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First-principles total-energy study of hydrogen adsorption on Be(0001)

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The adsorption of atomic hydrogen on the Be(0001) surface is studied using an *ab initio* pseudopotential method. The two hollow sites, the bridge site, and the on-top site are considered. We find that the bridge site has the lowest energy among the sites considered, in agreement with a recent experiment. The preference for the bridge site is the result of the attractive p potential of the substrate Be atoms. The calculated frequencies of hydrogen vibration perpendicular to the surface are compared with electron energy-loss spectroscopy measurements. The energetics of the hydrogen going into the subsurface octahedral site is investigated; the subsurface site is found to be at a much higher energy than the surface site. The surface energy and the work function of the clean Be(0001) surface are also calculated.

I. INTRODUCTION

The study of the adsorption process has continually received intensive experimental and theoretical attention. The adsorption of hydrogen on a metal surface presents a particularly simple physical system for theoretical investigation of substrate-adsorbate interaction because of the simple electronic structure of the hydrogen atom. Up until now, the experimental and theoretical efforts on hydrogen adsorption study have been focused on transition-metal surfaces. Realistic first-principles calculations have been performed for hydrogen on surfaces of various transition metals, e.g., W, Ni, Pd, and Ru.[1-4] This is partly owing to the technological importance of these systems; the transition metals are used in processes such as catalysis. The study of hydrogen adsorption on simple (sp) metals is also important. For example, the lightweight metals are ideal as a hydrogen storage medium because of their high concentration of hydrogen per unit weight. A desirable property is good absorption and desorption kinetics, which is influenced by the metal-hydrogen interaction at the surface. However, few experimental adsorption studies on simple metal surfaces were performed until recently.[5,6] Theoretically, surface adsorption on free-electron-like metals such as Na, Mg, and Al are relatively easy to treat and were investigated early by using the jellium model for the metal substrate, and including the effect of the lattice potential (pseudopotential) via first-order perturbation.[7] On the other hand, more of a first-principles approach is needed to treat a metal substrate of first-row elements such as Li and Be, because they have relatively strong pseudopotentials.

In this paper, we report the result of our first-principles calculation of the adsorption of atomic hydrogen on the Be(0001) surface. This system is chosen because there exist recent experimental results on this system.[6] Although the electronic configuration of the Be atom is simple, the Be crystal exhibits some unusual physical properties.[8] Its electronic band structure and density of states are different from the free-electron-like metals.[8] The interaction between Be and H is also quite unusual. BeH_2 was thought to consist of chains which contain hydrogen bridges, and covalent bonding was postulated.[9] However, a recent experiment determined the structure to be body-centered orthorombic, in which each unit cell contains 12 corner-sharing BeH_4 tetrahedra.[10] The structure has no analog among other tetrahedra-forming materials such as BeF_2, SiO_2, and GeO_2.[10] It is thus interesting to investigate the bonding between Be and H. Direct theoretical study of the electronic bonding in this crystal using a first-principles method is difficult because of the large unit cell. The investigation of hydrogen adsorption on Be offers an opportunity to study some aspects of the bonding between hydrogen and beryllium.

There are previous theoretical treatments of H/Be(0001). Bagus and co-workers[11] have made extensive investigations using the cluster model. However, their calculated adsorption energy of hydrogen suffered large nonuniform variations from one cluster size to another.[11] The slab geometry commonly used in first-principles calculations was employed in the work of Angonoa *et al.*[12] using the self-consistent-field Hartree-Fock (SCF-HF) method. Although a few results were given for the adsorption energy and the bond distance, their work was focused on the electronic structure. No attempt was made to determine the stable adsorption site due to a relaxed tolerance used to reduce the computational cost, which severely limited the accuracy of the calculated total energy.[13] Furthermore, the adsorption in the bridge site, which is important in the present system, was not considered. Ray and Plummer[6] have recently performed various experiments on chemisorbed atomic hydrogen on the Be(0001) surface. In particular, the vibrational frequencies of the adatom were measured using the electron-energy-loss spectroscopy (EELS) technique. Different vibrational modes were observed at low and high coverages. The low-coverage vibrational mode was tentatively assigned to the bridge site.[6] The result of the cluster calculations of Bagus and co-workers[11] is in contradiction to this assignment.

