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H-induced reconstructions on Pd(110)

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The (110) surface of many transition metals undergoes reconstructions either on the clean substrate or induced by adsorbates. The reconstructions can be induced by a variety of strongly bound adsorbates, e.g., H, O, S, and alkali-metal atoms. In this work, H/Pd(110) is chosen as a prototype of such reconstructions. The pairing-row and missing-row reconstructions are studied in a wide range of coverages, $\theta = 0.5-1.5$ ML, by using density-functional theory with the local-density approximation and the generalized gradient approximation. The driving force for the reconstructions is also analyzed in detail. The pairing-row reconstruction is driven essentially by the repulsion between the hydrogen atoms adsorbed in the same trough while the driving force for the missing-row reconstruction is the better adsorbate-substrate interaction on the reconstructed surface. [S0163-1829(98)02919-1]

I. INTRODUCTION

Understanding molecular-surface interaction is one of the key issues for surface science and, in particular, for heterogeneous catalysis. Surface crystallography has evidenced that a rigid substrate approximation is not always appropriate to describe surface reactions. The chemisorption of reactants can make dramatic modifications of the substrate, e.g., relaxations and/or reconstructions that create new reactive sites and sometimes close some active centers for certain species as happening in some surface oscillatory reactions. It is now well known that the (110) surface of many fcc transition metals undergoes reconstructions either spontaneously or induced by adsorbates. However, there is still little theoretical insight gained to understand the driving force of the reconstructions. In the present work, the H/Pd(110) system is chosen to serve as a prototype for the reconstructions induced by a strongly bound adsorbate. Moreover, this system has many important applications, e.g., catalysis of hydrogenation reactions and hydrogen storage.[1,2]

Now, it is established from experimental investigations[3–11] that the chemisorption of hydrogen can induce two types of reconstructions on the Pd(110) surface: pairing-row and missing-row. Early experimental works were made by a variety of techniques: low-energy electron diffraction (LEED),[3,6–8] He-scattering and low-energy-ion-scattering spectroscopies,[4,5] and high-resolution electron-energy-loss spectroscopy (HREELS).[9] Recently, scanning-tunneling spectroscopy (STM) (Refs. 10 and 11) has been also used to study H-induced reconstructions on Pd(110). It was concluded from early experimental results that reconstructions take place at coverages higher than $\theta = 1$ monolayer (ML). Only very recently, experimental evidence has appeared for the missing-row reconstruction in a large range of hydrogen coverages.[11] Another important piece of experimental information is that the missing-row reconstruction takes place at higher temperatures than the pairing-row reconstruction. This is a clear indication that the missing-row reconstruction is an activated process. Now, the way in which the substrate reconstructs has been deduced unambiguously from the experimental studies. However, the structure of hydrogen atoms on the reconstructed surface is not so well established. This is essentially due to the difficulty to ''see'' directly the hydrogen atoms by most experimental techniques. Although some conjectures have been made, the exact structures of H atoms on the reconstructed Pd(110) surface remain an open problem. One issue of the present work is to find out stable adsorption patterns on the reconstructed substrate by *ab initio* calculations.

Theoretical studies have also been carried out. Semiempirical calculations were made for the clean Pd(110) and its missing-row reconstruction.[12] *Ab initio* calculations were performed for low-index clean and H-covered unreconstructed surfaces of palladium.[13–22] In a very recent paper,[23] Tománek, Wilke, and Scheffler have reported a study on the H-induced polymorphism of Pd(110) which results from the H-induced pairing-row and missing-row reconstructions. Although a few common issues are addressed also in the present work, we will show that some interesting and important issues are overlooked in Ref. 23. Here, we present a more thorough investigation and show that the polymorphism of Pd(110) induced by the chemisorption of hydrogen is even richer and it takes place not only at the high coverage as reported in Ref. 23 but also at lower coverages. A fundamental theoretical issue is what is the driving force for the reconstructions. Previous theoretical efforts have been made on this problem in the case of the missing-row reconstruction of transition-metal surfaces induced by alkali metals.[24,25] Jacobsen and Norskov[24] advocated that the driving force comes from the higher chemisorption energy upon a reconstructed substrate. An alternate view[25] is based on the charge transfer between the adsorbate and the substrate and the driv-

TABLE I. Sufarce energy and geometry of unreconstructed Pd(110). Δd_{ij}: relaxation of the spacing between the ith and jth layers.

	Present work						
	LDA	GGA	Tománek *et al.*[23]	LMTO[17]	Experimental		
Δd_{12} (%)	-9.1	-8.6	-8.2	-5.3	-5.1 ± 1.5[a];	-6 ± 2[b];	-5.7 ± 2[c]
Δd_{23} (%)	$+3.3$	$+3.7$	$+0.7$		$+2.9\pm1.5$[a];	$+1\pm2$[b];	$+0.5\pm2$[c]
σ (eV)	1.476	1.089	1.27[d]; 1.1[e]	1.33			

[a] Reference 7.
[b] Reference 36.
[c] Reference 37.
[d] LDA value.
[e] GGA value.

ing force is attributed to the effect of the electric field resulting from this charge transfer. Compared to the alkali-metal atoms, the hydrogen atom has very different atomic size and electronegativity. So, it is not clear at all if the conclusions from the previous works apply also to account for the H-induced reconstructions. This is another issue to be addressed in this work.

II. THEORETICAL APPROACH

The approach used in this work is the density-functional theory with the local-density approximation (LDA) and the generalized gradient approximation (GGA) implemented in the Vienna *Ab initio* Simulation Program (VASP).[26,27] The exchange-correlation functional we used for the LDA is the Perdew-Zunger parametrization[28] of the quantum Monte Carlo simulation of Ceperley and Alder,[29] and for the GGA the functional known as Perdew-Wang91.[30] With the use of Vanderbilt's ultrasoft pseudopotentials,[31,32] the wave functions are expanded in plane waves. Thanks to the efficiency of the ultrasoft pseudopotentials, we are able to use a cutoff energy equal to 200 eV for the plane-wave basis. Careful check calculations are carried out and show that this cutoff energy leads to 1 mRy convergence for cohesive and adsorption energies. Recently, we have applied this approach to study the chemisorption of H and the dissociation of H_2 on the Pd(111) surface.[21,22] Satisfactory results have been obtained. For the present work, we use the same pseudopotentials as used in the previous works. The details concerning the pseudopotentials can be found in Ref. 21. The Brillouin zone integration is made on a $9\times5\times1$ grid of Monkhorst-Pack special k points.[33] To model surfaces, we adopt the slab supercell approach. Test calculations were carried out with slabs up to nine Pd layers. The results of these test calculations show that well converged results can be obtained with a slab of seven Pd layers and a vacuum space corresponding to five ideal bulk Pd layers. We present only the results for this size of cell. The calculation of Hellmann-Feynman forces allows full geometry optimizations to be performed easily.

