

Structure of the H-induced vacancy reconstruction of the (0001) surface of beryllium

Karsten Pohl* and E. Ward Plummer

*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996
and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

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A unique chemisorption structure has been determined for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ H-Be(0001) phase formed at a saturation coverage of 1 ML and $T\leq 270$ K. The analysis of low-energy electron diffraction data shows that $\frac{1}{3}$ of the Be top layer atoms are removed to form a honeycomb structure of Be vacancies. Each vacancy is decorated by three H adatoms bonded in tilted bridge sites with a H-Be bond length and angle of 1.53 \AA (± 0.2) and 42° (± 10), respectively. [S0163-1829(99)50208-7]

The general interest in the interaction of hydrogen with metal surfaces is motivated by its technological importance and its tractability by *ab initio* theoretical methods. Experimentally one of the most challenging aspects of the study of H is the determination of its bonding configuration, especially when the substrate surface reconstructs, because hydrogen is a very weak scatterer and has the ability to bond in many different configurations. As Pauling points out,¹ the covalent radius of the hydrogen atom is more variable than that of other atoms, ranging from 0.28 \AA for a more ionic molecule such as H-F to 0.37 \AA for H₂. In dihydride complexes, H radii of up to 1.1 \AA are observed.² A value of 0.30 \AA is found for diatomic metal-hydride molecules. Moreover, hydrogen is able to form bulk phases with a variety of metals, a well-studied example is palladium. The bond length for Pd-H in the β -hydride phase is 2.01 \AA which corresponds to a hydrogen radius of 0.64 \AA ,³ twice the size of ordinary H.

Spectroscopic methods of structural chemistry are able to measure interatomic distances with extremely high precision of about 0.001 \AA . For adatoms chemisorbed on surfaces, the atomic positions can usually be determined reliably to within a few 0.01 \AA depending on the method. However, hydrogen is special and the assignment of the precise adsorption site is very difficult.⁴ Atomic beam diffraction⁵ and time-of-flight scattering and recoiling spectroscopy⁶ seem to be the most sensitive techniques to the presence of H. High-resolution electron-energy-loss spectroscopy (HREELS) will supply information of the adsorption site symmetry, while H is nearly invisible to all other structural probes utilizing scattering and diffraction techniques—in particular to x rays.

Although low-energy electron diffraction (LEED) has been able to determine the hydrogen adsorption site on metal surfaces with a precision of a few 0.1 \AA ; this has been achieved only for systems where the substrate reconstruction is small, i.e., atomic displacements of less than a few 0.01 \AA ; see e.g., Ref. 7. A strong restructuring of a metal surface upon hydrogen adsorption, however, is a rather normal behavior as has been shown for numerous systems. They can be of the displacive type, as for W(100), Ni(110), and Cu(100),⁸ but also bond-breaking reconstructions have been observed for Pd(110), Ni(110), and Fe(211).⁹ It has been practically impossible for LEED to determine the adsorption site for these very important systems, because the diffracted intensity is dominated by the strong scattering from the reconstructed substrate.

We have been able to determine the H binding sites on a strongly reconstructed beryllium surface via LEED because the weak electron-scattering strength of Be, with $Z=4$, is comparable to that of H. The saturation of the Be(0001) by 1 ML of atomic hydrogen at temperatures $T\leq 270$ K induces a $(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern. Multiple-scattering analysis of the I - V spectra shows that $\frac{1}{3}$ of the Be top layer atoms are removed to form a honeycomb structure of Be vacancies. Each vacancy is decorated by three H adatoms bonded in bridge sites with a H-Be bond length of 1.53 \AA (± 0.2) tilted by $\vartheta=42^\circ$ (± 10) toward the threefold hcp sites. The achieved precision in the determination of the structure allows for a description of the complete adsorption geometry as well as the vibrational motion of the H adatoms above the strongly reconstructed Be(0001) surface. The results are in excellent agreement with recent first-principles calculations by Stumpf and Feibelman.¹⁰

