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Adsorption of hydrogen on Pt(100) at low temperatures

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Abstract

We have investigated the structure of the hydrogen-covered Pt(100) surface by high-resolution helium diffraction and compared it with the clean one. At surface temperatures below 250 K hydrogen adsorption leads to characteristic changes in the surface structure, as observed also by other authors [1–5]. While this structure was previously denoted as "(1 × 1)-like", our He-diffraction patterns clearly show, that the reconstruction is not removed at temperatures below 250 K. The diffraction patterns of the hydrogen-covered surface are compared to those obtained for the reconstructed Pt(100)-hex surface and the unreconstructed clean Pt(100)(1 × 1) surface (hydrogen coverage < 1%) The corrugation functions for these three surfaces were obtained using the eikonal approximation. The modified surface corrugation of the "(1 × 1)-like" structure is interpreted as a charge redistribution caused by the adsorbed hydrogen on the surface.

Keywords: Atom–solid interactions, scattering, diffraction; Atom–solid scattering and diffraction – elastic; Surface relaxation and reconstruction

1. Introduction

Metal surfaces reconstruct to minimize their surface free energy. In order to compensate for the reduced coordination of the surface atoms, the atomic arrangement in the outermost layers may differ from a mere continuation of the bulk structure. For clean single crystals of fcc metals surface reconstructions have been observed, for instance, for the (100) and (110) surface of Ir [6,7,11], Pt [7,8,12], Au [9,10,13] and for the (111) surface of Au [14] and Pt [15]. The atomic arrangement of the atoms in the surface sensitively depends on various factors, such as surface temperature or presence of adsorbates. On the other hand, the structural changes at the surface may alter the surface properties as, for instance, electronic properties or surface reactivity. In order to study the effect of the surface reconstruction it is necessary to first characterize the structure as well as to find recipes by means of which the surface structure can be changed in a reproducible way. In this context, particular effort has been devoted to the lifting of the stable surface reconstruction.

A well-known example is the (100) surface of platinum. After applying the initial cleaning procedure, including cycles of sputtering and heating, two different reconstructed states can be prepared starting

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from the rough (1 × 1) structure obtained after Ar^+-ion bombardment at room temperature: Heating the crystal above 400 K produces the *metastable* Pt(100)-hex phase which, upon further heating to 1100 K, is transformed into the *stable* Pt(100)-hex-R0.7°C phase, also denoted hex-rot phase [7,16]. In these structures the top-layer platinum atoms rearrange themselves to form a hexagonal, close-packed, buckled layer on top of the second layer, which retains the bulk structure. In the case of the stable hex-rot phase the first layer is in addition rotated by 0.7°. Both structures show complex LEED patterns with intense spots at 1/5th of the distance between the bulk spots, but a different fine structure in the spot splitting. Concerning the precise structure of these surfaces, different authors obtained slightly different unit cells. The Pt(100)-hex phase was described by a (5 × 20) [1], (5 × 25) [3] and c(26 × 150) [17] unit cell. For the Pt(100)-hex-R0.7° structure different coincidence unit cells were proposed as, for instance, the $\left(\begin{smallmatrix}13 & -1\\ 18 & 43\end{smallmatrix}\right)$ structure in Ref. [17], and detailed X-ray studies have well characterized the temperature-dependent behavior of this structure [18,19].