III. RESULTS AND DISCUSSIONS

A. Clean Pd(110) surface

Previous *ab initio* studies on the low-index surfaces of palladium and the adsorption of hydrogen on these surfaces have been made with several different approaches.[13–23] In particular, the clean Pd(110) surface has been studied by Methfessel, Hennig, and Scheffler[17] with the full-potential linear-muffin-tin-orbital (FP-LMTO) method. In the work on the chemisorption of H on the unreconstructed Pd(110) surface by Tománek, Sun, and Louie,[16] results for the clean Pd(110) surface have been reported as well. We started also by the clean Pd(110) surface but focused on examining the possibilities of its eventual reconstructions. The possibilities considered are pairing-row and missing-row reconstructions. A variety of geometries with different paired distances between $[1\bar{1}0]$ Pd rows are examined. No pairing-row reconstruction is found for the clean Pd(110) surface. The forces on the tentatively paired rows always bring them back to the unreconstructed structure. While LDA predicts a slightly more stable missing-row structure, GGA gives a more stable unreconstructed structure by 5 meV (per unit cell). Up to now, no experimental evidence exists for *spontaneous* missing-row reconstruction of the clean Pd(110) surface. However, Dhanak *et al.*[34] have shown that (1×2) and (1×3) missing-row structures of the clean Pd(110) surface can be prepared by oxygen adsorption. The important point to note in the results of Dhanak *et al.* is that when oxygen is removed after inducing the reconstruction, the missing-row reconstructed structures on the clean surface remain. Moreover, it has been reported that a small step-formation energy is found experimentally on the clean Pd(110) surface.[35] These experimental results together with our result indicate clearly a strong proclivity of the clean Pd(110) surface for the missing-row reconstruction. So, this missing-row structure should be considered as a metastable state which can compete with the unreconstructed one. Our results for the clean Pd(110) surface are summarized in Table I along with some experimental results[7,36,37] and some previous theoretical estimations.[17,23] We find oscillating relaxations as found experimentally. The contraction of the topmost interlayer spacing is somewhat overestimated. Taking into account the experimental errors, the overall agreement between our results and the experimental ones is satisfactory. The surface energy σ is defined as

$$\sigma=(E_{\mathrm{slab}}-N_{\mathrm{atom}}E_{\mathrm{bulk}})/2,$$

where E_{slab} is the total energy of the slab, E_{bulk} the total energy of the bulk crystal per atom, and N_{atom} the number of

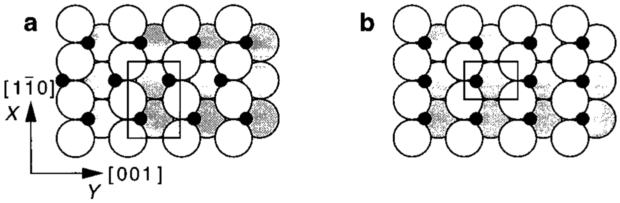

FIG. 1. Top view of H adsorption patterns on the unreconstructed Pd(110), $\theta = 1$ ML. (a) (2×1) H/Pd(110) superstructure; (b) (1×1) H/Pd(110). The unit cells used for calculation are indicated.

atoms in the slab. There is also a good agreement between our results and those of the other theoretical investigations.[17,23]

B. Chemisorption of H on unreconstructed Pd(110)

All the experimental studies have indicated that the surface concentration of hydrogen plays an important role in the H-induced reconstruction. At $\theta = 1$ ML, a (2×1) superstructure of hydrogen atoms is formed on the unreconstructed Pd(110) surface. A proposed arrangement of H atoms for this structure is shown in Fig. 1(a). Besides this zigzag chain arrangement, there is of course the (1×1) H straight chain arrangement with all the H atoms occupying also the threefold sites [see Fig. 1(b)]. Previously, Tománek, Sun, and Louie[16] have carried out *ab initio* calculations for the chemisorption of hydrogen on Pd(110). Their study is limited to the (1×1) unreconstructed surface for a variety of adsorption sites except the threefold one as shown in Figs. 1(a) and 1(b). In fact, the threefold site is the most stable on the (1×1) unreconstructed substrate. We have carried out calculations for both the structures [Figs. 1(a) and 1(b)] and found that the zigzag chain structure is more stable than the straight chain by 29 meV/H (LDA). This is in entire agreement with experiments.[4,7] This zigzag superstructure can be accounted for in the following way: the electron transfer from the substrate to H atoms creates dipoles localized near the adsorbates. The electrostatic interaction between these dipoles is repulsive. The zigzag arrangement of H atoms on one hand keeps the adsorbates as far away as possible and on the other hand makes the screening of the electrostatic interaction done more efficiently by the intervening Pd atoms. These two effects decrease all the dipole-dipole repulsion between the adsorbates. The results for the stable (2×1) H/Pd(110) superstructure are given in Table II. The adsorption energy per adsorbate, E_{ad}, is defined in such a way that it can be directly compared to experimental results,

$$E_{\mathrm{ad}} = \{E[\mathrm{Pd}(110)] + N_{\mathrm{H}}E[\mathrm{H}_2]/2 - E[\mathrm{H/Pd}(110)]\}/N_{\mathrm{H}}, \tag{1}$$

where N_{H} is the number of hydrogen atoms in the slab H/Pd(110). It is well known that the error of LDA for $E[\mathrm{H}_2]$ is quite large. For calculating the LDA value of E_{ad} given in Table II, we have used the experimental value of $E[\mathrm{H}_2]$. The LDA adsorption energy thus obtained is in very good agreement with the GGA value and the experimental result.[38] The bond distance between H and Pd atoms is somewhat underestimated. Nevertheless, it is worth noting that the local environment of the threefold site is similar to that on the Pd(111) surface where the Pd-H distance is 1.8 Å.[39] The adsorption of H reduces the amplitude of the substrate relaxation compared to that of the clean surface. This is a quite general effect of chemisorption on the substrate relaxation. Δd_{12} and Δd_{23} are in good agreement with the experiment results. For comparison, the results of Tománek *et al.*[23] are also put in Table II. The energetic results in Ref. 23 are expressed in terms of the clean surface energy, E_s^0, and the surface energy of the H-covered surface, E_s (see Ref. 23 for their precise definitions). These surface energies are related to the adsorption energy defined in Eq. (1) by $E_{\mathrm{ad}} = 2(E_s^0 - E_s)$. There is a qualitative agreement between our results and those of Tománek *et al.*

C. H-induced pairing-row reconstruction

At the coverage $\theta = 1$ ML, we have studied an attempted pairing-row reconstruction as shown in Fig. 2(a). This structure can be obtained from the zigzag chain [Fig. 1(a)] in a straightforward way by pushing some [1$\bar{1}$0] Pd rows together. However, no stable reconstructed structure of this kind was obtained. The forces exerted on the approached rows bring them back to the unreconstructed structure. When the coverage is increased to $\theta = 1.5$ ML, the threefold sites in Fig. 2(a) are saturated, and a reconstruction as shown in Fig. 2(b) takes place. As we have mentioned in the Introduction, it is not easy to determine the arrangement of H atoms by experimental techniques. Different conjectures have been made. Rieder, Baumberger, and Stocker[4] have proposed a pairing-row structure as shown in Fig. 2(c). From our calculations, this pairing-row structure cannot exist. The structure shown in Fig. 2(c) can be obtained from that shown in Fig. 2(b) by separating the paired rows and pushing them away continuously until the structure given in Fig. 2(c) is reached. In doing this, the pushed rows are exerted by large forces which always bring them back to the pairing-row structure given in Fig. 2(b). To interpret their STM results, Yoshi-

TABLE II. Adsorption energy and geometry of the superstructure (2×1)H/Pd(110), $\theta = 1$ ML. d_{H}: height of H with respect to the top Pd layer. $d_{\mathrm{H\text{-}Pd}}$: distance between H and Pd atoms.

