

phys. stat. sol. (a) **159**, 225 (1997)

Subject classification: 68.35.Bs; S1; S1.1; S1.2

Hydrogen on Metals: Adsorption Sites and Substrate Reconstructions

K. HEINZ¹) and L. HAMMER

*Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7,
D-91058 Erlangen, Germany*

(Received May 31, 1996)

By various representative examples the structural properties of hydrogen adsorption on transition metal surfaces are illustrated. It is shown that the occurrence of hydrogen induced substrate reconstruction is rather the rule than the exception. In many cases the reconstruction is weak with atomic displacements of a few 1/100 Å only. However, also strong reconstructions can take place with displacements > 0.1 Å and/or even removal of substrate atoms. Also, reconstructions already existing for the clean surface can be drastically modified and even switched in symmetry. At full coverage, atomic displacements add up to modify the vertical relaxation of interlayer distances of the clean surface towards the bulk layer spacing and in this sense hydrogen acts to restore the truncated surface bonds. No induced registry shifts of layers are observed. The structural influence of hydrogen seems to extend and to be limited down to about the second to third layer. It apparently is accompanied by a redistribution of electronic charges within the surface leading to unforeseen changes of the electronic work function. The adatoms have a strong tendency to occupy high symmetry or highly coordinated sites with bond lengths according to a hydrogen radius of 0.5 to 0.7 Å.

1. Determination of Hydrogen Adsorption Structures

For the quantitative understanding of surface properties the knowledge of the surface structure is crucial, as well known. Its determination generally is a complex problem for chemisorption systems and this holds also for hydrogen adsorption. The chemical reactivity of hydrogen is high enough to make the adatoms perturb the energy balance of bonds within the surface, eventually leading to a more or less pronounced surface reconstruction. Obviously, the determination of the adsorption structure must include the modified substrate. This, in many cases, is equivalent to the determination of a rather large number of structural parameters. Also, as the adsorbate induced perturbation might not be limited to the top substrate layer, a structure sensitive method is needed which provides information on a whole surface slab of a certain thickness. Equivalently, such a method must use a probe which penetrates somewhat into the surface. This is in particular true for low energy electrons, and in fact recent progress in both accuracy and precision of intensity measurements and model calculations has led to a number of complete structure determinations by low energy electron diffraction (LEED). Photoelectron diffraction has been applied as well. Of course, in principle also other penetrating particles as in transmission channeling and ion scattering could be used and in fact were successfully applied (for a catalogue-like overview of analyses using different methods see [1]). It is also important to mention that helium and neon diffraction has been success-

¹) e-mail: kheinz@fkp.physik.uni-erlangen.de

fully used to investigate the structure of hydrogen adsorption systems (see e.g. [2]). However, the missing penetration of particles into the surface limits the extractable information to the very surface, i.e. to its corrugation due to or induced by hydrogen from which the hydrogen adsorption site could be retrieved in a number of cases.

