

Hydrogen on W(110): an adsorption structure revisited

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Abstract

We present a quantitative study of the atomic structure of the clean and H-covered W(110) surface employing an analysis of low-energy electron diffraction (LEED) as well as density functional theory (DFT) calculations. Our results give no evidence of a noteworthy reconstruction of the W(110) surface upon H-adsorption, and thus discard the widely accepted model of a H-induced lateral shift of the top layer based on earlier LEED data. Moreover, we offer a reinterpretation of the latter which goes along without such a surface reconstruction. In detail, we find good agreement between the LEED analysis and the DFT calculations on a small contraction of the first interlayer distance by about 3% for the clean surface, which is reduced to half this size at full H coverage. Hydrogen itself is found to be adsorbed in quasi-threefold coordinated hollow sites at a height of about 1.20 Å above the first substrate layer. © 1997 Elsevier Science B.V.

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1. Introduction

When hydrogen is made to adsorb on a crystalline surface in the submonolayer regime, in most cases only a local displacement of substrate atoms surrounding the adsorbate is observed. At full monolayer coverage these displacements add up to a homogeneous change of the topmost interlayer spacing. In all known cases, this de-relaxation of the surface is towards the bulk value of the interlayer distance. However, there are also some examples where hydrogen induces severe displacements and even bond-breaking surface modifications like row pairing or missing-row reconstructions (e.g. H/Ni(110) [1,2], H/Fe(211) [3]) as well as dimer-

ization of surface atoms (e.g. H/W(100) [4,5]). A very special and so far unique case seems to be the adsorption of hydrogen on W(110), where a uniform lateral shift in the $[1\bar{1}0]$ direction was reported by Chung et al. [6] to occur for the whole top layer when the hydrogen coverage exceeds half a monolayer. This conclusion was drawn from an asymmetry in the intensities of LEED spots, which are symmetrically equivalent for the clean surface. Of course, such a registry shift should be equally probable in the $[1\bar{1}0]$ and $[\bar{1}10]$ directions, but without causing any asymmetry of the LEED intensities by domain averaging. Therefore a sufficient number of surface imperfections such as steps or other defects was required by Chung et al. to lift the mentioned degeneracy of left- and right-hand side domains. One can argue that for that

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reason, the observation has not been confirmed by other groups for W(110) [7,8], or for the similarly behaving Mo(110) surface [9]. However, indirect evidence for the registry shift was deduced from the coverage dependence of surface core-level shifts [10] as well as from the missing anisotropy in surface diffusion [11], where the results can be easily explained by a symmetry breakdown. On the other hand, there are also investigations which are hardly compatible with a registry shift reconstruction. For instance, the phonon dispersion in the $[1\bar{1}0]$ direction (i.e. the proposed registry shift direction) is very similar to that of other “ordinary” systems [12,13], and an anomaly is observed only in the perpendicular $[001]$ direction. Also, low-energy electron reflectivity measurements are in contrast to a lateral reconstruction [7] and high-energy ion scattering finds no significant surface peak, as would be expected for such a type of reconstruction [14,15]. Therefore, it appears necessary to reinvestigate the adsorption system by means of a full dynamical LEED structure analysis to prove and, if present, to quantify the top-layer shift. Moreover, with the sensitivity achieved nowadays by this method, it can also be expected to determine the adsorption site of the hydrogen atoms, despite the weak scattering strength of hydrogen and the nonexistence of superstructure spots [16]. Since imperfections, always present at a real surface, may have a crucial influence on the properties of the adsorption system H/W(110), as mentioned above, we have also carried out density functional theory (DFT) calculations to study the properties of an ideal surface. Moreover, these calculations also provide the course of the total energy versus the lateral displacement of surface atoms, and thus visualize the absolute energy gain of the proposed reconstruction.

We have restricted our investigations to the fully covered (1×1) -H phase and, for comparison, the clean (1×1) surface. Thus, we do not have to deal with the ordered superstructures (2×1) -H and (2×2) -3H which develop at low temperatures at $\Theta=0.5$ and $\Theta=0.75$, respectively [8,9]. Such superstructures usually induce additional local reconstructions within the substrate, thus rendering a safe detection of the hydrogen position difficult at best, and sometimes even impossible

[16]. In the following we describe details of the LEED and DFT studies in Sections 2 and 3, respectively. In Section 4 we discuss our results and give an alternative interpretation of the observations of Chung et al. [6]. A short summary concludes the paper.

2. LEED analysis

In order to test the predicted top-layer shift of the hydrogen-covered W(110) surface, a LEED structure analysis which was as precise as possible was carried out for the (1×1) -H phase. As a test of the precision of the structure determination and the quantification of the hydrogen-induced modifications of the surface structure, we first reanalyzed the structure of the clean (1×1) surface. A very early LEED analysis by Van Hove and Tong [17] indicated that the clean surface maintains the bulk structure, i.e. the tungsten atoms at the surface neither settle into sites of higher coordination nor relax significantly in the vertical direction.

In the analyses of both the clean and fully hydrogen-covered surfaces, special emphasis was placed on the determination of any possible top-layer shift of tungsten atoms. In order to minimize the error limits in particular for this lateral displacement, large databases as well as very good theory-experiment fits are required. Both are equally important for the determination of the hydrogen adsorption site in the case of the (1×1) -H phase since tungsten is a very strong scatterer as compared to the weak contribution of the hydrogen atoms, and no extra spots are available. In the following paragraph, details of the experiments and intensity calculations are given, whilst in the Section 2.2 the results of the structure analyses are described.