The Pt(100) surface has been of considerable interest ever since the discovery of Bonzel et al. in (1975) [20,21], that a metastable, clean (1 × 1) surface structure can be prepared from the reconstructed clean surface by a combination of various adsorption and desorption processes. In brief, the reconstruction is lifted by first adsorbing NO or CO at room temperature, followed by a short heating to ~ 400 K (where the molecules dissociate), and finally removing the remaining oxygen by titration with hydrogen. The transformation from the reconstructed platinum surface to the (1 × 1) structure is not understood in detail, but the main features are known and have also been studied on the atomic scale by scanning tunneling microscopy (STM) [22]. The adsorption of NO or CO affects the surface free energy in such a way that Pt atoms are preferentially removed from the 20% denser surface layer, forming new terraces on top of the surface. In this case a *complete* lifting of the reconstruction is reached and all platinum atoms occupy bulk lattice positions. Norton et al. [1] reported, that a (1 × 1) surface structure might also be obtained by hydrogen adsorption at low temperatures, however, with a lower degree of perfection as indicated by the persistence of broad LEED spots at 1/5th positions. Nielsen et al. [3] and later Pennemann et al. [4] have investigated the hydrogen adsorption on the reconstructed Pt(100) surface at low temperatures. They reported LEED patterns with only weak superstructure features, which they described as stripes or elongated spots. These always present residual superstructure spots were assumed to originate from an *incomplete* lifting of the reconstruction. The two distinct (1 × 1) structures, i.e. the (1 × 1) structure prepared using NO or CO and the so-called "(1 × 1)-like" structure obtained after hydrogen adsorption also differ in their chemical reactivity and electronic properties [3–5].

In connection with the different nature of the (1 × 1) and "(1 × 1)-like" surfaces two experimental observations deserve special attention [2–4]. First, the temperature at which the transition from the "(1 × 1)-like" surface to the reconstructed surface occurs is about 350 K [23], while the Ar^+-ion-bombarded surface transforms into a poorly ordered (1 × 5) surface only at a temperature above 400 K. Thermal desorption measurements by Pennemann et al. [4] further revealed that the transformation of the "(1 × 1)-like" phase takes place just at the temperature where the hydrogen desorbs from the surface. Hence, the "(1 × 1)-like" phase seems to exist only in presence of hydrogen on the surface. The second and more significant point is an observation reported by Nielsen et al. [3]. Upon heating to 400 K the "(1 × 1)-like" structure always transforms directly back into exactly that reconstructed phase (hex or hex-rot) from which it was created: This "memory effect" would not be expected if the "(1 × 1)-like" phase were a true (1 × 1) phase. The true (1 × 1) phase always first transforms into the hex phase and only at higher temperatures (~ 1100 K) into the hex-rot phase [7]. Due to the low adsorption temperatures it may, however, be possible that in contrast to the adsorption procedures at room temperature (e.g. Ref. [20]) specific defects (e.g. steps with certain orientations [19]) are frozen in and favor the return to the same type of reconstructed phase from which the "(1 × 1)-like" was created.

Thus, it is not clear so far whether the adsorption of hydrogen at low temperatures leads to a partial removal of the surface reconstruction or what other possible structural changes might occur. Using thermal energy He diffraction we have investigated the structure of the reconstructed Pt(100) surface after hydrogen adsorption at temperatures between 25 and 250 K and compared it to the (1 × 1) phase obtained after lifting the reconstruction with NO.

2. Experimental

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base-pressure of about 1×10^{-10} mbar. Besides the facilities for He-scattering the chamber is equipped with a combined LEED/Auger system and a sputter-gun. The sample crystal is mounted on an *xyz*-manipulator and can be rotated around its three principle axes. The crystal can be heated up to 1600 K by electron bombardment and cooled to 25 K by means of a He cryostat connected to the sample holder by a copper braid. For the measurements reported below the energy of the incoming He beam was 69.8 meV and the total scattering angle was fixed at $\vartheta_i + \vartheta_f = 90°$. The diffraction profiles were all taken along the $\langle 01\bar{1} \rangle$ direction of the crystal. The Pt(100) crystal was prepared in situ by heating for several hours at 900 K in an oxygen atmosphere of about 1×10^{-8} mbar, followed by several cycles of sputtering with 1 keV Ar^+ ions and subsequent annealing at temperatures between 900 and 1300 K. The cleanliness of the crystal was controlled by monitoring the intensity of the specularly reflected He beam, which constitutes a sensitive measure for surface defects and impurities [24]. The well-prepared surface exhibited an ordered Pt(100)-hex structure as seen from the He-diffraction profiles shown in Fig. 1. The peaks at 1/5th positions of the integer-order peaks indicate the five-fold periodicity of the hex-reconstructed surface along the $[01\bar{1}]$ direction. (The additional peaks near the (0, 0) peak are explained by the more complex structure of the reconstruction [17], which will be neglected in the present discussion.) Some adsorption experiments were also conducted on the Pt(100)-hex-R0.7° surface which is obtained by heating the crystal to temperatures above 1100 K. This structure is characterized by a splitting of the diffraction peaks caused by the slight rotation of the first layer. After hydrogen adsorption on both reconstructed phases almost identical He-diffraction patterns were obtained. Since the Pt(100)-hex surface is easier to prepare, most of the experiments were performed on this phase.