The clean Be(0001) surface was prepared in vacuum via repeated sputter-anneal cycles at 700 K and monitored by HREELS and Auger electron spectroscopy. The hydrogen doser consisted of a 0.25 mm tungsten filament heated to 1800 K. The filament was surrounded by a coaxial molybdenum tube through which H₂ was passed. The absolute atomic hydrogen coverage was determined by nuclear reaction analysis (NRA), an accelerator-based technique in which the proton flux from the nuclear reaction $D(^3\text{He},p)^4\text{He}$ on the deuterium covered surface is compared to the flux from a standard of known deuterium coverage.¹¹ The absolute coverage is an important constraint in our search for a trial structure which best correlates with the LEED data. In our LEED I - V experiment we measured intensity vs energy spectra for the hydrogen saturated surface at $T=130$ K by Video-LEED at normal incidence in an energy range of 20–250 eV for 24 diffracted beams of the H-induced $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure. The observed LEED pattern exhibited sixfold symmetry indicating natural averaging over the two possible terminations (A or B) of the threefold symmetric hcp(0001) surface. Averaging of symmetry-equivalent beams led to two integer-order, (10) and (11), and two fractional-order, $(\frac{1}{3}\frac{1}{3})$ and $(\frac{2}{3}\frac{2}{3})$, beam profiles with a total energy range $\Delta E=390$ eV ($R_p<0.1$ between equivalent beams). The diffraction intensity of the superstructure (half-order) spots is of the same magnitude as the substrate (integer-order) spots, strongly suggesting that the substrate is reconstructed; see Fig. 1(a).

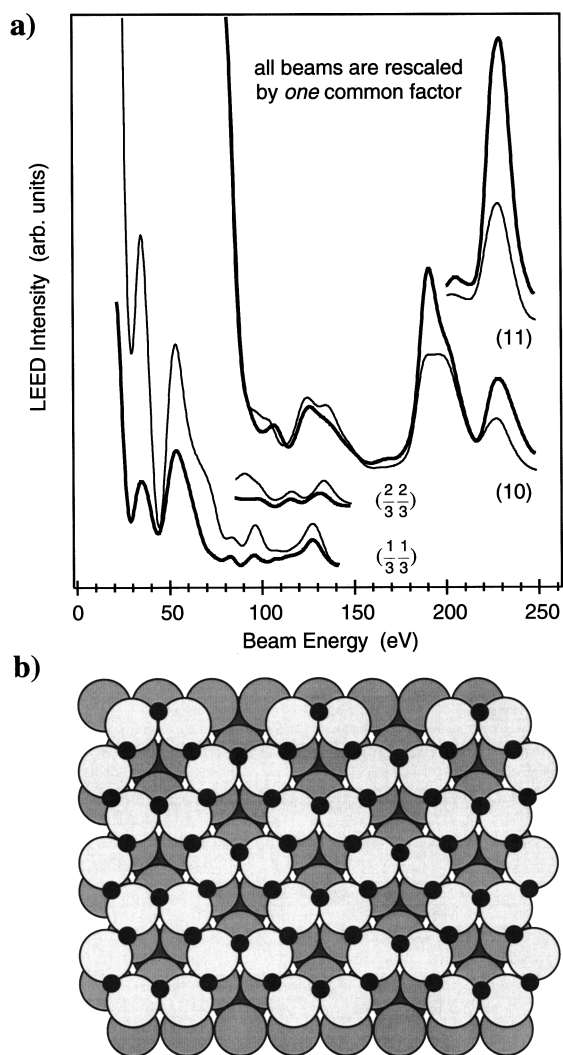


FIG. 1. (a) Comparison of the measured LEED I - V spectra (thick lines) to the calculated diffraction intensities (thin lines) for the optimized adsorption structure. The I - V curve pairs are shifted for display but the relative intensity scale is conserved, i.e., only one common scaling factor for all beams in the experimental and theoretical beam set is used. (b) Top view of the best fit $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorption structure for 1 ML H (small filled circles) on the first three layers (large shaded circles) of the Be(0001) surface. Each vacancy in the honeycomb structure is decorated by three H adatoms in near-hcp sites.

The analysis of the LEED I - V spectra was carried out using standard multiple-scattering algorithms.^{12,13} Atomic-scattering matrices were calculated from a maximum of 14 phase shifts, which we derived from bulk potentials,¹³ and were renormalized for thermal vibrations using a Debye temperature Θ_D converted into isotropic root-mean-square displacements $\langle u \rangle_H$ for the H adatoms, and $\langle u \rangle_1$, $\langle u \rangle_2$, and $\langle u \rangle_b$, for the first two Be layers and the bulk, respectively. We used the method of tensor LEED (Ref. 14) for the structural search, in which the position of nine atoms were individually optimized, three per two-dimensional unit cell in the H adlayer and the first two Be layers, respectively. The agreement between measured and calculated I - V curves were quantified by the Pendry R factor, R_p .¹⁵