		E_{ad} (eV/H)	d_{H} (Å)	$d_{\mathrm{H\text{-}Pd}}$ (Å)	Δd_{12} (%)	Δd_{23} (%)
Present work	LDA	0.497	0.29	1.80	−2.4	+2.7
	GGA	0.494	0.25	1.81	−1.9	+3.2
Tománek *et al.* (Ref. 23)		0.64[a]		1.8	−3.2	+1.4
Experiment (Ref. 7)		0.5[b]	0.6±0.1	2.0±0.1	−2.2	+2.9

[a] Calculated according $E_{\mathrm{ad}} = 2(E_s^0 - E_s)$.
[b] Reference 38.

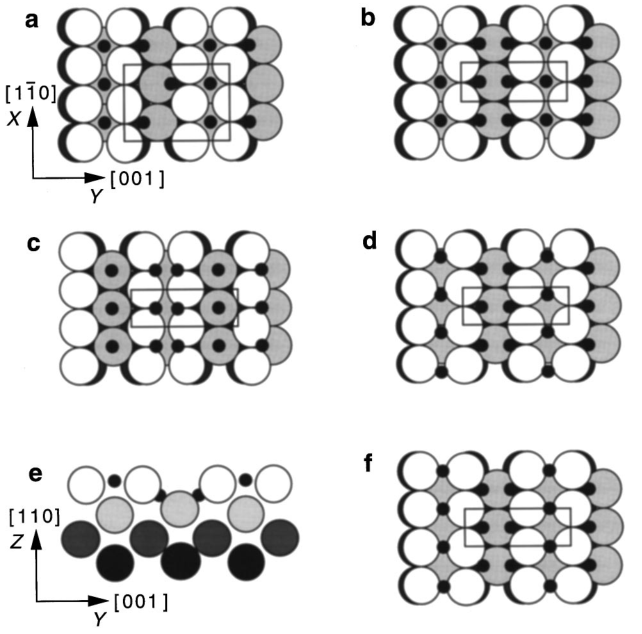

FIG. 2. Top view [exceptionally (e) is a side view] of different H adsorption patterns on the pairing-row reconstructed Pd(110), $\theta=1$ ML for (a) and $\theta=1.5$ ML for (b)–(f).

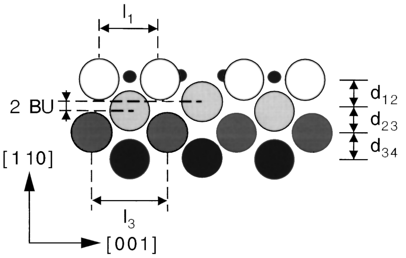

FIG. 3. Side view of the structure given in Fig. 2(b).

nobu, Tanaka, and Kawai[10] have suggested recently the structure shown in Fig. 2(d) for the pairing-row reconstruction. A structure with threefold hydrogen atoms placed on subsurface sites was also proposed for the pairing-row reconstruction.[2] This structure looks exactly the same as Fig. 2(b) from the top and Fig. 2(e) provides a side view to show clearly this arrangement. We have also carried out careful searches for these two structures but it turned out that none of them corresponds to a true energy minimum. In their recent paper,[23] Tománek, Wilke, and Scheffler have reported a pairing-row structure at $\theta=1.5$ ML as depicted in Fig. 2(f). In this adsorption pattern, 1 ML of H atoms are adsorbed on the threefold sites as in Fig. 2(b) and the other 0.5 ML on the long bridge sites [see Fig. 2(f)]. We did not find that this structure is stable. In fact, it is a saddle point and a slight displacement leads the H atom to slide to the fourfold site. So, the only stable structure we have found for the pairing-row reconstruction at $\theta=1.5$ ML is that shown in Fig. 2(b). This is also the generally accepted structure of the H-induced pairing-row reconstruction of Ni(110).[40] The results of the pairing-row reconstruction are summarized in Table III. The distance between the fourfold H atom and the nearest Pd atom on the top layer is equal to 2.11 Å, which is comparable to the H-Pd distance of the fourfold H on a Pd(100) surface.[41] In fact, the fourfold label is the generally used one despite the fact that the distance between the H atom and the second-layer Pd atom just beneath is much shorter (see Table III). The height of the H atom on the threefold site is reduced by 0.09 Å compared to that in the (2×1) H/Pd(110) superstructure. A quite important buckling distortion is observed for the second Pd layer. This buckling is characterized by the distance BU (see Fig. 3). It is interesting to note that the buckling together with the height adjustment of the threefold H atoms takes place in such a way to keep the H-Pd distance of the threefold site around 1.80 Å as in the case of (2×1) H/Pd(110). The distance between the paired rows on the top Pd layer is reduced (Δl_1 in Table III) by 0.68 Å with LDA and 0.74 Å with GGA. This reduction is overestimated compared to the experimental estimation.[6] We observe also an opposite lateral shift on the third Pd layer, $\Delta l_3=0.04$ Å (LDA); 0.22 Å (GGA). Although this lateral shift of the third

TABLE III. Results of the H-induced (1×2) pairing-row reconstruction, $\theta=1.5$ ML. d_H: height of H over the threefold site. d'_H: height of H over the fourfold site. $d_{\text{H-Pd}}$: distances between the threefold H atom and the first and second Pd layers. $d'_{\text{H-Pd}}$: distances between the fourforld H atom and the first and second Pd layers.

	Present work		Tománek *et al.* (Ref. 23)	Experiment (Ref. 6)
	LDA	GGA		
E_{ad} (eV/H)	0.460	0.469		
d_H (Å)	0.20	0.16		
d'_H (Å)	0.14	0.09		
$d_{\text{H-Pd}}$ (Å)	1.79; 1.79	1.82; 1.81		
$d'_{\text{H-Pd}}$ (Å)	2.11; 1.81	2.13; 1.83		1.97[a]
BU (Å)	0.25	0.28	0.15	0.15 ± 0.05
Δl_1 (Å)	-0.68	-0.74	-0.64	-0.40 ± 0.05
Δl_3 (Å)	$+0.04$	$+0.22$		
d_{12} (Å) and Δd_{12}	1.43; $+4.4\%$	1.47; $+5.0\%$		1.37 ± 0.03
d_{23} (Å) and Δd_{23}	1.39; $+1.3\%$	1.42; $+1.8\%$		1.47 ± 0.03
d_{34} (Å) and Δd_{34}	1.40; $+2.5\%$	1.45; $+3.8\%$		1.37 ± 0.03

[a] Reference 41.

