),10(c)} Those algorithms depend on three Hermite-Gaussian basis sets, one to expand the Kohn-Sham orbitals (the KS basis), an auxiliary one to expand the electron number density (the Q basis), and a second auxiliary one to expand the LDA exchange-correlation kernels (the XC basis).

The $9s5p$ KS basis for Be was the same as used in previous Be 1L studies,^{10(b)} while the $3s1p$ H basis was as in Ref. 10(a), namely, Van Duijneveldt's $3s$,¹¹ augmented by a p with exponent 1.000. The Q bases were generated primarily according to Dunlap's rule,^{10(b)} i.e., $9s5d$ for Be and $3s1d$ for H. The XC basis for Be was $4s2d$ and $2s1d$ for H. The Be XC basis was generated from the KS basis by removing the first, third, fifth, seventh, and ninth s functions, and the first, third, and fifth d functions, and leaving the exponents unaltered in the remaining functions, except for the most diffuse d , which is changed from 0.17 to 0.12.

The calculations utilized 21 points in the irreducible wedge of the two-dimensional Brillouin zone. All were converged to an iteration-to-iteration shift in total energy of $1 \mu\text{hartree}$. We have introduced the Broyden-II convergence stabilization algorithm¹² in the self-consistent segment of FILMS, both to reduce the total number of iterations required (roughly a factor of 2 is achieved) and to stabilize otherwise nearly nonconverging cases.

III. RESULTS

We show the total energy as a function of lattice constant $a_s = 2a_{\text{NN}}$ of the BeH_2 1L in Fig. 2. The calculated equilibrium value for a_s is 5.51 a.u., at which spacing the

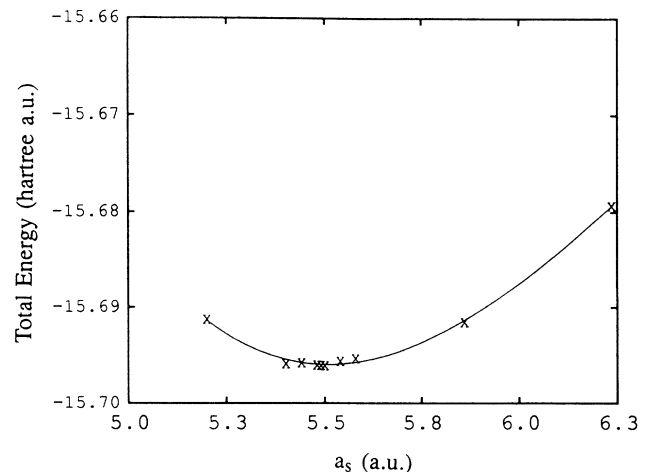


FIG. 2. The total energy as a function of a_s for the BeH_2 monolayer.

TABLE I. Be-H and H-H equilibrium distances for monolayers and clusters from various calculations as referenced, along with a relevant molecular bond length.

Source	a_{BeH} (a.u.)	a_{HH} (a.u.)
This work	2.75	3.90
Seel <i>et al.</i> (Ref. 7)	2.93	4.14
Press <i>et al.</i> (Ref. 3)	2.82	3.99
Yu and Lam (Ref. 4) (semicond.)	3.01	4.25
Yu and Lam (Ref. 4) (metal)	4.25	4.25
BeH molecule ^a	2.53	
Hexagonal H 1L		2.65

^aR. Colin and D. DeGraf, *Con. J. Phys.* **53**, 2142 (1975).

calculated total energy per cell is -15.696085 hartree (from a third-degree polynomial fit to the calculated energies). The calculated equilibrium intraplanar force constant, $\partial^2 E / \partial a_s^2|_0$, is 8.91×10^{-2} hartree/a.u.² (also from a third-degree polynomial fit). With respect to equilibrium 1L Be and two H 1L's, the BeH₂ 1L is thus bound by 0.04 hartree/cell.

The equilibrium value for a_s corresponds to H-H distance of 3.90 a.u. and a Be-H distance of 2.75 a.u. What is particularly interesting for the Overhauser conjecture¹ is that we find an a_{HH} below the Switendick² empirical threshold of 3.97 a.u. for stable metal hydride a_{HH} 's. Since none of the metal hydrides on which that threshold is based is a high- T_c superconductor, it has been believed that an a_{HH} substantially smaller than the Switendick threshold is a necessary condition for a hydrogenic high- T_c superconductor. Unfortunately, Overhauser's conjectured LiBeH₃ structure requires $a_{\text{HH}} = 3.40$ a.u., well below what we calculate.

Table I compares calculated equilibrium values of a_{HH} and a_{BeH} . There one sees that the only other work specifically on 1L BeH₂, the HF calculation of Seel *et al.*,⁷ finds $a_{\text{HH}} = 4.14$ a.u., more than 6% longer than

our result and well above the Switendick threshold. In fact, the only other calculation on a Be-H system of any kind even to find a value at the Switendick threshold is the UHF cluster designated as 2c in Ref. 3. Notice, also, that the H ions are not particularly "large" in our calculation, since a_{HH} for the hexagonal H 1L is much smaller than in the BeH₂ 1L.