We have calculated the adsorption energy of the hydrogen at different adsorption sites and found that the bridge site is favored over the two hollow sites and the on-top site, in agreement with experiment.[6] Our calculation also gives results for the equilibrium Be—H bond distances, which can be compared with the bond distances in crystalline BeH_2, and the frequencies of hydrogen vibration perpendicular to the surface, which can be compared with the EELS experiment. The energetics for the hydrogen going into the subsurface sites is also investigated; we find that it is highly unfavorable for the hydrogen to be in the subsurface octahedral site. By using a slab of Be thicker than used in previous calculations, we obtain a result for the surface energy of clean Be(0001) surface, which is an important parameter of the surface. We also calculate the work function of the Be(0001) surface and find it in good agreement with experiment. The rest of the paper is organized as follows. A general description of our supercell calculation is described in Sec. II. The results of our calculation are given in Sec. III, and Sec. IV concludes the paper with a discussion.

II. CALCULATION

Our calculation uses an *ab initio* pseudopotential method[14] within the density-functional formalism.[15] The Hedin-Lunqvist form for the exchange-correlation potential[16] is employed. Calculations are performed self-consistently in a plane-wave basis.[17] The pseudopotentials are generated via the method of Hamann, Schlüter, and Chiang.[18] The pseudopotential of the Be atom is generated in the electronic configuration of $1s^2 2s^1 2p^1$ and has been used previously in the calculation of bulk Be crystal.[8] By allowing both the a and c axes to relax, the calculated equilibrium lattice parameters of the Be crystal are in agreement with experiments to within 2%.[8] The supercell method[19] is used in the present calculation. In this method, slabs which are comprised of a substrate, adsorbed atoms, and vacuum regions are arranged periodically in the direction perpendicular to the surface. A surface calculation is thus treated on an equal footing with a bulk calculation; the same code can be used for both calculations. In the present work, there are four Be layers in a slab and the slabs are separated by a vacuum region which has a thickness equivalent to that of six Be layers. One hydrogen layer is then adsorbed onto either surface of the Be slab. We assume that the Be atoms reside at their bulk positions, and we use the experimental values for the lattice constants.[20] Advantage is taken of the inversion symmetry associated with an even-layer slab. We have performed calculations with the hydrogen atoms in the four symmetry adsorption sites, i.e., the two hollow sites (hcp site, with a Be atom directly underneath; fcc site, without a Be atom underneath), the bridge site, and the on-top site. With a kinetic-energy cutoff of 20 Ry for the plane-wave basis, the median size of the Hamiltonian matrices is $\sim 800 \times 800$. The result is considered self-consistent when the potentials in the last two iterations differ by about 1 mRy. We find that the total energy differs by less than 0.01 mRy in the last two iterations. The convergence of our result on the number of **k** points used in the surface Brillouin-zone (SBZ) summation and on the kinetic-energy cutoff are tested and are discussed along with the results below. Because of computational limitations, the calculations are performed in the high-coverage limit, and one H per surface Be atom ($\Theta = 1$), where the adsorbed H atoms form a two-dimensional triangular $p(1\times1)$ lattice on the surface.