2.1. Sample preparation, LEED intensity measurements and calculations

The experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure below 5×10^{-11} mbar. It was equipped with a four-grid back-view LEED optics which was also used in a retarding field mode for Auger electron

spectroscopy (AES). The sample holder allowed both cooling of the sample down to below 100 K by direct contact to a liquid-nitrogen reservoir and heating up to 3000 K by electron bombardment from the rear. The temperature was measured using a WRe3%–WRe25% thermocouple attached directly to the sample. Precise adjustment of the crystal position in order to ensure normal incidence of the primary electron beam was enabled by three linear and two rotational degrees of freedom of the sample manipulator. In order to exhaust bulk carbon impurities, the crystal was heated to 1500 K in an oxygen ambient of 2×10^{-7} mbar for 5 h. The remaining oxygen was removed by a flash to 2600 K. Several cycles of argon sputtering and annealing finally resulted in a (1×1) LEED pattern with very sharp spots and low background. No traces of contamination could be observed by AES. During the experiments, short flashes to 2600 K were sufficient to remove residual gas contaminations and to restore the clean surface.

Saturation coverage of hydrogen had to be achieved with the lowest possible degree of impurities. Thus, deposition was performed at a pressure of 8×10^{-9} mbar of hydrogen for about 15 min, beginning with a short flash of the crystal to 1500 K in hydrogen ambient to ensure the desorption of residual gas contaminations. There was immediate adsorption of hydrogen during the cooling process towards liquid-nitrogen temperature. Using this procedure we automatically provide some thermal energy to enable the surface to overcome possible activation barriers for reconstruction. After this hydrogen deposition, the crystal also showed a (1×1) structure without any residuals of superstructure spots developing at intermediate coverages [8,9].

Additionally to the above adsorption procedure, we also adsorbed hydrogen conventionally at low temperatures under continuous LEED observation. With both preparations we did not find any asymmetry developing with hydrogen coverage in the intensities of equivalent LEED beams. Thus, we can conclude that our sample must have fewer imperfections as compared to that of Chung et al. [6]. LEED intensity curves were measured at liquid-nitrogen temperature, using a video-based and computer-controlled technique as described in

detail previously [18,19]. This technique offers automated spot tracking with sweeping energy as well as background subtraction. LEED intensities for a total of eight different beams can be recorded practically simultaneously as a function of the electron energy, whereby the primary beam current is measured in parallel. All data points taken for this analysis were averaged over four subsequent video frames in order to improve the signal-to-noise ratio. This led to an effective speed of measurement of 80 ms per energy point and beam, being sufficiently rapid to neglect any residual gas adsorption. The primary electron energy was scanned in the range 50–550 eV in steps of 0.5 eV and the beams were recorded from their first appearance on the LEED screen. Subsequently, the spectra were smoothed and corrected for the energy dependence of the primary beam current.

The quality of the LEED intensity data was further enhanced by averaging the spectra of symmetrically equivalent beams [19,20], because intensity changes due to deviations from the normal incidence of the primary electron beam depend almost linearly on the angle of misalignment as long as the latter is sufficiently small. Pendry R -factors [21] in the range $0.02 \leq R_p \leq 0.12$ between single symmetrically equivalent beams indicate only small misalignments of less than $\Delta\theta = 0.2^\circ$. Experience from other systems shows that for such small misalignments the averaged spectra resemble the true normal incidence spectra within $R_p \leq 0.01$, and thus justify the procedure. All datasets were taken several times and after different preparation procedures in order to ensure reproducibility, which was typically better than $R_p = 0.05$ between different datasets. Using this procedure, data bases of non-equivalent beams for the theory–experiment comparison were achieved with total widths $\Delta E = 2390$ eV and $\Delta E = 1940$ eV for the clean and hydrogen-covered surfaces, respectively.

Standard full dynamical computer programs [22] were used for the calculation of $I(E)$ spectra. The maximum energy of 550 eV requires the use of 13 relativistically calculated and spin-averaged phase shifts for both tungsten and hydrogen, which was checked to be sufficient even for such a strong scatterer as W. All phase shifts were temperature-

corrected using the same bulk Debye temperature for tungsten, $\Theta_W = 380$ K, as in the earlier LEED analysis of Van Hove and Tong [17]. For hydrogen a value of $\Theta_H = 4000$ K was applied, assuming that the adsorbate adopts the vibrational amplitude of the substrate. Additionally, the Debye temperature of the first W layer was refined in the course of the structural analysis, resulting in a best-fit value of $\Theta_S = 200$ K for both analyses.

All layer diffraction matrices were calculated by the matrix inversion method [22], and the layers were stacked using the layer doubling scheme [23] to produce the full surface diffraction. Electron attenuation within the crystal was simulated by introducing a constant imaginary part of the inner potential, which was fitted to be $V_{oi} = -6.5$ eV for the clean as well as the hydrogen-covered phase. The real part of the inner potential was automatically adjusted by the fit routine as a constant value. For the quantitative theory–experiment fit the Pendry R -factor R_p [21] was applied. The limits of error for the structural parameters determined were estimated by its variance $\text{var}(R_p) = R_{\min} \sqrt{8V_{oi}/\Delta E}$.