As the method applied by the present authors is LEED, we focus on the problem of hydrogen adsorption structure determination by this tool a bit more closely (for details see e.g. [3]). Unfortunately, hydrogen is a weak electron scatterer. Its scattering cross section is about two orders of magnitudes smaller than that of e.g. transition metal atoms and this puts substantial demands to the structural analysis. If the adatoms – in the submonolayer regime – would form a superstructure without affecting the substrate, “only” an experimental problem would result, i.e. the reliable measurement of weak extra spot intensities. The subsequent intensity analysis would be straightforward. Unfortunately, however, to the authors’ knowledge this case, though sometimes assumed, never really takes place. Instead, as mentioned above, substrate atoms are displaced or removed from the surface. Even if the displacements are small, i.e. of the order of several $1/100 \text{ \AA}$, the extra scattering from the perturbed substrate can become larger than the pure hydrogen scattering, though the latter is not yet negligible. Then extra spot intensities can be measured more easily, but a problem appears on the theoretical side: The induced local reconstruction, i.e. the structure of the local adsorption cluster including the adsorbed atom, might be (and generally is) rather complex, and the best fit model parameters have to be found in a multi-parameter space. We will give an example for that in the next section. A special case results when more and more hydrogen atoms are made to adsorb and a full monolayer is formed. Then the local reconstructive displacements add up, eventually resulting in only a modified interlayer distance relaxation and/or (at least in principle) a registry shift of layers. As a consequence, the resulting adsorption structure is rather simple but – with no extra spots present – has to be retrieved from integer order spot intensities which are dominated by the substrate. We focus on such a case in the third section. In particular we deal with the case of $\text{W}(110)\text{-(}1 \times 1\text{)-H}$, which is the only one, for which a hydrogen induced registry shift has ever been reported. As will be shown, the occurrence of such a shift must be ruled out on the basis of a new LEED analysis, additionally confirmed by first principle calculations. Eventually, in Section 4 we address the case of strong induced reconstructions or switching of existing ones, where the extra scattering from the reconstruction cluster highly dominates the scattering into superstructure spots. This makes the determination of the hydrogen adsorption site impossible leaving access to the reconstruction parameters, only.

2. Weakly Reconstructed Substrates in the Submonolayer Coverage Regime

In many and possibly most cases hydrogen interacts only moderately with transition metal surfaces, in particular when the latter are close or nearly close packed. A representative case is $\text{Ni}(111)\text{-(}2 \times 2\text{)-}2 \text{ H}$ which was first analyzed by LEED years ago [4], when one could not imagine that a close packed surface could be induced to reconstruct. Not surprisingly, the quality of the theory–experiment achieved was limited and in particular, the level of calculated extra spot intensities did not meet that of measured data. The reinvestigation of the systems allowing for substrate atom displacements in fact revealed a slight substrate reconstruction and brought the level of extra spot intensities to the observed value (3% of substrate spots on average) [5]. As displayed on the left of

Fig. 1 (and also found in the earlier investigation [4]), the adatoms reside both in three-fold symmetric h.c.p. and f.c.c. sites forming a honeycomb arrangement. Hydrogen coordinated nickel atoms are lifted by 0.04 \AA making the top substrate layer buckle and so