III. RESULTS

A. Clean surface

Two physical quantities of the clean Be(0001) surface are calculated: the surface energy and the work function of the clean surface. The Be(0001) surface is known not to reconstruct and the surface relaxation is minimal.[21] The surface energy per surface atom is obtained by taking half of the difference between the total energy per cell from the surface calculation and the total energy for the number of Be atoms in a cell from the bulk calculation. The $\frac{1}{2}$ comes from the fact that each slab has two surfaces. We obtain a surface energy of 0.60 eV per surface atom, or 2.1 J/m^2. Various convergence tests confirm that this is an accurate evaluation. When the number of **k** points in the ($\frac{1}{4}$) irreducible part of the surface Brillouin zone (ISBZ) is increased from 12 to 20, the surface energy lowers by only 0.005 eV per surface atom. The cutoff energy of 20 Ry is sufficient for the clean surface, since the bulk calculation is already well converged at a cutoff energy of 10 Ry.[8] In fact, we obtained an increase in the surface energy of only 0.001 eV when the cutoff energy is 25 Ry. The convergence of the surface energy is also checked by increasing the Be slab to six layers, which results in a change of only -0.015 eV per surface atom. The convergence with respect to the vacuum size is also tested; when the thickness of the vacuum region is increased from equivalent of six layers to eight layers, the surface energy increased by 0.02 eV per surface atom. The surface energy obtained is thus converged to within 3%.

Experimental determination of surface energy is difficult. To our knowledge, an experimental value for the surface energy of Be(001) is not available. Theoretical evaluation of surface energies has been performed for some transition metal surfaces.[22] For comparison, our calculated value for Be(0001) (2.1 J/m^2) is smaller than that of the Ru(0001) surface[22] (3.0 J/m^2) by 30%. The surface energy can be estimated from the cohesive energy of the crystal by viewing the formation of a solid from separate atoms in a certain way.[22] Assume each atom is a sphere with the radius determined by the bulk atomic volume. When the atoms come together to form a solid, the surfaces of the atoms are eliminated and the surface energies are released, inducing binding. The surface energy per unit area is thus equal to the cohesive energy divided by the area of the spherical surface of an atom. This estimate gives a value of 2.7 J/m^2 for Be(0001), which is 29% larger than the calculated value. A similar estimate for Ru(0001) is 25% greater than the first-principles calculation.[22]

The work function of Be has been a matter of controversy. Experiments have turned out a wide range of values. An earlier standard reference[23] recommends a value of 3.92 eV. More careful experiments performed thereafter give 5.08±0.08 eV and 4.98±0.10 eV for polycrystalline films, and 5.10±0.02 eV for a single-crystal surface.[24] The work function is the energy difference between the Fermi level and the vacuum level. In our calculation, the vacuum level is taken to be the potential energy in the middle of the vacuum region averaged in the directions parallel to the surface. We obtain a work function of 5.1 eV. Our result has an inherent uncertainty of about 0.1 eV. When the number of **k** points is increased from 12 to 20, we obtain 5.0 eV for the work function. Our calculation agrees well with the more recent experimental values as quoted above.

There have been theoretical studies of monolayer and dilayer thin films of Be.[25,26] Since these films are not thick enough to simulate the bulk of the Be crystal, a total-energy calculation can only give the cohesive energy for the particular films; the surface energy of the Be(0001) surface cannot be determined. Surprisingly, the calculated work functions of the thin films are fairly close to the experimental value for the semi-infinite metal. The work of Boettger and Trickey,[25] using a method that employs fitting of charge density and potential to Gaussian-type functions, gave 4.80 and 5.11 eV for the monolayer and dilayer films, respectively. The geometry of the films was determined by minimizing the total energy.[25] The linear-augmented-plane-wave calculation of Wimmer[26] obtained a value of 5.19 eV for a monolayer film (a lattice constant of $a = 4.20$ a.u. is used as opposed to the experimental value of 4.32 a.u.). These are all local-density-functional calculations employing the Hedin-Lundqvist correlation potential.[16] These values are in close agreement with each other and with the experimental value for the Be(0001) surface. The difference of 0.39 eV between the two monolayer results probably arises from the slightly different geometries and possibly a contribution due to different methodology. Calculation of a monolayer film of other alkaline-earth metals[26] also shows similarly good agreement of the work function with the experimental values. At present, there is no clear explanation of why the thin-film results agree so well with experiment.