For both the clean and hydrogen-saturated (1×1) phases, the number of possible structural models is decisively restricted from the outset. Reasonably, the only structural parameters to be varied for the clean surface were the interlayer distances $d_{i,i+1}$ between the four uppermost W layers ($i = 1, 2, 3$), and a possible top-layer registry shift y_1 in the $[1\bar{1}0]$ direction (cf. Fig. 1b). After a best-fit geometry was found, non-structural parameters such as the surface Debye temperature and the imaginary part of the inner potential were optimized. Subsequently, all structural parameters were readjusted again. For the (1×1) -H phase, the adsorption height d_H and the lateral position of the hydrogen atoms are additional parameters which had to be varied independently. Four highly symmetrical adsorption sites (top, short- and long-bridge, threefold hollow) as sketched in Fig. 1c were tested, (i.e. for each site, a full parameter optimization as described above was performed). In a final refinement, the lateral parameter y_H (see Fig. 1b) was varied in order to allow for hydrogen shifts from the ideal high-symmetry positions. In

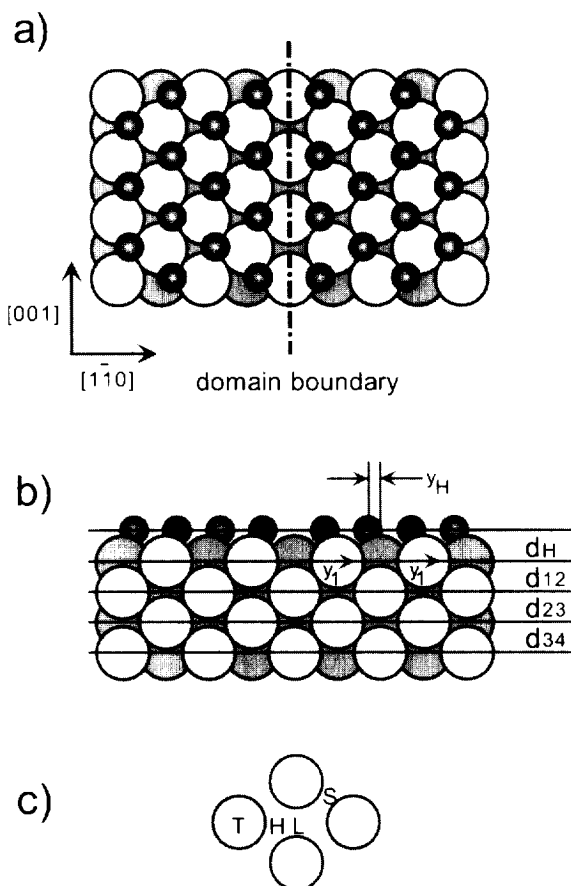


Fig. 1. (a) Two domains of the best-fit model for the (1×1) -H phase of W(110) in top view. (b) Side view of the (1×1) -H phase of W(110) indicating all relevant structural parameters. (c) Schematic drawing of all possible highly symmetric adsorption sites of hydrogen (top (T), short-bridge (S), long-bridge (L), threefold hollow (H)).

this latter procedure, all other structural and non-structural parameters were kept constant.

2.2. Structural results of the LEED analyses

In both analyses a remarkable good agreement between calculated best-fit and experimental spectra could be achieved, as demonstrated in Fig. 2 for selected beams. The quality of the fit is also reflected by low values of the best-fit R -factors, $R_p = 0.13$ and $R_p = 0.12$ for the clean and hydrogen-saturated (1×1) phases, respectively. As the most remarkable result of the LEED analyses,