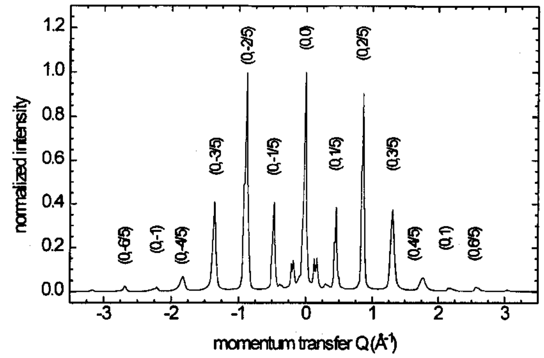

Fig. 1. Normalized He-diffraction scan of the bare Pt(100)-hex surface taken along the $[01\bar{1}]$ direction for a He beam energy of 69.8 meV and a surface temperature $T = 300$ K. The diffraction peaks at 1/5th-order positions are characteristic of the hexagonal reconstructed surface. Note the slightly higher intensity of the 6/5 peak as compared to the (0, 1) peak.

3. Results and discussion

Following the recipes of Bonzel et al. [20] and Norton et al. [2] the unreconstructed Pt(100)(1 × 1) phase can be prepared by NO adsorption in two slightly different ways. We took advantage of the sensitivity of the specularly reflected He beam with respect to the presence of adsorbates on the surface [24] for a modification of the recipes in order to ensure the lowest possible H coverage on the unreconstructed surface. In the present case NO was adsorbed at room temperature until the specular He intensity stopped decreasing, indicating the saturation of the surface. Then the sample was flashed to 400 K to dissociate the NO leaving only oxygen adsorbed on the surface. Finally, the oxygen was removed by exposing the surface to H at room temperature until the specular He intensity stopped increasing. From the height of the specular He intensity we can estimate that the terrace coverage of adsorbed H and O after this preparation is less then 1%. The capability of the thermal He scattering to detect small amounts of adsorbates (in particular hydrogen) allows to prepare an almost adsorbate-free unreconstructed Pt(100) surface. A more detailed discussion of the procedure will be given in a forthcoming paper [25]. Fig. 2 shows the He diffraction profile along the [01$\bar{1}$] direction of the so prepared Pt(100)-(1 × 1) surface. Besides the specularly reflected He beam (0, 0) only the first order peaks (0, 1) and (0, −1) are visible and no superstructure peaks can be detected in between anymore. LEED pictures obtained from this ordered (1 × 1) structure also exhibited spots only at the bulk positions, in agreement with LEED patterns reported by Norton et al. [2]. In the following, the diffraction scan in Fig. 2 is taken as a reference for the well-ordered and clean Pt(100)(1 × 1) surface structure to which structures of the surfaces obtained after the attempts to lift the reconstruction by using hydrogen alone, are compared.

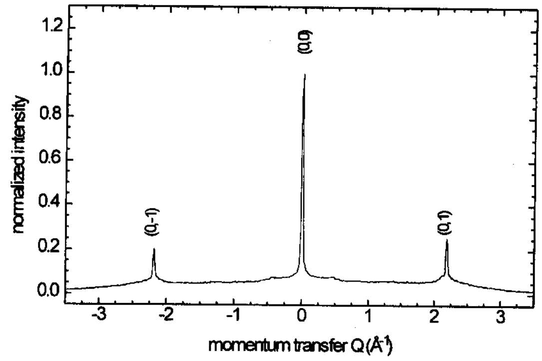

Fig. 2. Normalized He-diffraction scan of the clean Pt(100)(1 × 1) surface obtained after NO adsorption and subsequent titration with hydrogen (see text). The profile is taken along the [01$\bar{1}$] direction with a He beam energy of 69.8 me V at a surface temperature $T = 300$ K. No superstructure peaks are seen between the integer-order peaks, indicating that the reconstruction is fully removed.