The Kohn-Sham band structure for the BeH₂ 1L along the high-symmetry lines of the two-dimensional Brillouin zone is in Fig. 3, along with a plot of the density of states. The system is clearly metallic with a work function of 4.1 eV. This is in quite marked disagreement with the results of Seel *et al.*⁷ which found a large band gap (about 7.5 eV).

It is easily seen that the metallic behavior we find is not a consequence of the well-known problem of KS band-gap underestimation.¹³ Though there are cases in which the KS band gap is reduced to zero or nearly so for systems known experimentally to be small-band-gap semiconductors [see Table I of Ref. 13(a) for convenience], there is no known example of a 5–7 eV reduction from the actual gap to the KS gap. Furthermore, the largest known spurious reduction is in NiO which involves a transition metal and, hence, another trait of the LDA, noninteger occupancy of atomic states. That problem is not relevant here. Instead, as we now will show, understanding both the disagreement of the HF film results with the present ones and the interpretation of the BeH₂ 1L band structure depends on a detailed comparison with the LDA band structure for bulk LiBeH₃.

The relevant LDA LiBeH₃ band structure is for the Be-centered structure found by Yu and Lam⁴ to be lowest in energy; see Fig. 2(a) of Ref. 4. In going from that bulk band structure to the BeH₂ in Fig. 3, all but one of the bulk bands are left essentially unaltered in shape. For these there is a simple lowering of the conduction band relative to the valence bands. (The top bulk valence band

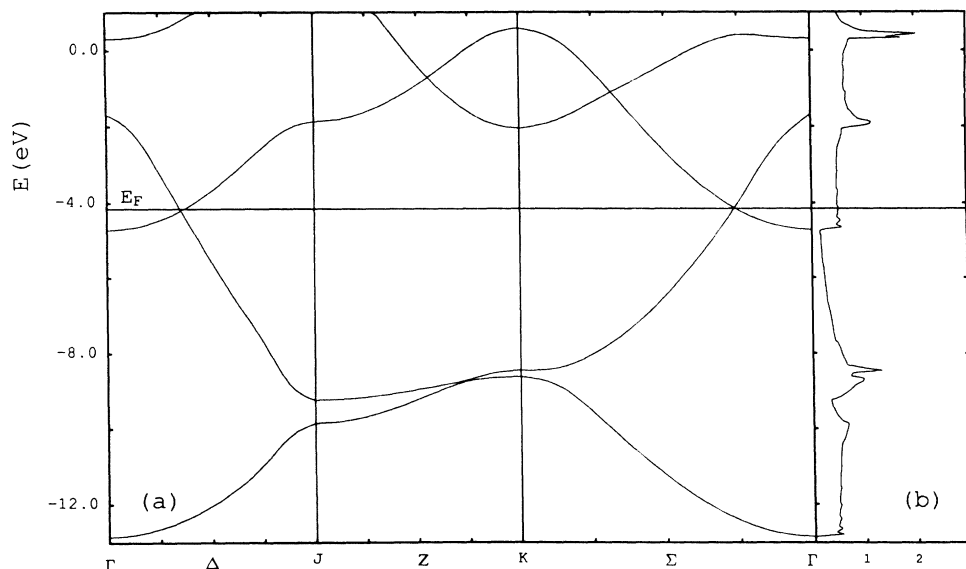


FIG. 3. Kohn-Sham band structure and DOS (states/eV cell) for the BeH₂ monolayer.

is associated with the H atoms which lie above and below the BeH_2 plane and thus does not appear in the $1L$ band structure.) This qualitative behavior is in good agreement with that found in the HF calculations by Seel *et al.*⁷ in going from the bulk to the $1L$. However, for LDA band structures, the bulk band gap is sufficiently small that the relative lowering of the conduction bands is, in itself, capable of producing weakly metallic behavior upon going over to the $1L$.

Comparison of our $1L$ band structure with the bulk band structure of Yu and Lam⁴ also reveals two singly degenerate $1L$ bands which do not appear in the bulk bands. The lower of the two has odd symmetry with respect to inversion through the x,y plane, is partially occupied, and cuts across the two bands derived from the highest valence band and lowest conduction band of the bulk. This band is responsible for the strong metallic character of the $1L$. Inspection of the orbital coefficients of the odd-symmetry band reveals that it is derived from the Be $2p_z$ state. A similar Be $2p_z$ band appears in the LDA band structure of hexagonal $1L$, $2L$, and $3L$ Be films.⁸ It has been identified unequivocally as a precursor to an experimentally observed surface state on the Be(0001) surface. Based on this correspondence with the Be(0001) $1L$ and the fact that the odd-symmetry band in Fig. 3 does not appear in the bulk band structure of LiBeH_3 , it is reasonable to identify that odd-symmetry band with the highly localized Be surface-state band.