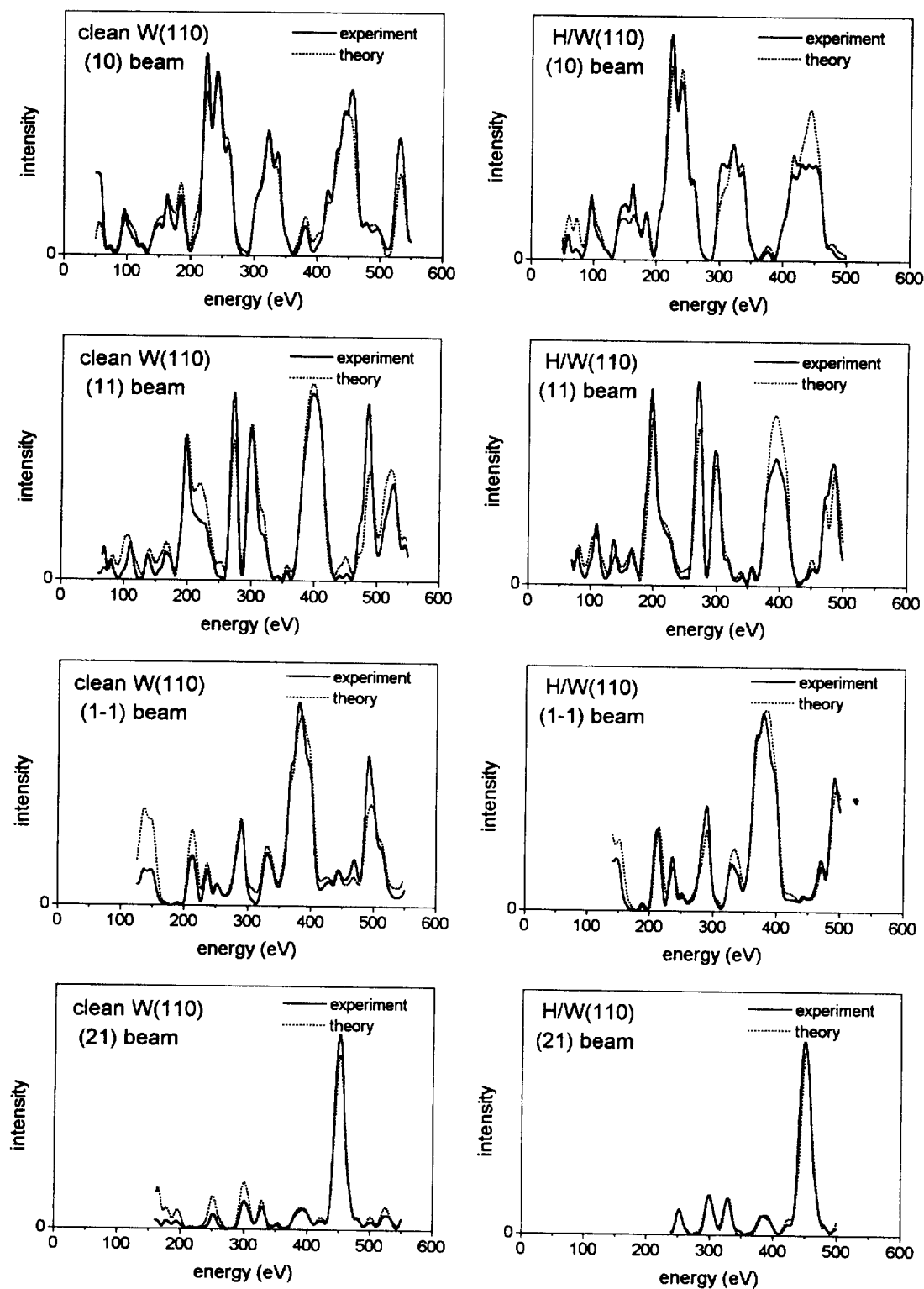


Fig. 2. Comparison of experimental (averaged over the symmetrically equivalent beams in each case) and calculated best-fit $I(E)$ spectra for some selected beams for the clean and hydrogen-saturated (1×1) phases.

we do not find evidence for the proposed top-layer shift reconstruction, either for the (1×1) -H phase or for the clean surface. In contrast, the tungsten atoms remain in their bulk positions, i.e. in the long-bridge sites of the layer below. This is with the exception of a small inward relaxation of the top layer by $\Delta d_{12}/d_0 = -3.1\%$ of the clean surface, which is partly lifted to only $\Delta d_{12}/d_0 = -1.7\%$ by hydrogen adsorption ($d_0 = 2.2364 \text{ \AA}$). No significant deeper-layer relaxations are observed. The statistical errors of the analyses as determined by the variance of the Pendry R -factor turn out to be much larger for the lateral parameters ($\sim 0.1 \text{ \AA}$) than for the vertical parameters ($\sim 0.01\text{--}0.02 \text{ \AA}$). This, however, is a quite usual characteristic of LEED analyses which are based on intensity data taken at normal incidence of the primary electron beam. Due to these error limits, we cannot exclude top-layer shifts smaller than about 0.1 \AA in both cases. However, we should mention that the minimum R -factors of both analyses are obtained right at the bulk-like position, as shown in Fig. 3. (Note that in the case of the (1×1) -H phase the R -factor curve becomes slightly asymmetric because of the adsorbed hydrogen atom breaking the symmetry of the long-bridge position, as discussed in detail below.)

Among the four distinct sites (Fig. 1c) tested for hydrogen adsorption, the lowest Pendry R -factor was achieved for the threefold hollow position, which provides the highest possible coordination for the hydrogen adsorbate (Fig. 1a). For this site, the height of the adsorbate layer above the substrate is found to be $d_H = 1.20 \text{ \AA}$. This corresponds to a hard-sphere radius of $r_H = 0.66 \text{ \AA}$ for the hydrogen atoms, which is in the range also found for hydrogen on other transition metals [24]. The best-fit R -factor for this threefold coordinated site is $R_p = 0.12$, with a variance of $\text{var}(R_p) = 0.02$. Thus, all structural models with a theory–experiment agreement of above 0.14 could be excluded merely by the statistical limits of error. This allowed us to reject the other three distinct adsorption sites for hydrogen under investigation, which produced comparably worse R -factors of $R_{\text{top}} = 0.22$, $R_{\text{short-bridge}} = 0.16$, and $R_{\text{long-bridge}} = 0.16$, respectively. Moreover, and besides these statistical arguments, all these models