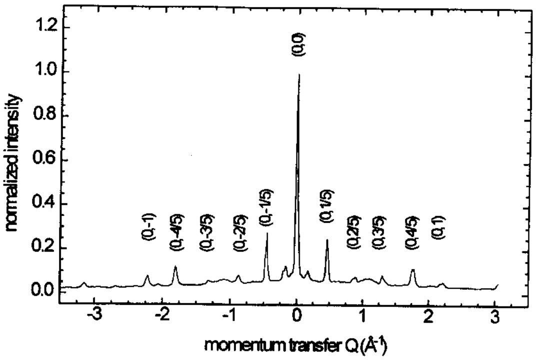

Fig. 3. Normalized He-diffraction scan of the Pt(100)-hex surface after 3 L hydrogen exposure at $T = 25$ K taken along the [01$\bar{1}$] direction with a helium beam energy of 69.8 meV at a surface temperature of $T = 25$ K. Compared to the clean reconstructed surface (Fig. 1) the intensity of the specular beam is reduced by a factor of 2.5. Note that at the 2/5th and 3/5th-order position only weak diffraction features are observed.

To answer the question whether it is possible to remove the Pt(100) reconstruction by hydrogen adsorption at low temperatures alone [1,3,4], we have carried out a series of adsorption and annealing experiments at surface temperatures between 25 and 250 K. We never obtained a He-diffraction scan similar to that of the clean (1 × 1) surface as can be seen, for instance, by comparing the diffraction profiles of Fig. 3 and Fig. 2. The diffraction scan in Fig. 3 shows the diffracted helium intensity in the [01$\bar{1}$] direction of the reconstructed Pt(100)-hex surface after exposure to 3 L (1 langmuir = 10^{-6} Torr · s) of hydrogen at a surface temperature of $T = 25$ K. While the intensity of the superstructure peaks (1/5th order peaks) is decreased relative to the integer-order peaks, the presence of all superstructure peaks indicates that the reconstruction has not been removed. It should be pointed out that some peaks, like the 2/5 or 3/5, are more strongly affected than other superstructure peaks. In addition, there is a broad feature at the (0, 1/2) positions. The same result was obtained for a larger exposures (up to 50 L) as well as after increasing the surface temperature up to 80 K. LEED patterns from the so-prepared surfaces exhibited broadened spots and weaker superstructure spots. Again, the intensity is reduced more strongly for the 2/5 and 3/5 spots than for the 1/5 and 4/5 spots. The 1/5th-order peaks in Fig. 3 are still as sharp as those of the Pt(100)-hex phase (Fig. 2). This indicates no significant disordering of the structure and no measurable decrease of the domain size which is still larger than 150 Å, as determined from the peak widths. The diffraction scan is somewhat different if hydrogen is adsorbed at temperatures above 80 K. As an example, Fig. 4 shows the scan after 3 L hydrogen exposure at a surface temperature $T = 105$ K. Similar patterns are obtained for all adsorption temperatures between 80 and 120 K and exposures up to 50 L. Some of the superstructure peaks, namely the 2/5, 3/5 and 6/5 peaks, have nearly disappeared. The broad half-order peaks are also not present. In contrast, the 1/5 and 4/5 peaks remain intense although a slight broadening as compared to

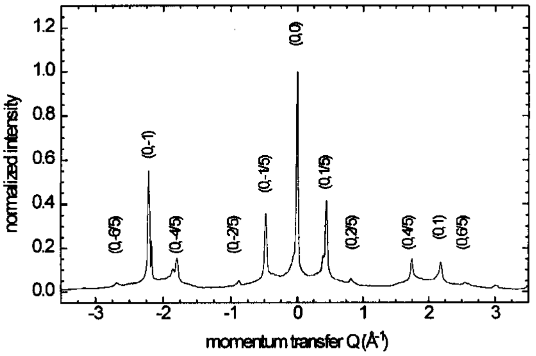

Fig. 4. Normalized He-diffraction scan of the Pt(100)-hex surface after 3 L hydrogen adsorption at $T = 105$ K taken along the $[01\bar{1}]$ direction with a He beam energy of 69.8 meV at a surface temperature of $T = 25$ K. No peak can be detected at the 3/5 position and the peaks at the 2/5 and 6/5 positions also have nearly disappeared.

the integer-order peaks is observed which, however, still indicates domain sizes of more than 110 Å. In the LEED patterns which correspond to the ones known from the literature [4] a weakening of the 2/5 and 3/5 spots and subsistence of broad spots at the 1/5 and 4/5 positions is observed.