B. Adsorption sites and energy

To determine the minimum-energy site of the adsorbed hydrogen, the total energy is calculated for the hydrogen at different sites and for various vertical distances h from the surface Be layer. The adsorption energy is obtained by taking half of the difference in the total energy of the slab with and without H, then subtracting out the calculated energy of an isolated hydrogen atom within the local-density approximation. We use the value -0.958 Ry for the energy of a H atom, calculated with the Ceperly-Alder correlation potential as parametrized by Perdew and Zunger.[27] The absolute value of the calculated adsorption energy may not be accurate because the local-density approximation cannot simulate the correlation effect adequately in both the atomic and adsorbate limits simultaneously. Hence, the absolute value of the calculated adsorption energy cannot be compared to the binding energy of the H_2 molecule so as to deduce whether the adsorption is dissociative or not. Experimentally, only atomic hydrogen is found to adsorb on the Be(0001) surface, i.e., the hydrogen molecule cannot be dissociated by the surface.[28] However, the relative adsorption energies for different sites are expected to be accurate. The dependence of the binding energies on the vertical distance is shown in Fig. 1. The curves are least-squares fits of polynomials in h to the calculated points. The equilibrium heights h_0 and the adsorption energies are obtained directly from the fit. They are summarized in Table I. The result indicates that the bridge site is the stable adsorption site. This is consistent with the assignment by Ray and Plummer[6] of the adsorption at low coverages (see below). The fcc and hcp sites are next in order, the adsorption energy for the fcc site being approximately 0.1 eV more negative than for the hcp site. A difference of the order of 0.1 eV between the two hollow sites seems to be typical for H adsorption on most close-packed metal surfaces.[29] The on-top site is the most unstable, with the adsorption energy being 0.5 eV higher than that for the hcp site. The distance between the adsorbed H and their nearest Be atoms, d, which is referred to here as bond distance, are calculated and are also listed in Table I. The bond distance decreases from the hollow sites to the bridge site, and to the on-top site, viz., as the number of nearest neighbors decreases. For the fcc and hcp sites, the bond distance is found to be ~1.6 Å, which is the value obtained for the Be-H distance in $LiBeH_3$ (assuming a cubic perovskite structure).[30] The calculated bond distance for the on-top site is 1.42 Å, which is still slightly greater than the 1.34 Å of the BeH molecule,[31] but coincides with the Be-H distances in crystalline BeH_2, which range from 1.38 to 1.44 Å.[10]

It is important to check the result using a different cutoff energy for the plane-wave basis, since the presence of hydrogen requires a large cutoff energy to arrive at a

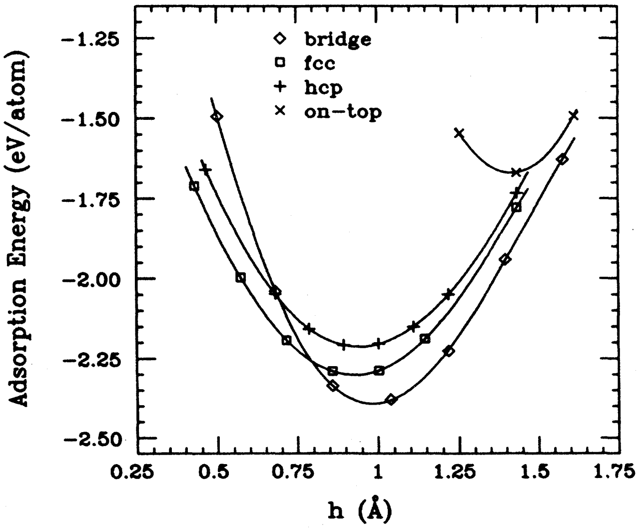

FIG. 1. Adsorption energy of H at different surface sites as a function of vertical distance between H and the surface Be layer. The adsorption energy is relative to the isolated hydrogen atom. The origin is at the surface Be layer.