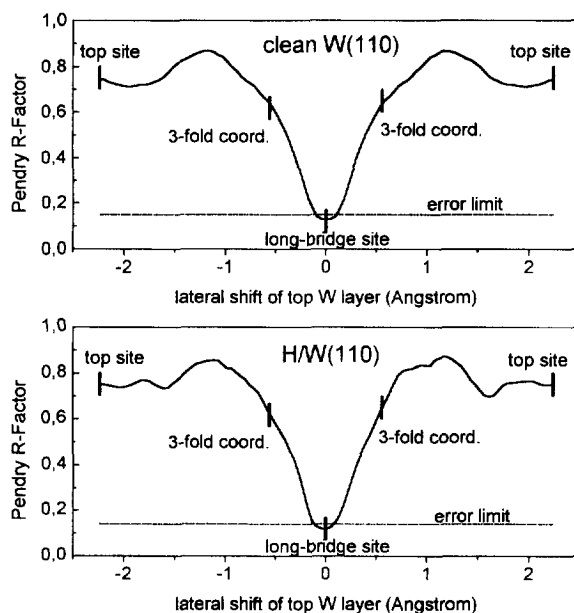


Fig. 3. Dependence of the Pendry R -factor R_p on the top W layer shift y_1 for the clean and hydrogen-covered W(110)- (1×1) H phases. In the latter case the adsorbate was kept fixed with respect to the first W layer, and thus simultaneously shifted. The positions of the top W layer with respect to the second W layer are noted. The long-bridge position corresponds to the layer stacking in the bcc structure.

led to the same or even smaller values for the adsorption height d_H , resulting in non-physical hard-sphere radii for hydrogen in short-bridge ($r_H = 0.45 \text{ \AA}$) and top sites ($r_H < 0$). Only the long-bridge site also resulted in a physically reasonable hydrogen radius of $r_H = 0.58 \text{ \AA}$.

The threefold coordinated site is not distinguished by symmetry (C_3) from any other position at the line between the long-bridge and the top site. Thus it may be that the hydrogen adsorbate actually does not prefer equidistant bond lengths to all three substrate atoms around the hollow site, but is shifted somewhat in the $[1\bar{1}0]$ direction. Since it turned out that not only the adsorption height d_H but also the other best-fit parameters for both the long-bridge and the threefold hollow site were practically identical, it appeared reasonable to fine-tune the lateral position of the hydrogen atoms along the coordinate y_H (cf. Fig. 1b) with all other parameters fixed at the best-fit values. The result of this variation is displayed in Fig. 4.

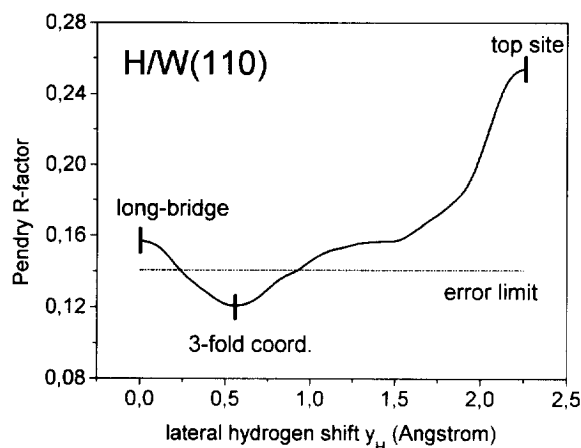


Fig. 4. Dependence of the Pendry R -factor on the lateral shift y_H of the hydrogen adsorbate along the $[1\bar{1}0]$ direction.

showing that a minimum of the R -factor is indeed obtained for the hollow site investigated. However, the statistical error for the parameter y_H , also indicated in Fig. 4, is $\Delta y_H = \pm 0.36$ Å, and is therefore far too large to rule out any slight shifts away from the ideally coordinated position. Table 1 summarizes the results for both the clean and the hydrogen-saturated phases.

Table 1

Compilation of structural parameters as defined in Fig. 1, resulting from the DFT and LEED analyses. For each system, the LAPW results for a five-, seven-, and nine-layer slab are presented

W(110)	DFT			LEED
	5 layers	7 layers	9 layers	
Δd_{12} (% d_0)	−4.1	−3.3	−3.6	$−3.1 \pm 0.6$
Δd_{23} (% d_0)	−0.2	−0.1	+0.2	0.0 ± 0.9
Δd_{34} (% d_0)	—	−0.4	−0.3	0.0 ± 1.0
(1 × 1)-H/W(110)	DFT			LEED
	5 layers	7 layers	9 layers	
Δd_{12} (% d_0)	−1.4	−1.3	−1.4	$−1.7 \pm 0.5$
Δd_{23} (% d_0)	± 0.0	+0.3	−0.3	0.0 ± 0.6
Δd_{34} (% d_0)	—	+0.3	−0.1	0.0 ± 0.9
y_1 (Å)	0.01	0.05	0.00	0.0 ± 0.1
d_H (Å)	1.12	1.11	1.09	1.20 ± 0.25
y_H (Å)	0.68	0.67	0.67	0.56 ± 0.36

3. DFT study

Our density functional theory calculations were performed using the local-density approximation for the exchange-correlation functional [25,26] and employing the full-potential linearized augmented plane-wave (LAPW) method [27]. Our code enables the efficient evaluation of the optimized geometry of stable and metastable structures by using a damped molecular-dynamics approach [28]. In order to check the accuracy, the substrate was modelled by three different slab systems: a five-, seven- and nine-layer slab. These slabs were repeated periodically and separated by a vacuum region of a thickness equivalent to four substrate layers. The geometry parameters are given in Fig. 1. For the potential, the (l, m) representation within each muffin-tin (MT) sphere was taken up to $l_{\max} = 4$ while the kinetic energy cut-off for the interstitial region was set to 64 Ry. We chose the plane-wave cut-off for the wave functions to be 12 Ry and employed an (l, m) representation in the MTs with $l_{\max} = 8$ for them. The MT radius for the W atoms was chosen to be 1.27 Å. For hydrogen, this radius was set to 0.48 Å. Fermi smearing with a broadening of $kT_{\text{el}} = 0.07$ eV was used in order to stabilize self-consistency and \mathbf{k} summation [29]. The valence and semi-core electrons were treated scalar relativistically, and the core states fully relativistically. The in-plane lattice parameter of the slab (3.14 Å), calculated without including zero-point vibrations, was in good agreement with the experimental bulk lattice parameters (3.163 Å [30] at room temperature). For the structure optimization we performed several calculations starting from different low-symmetry geometries in order to reduce the risk of getting trapped in a metastable geometry. Our results for different slab sizes are listed in Table 1. Note that the error range of the LAPW-calculated structure parameters was ± 0.02 Å, which is about 1% of the bulk interlayer spacing d_0 .