Short heating for about 1 min at temperatures between 150 and 250 K of the hydrogen-covered surface always yielded a diffraction pattern as shown in Fig. 5, where now the 2/5 and 3/5 peaks have completely disappeared and only those superstructure peaks are visible that are direct neighbors of the integer-order peaks, such as the 1/5, 4/5 and 6/5 peaks. Since these peaks are closest to the bulk spots they could sometimes not be resolved in our LEED system leading to the impression of elongated spots at the bulk positions. This is in fact in agreement with the LEED observations reported by Nielsen et al. [3] and Norton et al. [2], but not with the pattern of a (1 × 1) surface (Fig. 2), where no superstructure spots are detected and only sharp bulk spots are retained. Based on the notation in Refs. [2,3] we also use the term "(1 × 1)-like" to describe this surface. As will be shown below, the underlying structure, however, is not likely to be accompanied by the removal of the Pt(100) reconstruction, as this name suggests. Finally, at temperatures above 250 K no hydrogen could be adsorbed on the reconstructed Pt(100) surface as indicated by an unchanged intensity of the specularly reflected helium beam.

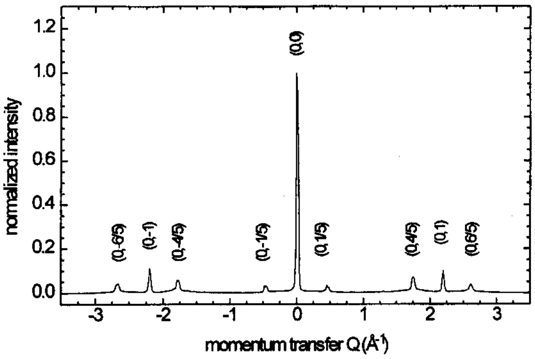

Fig. 5. Normalized He-diffraction scan of the Pt(100)-hex surface after 3 L hydrogen adsorption at $T = 110$ K and short annealing at $T = 150$ K (~ 1 min) taken along the $[01\bar{1}]$ direction with a He beam energy of 69.8 meV at a surface temperature of $T = 25$ K. No peaks are detected at the 2/5 and 3/5 positions, but strong superstructure peaks are observed at the nearest 1/5th positions on both sides of each integer-order peak.

In all cases the hydrogen-induced surface structures transformed back to the reconstructed Pt(100)-hex phase after heating the crystal to about 330 K. Similarly, if the Pt(100)-hex-rot phase was used for the preparation, the surface transformed at around the same temperature back into the original hex-rot phase, as seen from the appearance of splitted superstructure peaks. This is also in agreement with the observations reported by Nielsen et al. [3].

The changes in the diffraction pattern due to hydrogen adsorption at low temperature cannot be attributed to a homogeneous lifting of the reconstruction since large reconstructed domains must remain intact in order to explain the sharp superstructure peaks. If we assume, on the other hand, that the preserved five-fold periodicity is found in large areas which are not covered by hydrogen, a proportional reduction of *all* superstructure peaks (relative peak intensities preserved) is expected. In our experiments this is clearly not the case. We thus have to assume that the superstructure remains intact below the adsorbed hydrogen. In contrast, the appearance of the broad peak at the half-order positions (0, 1/2) and (0, −1/2) may indicate the formation of small domains of (2 × n) character. Because of the width and low intensity of the peak it cannot be excluded that Pt atoms are involved in this change of periodicity. These small domains (with sizes of about 30 Å according to the peak width) do obviously not appear