With the identification of the odd-symmetry $1L$ band as a Be surface state, it is straightforward to understand the behavior of the $1L$ relative to the bulk. When the BeH_2 layer is embedded in the solid, the electrons are confined in a relatively small volume of space. With that constraint, the lowest energy configuration is largely ionic in character with a significant transfer of electrons from the Be atom to the two H atoms and a band gap arises in the solid. When the surrounding medium is removed to produce the BeH_2 $1L$, it is then energetically preferable for some of the electron charge to be transferred into the vacuum region by occupying the Be surface state, which is intrinsically metallic in nature. The transfer of charge into the vacuum and away from the Be nucleus then produces a potential well near the nucleus which in turn results in a lowering of the Be-derived conduction bands (such as the singly degenerate band which appears near the vacuum level of the $1L$ but is not seen in the bulk LDA bands of Yu and Lam⁴).

While the differences between the LDA bulk band structure found by Yu and Lam⁴ and the LDA $1L$ band structure are easily accounted for, it is difficult to understand how HF theory used by Seel *et al.*⁷ and LDA theory could produce such radically different results for both the bulk and the $1L$. Given the importance of the Be $2p$ state in determining the behavior of the $1L$, the most obvious candidate for the source of the discrepancy between the HF results of Ref. 7 and the present results is the use of a very small basis set in Ref. 7 (which used only one rather tight p exponent). To test this conjecture, we repeated our calculation using as the KS basis the same contracted Gaussian orbital basis set used in Ref. 7, in conjunction with very rich Q and XC fitting function

basis sets which were tested carefully for their adequacy and quality. That restricted KS basis set produces a LDA $1L$ band structure (at the same lattice constant as used by Ref. 7) which is qualitatively the same as that obtained by Ref. 7, except that the conduction bands are lowered relative to the valence band to produce a band gap of only 1.32 eV as opposed to the HF gap of about 7.5 eV. It is particularly significant that use of the restricted KS basis causes the Be surface-state band to be shifted up in energy by about 6.5 eV relative to the valence bands and to be reduced in width from about 4 to 1.2 eV, in reasonable agreement with Ref. 7. Thus it is rather clear that the small basis set used in Ref. 7 is incapable of producing metallic behavior in the BeH_2 $1L$, and may therefore be inadequate to describe bulk LiBeH_3 properly as well.

This comparison of the $1L$ bands using our rather rich basis set and the small basis set used in Ref. 7 is of some more general importance, since small basis sets also have been used to study hexagonal films of Be.¹⁴ A related problem may be the reported strong sensitivity of calculated band energies¹⁵ to small changes in basis set exponents exhibited by a version of the code used in Ref. 7. An earlier analysis of this problem is in Ref. 8.

We find the density of states at the Fermi level for the BeH_2 $1L$ to be 0.52 states/eV, as compared with 0.34 states/eV for the bare Be $1L$.^{10(c)} The shape of the density of states (DOS) (Fig. 3) is rather interesting. The peak from Be $2s$ together with the p_z surface-state precursor,⁸ found just below ϵ_F in the Be $1L$, is broken apart in $1L$ BeH_2 . The Be $2s$ component is shifted down roughly 4 eV, where it comes close to the H s -type valence band on the zone boundary to produce a double peak. Meanwhile, the flat p_z stays about where it was in the Be n layers,⁸ thus generating a step in the DOS about 1 eV below ϵ_F . The result is that the BeH_2 $1L$ is predicted to be a rather better metal than is the Be $1L$. Interestingly for Overhauser's conjecture about superconductivity, while there is not a strongly peaked DOS at the Fermi surface, there is a broad plateau. These features differ dramatically from the cluster DOS of Ref. 3, which seems to be dominated by localized H states.

IV. CONCLUSIONS

The only other BeH_2 $1L$ results (Seel *et al.*⁷) differ qualitatively from ours. We obtain a metallic BeH_2 $1L$ while they predicted wide-band-gap insulating behavior. The difference is strongly dependent on the choice of basis set. In particular, LDA calculations seem to represent the key Be surface state correctly, whereas Hartree-Fock calculations with the basis sets used so far do not. We cannot speculate on the outcome of a HF calculation with a rich basis, but with the behavior of the BeH_2 plane as a key issue in understanding LiBeH_3 , such a calculation would be timely.

Assuming that the LDA calculations on bulk LiBeH_3 by both Yu and Lam⁴ and by Martins⁵ and the BeH_2 $1L$ calculations reported here are all equally reliable (as we

believe they are), there are important implications. By analogy with the behavior of the Be surface state on Be(0001), we have good reason to expect that the Be surface state evident in Fig. 3 will persist even when the BeH₂ 1L forms the surface of a thicker film. This suggests that if one were to prepare a sample of LiBeH₃ in the cubic perovskite structure so as to expose a square BeH₂ plane, the resulting system would be a bulk insulator with a conducting surface. It should be possible to produce a similar result by depositing an epitaxial 1L of BeH₂ on a square symmetry surface of an insulating sub-

strate. Thus several rather subtle tests of the BeH₂ 1L band structure predicted in Fig. 3 should be achievable.

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