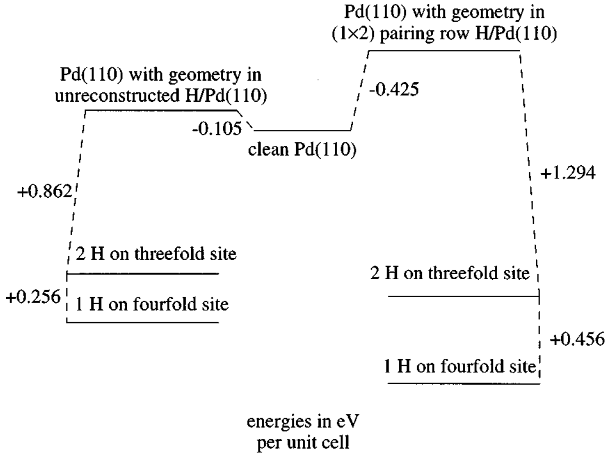

FIG. 4. Interaction energy decomposition analysis of the driving force for the pairing-row reconstruction at $\theta = 1.5$ ML.

Pd layer has been anticipated by Kleinle *et al.*,[6] they did not take it into account in their fittings of LEED intensity/energy (I/V) profiles to determine the geometry parameters. The surface layer reorganization due to the reconstruction produces also a perpendicular relaxation involving more substrate layers. This can be seen from Δd_{12} to Δd_{34}. The variation tendency from Δd_{12} to Δd_{34} given by our calculation does not agree well with that found experimentally. The reason for this disagreement is unclear and certainly needs to be clarified by further investigations.

After finding out the stable structure of the pairing-row reconstruction, an important question we can ask is what is the driving force for the reconstruction? Intuitively, one can think that the pairing-row reconstruction results in a better interaction between the fourfold H atoms and the Pd atoms on the approached rows.[42] In order to examine this hypothesis, we have made an analysis of the reconstruction by a decomposition of interaction energies. The analysis can be schematized in Fig. 4. We started from two frozen substrates: one with the unreconstructed structure and the other with the reconstructed one. The threefold and fourfold H atoms are separately adsorbed on the two frozen substrates to assess their contributions. Here, the underlying assumption is that these contributions can be considered as additive. We have found that the difference between the adsorption energy on the reconstructed surface and that on the unreconstructed one has nearly a perfect additivity. The interaction energy is increased quite similarly for the threefold (0.22 eV) and the fourfold (0.20 eV) sites. The contribution from the threefold site is, however, dominant due to the fact that there are two threefold sites in the unit cell. It turns out that the pairing-row reconstruction is mainly driven by the release of the dipole-dipole repulsion between the threefold H atoms on the two neighboring chains in the same trough. From this analysis comes another interesting thing. It is easy to see (Fig. 4) that the interaction between the substrate and the threefold H atoms alone can already overcompensate the energy cost for reconstructing the substrate. This implies that a pairing-row reconstruction such as that shown in Fig. 5 should exist if our analysis is valid. To check this, calculations were carried out to look for such a reconstruction at $\theta = 1$ ML. Remarkably, we indeed found it and its existence shows that our decomposition analysis is not only explanatory but also predictive. The results for this reconstruction are given in Table IV. This pairing-row structure is nearly degenerate energetically (only 30 meV/H higher from LDA) with the zigzag (2×1) superstructure on the unreconstructed substrate [Fig. 1(a)]. The most marked geometry difference between the pairing-row reconstruction at $\theta = 1$ ML and that at $\theta = 1.5$ ML is that the [110] Pd rows are less paired at the lower coverage. To our knowledge, this pairing-row reconstruction at $\theta = 1$ ML has never been reported. We think it deserves some experimental investigations. If the pairing-row reconstruction at $\theta = 1$ ML and that at $\theta = 1.5$ ML can coexist as different patches on Pd(110), the quite large disagreement on Δl_1 between our calculated values and the experimental estimation might be partly understood. In this case, the experimental result is an average value of Δl_1's for the patches at $\theta = 1$ ML and $\theta = 1.5$ ML. We emphasize that this is just a speculation which cannot account totally for the discrepancy and hope that it will motivate further experimental investigations. The fact that the stable pairing-row structure at $\theta = 1$ ML is that given in Fig. 5 instead of that shown in Fig. 2(a) provides further support to our conclusion that the driving force is the dipole-dipole repulsion between adsorbates rather than the better interaction between the fourfold H atoms and the substrate. Otherwise, the structure given in Fig. 2(a) would be more stable.

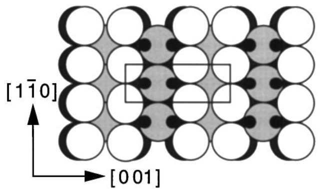

FIG. 5. H-induced pairing-row reconstruction at $\theta = 1$ ML.

D. H-induced missing-row reconstruction

Experimental investigations[6,10,11] have shown that the chemisorption of hydrogen can induce (1×2) and (1×3) missing-row reconstructions. In this work, we will restrict ourselves to the (1×2) missing-row reconstruction. To our knowledge, no experiment has been able to show the arrangement of H atoms on the reconstructed surface. Upon missing-row reconstruction, (111) facets are created. As it is known that on the Pd(111) surface the most stable site is the threefold one, we will consider only different adsorption pat-

TABLE IV. Results of the H-induced (1×2) pairing-row reconstruction, $\theta = 1.0$ ML.

	Present work (LDA)
$E_{\rm ad}$ (eV/H)	0.467
$d_{\rm H}$ (Å)	0.28
$d_{\rm H\text{-}Pd}$ (Å)	1.78
BU (Å)	0.16
Δl_1 (Å)	-0.46
Δl_3 (Å)	$+0.10$
d_{12} (Å) and Δd_{12}	1.34; -2.1%
d_{23} (Å) and Δd_{23}	1.40; $+2.2\%$
d_{34} (Å) and Δd_{34}	1.38; $+0.7\%$

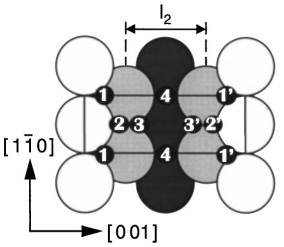

FIG. 6. Different adsorption patterns of hydrogen on the missing-row reconstructed Pd(110), $\theta = 1$ ML.