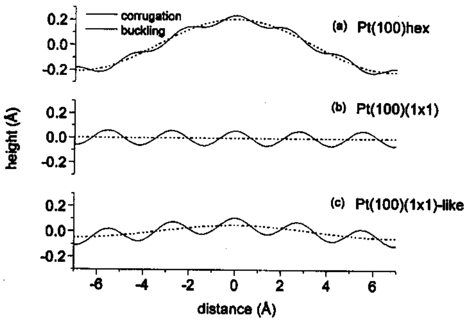

Fig. 6. Best-fit one-dimensional corrugation function calculated from the values in Table 1 for the three Pt(100) structures. The solid line is the sum over all terms in Eq. (1), the dashed lines shows the surface buckling with periodicity $5a$ only (third term in Eq. (1), corrugation amplitude ζ_3).

at adsorption temperatures above 100 K as can be concluded from the fact that no half-order peaks are present in Figs. 4 and 5.

In the following we will discuss a simple model which can explain quantitatively the intensity distribution for the "(1 × 1)-like" structure obtained after adsorption above 100 K and subsequent annealing (Fig. 5). In order to interpret the He-diffraction profiles one has to consider the possible modification of the surface corrugation induced upon hydrogen adsorption. To this end corrugation functions for the reconstructed Pt(100)-hex, the (1 × 1) and the "(1 × 1)-like" surface structures were fitted to the He-diffraction scans. A simple, one-dimensional hard corrugated wall model was used to describe the surface, and the diffraction profiles were calculated within the eikonal approximation [26].

We assume a homogeneous surface morphology. The Pt(100)-hex reconstruction is described in a simplified manner by a (1 × 5) unit cell, in which 6 Pt atoms in the topmost layer are placed above 5 atoms in the second layer. The stress in the surface caused by the 20% increased packing density in the topmost layer is partially compensated by a buckling of the first layer with a period of $5a$, where $a = 2.77$ Å is the Pt nearest-neighbor distance in the bulk. In the case of a (1 × 1) structure (i.e., if the Pt reconstruction is lifted) all atoms have the same distance a and the first layer should no longer be buckled with a $5a$ periodicity. On the other hand, for the "(1 × 1)-like" phase some buckling still remains, otherwise the peaks at the 1/5th positions would not be observed. Based on these arguments we took the following ansatz for the corrugation function:

$$\zeta(x) = \frac{1}{2}\zeta_1 \cos\left(\frac{2\pi}{a}x\right) + \frac{1}{2}\zeta_2 \cos\left(\frac{2\pi}{\frac{5}{6}a}x\right) + \frac{1}{2}\zeta_3 \cos\left(\frac{2\pi}{5a}x\right), \qquad (1)$$

including all expected periodicities with periods a (row distance on Pt(100)(1 × 1)), $5a/6$ (row distance on Pt(100)-hex) and $5a$ (top-layer buckling of Pt(100)-hex), respectively (see Fig. 6). Table 1 displays the values for the corrugation amplitudes ζ_1, ζ_2 and ζ_3 obtained from the best fits to the measured intensities (cf. Figs. 1, 2 and 5). All 1/5th-order peaks between the (0, $-6/5$) peak and the (0, $6/5$) peak are included. A comparison of the measured and calculated integral intensities is given in Fig. 7 for the diffraction profiles in Figs. 1, 2 and the well-annealed "(1 × 1)-like" structure in Fig. 5. As reliability factor we used:

$$R \equiv \frac{1}{(2N+1)} \sqrt{\sum_{k=-N}^{N} \left(I^{\exp}(k) - I^{\mathrm{calc}}(k)\right)^2}, \qquad (2)$$

where $2N+1$ is the number of diffraction peaks considered in the calculations and $I^{\exp}(k)$ is the measured integrated intensity of the kth peak. Although the calculated intensities differ at some positions from the measured ones, this simple model can

Table 1
Calculated corrugation amplitudes and reliability factors

	ζ_1 (Å)	ζ_2 (Å)	ζ_3 (Å)	R factor
Pt(100)-hex	< 0.01	0.06	0.42	0.035
Pt(100)(1 × 1)	0.12	< 0.01	< 0.01	0.0077
Pt(100) "(1 × 1)-like"	0.12	< 0.01	0.1	0.035

The table contains the values of the corrugation amplitudes ζ_1, ζ_2 and ζ_3 in Eq. (1) obtained from the best-fit to the diffraction data as well as the corresponding reliability factors R. For the calculation the eikonal approximation was used and all 1/5th-order peaks between the (0, $-6/5$) peak and the (0, $6/5$) peak were included in the fit. The corrugation function $\zeta(x)$ and the R factor are defined by Eq. (1) and Eq. (2), respectively.