TABLE I. Calculated adsorption energy, equilibrium distance of hydrogen from the surface, the Be—H bond distance, and the vibrational excitation energy of hydrogen.

Adsorption site	E_{ad} (eV)	h_0 (Å)	d (Å)	$h\nu$ (meV)
Bridge	−2.39	0.98	1.51	168 (178[a])
fcc	−2.30	0.93	1.61	140
hcp	−2.21	0.94	1.62	137
On-top	−1.67	1.42	1.42	197

[a]Effect of substrate motion is included. See text for details.

good convergence. We have done this by repeating the calculation for the bridge site and the two hollow sites with a cutoff energy of 25 Ry. The hydrogen-substrate distances are fixed at the equilibrium values obtained with the 20-Ry cutoff energy.[32] The adsorption energy increases by 0.161, 0.175, and 0.173 eV for the bridge, fcc, and hcp sites, respectively. Thus, the difference between the adsorption energies for the bridge site and for the fcc site decreased by only 0.014 eV. This is a small value compared to the adsorption energy difference itself indicating that the ordering of the adsorption energies will probably be the same when a larger cutoff energy is used. The change in the calculated adsorption energy with respect to the number of **k** points in ISBZ is also found to be small (~0.01 eV).

C. Vibrational frequency of H

With the fitted analytic potential energy as a function of h, the energy levels of the H vibration perpendicular to the surface are evaluated by diagonalizing the Hamiltonian matrix for the H motion in the basis of the simple-harmonic-oscillator eigenfunctions. The calculated excitation energies are listed in Table I. The uncertainty in the frequency is about 2 meV, as inferred from using different fitting polynomials. The deviation from the harmonic frequencies due to the higher-order terms is only 2–3 meV for the hollow sites and ~5 meV for the bridge site.

The measurement of vibrational frequencies of H has been made using the EELS technique for different surface coverage by Ray and Plummer.[6] They observe a high-frequency mode of 185 meV at low H coverages (the exact coverages are not known). As the coverage increases, this mode disappears and two new vibrational modes of lower frequencies are observed at 158 and 170 meV. They have tentatively assigned the low-coverage mode to the bridge site and the high-coverage modes to a tilted bridge site. As discussed above, our calculated adsorption energies are consistent with the assignment of the bridge site to the low-coverage mode. The hydrogen vibrational frequency for the bridge site in the present calculation is 168 meV. This is smaller than the experimental value by 17 meV. This discrepancy can be resolved by recognizing two major differences between the experimental situation and our calculation. First, the dynamics of the Be substrate is not taken into account in our calculation. In reality, the hydrogen oscillation couples to the substrate. Due to the small mass of Be, this can have a large effect. We have simulated this effect by using pair interactions between H and their nearest-neighbor Be atoms and between Be atoms. The force constant for nearest-neighbor H-Be interaction is 12.9×10^4 dyn/cm, chosen so that the vibrational frequency equals the value obtained from our first-principles calculation, 168 meV, when Be atoms are assumed to be stationary. The force constants between the substrate Be atoms are obtained from a previous study of the bulk Be phonon spectrum.[33] The result indicates that an increase of around 10 meV is obtained when the dynamics of the substrate is taken into account. Since the substrate force constants ($\sim3\times10^4$ dyn/cm) are much smaller than the Be-H force constant, the 10-meV increase is due mainly to the reduced mass effect. Indeed, the resulting frequency changes very little when the Be-Be force constants are set identically to zero. The second factor which contributes to the difference between experiment and theory is that the experimental frequency is obtained at low coverage while our calculation is performed for a $p(1\times1)$ lattice corresponding to unit coverage. In the present system, the frequency is experimentally observed to decrease with increasing hydrogen coverage; the 185-meV oscillation was seen to shift to 181 meV, as coverage increases, before it disappears.[6] This change in the frequency could arise from the redistribution of charge density around the hydrogen under consideration, due to the occupation of nearby sites. In the absence of any knowledge of hydrogen coverage in the experiment, we do not know what the shift would be at unit coverage. However, the theoretical result, 178 meV, taking into account the effect of the substrate is sufficiently close to the experimental value of 181 meV, the frequency of this vibration mode before it disappears.