terns with H atoms occupying the threefold sites. Three types of threefold sites are indicated in Fig. 6. Site 1 has two neighbor Pd atoms from the top layer and the other Pd atom from the second layer, site 2 has one Pd atom from the top layer and two Pd atoms from the second layer, and site 3 involves two Pd atoms from the second layer and the other Pd atom from the third layer. Several structures formed from some combinations of these sites at $\theta = 1$ ML are considered. In Table V, the energetic stability of these structures is given, which can be explained essentially by the dipole-dipole repulsion between the adsorbates if the screening of the electrostatic interaction by the [110] rows is taken into account. Two structures ($11'$ and $12'$) are more stable than the zigzag (2×1) superstructure and the three others have about the same stability. The adsorption pattern $11'$ is the most stable one and is more stable by 62 meV/H than the (2×1) superstructure. So it is the most stable structure among all the adsorption patterns we have considered at $\theta = 1$ ML. In fact, the zigzag (2×1) superstructure corresponds to a metastable state and there is a sufficient energy barrier between it and the most stable missing-row structure so that the (2×1) superstructure has been experimentally observed. Experimental investigations[6,10] indeed show that the missing-row reconstruction takes place at higher temperatures and that once it occurs, it remains even when the system is brought back to a lower temperature. This indicates that the missing-row structure corresponds to a lower energy minimum. The results obtained in the present work conform perfectly with this. The geometry of the $11'$ structure is presented in Table VI. We see that the H atom is adsorbed in fact in a pseudothreefold site. The first value for $d_{\text{H-Pd}}$ is the distance between the H atom and the Pd atom on the first layer and the other value for the distance from the H atom to the second-layer Pd. For the missing-row reconstruction, there is only a very slight buckling distortion on the third Pd layer, BU=0.03 Å. We obtain also a lateral shift on the second Pd layer. This lateral shift is a contraction of the distance between two [110] rows just below the missing row. Only very small perpendicular relaxations are observed.

We have also studied a missing-row structure at $\theta = 1.5$ ML. The considered adsorption pattern is $11'$ (the most stable one at $\theta = 1$ ML) with an added H atom placed at the site 3 (Fig. 6) in order to keep large distances between H atoms to minimize their repulsion. We found that this structure is more stable by 40 meV/H than the pairing-row structure in Fig. 2(b). In their recent work,[23] Tománek, Wilke, and Scheffler have considered only one H-induced missing-row structure, which corresponds to the adsorption pattern denoted by $22'4$ in our notation given in Fig. 6. This structure is reported to be also more stable than the pairing-row structure at $\theta = 1.5$ ML.

TABLE V. LDA adsorption energy of different hydrogen adsorption patterns on the missing-row reconstructed Pd(110), $\theta = 1$ ML.

Adsorption pattern	$1\,1'$	$1\,2'$	$2\,2'$	$1\,3'$	$1\,3$	$3\,3'$
E_{ad} (eV/H)	0.559	0.511	0.496	0.491	0.481	0.359

TABLE VI. Adsorption energy and geometry of $1\,1'$ adsorption pattern on the missing-row reconstructed Pd(110), $\theta = 1$ ML.

	Present work	
	LDA	GGA
E_{ad} (eV/H)	0.559	0.564
d_{H} (Å)	0.24	0.19
$d_{\text{H-Pd}}$ (Å)	1.82;1.79	1.85;1.80
BU (Å)	0.03	0.03
Δl_2 (Å)	-0.10	-0.11
d_{12} (Å) and Δd_{12}	1.36;-0.7%	1.41;$+0.6\%$
d_{23} (Å) and Δd_{23}	1.36;-0.9%	1.39;-0.6%

It was believed that hydrogen can induce missing-row reconstructions only at high coverages. However, as we have seen earlier, the clean Pd(110) has already a large tendency to reconstruct. It can be expected that a small gain in adsorption energy will be sufficient to stabilize the reconstructed substrate. Therefore, we have also studied a missing-row reconstruction at $\theta = 0.5$ ML. The considered adsorption pattern is shown in Fig. 7. This structure has been recently found experimentally for the oxygen induced (1×2) missing-row reconstruction of Pd(110).[43] Comparing with the same adsorption pattern on the unreconstructed substrate, we found again that this missing-row structure is more stable by 35 meV/H (LDA). In a very recent work, Kampshoff *et al.*[11] have found experimental evidence for missing-row reconstructions of Pd(110) induced by hydrogen at coverages lower than $\theta = 1$ ML. Our results here supply further evidence from *ab initio* calculations.

It is well known that (1×2) and (1×3) missing-row reconstructions can be induced also by alkali metals. Previous efforts have been made to study the driving force for these reconstructions.[24,25] Fu and Ho[25] have proposed an electron-donation mechanism to account for the alkali-metal-induced missing-row reconstruction on the (110) surface of $3d$ and $4d$ fcc metals. In this mechanism, the driving force is attributed to the electron transfer between the adsorbates and the substrate and the effect of the electric field thus created

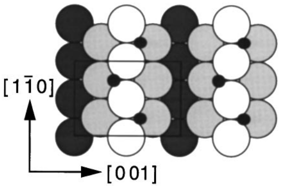

FIG. 7. Adsorption pattern of hydrogen on the missing-row reconstructed Pd(110), $\theta = 0.5$ ML.

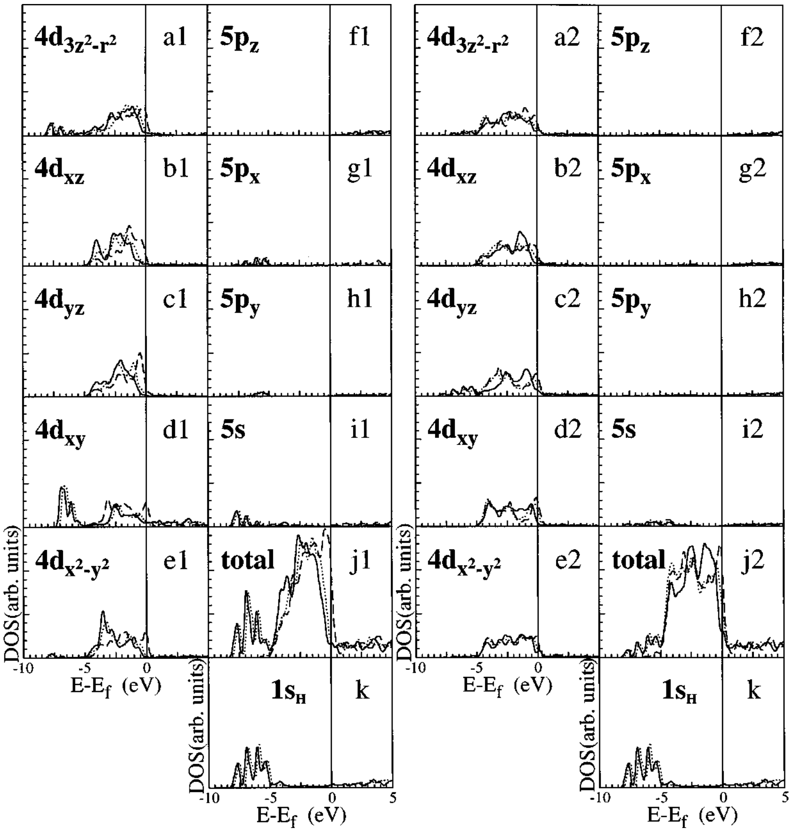

FIG. 8. Local DOS's of the H-covered (1×2) missing-row surface (full line) at $\theta=1$ ML, of the same adsorption pattern as in the MR structure but on the unreconstructed surface (dot line) at $\theta=1$ ML, and of the clean unreconstructed surface (dash line). (a1)–(j1) Projections localized on the first-layer Pd atom. (a2)–(j2) Projections localized on the second-layer Pd atom. (k) Projection on the H atom.