Based on the $(\sqrt{3} \times \sqrt{3})R30^\circ$ symmetry of the observed

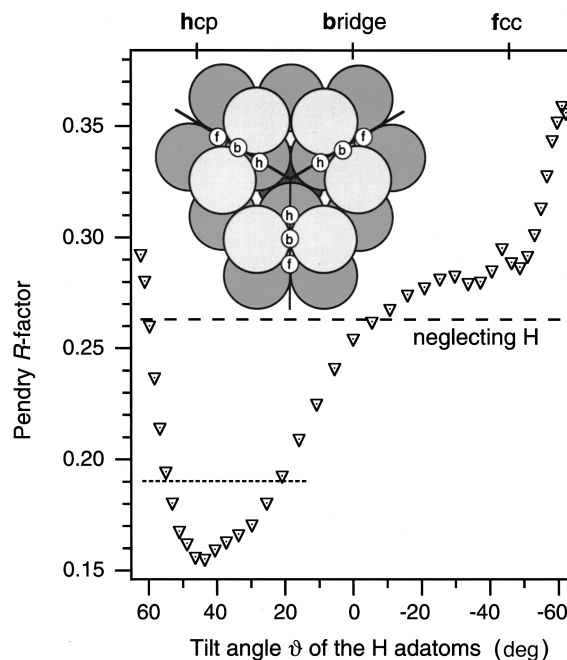


FIG. 2. Pendry R factor as a function of the tilt angle ϑ of the H atom with respect to the bridge site; in comparison the best R factor achieved for an independent search in which H is ignored ($R_p = 0.263$) is given by the dashed line. The dotted line indicates the significance level at $R_p^{\min} \pm \sigma$. The trajectory along which the lateral H adsorption position, Y_H , is determined, passing through the hcp, bridge and fcc site is shown in the inset.

LEED pattern and the known coverage of 1 ML, an initial survey of H adsorption sites on an unreconstructed Be surface was carried out. All models based on an unreconstructed substrate gave uniformly poor agreement between the calculated and measured diffraction intensity ($R_p \geq 0.36$). In addition, the calculated ratio of energy averaged intensities of the fractional-order spots relative and the integer-order spots, $\nu = \langle I \rangle_{\text{frac}} / \langle I \rangle_{\text{int}} \approx 0.3$, is too small by a factor of about 3. Introducing a buckling of the unreconstructed surface does not improve the agreement between theory and experiment ($R_p \geq 0.35$) and the fractional-order spots are only 40% as intense as measured ($\nu \approx 0.4$). Only the removal of $\frac{1}{3}$ of the Be surface atoms to create a honeycomb structure of Be vacancies raised the intensity ratio to about unity and dropped R_p to 0.18. This structure is shown in Fig. 1(b). Finally, we tested a $\frac{2}{3}$ ML vacancy model, and a registry change in the hcp stacking sequence for all models, which could be caused by the massive mass transport of Be atoms to step edges. However, models of this sort have a poor $R_p \geq 0.33$.

The H adsorption site had to be optimized simultaneously with all of the Be atomic positions, in order to distinguish between the many models tested. The assumed conservation of threefold symmetry throughout our search limited the allowable adsorption site of the three H atoms per unit cell to a position on a line connecting a fcc adsorption site through a bridge and passed a hcp site, as indicated in the inset of Fig. 2. We plotted the change in the R factor with the H adsorption site along this trajectory in Fig. 2; the deep minimum in the vicinity of the hcp site shows unambiguously that an accurate positioning of the H atoms on the honeycomb vacancy structure is possible. The lateral displacement

TABLE I. Best-fit parameters and comparison to theoretical predictions (Ref. 10) for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure for 1 ML of H: $D_{\text{H-Be}}$ is the shortest H-Be distance, h_{H} is the vertical height of the adatoms above the first Be plane, Y_{H} is the lateral displacement, and ϑ the tilt angle from the bridge site ($\tan \vartheta = Y_{\text{H}}/h_{\text{H}}$, $D_{\text{H-Be}} = \{(h_{\text{H}} + Y_{\text{H}})^2 + a^2/4\}^{1/2}$). $\Delta d_{ii+1}/d_0$ give Be-Be interlayer relaxations. $\langle u \rangle_b$ should be compared to 0.094 \AA which is converted from $\Theta_D = 1400 \text{ K}$, the tabulated bulk Debye temperature for Be (Ref. 19).