Depending on the size of the slab, we found a H-adsorption induced top-layer shift of $0.0 \text{ Å} \leq y_1 \leq 0.05 \text{ Å}$ towards the adsorbed hydrogen atom. Even if this shift y_1 is non-zero, it is doubtful that it can be resolved experimentally due to zero-point vibrations. We analyzed this aspect by per-

forming calculations using a H/W(110) slab with seven substrate layers, for which we obtained the maximum shift. First, we induced a rigid top-layer shift y_1 . Then, the surface was relaxed keeping only the substrate $[1\bar{1}0]$ coordinates y_1 and $y_2=y_3=0$ Å fixed. The calculated total energies are shown in Fig. 5, where we also depict the first three vibrational eigenstates of top-layer W atoms evaluated from a harmonic expansion of the total energy $E^{\text{tot}}(y_1)$. As $k_B T \approx 9$ meV at 100 K, being in the order of one quantum $\hbar\omega$ of the thermal vibration, we expect thermal fluctuations y_1 of up to ± 0.1 Å, which is larger than the marginal top-layer shift found in some of the slab calculations.

4. Discussion

It is interesting that the agreement between LEED and DFT results is very good with respect to all geometrical parameters of the analyses. This proves that both methods are now highly developed to provide quantitatively accurate data. This agreement also indicates that for both methods, the levels of accuracy and precision which in principle can be different because of possible sys-

tematic errors, are nowadays practically identical. The good correspondence further tells us that neither surface defects nor the kinetics of surface diffusion play a relevant role, because they are not considered in the DFT study but should show up in the experiment if present.

As the most remarkable result we find that there is no or at most a marginal lateral shift of the topmost tungsten layer occurring with hydrogen adsorption. So, the question arises as to whether there is a way to solve the apparent contradiction to the results of Chung et al. [6]. As already mentioned, they found a remarkable asymmetry in the intensities of LEED spots equivalent for the clean surface, which develops with hydrogen exposure at coverages exceeding half a monolayer. Since our results correspond to saturation coverage only, we restrict the following discussion to that case.

The experimental finding of Chung et al. [6] requires an unequal distribution of right- and left-hand side domains, most probably caused by surface imperfections such as steps, as also stated by the authors. Otherwise, averaging over the contributions of different domains would always enforce degeneracy of the experimental LEED intensity spectra. As a second constraint, the $(1\bar{1}0)$ mirror plane must be removed by hydrogen adsorption. This cannot be achieved by hydrogen itself as long as it is adsorbed in top or long-bridge sites. The latter sites, however, were assumed by Chung et al., supported by apparently unreliable effective-medium theory results [31] (where hydrogen is found to delocalize symmetrically around the long-bridge site) as well as by analogy to W(100) [32,33]. With this supposition, the conclusion of a top-layer shift was the only possibility to explain the experimental evidence of non-degenerate intensity spectra. However, the adsorption of hydrogen in a hollow-site position as found in our study directly breaks the symmetry of the $(1\bar{1}0)$ mirror plane, and does not necessarily require a substrate reconstruction. However, as hydrogen is known to be a comparatively weak scatterer, the induced effect on the LEED intensities might be expected to be very small. On the other hand, it cannot be totally negligible, otherwise we would not have

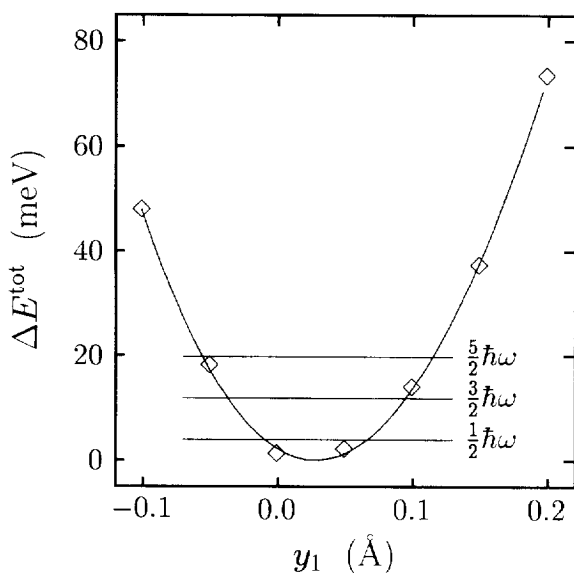


Fig. 5. Change of total energy E^{tot} versus a rigid top-layer shift y_1 . Also shown are the first three oscillator excitations.

found any sensitivity on the adsorption site in our LEED analysis.