near the substrate. The main conclusion is that the (1×2) reconstructed structure is stabilized when the electron transfer takes place from the adsorbates to the substrate and the (1×1) unreconstructed structure is stabilized when the inverse electron transfer occurs. The results we obtained in the present work show clearly that this mechanism does not apply to the system considered here. In the adsorption process studied here, the electron transfer takes place from the substrate to the adsorbates. Moreover, a recent experimental study[43] has shown that oxygen (a quite electronegative element) can induce also (1×2) missing-row reconstruction. Although the electron-donation mechanism proposed by Fu and Ho[25] accounts quite well for some reconstructions induced by alkali metals, the nature of the driving force is more subtle than what can be described by this simple mechanism. In the next subsection, we are going to provide evidence from the analysis of the electronic structures that reveals that the driving force comes essentially from the better adsorbate-substrate interaction on the reconstructed surface.

E. Electronic structure—Microscopic nature of the adsorbate-substrate interaction

A detailed analysis of the modifications of electronic structure resulting from reconstructions is carried out to understand better the microscopic nature of the driving force. In Fig. 8, the local density of states (DOS) for the missing-row reconstructed structure $(11')$ at $\theta=1$ ML (full line) is plotted and compared with that of the same chemisorption pattern but on the unreconstructed substrate (dot line) and that of the unreconstructed clean surface (dash line). In Fig. 8 and all subsequent ones for DOS, the energy origin corresponds to the Fermi level obtained for the unreconstructed clean Pd(110) and the changes in work function are taken into account when plotting DOS's of different H-covered surfaces. The local DOS's presented in Fig. 8 show clearly the orbitals involved in the adsorbate-substrate interaction. The s orbital of the hydrogen atom interacts mainly with the $4d_{xy}$, $4d_{3z^2-r^2}$, and $5s$ of the two neighbor Pd atoms on the first layer [see Figs. 8(d1), 8(a1), and 8(i1)] and to a less extent with $4d_{x^2-y^2}$, $5p_x$, and $5p_y$. The interaction of the H atom with its neighbor Pd atom on the second layer takes place essentially between the s orbital of H and the $4d_{yz}$ of the Pd atom [see Fig. 8(c2)]. The results given in Fig. 8 show clearly that there is an overall shift of energy levels toward lower energies in the case of the chemisorption on the reconstructed substrate compared to the case of that on the unreconstructed one. This is the evidence that the adsorbate interacts better with the reconstructed surface.

The local DOS's for the pairing-row reconstruction at $\theta=1.5$ ML are presented in Fig. 9 (full line). For comparison, the results for the same adsorption pattern on the unreconstructed substrate (dot line) are also plotted as well as the local DOS's of the clean Pd(110) (dash line). The DOS's localized on the Pd atom of the first layer are presented in Figs. 9(a1)–9(j1), which are not very different from those given in Figs. 8(a1)–8(j1). The local DOS's for the second-layer Pd atom bonding to the threefold H atom are given in

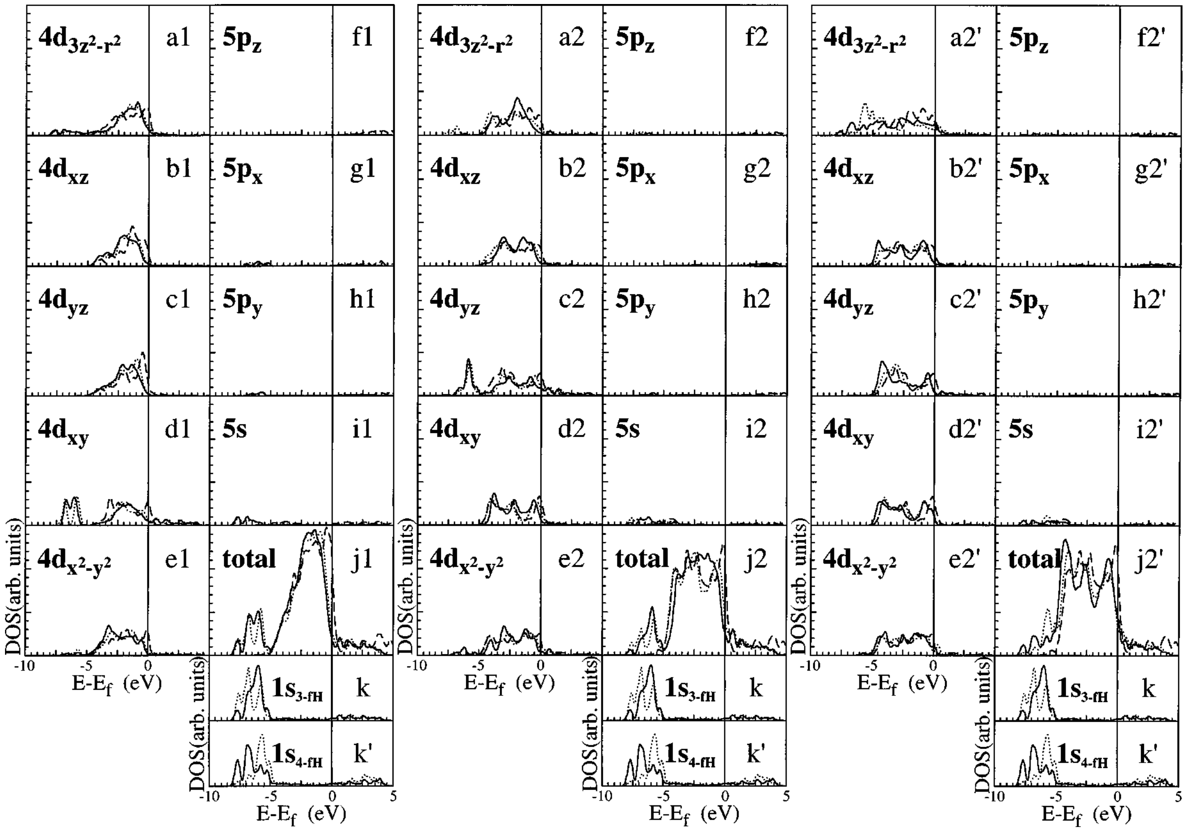

FIG. 9. Local DOS's of the H-covered pairing-row surface (full line) at $\theta = 1.5$ ML, of the same adsorption pattern as in the PR structure but on the unreconstructed surface (dot line), and of the clean unreconstructed surface (dash line). (a1)–(j1) Projections localized on the first-layer Pd atom. (a2)–(j2) Projections localized on the second-layer Pd atom coordinated with the threefold H atom. (a2)–(j2) Projections localized on the second-layer Pd atom coordinated with the fourfold H atom. (k) Projection on the threefold H atom. (k) Projection on the fourfold H atom.