The calculated adsorption frequencies at the fcc and hcp sites are almost the same (they differ by only 3 meV). This is in agreement with other work on close-packed metal surfaces. The two lower frequencies, 158 and 170 meV, which appear at high coverages exhibit a splitting of 12 meV. Thus they are not likely to be associated with the hcp- and fcc-site adsorptions. The assignment of these modes to the hollow sites would also contradict our calculated adsorption energies (Table I). These modes were assigned to a tilted bridge site by Ray and Plummer,[6] which is not considered in the present work due to computational limitations.

D. H in the subsurface site

In order to study the energetics of H going into the bulk, the adsorption energy is calculated for several H positions along the straight line which connects the surface site to the subsurface octahedral site. The result is shown in Fig. 2. The hydrogen has to overcome a rather large energy barrier (~1.6 eV) to go into the subsurface octahedral site from the fcc site. The potential well around the octahedral site is very shallow (0.2 eV). There is a difference of 1.4 eV between the potentials at the octahedral site and at the fcc site. Note that the potential curve in Fig. 2 is derived by placing a layer of hydrogen parallel to the surface. When a single hydrogen atom

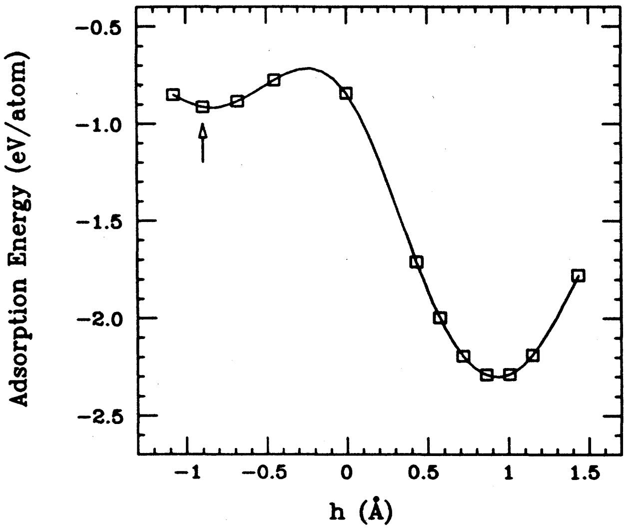

FIG. 2. Adsorption energy as a function of the coordinate of H perpendicular to the Be(0001) surface for H along the path which connects the subsurface octahedral site (indicated by arrow) and the surface fcc site. The origin is at the surface Be layer.

moves beneath the surface, the lattice may distort around it; the energy barrier and the energy of hydrogen in the subsurface site with respect to the surface site could be smaller than the calculated values given above. However, it is still unlikely that hydrogen will go below the surface at low coverages ($\Theta \leq 1$). But, at much higher coverages, the repulsion between H on the surface may make it energetically favorable for some of the hydrogen to occupy the subsurface sites. A theoretical investigation of such a situation was recently performed for H/Ru(0001) by Chou and Chelikowsky.[4]

IV. DISCUSSION

The EELS experiment of Ray and Plummer[6] showed that atomic hydrogen adsorbs in the bridge site at low coverage. The comparison of the adsorption energies from the present calculation supports this assignment. Due to the computational limitations, the calculations are performed by a monolayer coverage of hydrogen. Because of the effective H-H interaction, the calculated adsorption energy at this high coverage is not necessarily the same as a similar calculation at low coverage—or in the extremity—for a single adatom. Such a calculation is very difficult using the present method because of the lack of symmetry and periodicity. To make sure that we make a sensible comparison with experiment, we used the same triangular lattice of adatoms, placed in different high-symmetry adsorption sites. This procedure will presumably reduce, if not eliminate, the contribution of the effective adatom-adatom interaction when the adsorption energy of different sites are compared.