In order to quantify the influence of the asymmetric hydrogen adsorption site for the comparison with the results of Chung et al., we have to compare the calculated LEED spectra for the now non-equivalent beams of one single domain before they are averaged, as routinely performed in the LEED analysis. Fig. 6 displays the respective curves for the (1,0) and ($\bar{1}$,0) beams which were also used in the investigation of Chung et al. [6]. Obviously they look very similar, in particular at higher energies above 100 eV, where the scattering cross-section of hydrogen indeed becomes negligible as compared to tungsten. At lower energies, however, there are remarkable differences in the intensity level as well as the exact position of the peaks to be observed, as demonstrated on an enlarged scale in the inset of Fig. 6. In particular, at a primary electron energy of 62 eV, where the asymmetry of the spots was monitored by Chung et al., the intensities of the non-equivalent beams differ by around a factor of three to four. Hence, the results reported by Chung et al. are definitely consistent with our results and with our explanations. The conclusively identified hollow site of hydrogen does not require the invocation of a top-layer shift as the symmetry is already broken.

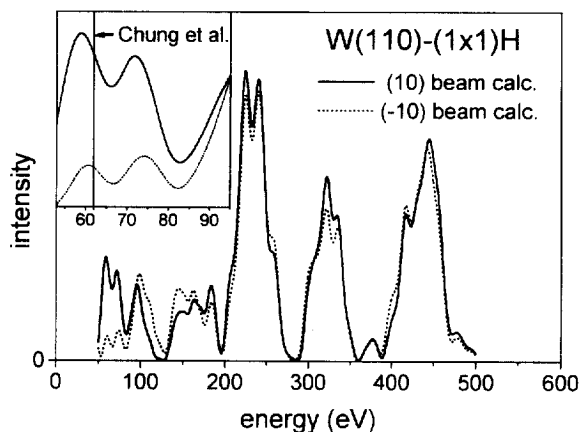


Fig. 6. Comparison of the LEED $I(E)$ spectra for the non-equivalent (1,0) and ($\bar{1}$,0) beams of the best-fit model for W(110)-(1 \times 1)H. The low-energy region is magnified in the inset, also showing the energy used in the investigation of Chung et al. [6].

Unfortunately, right in the above-mentioned energy region, our LEED calculation fails to produce the exact intensity level of the experimental (1,0) beam. Since the latter was averaged over all symmetrically equivalent beams, this effect has nothing to do with an asymmetry between the (1,0) and ($\bar{1}$,0) beams which could not be found at all in our experiments, as already outlined. We tentatively attribute this discrepancy to some residual disorder within the H adlayer which might lead to significant lower experimental intensities in a regime where hydrogen scattering becomes dominant, as discussed in the following. (For adsorbate structures, it frequently occurs that calculated superstructure spot intensities are higher by a factor of up to 2–3 than experimental values.)

The differences between the two spectra displayed in Fig. 6 might come as a surprise even to the LEED specialist. This is because the electron scattering cross-section of hydrogen is only in the percentage region of that of tungsten atoms. The reader should recall that the amplitudes of hydrogen and tungsten layers rather than their intensities interfere. Consequently, in a simplified and kinematic picture, the square root of the differential cross-section (i.e. the atomic scattering amplitude $f(\theta)$) in the direction of the beam under consideration is a more relevant quantity for comparison. Due to the complex multiple intra-atomic scattering, the angular dependence of $f(\theta)$ in the backwards direction is rather modulated for many-electron atoms such as tungsten, which is different from the smooth behaviour of hydrogen scattering. The numerical evaluation of the modulus of the scattering factor back into the (1,0) direction shows that around 60 eV the value for tungsten scattering is only 20% larger than that for hydrogen. Of course, because it is kinematic, this consideration does not reflect the full surface diffraction scenario. Therefore, in order to gain more insight on the basis of full dynamical diffraction, we calculated the diffraction from the isolated hydrogen layer back into the (1,0) direction and compared it to the amplitude diffracted into the same direction from the tungsten substrate, both for normal incidence of the primary beam. Full dynamical intralayer scattering was considered for hydrogen as well as tungsten layers (though it is

not very important in the case of hydrogen), and full interlayer diffraction within the tungsten substrate was allowed for. The contribution of the substrate was reduced according to the attenuations of electrons when travelling between the hydrogen layer and the substrate. Fig. 7 displays the result for the modulus of the diffraction amplitude in each case. Evidently, at around 60 eV the contribution of the hydrogen layer is about the same strength as that of the substrate. As a consequence, the interference of both can significantly affect the total intensity. Near 150 eV, the modulus of the hydrogen amplitude is still half of that of the substrate, but then decreases rapidly. These features undoubtedly demonstrate the non-negligible role of hydrogen scattering in the low-energy region. Further influence of hydrogen could come through forward diffraction by the hydrogen layer for the impinging primary beam towards the substrate and for the wavefield coming back from the substrate, neither of which are considered in the calculations displayed in Fig. 7.