Figs. 9(a2)–9(j2). Here, some new feature appears: besides its interaction with $4d_{yz}$, the s orbital of the threefold H atom interacts now also with the $4d_{x^2-y^2}$ orbital. This is essentially due to the important buckling of the second Pd layer, which moves up the row bonding to the threefold H atoms and allows this orbital interaction to take place. Figures 9(a2′)–9(j2′) show the DOS's localized on the second-layer Pd-atom bonding to the fourfold H atom. Here, we see that the orbital interactions take place between the s orbital of H and the $4d_{3z^2-r^2}$ and the $5s$ of Pd. The results presented in Fig. 9 do not give indication for a better interaction of the adsorbate with the reconstructed substrate. This can be considered as a support to our conclusion made in Sec. III C that the driving force for the pairing-row reconstruction is mainly due to the electrostatic adsorbate-adsorbate repulsion. It is to note that such adsorbate-adsorbate interaction can hardly be evidenced in the density of states.

Finally, the local DOS's for the (2×1) zigzag superstructure of H on the unreconstructed Pd(110) are presented in Fig. 10 (full line) together with those of the (1×1) straight chain adsorption structure (dot line) as well as those of the clean substrate (dash line). The interaction of the hydrogen atom with the second-layer Pd atom takes place between the s orbital of the hydrogen and the $4d_{yz}$, $4d_{3z^2-r^2}$, and $5s$ of the Pd atom in a quite similar way to the previous cases. For the interaction of the H atom with the Pd atom on the first layer, the overlap between the s orbital of the H atom and the $4d_{xy}$ of the Pd atom plays again an important role [see Fig. 10(d1)]. Moreover, this orbital interaction imposes different constraints for the signs of the wave functions of the hydrogen atoms as shown in Fig. 11. For the (1×1) straight chain arrangement, the signs of the wave functions alternate on neighboring H atoms [see Fig. 11(b)] while the signs of the wave functions of H atoms remain the same on the (2×1) zigzag chain [see Fig. 11(a)]. The alternating sign pattern is unfavorable for the bonding with $4d_{3z^2-r^2}$ and $5s$ of the Pd atoms but favorable for the bonding with $5p_x$ in the arrangement depicted in Fig. 11(c). The results given in Fig. 10 confirm the bonding picture we describe here. Figures 10(a1) and 10(i1) show clearly that the zigzag chain structure yields more stabilizing interaction of the s orbital of the H atom with $4d_{3z^2-r^2}$ and $5s$ of the Pd atom while its interaction with $5p_x$ is more stabilizing for the (1×1) straight chain arrangement [see Fig. 10(g1)]. The (2×1) zigzag arrangement on one hand decreases adsorbate-adsorbate repulsion and on the other hand allows the hydrogen atoms to interact favorably with more orbitals of the Pd atoms on the first layer. This is why the zigzag chain arrangement is more stable than the straight chain.

IV. CONCLUSIONS

In the present work, we have studied in detail the chemisorption of hydrogen on the (110) surface of palladium by *ab*

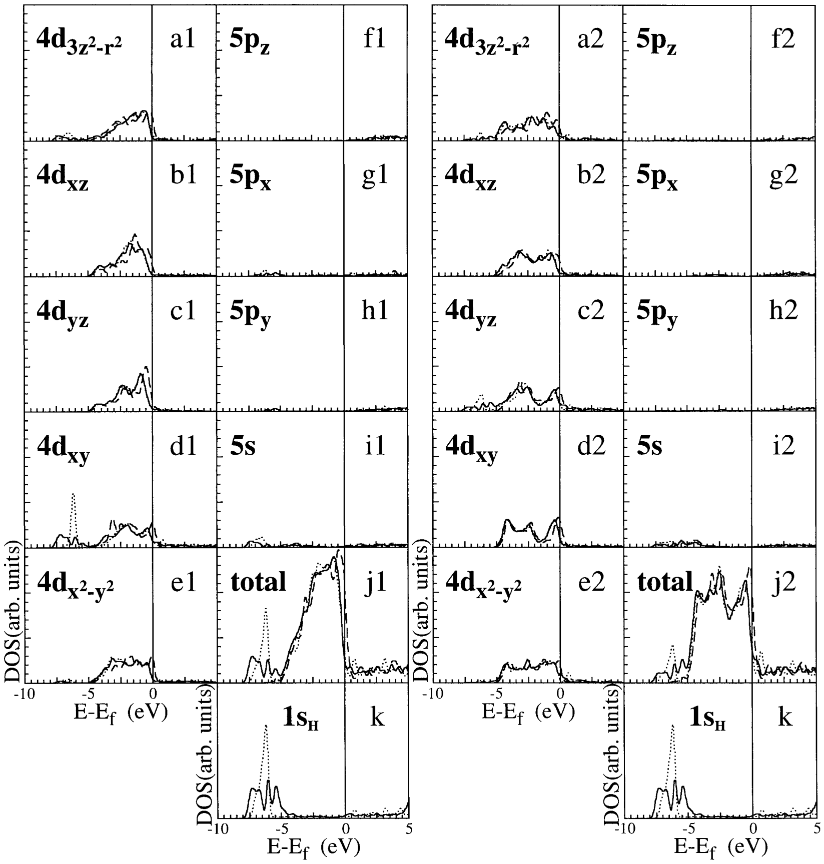

FIG. 10. Local DOS's of the (2×1) zigzag chain superstructure of H atoms on unreconstructed Pd(110) (full line) at $\theta=1$ ML, of the (1×1) straight chain arrangement of H atoms on the unreconstructed Pd(110) (dot line) at $\theta=1$ ML, and of the clean unreconstructed surface (dash line). (a1)–(j1) Projections localized on the the first-layer Pd atom. (a2)–(j2) Projections localized on the second-layer Pd atom. (k) Projection on the H atom.

initio calculations. A quite unique character of the Pd(110) surface is that it does not undergo spontaneous reconstructions like Pt and Ir but has a large proclivity to reconstruct. This tendency is reflected through the quasidegenerate energetic stability of the unreconstructed (1×1) substrate and the (1×2) missing-row reconstructed clean surface. At $\theta=1$ ML, we find that the most stable chemisorption pattern on the unreconstructed substrate is a (2×1) superstructure with H atoms arranged in zigzag chains around the [110] Pd rows. The results obtained in this work allow us to understand why this (2×1) superstructure is more stable than the (1×1) straight chain adsorption pattern. On one hand, the (2×1) zigzag arrangement decreases the adsorbate-adsorbate repulsion resulting from the partial electron transfer from substrate to adsorbates and, on the other hand, the analysis of electronic structure shows that in the zigzag structure, the hydrogen atoms can interact favorably with more orbitals of the substrate.