	Experiment	Theory
$D_{\text{H-Be}}$ (\AA)	1.53 ± 0.2	1.44
h_{H} (\AA)	0.79 ± 0.12	0.69
Y_{H} (\AA)	0.71 ± 0.3	0.58
ϑ (deg)	42 ± 10	40
$\Delta d_{12}/d_0$ (%)	$+0.6 \pm 1.1$	+4.5
$\Delta d_{23}/d_0$ (%)	$+1.65 \pm 1.3$	+1.1
$\langle u \rangle_{\text{H}}$ (\AA)	0.25 ± 0.03	
$\langle u \rangle_1$ (\AA)	0.21 ± 0.03	
$\langle u \rangle_2$ (\AA)	0.09 ± 0.02	
$\langle u \rangle_b$ (\AA)	0.08 ± 0.01	

is given by the tilt angle of the H-Be bond from the bridge site ϑ . For comparison, we added the best R factor achieved for an independent search in which we ignored H altogether. The results of a full refinement of all the structural parameters are summarized in Table I. The very good agreement between our results and the structural values of the first-principles calculation of Stumpf and Feibelman¹⁰ is obvious, especially for the hydrogen adsorption geometry. However, the very large top layer expansion (+4.5%) predicted by the local-density approximation (LDA) calculation was not found in our experiment. This might be an indication that the corrugated geometry of the Be top layer reconstruction requires a more sophisticated theoretical treatment of exchange and correlation within the LDA formalism. Gradient corrections to the charge density could make up for part of the difference, as was suspected on the missing-row reconstruction of the clean Be(11 $\bar{2}$ 0) surface.¹⁶ Alternatively, this discrepancy might be associated with thermal effects, given that the calculation is for $T=0 \text{ K}$ and the experiment is performed at $T=130 \text{ K}$. Thermal effects are important for the interplanar spacing of clean Be(0001).¹⁷

In addition to the structural parameters, the thermal displacements in the surface region were determined. The vibrations of the Be atoms changed slightly from the clean surface: In the now reconstructed top layer, every Be atom lost three out of its six in-plane nearest neighbors but gained three strong H bonds which resulted in enhanced vibrational amplitudes of the top layer atoms; see Table I and Ref. 17. The mean-square displacements in the second layer Be layer are slightly smaller than observed on the clean surface, keeping in mind that the interlayer distances are also reduced. The analysis was sensitive enough to also investigate the hydrogen vibrations; we find them to be 10% larger than the Be surface amplitudes. The mean-square displacements of the H adatoms $\langle u \rangle_{\text{H}}^{\text{LEED}} = 0.21 \text{ \AA}$ can be compared to an experimentally derived value of $\langle u \rangle_{\text{H}}^{\text{EELS}} = 0.23 \text{ \AA}$ from the vibrational frequencies of the H-Be losses as seen in HREELS under the simple assumption that the adsorption potential is that of a three-dimensional harmonic oscillator.¹¹

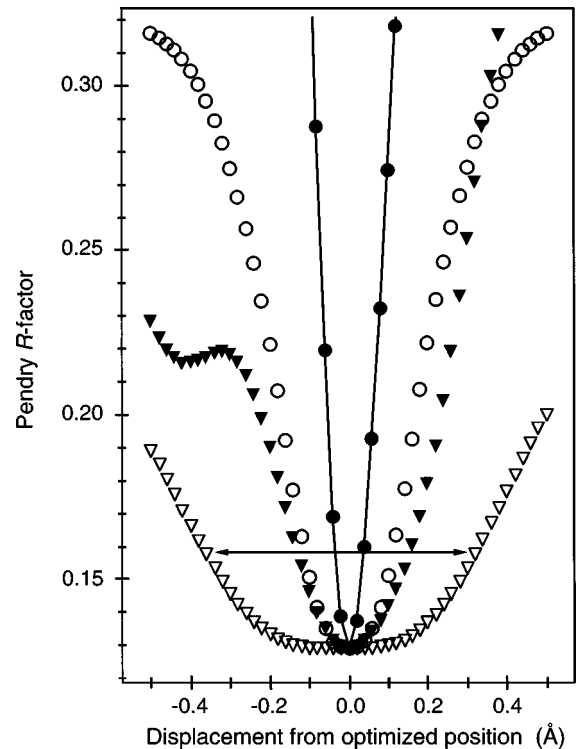


FIG. 3. Comparison between the sensitivities to the normal (open) and lateral (filled) beryllium (circles) and hydrogen (triangles) positioning. The solid arrows indicate the line of significance at $R_p^{\text{min}} \pm \sigma$.