It is worth noting that Chung et al. also observed the described intensity asymmetry in the submonolayer regime, i.e. in the coverage range 0.5–1, which was not subject of the present investigation. However, also in this regime adsorption in three-fold coordinated hollow sites of a single domain accounts for the experimental observation without the need of a registry shift. Initially, defects induce

the preferential occupation of only one type of site. At sufficiently high coverage, hydrogen–hydrogen interaction enforces further occupation of the same sites. As a consequence, the degeneracy of beams which are symmetrically equivalent for the clean surface is lifted. However, the asymmetry should become weaker and weaker with decreasing coverage because the hydrogen–hydrogen interaction becomes too weak to make H atoms reside exclusively in one type of site. As soon as the second type of site starts to become occupied, the observed asymmetry will be reduced. In fact, this is the finding of Chung et al.

As a consequence of our results, H/W(110) proves to be an “ordinary” adsorption system.

For the clean W(110) surface we observe an inward relaxation of about 3–4% of d_0 , which appears rather large for a quasi-hexagonal close-packed surface [24]. However, for transition metals one should take into consideration the influence of the d-electrons. For elements in the middle of the d-rows, the important mechanism is the relation between bond-strength and coordination. The bonding between atoms becomes stronger when the number of neighbours decreases. This is because the bonding electrons can then concentrate on less numerous bonds and need not oscillate between many different binding geometries. With increasing bond strength, however, the atomic distances decrease. So, at the surface with its reduced coordination, interlayer distances should be reduced.

On this qualitative basis, a non-vanishing first-layer contraction, as found in our investigation for the clean W(110) surface, can be easily understood. Nevertheless, our results contrast with those of a previous LEED study by Van Hove and Tong [17], who found no relaxation of the topmost layer. However, this analysis goes back to the very early days of LEED structure determinations, where, as state-of-the-art at that time, the comparison of experimental and calculated spectra had to be performed on a subjective visual base without any quantitative measure such as an *R*-factor. Moreover, the acquisition of experimental data with a movable Faraday cup (by Lagally et al. [34,35]) was very time-consuming, as already pointed out by the experimentalists [35]. So, resid-

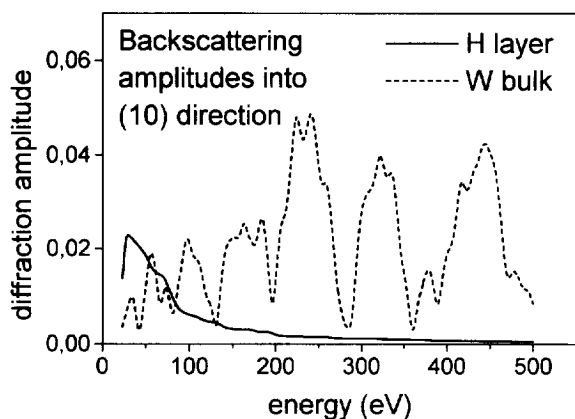


Fig. 7. Comparison of the modulus of the diffraction amplitudes of an isolated hydrogen layer and of the tungsten substrate for the (1,0) beam.

ual gas adsorption might have contaminated the surface during the measurements, which in general is known to reduce surface relaxations. On this basis, we think that a discrepancy with the earlier LEED analysis of not more than $3\%d_0 \approx 0.07 \text{ \AA}$ in the surface relaxation may still be regarded as a fair agreement. This, however, does not hold for the results of a more recent ARXPS study by Kim et al. [36], who even report a 1.1% ($\pm 2.2\%$) outward relaxation for the clean W(110) surface. We have no explanation as yet for this clear contradiction of our values.

As shown, a saturation coverage of hydrogen on W(110) reduces the first-layer relaxation amplitude significantly (by a factor of two). This trend towards an unrelaxed bulk-like termination upon hydrogen adsorption is quite general, and has been observed for a number of metal surfaces (see, e.g., Ref. [16]). It can be explained qualitatively by a partial refilling of the dangling d-bonds at the surface due to the adsorption of hydrogen. To a certain extent this will restore the bulk-like environment for the first substrate layer. Consequently, we have a de-relaxation of the distance of the first two surface layers by about $2\%d_0$, resulting in a layer contraction of $\Delta d/d_0 = 1\text{--}2\%$.

Hydrogen itself is found to be adsorbed in or near the threefold coordinated hollow site with a covalent radius of 0.66 \AA . This is in agreement with the results for other hydrogen-covered bcc(110) surfaces like iron [37,38], molybdenum [39] and $\text{Mo}_{0.75}\text{Re}_{0.25}$ [40]. The calculated adsorption energies for both bridge positions as well as the top site are, similarly to the H/Mo(110) system [41], several 100 meV lower. The DFT study, which presumably is of higher accuracy with respect to the exact hydrogen position than LEED, indicates a slight shift of about 0.1 \AA from the ideally threefold coordinated site towards the top position. As this is within the error limits of our LEED analysis, such a small shift off the ideally coordinated site might be possible.

5. Conclusion

In the present paper we have demonstrated that the clean as well as the fully hydrogen-covered

W(110) surface exhibit quite ordinary structures. In particular, we show that the top layer does not undergo a noteworthy lateral-shift reconstruction upon hydrogen adsorption as postulated previously. Moreover, we were able to present an alternative interpretation of the previous measurements on the basis of LEED intensity calculations. The structural parameters derived from the LEED intensity analysis and from density functional theory are in excellent quantitative agreement. The clean W(110) surface was found to exhibit a 3–4% inward relaxation, which is reduced to about $\Delta d/d_0 = 1\text{--}2\%$ at saturation coverage of hydrogen. The adatom adsorbs on a threefold coordinated site $1.1\text{--}1.2 \text{ \AA}$, above the substrate.

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