In the literature, various adsorption structures have been proposed for the hydrogen-induced pairing-row reconstruction on Pd(110). We have examined carefully a large variety of geometries for the pairing-row reconstruction and identified only one stable pairing-row structure at $\theta=1.5$ ML. Moreover, we show that the chemisorption of hydrogen can induce also a pairing-row reconstruction at $\theta=1$ ML. The issue concerning the origin of the driving force for the pairing-row reconstruction is addressed in two ways: (i) an energetic analysis to estimate the different contributions from threefold and fourfold H atoms and (ii) an analysis based on the electronic structure. These analyses allow us to conclude that the H-induced pairing-row reconstruction is essentially driven by the repulsion between the H-atoms adsorbed in the same trough.

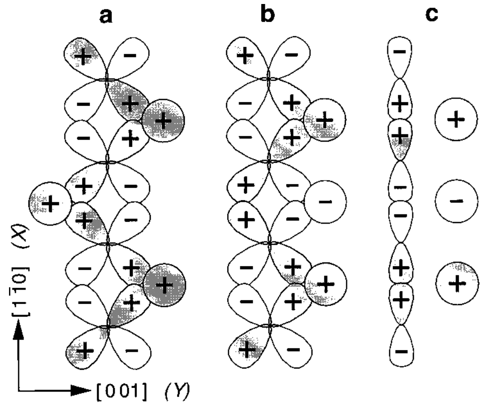

FIG. 11. Interactions of s orbital of the H atom with (a) $4d_{xy}$ of the first-layer Pd atom in a zigzag chain pattern, (b) $4d_{xy}$ of the first-layer Pd atom in a straight chain pattern, (c) $5p_x$ of the first-layer Pd atom in a straight chain pattern.

It was believed that the chemisorption of hydrogen induces missing-row reconstruction only at high coverages. In the present work, we have studied the H-induced missing-row reconstruction in a large range of surface concentrations of the hydrogen from $\theta = 0.5$ ML to $\theta = 1.5$ ML and found out a rich variety of missing-row reconstructed structures. In fact, this rich polymorphism is due to the large proclivity of the clean Pd(110) surface to reconstruct. So, the chemisorption of a small amount of hydrogen can already stabilize the reconstructed substrate. The (1×2) missing-row reconstruction creates (111) facets on which various nearly degenerate adsorption patterns can be formed. This is another factor that accounts for the H-induced polymorphism. The analysis of the electronic structure clearly shows that the driving force for the missing-row reconstruction is the better adsorbate-substrate interaction on the reconstructed surface.

ACKNOWLEDGMENTS

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[1] K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).

[2] K. Christmann, in *Hydrogen Effects in Catalysis-Fundamentals and Practical Applications*, edited by Z. Paál and P. G. Menon (Marcel Dekker, New York, 1988).

[3] M. G. Cattania, V. Penka, R. J. Behm, K. Christmann, and G. Ertl, Surf. Sci. **126**, 382 (1983).

[4] K. H. Rieder, M. Baumberger, and W. Stocker, Phys. Rev. Lett. **51**, 1799 (1983).

[5] H. Niehus, C. Hiller, and G. Comsa, Surf. Sci. **173**, L599 (1986).

[6] G. Kleinle, M. Skottke, V. Penka, G. Ertl, R. J. Behm, and W. Moritz, Surf. Sci. **189/190**, 177 (1987).

[7] M. Skottke, R. J. Behm, G. Ertl, V. Penka, and W. Moritz, J. Chem. Phys. **87**, 6191 (1987).

[8] J. W. He and P. R. Norton, Surf. Sci. **195**, L199 (1988).

[9] T. H. Ellis and M. Morin, Surf. Sci. **216**, L351 (1989).

[10] J. Yoshinobu, H. Tanaka, and M. Kawai, Phys. Rev. B **51**, 4529 (1995).

[11] E. Kampshoff, N. Waelchli, A. Menck, and K. Kern, Surf. Sci. **360**, 55 (1996).

[12] S. M. Foiles, Surf. Sci. **191**, L779 (1987).

[13] S. G. Louie, Phys. Rev. Lett. **40**, 1525 (1978).

[14] S. G. Louie, Phys. Rev. Lett. **42**, 476 (1979).

[15] D. Tománek, S. G. Louie, and C. T. Chan, Phys. Rev. Lett. **57**, 2594 (1986).

[16] D. Tománek, Z. Sun, and S. G. Louie, Phys. Rev. B **43**, 4699 (1991).

[17] M. Methfessel, D. Hennig, and M. Scheffler, Phys. Rev. B **46**, 4816 (1992).

[18] S. Wilke, D. Hennig, and R. Löber, Phys. Rev. B **50**, 2548 (1994).

[19] S. Wilke and M. Scheffler, Surf. Sci. **329**, L605 (1995).

[20] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995).

[21] W. Dong, G. Kresse, J. Furthmüller, and J. Hafner, Phys. Rev. B **54**, 2157 (1996).

[22] W. Dong and J. Hafner, Phys. Rev. B **56**, 15 396 (1997).

[23] D. Tománek, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **79**, 1329 (1997).

[24] K. W. Jacobsen and J. K. Norskov, Phys. Rev. Lett. **60**, 2496 (1988).

[25] C. L. Fu and K. M. Ho, Phys. Rev. Lett. **63**, 1617 (1989).

[26] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **48**, 13 115 (1993); **49**, 14 251 (1994).

[27] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[28] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[29] D. M. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[30] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[31] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[32] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).

[33] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[34] V. R. Dhanak, G. Comelli, G. Paolucci, K. C. Prince, and R. Rosei, Surf. Sci. **260**, L24 (1992).

[35] H. Hörnis, J. D. West, E. H. Conrad, and R. Ellialtioglu, Phys. Rev. B **48**, 14 577 (1993).

[36] C. J. Barnes, M. Q. Ding, M. Lindroos, R. D. Diehl, and D. A. King, Surf. Sci. **162**, 59 (1985).

[37] R. D. Diehl, M. Lindroos, A. Kearsley, C. J. Barnes, and D. A. King, J. Phys. C **18**, 4069 (1985).

[38] H. Conrad, G. Ertl, and E. E. Latter, Surf. Sci. **41**, 435 (1974).

[39] T. E. Felter, E. C. Sowa, and M. A. Van Hove, Phys. Rev. B **40**, 891 (1989).

[40] B. Voigtländer, S. Lehwald, and H. Ibach, Surf. Sci. **208**, 113 (1989).

[41] F. Besenbacher, I. Stensgaard, and K. Mortensen, Surf. Sci. **191**, 288 (1987).

[42] M. A. Van Hove and G. A. Somorjai, Surf. Sci. **299/300**, 487 (1994).

[43] B. Brena, G. Comelli, L. Ursella, and G. Paolucci, Surf. Sci. **375**, 150 (1997).