In order to quantify the sensitivity of our analysis, we evaluate the variance of the achieved $R_p^{\text{min}} = 0.13$, according to $\sigma(R_p) = R_p^{\text{min}} \sqrt{8 V_{0i} / \Delta E} \approx 0.03$.¹⁵ Thus, the result is of similar accuracy as our recent analysis of the clean Be(0001) surface, which yielded $R_p^{\text{min}} = 0.13$.¹⁷ The sensitivity to the H positions in comparison to the beryllium top layer atoms is shown in Fig. 3 where the variation of the R factor with the atomic displacements around the optimized positions is shown. The error in the structural parameters relating to the normal and parallel components of the atomic positions with respect to the surface is given by the intersection of the curves with the line of significance at $R_p^{\text{min}} \pm \sigma$. The uncertainty in the H-Be bond length will be dominated by the error in the lateral H displacement, $\Delta(H_{\parallel}) \approx \pm 0.30 \text{ \AA}$, since the accuracy of the normal position is about three times more precise, $\Delta(H_{\perp}) \approx \pm 0.12 \text{ \AA}$. Overall, the sensitivity to the atomic positions of Be atoms is three times as high as to hydrogen atoms $\Delta(\text{Be}_{\parallel}) \approx \pm 0.10 \text{ \AA}$ and $\Delta(\text{Be}_{\perp}) \approx \pm 0.03 \text{ \AA}$. The measured H-Be bond length of 1.53 \AA (± 0.2) is in good agreement with the interatomic distance that can be calculated by adding the covalent and metallic radius of H (0.37 \AA) and Be (1.12 \AA), respectively to 1.49 \AA .¹

Reducing the atomic number Z of the substrate obviously enhances the sensitivity to hydrogen in LEED. However, Z is not a sure guide for the low-energy electron scattering strength and the detailed angular dependence of the atomic-scattering strength or t matrix has to be considered.¹⁸ Most LEED observations are done close to the backward scattering direction. The intensity which is scattered in the forward direction undergoes more inelastic scattering events and is removed from the incident beam very quickly as it penetrates

deeper in the bulk. We found that the ratio of backward-scattering to forward-scattering amplitudes, $Q = |f(\pi)|^2/|f(0)|^2$, at a typical LEED energy of 150 eV is as small for Be atoms as for H, $Q_{\text{Be}} \approx 0.006$ and $Q_{\text{H}} \approx 0.004$, respectively, while a factor of 2 higher for Al, $Q_{\text{Al}} \approx 0.021$, and much larger for Ni and Cu, $Q_{\text{Ni}} \approx 0.11$ and $Q_{\text{Cu}} \approx 0.098$, respectively. This shows that the major diffraction contribution of small Z elements arise from forward-scattering events. Thus, electrons scattered by the surface atoms are primarily directed toward the bulk. This behavior explains the low-scattering intensities for hydrogen and beryllium and why the sensitivity to the atomic positions of both elements are of comparable magnitude. Moreover, we have to bear in mind that the physics of the hydrogen-metal interaction lies in the representation of the scattering potential. Conventional LEED calculations are based on a muffin-tin approximation, which assumes a spherical symmetric potential. It would be very interesting to understand why this model works so well given the inhomogeneous and non-spherical nature of the H-metal bond.

In summary, we found a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase by saturating the Be(0001) surface with 1 ML atomic hydrogen. Based on NRA absolute coverage measurements, we have determined the adsorption structure to be a unique honeycomb

array of $\frac{1}{3}$ ML Be vacancies each decorated by three H atoms. The adsorption configuration of atomic hydrogen on a strongly reconstructed surface could be precisely determined by LEED, because of the low atomic number Z of the substrate. The measured H-Be bond length of 1.53 Å (± 0.2) is in good agreement with the interatomic distance calculated by adding the covalent and metallic radius of H (0.37 Å) and Be (1.12 Å), respectively to 1.49 Å.¹ This strong, short covalent H-Be bond induces the vacancy formation in the Be(0001) surface by rearranging the surface valence charge density and reducing the large tensile stress of the unreconstructed surface. In addition to the adsorption geometry, we determined the vibrational properties of H adatoms. In accordance with our HREELS measurements,¹¹ we found the vibrational amplitudes of the adatoms to be of the same order as the enhanced vibrations of the atoms in the top layer of the substrate.

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*Present address: Sandia National Laboratories, Livermore, CA 94550.

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