Previous studies of hydrogen on close-packed transition-metal surfaces have generally found that hydrogen adsorbs onto either the fcc or hcp site. A preliminary study of H/Mg(0001) by present authors[34] also concluded that the fcc site is preferred to the hcp site and the bridge site. The present system is different in that hydrogen prefers the bridge site to the hollow sites. It is of interest to see what causes the difference between H/Be(0001) and H/Mg(0001), since the structure of the substrate is the same and both Be and Mg atoms have two *s* electrons in the outermost electronic shell. To do this, we examine the various components of the total energy. In general, it is difficult to determine which energy component is responsible for the particular order of stability of the adsorption sites in a total-energy calculation. This is because the components of the total energy for two sites can differ by 1–2 orders of magnitude greater than the difference between the total energies. On the other hand, the difference in the band-structure term of the total energy is usually small. For instance, in the H/Mg(0001) system, we find that the band energy for the fcc site is only about 0.03 eV per hydrogen atom lower than those of the hcp and bridge sites, while the difference in the adsorption energy is 0.1 eV. In the case of H/Be(0001), however, we find two distinct features when the components of the total energy for the bridge site are compared with those of the fcc site. First, the band-structure energy for the bridge site is lower than that of the fcc site by about 0.2 eV per hydrogen atom. Second, a similar large difference (0.6 eV per hydrogen atom) in the nonlocal part of the ionic energy is also found between the two sites [which is very small in the case of H/Mg(0001)]. The nonlocal pseudopotential in both cases is of *p* character. (The nonlocal *d* potential is not generated since the effect is expected to be negligible.) Because of the lack of orthogonality with the core state (there is no core state of *p* character) in Be, the *p* potential is very attractive. Magnesium, on the other hand, does have a 2*p* core state, resulting in a less-attractive *p* potential. The correlation of the lower band-structure energy and the nonlocal part of the ionic energy for the bridge site in H/Be(0001) suggests that the attractive *p* potential in Be favors the adsorption of hydrogen in the bridge site over the hollow sites. To substantiate this point, we repeated the calculation for H/Be(0001) with only the local potential for Be (i.e., by equating the *p* potential to the *s* potential). With the hydrogen atoms in their respective equilibrium positions as determined before, the result indicates that the fcc site would be lower than the bridge site by about 0.2 eV/atom if the nonlocal potential is neglected. This confirms the above conjecture that the nonlocal potential (of *p* character) is important for the selection of the adsorption site by hydrogen.

In summary, we have studied the hydrogen adsorption on the Be(0001) surface using an *ab initio* pseudopotential approach. From the calculation of the four high-symmetry adsorption sites, we conclude that the bridge site is the stable adsorption site, in agreement with experiment.[6] The attractiveness of the *p* potential of Be is found to be responsible for the preference of the bridge site. The bond lengths as well as the phonon frequencies are calculated. Results are also obtained for the surface energy and work function of the clean surface. The calculated quantities are in good agreement with available experimental value. Further work is necessary for the elucidation of the coverage dependence of the adsorption.

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[32] From our experience with previous calculations, the equilibrium distance is accurate within a few percent even at low cutoff energy. Furthermore, the change in the adsorption energy resulting from the change of equilibrium distance is small in this case. For instance, even if h_0 changes by 0.1 a.u., the energy changes only by 10 meV for the bridge site as estimated from the calculated frequency. Therefore, it is valid to compare the difference in the adsorption energy between two sites calculated at these fixed positions only.

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