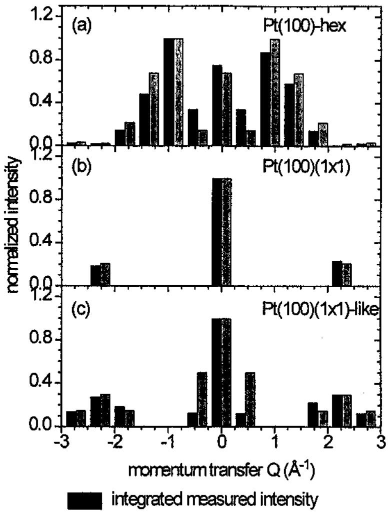

Fig. 7. Comparison between experimental He-diffraction intensities and the best-fit intensities calculated within the eikonal approximation and using the corrugation function in Eq. (1). The parameters for ζ_1, ζ_2 and ζ_3 are given in Table 1. All measurements were normalized to 1: (a) Pt(100)(1 × 1), (b) Pt(100)-hex, (c) "(1 × 1)-like" Pt(100) surface.

explain the main characteristics of the diffraction profiles, such as the higher intensity of the (0, 6/5) peak as compared to the (0, 1) peak in the diffraction pattern of the Pt(100)-hex surface. Here the corrugation amplitude ζ_3 of the surface buckling is in good agreement with the value of 0.4 Å as measured by scanning tunneling microscopy (STM) [22,27]. For the reconstructed Au(100) surface, whose structure is very similar to that of the Pt(100) surface, a corrugation amplitude for the surface buckling of 0.5 Å was reported [28]. The value $\zeta_2 = 0.06$ Å for the Pt(100)-hex surface is also not unrealistic if it is compared with corrugation amplitudes expected for close-packed metal surfaces, like Ag(111) and Pt(111) with values around 0.01 Å [29]. In contrast, a small surface buckling still persists on the "(1 × 1)-like" surface. The presence of peaks at integer and neighboring 1/5th-order position in the diffraction pattern of the "(1 × 1)-like" structure (see Fig. 5) requires a corrugation function with two components; one with periodicity a (ζ_1) and the other with $5a$ (ζ_3) (Table 1 and Fig. 6c). At first sight this seems to point to a removal of the reconstruction restoring the original bulk Pt spacing by the component $\zeta_1 = 0.12$ Å. However, the other component of the corrugation function $\zeta_3 = 0.1$ Å, which is necessary to obtain intensities at fifth-order positions, must be considered as well. It corresponds to the buckling of the reconstructed hexagonal surface structure (cf. Fig. 6a) and should be absent for a flat well-ordered (1 × 1) surface structure (cf. Table 1 and Fig. 6b).

A strong argument against the lifting of the reconstruction in the "(1 × 1)-like" phase is the fact that specular peak profiles at anti-phase scattering conditions showed no side peaks on the "(1 × 1)-like" phase in contrast to what is observed for the (1 × 1) surface after removal of the reconstruction [25]. In the latter case the Pt atoms expelled from the surface during the lifting of the reconstruction aggregate into Pt islands on top of the surface, which then lead to the observed side peaks in the anti-phase peak profile. Consequently, we infer that in the "(1 × 1)-like" structure the top-most layer is still densely packed and, hence, that the reconstruction is not removed.

As already discussed, our results can not be explained by a *partial* removal of the reconstruction. If one part of the surface is unreconstructed while the other part is not, a superposition of the corresponding profiles and corrugation functions (cf. Figs. 7a and 7b and Figs. 6a and 6b, respectively) would be expected. In particular, a component of the corrugation function with a periodicity of $5a/6$ from the reconstructed part, should have been observed. This was not the case in our investigations. In contrast, a strong change of the relative intensities of the fifth-order peaks, even the complete disappearance of some of them, is observed.

To understand the origin of the structural changes in the "(1 × 1)-like" phase as compared to the structures of the unreconstructed (1 × 1) phase and the reconstructed hex phase, respectively, we recall that only in the "(1 × 1)-like" case the surface is covered with hydrogen. This, together with the strong dependence on the annealing and adsorption procedure (Figs. 2–5), should be considered in the interpretation of the "(1 × 1)-like" phase.

From the experiments, calculations and the above discussion we infer that the "(1 × 1)-like" surface is reconstructed even after annealing to 250 K, but due to the presence of H adatoms a relaxation takes place. The corrugation of the hexagonal reconstructed surface is changed upon the adsorption of hydrogen so that it becomes flatter and instead of the periodicity of $\frac{5}{6}a$ a corrugation with "bulk" periodicity a is obtained. This, however, does not necessarily mean that one of the 6 top layer atoms in the unit cell has been removed: since the He-atoms are sensitive to the electron density above the surface [30,31] and not to the atoms themselves, the changes of the corrugation only imply a corresponding change of the lateral distribution of the electron density. A possible explanation would be the smoothening of the corrugation by charge redistribution upon hydrogen adsorption similar to the mechanism proposed by Finnis and Heine [32] (see also Baddorf et al. [33]). They proposed for the removal of a (110) surface relaxation by hydrogen adsorption a smoothening of the surface electron density due to the fact that the electrons of the hydrogen atoms must be included in the charge transfer that minimizes the surface free energy.

If we assume a hydrogen saturation coverage of approximately 1 around 120 K (where $\theta = 1$ corresponds to 1.28×10^{15} atoms/cm^2) [23,2], a possible arrangement of the hydrogen atoms on top of the Pt surface is shown in Fig. 8, where the H atoms are separated at a distance a. The hydrogen on top of the reconstructed surface induces a charge transfer in order to minimize the surface free energy by a smoothening of the corrugation. However, this also affects the atomic relaxation in the top-most layers. The resulting electronic corrugation is therefore mediated by a vertical movement of the Pt atoms in combination with a redistribution of the electron density as indicated by the arrows in Fig. 8.

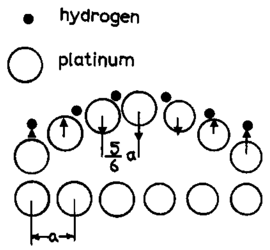

Fig. 8. Tentative model of the hydrogen-covered "(1×1)-like" Pt(100) surface: Six Pt atoms of the top-most platinum layer are placed above five atoms in the second layer. Due to the increased surface density the first Pt layer is buckled. Five hydrogen atoms are adsorbed on the surface in such a way that the surface corrugation (buckling) is effectively reduced.

Note, that the thermal desorption measurements in Ref. [4] show different desorption peaks, in agreement with the existence of different adsorption sites implied by the simple model in Fig. 8. Although the model proposed here can explain the experimental observations, we cannot exclude that, for instance, subsurface sites for hydrogen are involved in the formation of the "(1 × 1)-like" phase. While we cannot determine the precise positions of the hydrogen atoms, there is strong evidence that the adsorption of hydrogen is responsible for the change in the surface corrugation, rather than the removal of the reconstruction (i.e., the expulsion of platinum atoms out of the top-most layer). We feel, that the notation "(1 × 1)-like" surface is misleading.

4. Conclusion

Adsorption of hydrogen at low temperatures and subsequent annealing up to 250 K does not lift the reconstruction of the Pt(100) surface. This conclusion has been drawn from thermal energy helium diffraction patterns. After hydrogen adsorption on both reconstructed phases, hex and hex-rot, the diffraction patterns differ from those of the unreconstructed (1 × 1) phase. A semiquantitative analysis suggests that the Pt top-layer superstructure persists, but that the electronic charge density at the surface is modified by the adsorbed hydrogen.

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