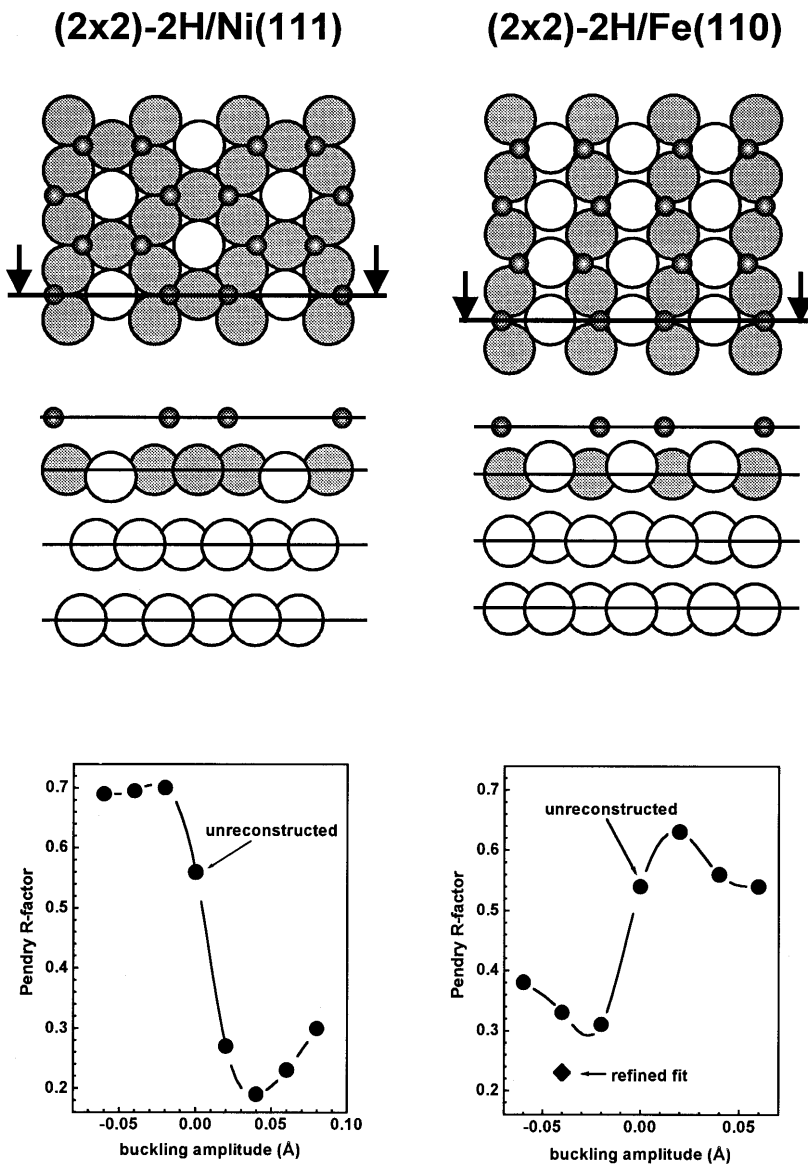


Fig. 1. Left: Adsorption structure of Ni(111)-(2 × 2)-2 H in on-top and side view (upper and middle panel, respectively). The bottom panel displays the dependence of the Pendry R -factor on the vertical displacement of hydrogen coordinated atoms (shaded). Right: Same as left except for Fe(110)-(2 × 2)-2 H. The point of further refinement in the bottom panel corresponds to the additional allowance for a buckling in the third layer. Small circles stand for H-atoms. Large circles indicate substrate atoms, whereby hatched ones are pulled out (left) or pushed into (right) the surface

contribute to spot intensities. The improvement of the theory–experiment fit achieved by this reconstruction is mirrored by the behaviour of the Pendry R -factor [6] given in the left bottom panel of Fig. 1. There is a dramatic decrease of the R -factor demonstrating the sensitivity of LEED to the surface modification. The detected reconstruction is beyond the limits of error estimated by the variance of the Pendry R -factor. The adsorption height is 0.98 Å above the substrate, however, this value is uncertain by ± 0.1 Å because of the weak hydrogen scattering.

One might expect that a similar reconstruction will take place in case of comparably close packed surfaces. However, the investigation of Fe(110)-(2 × 2)-2 H, a phase which develops at temperatures below 80 K [7], tells us that nature is not that simple [5]. As demonstrated by the models on the right-hand side of Fig. 1, hydrogen atoms again adsorb in three-fold coordinated sites as also found earlier for a (2 × 1) phase developing at higher temperatures [8]. Our analysis finds the adatoms laterally shifted by 0.14 Å off the ideal three-fold coordinated site towards the two-fold bridge site. This slight change of coordination seems to concentrate the hydrogen induced displacements to the bridge atoms which in fact move by 0.04 Å. However, in contrast to the case of Ni(111)-(2 × 2)-2 H and obvious from the reversed shape of the R -factor behaviour, hydrogen coordinated iron atoms are pushed into the surface (instead of being pulled out), i.e. the reconstruction amplitude is of different sign. Interestingly, this correlates with the different sign of work function changes induced by hydrogen on the two surfaces, i.e. $\Delta\varphi = -60$ meV for H/Fe(110) [9] and $\Delta\varphi = +165$ meV for H/Ni(111) [4]. In particular this tells that caution has to be paid when interpreting work function changes in terms of charge transfer to or from the substrate: Redistribution of charges within the surface due to some induced substrate reconstruction may add or even dominate.

There is a number of other examples with weak substrate reconstructions induced in the submonolayer regime. LEED proves to have a good chance to determine both the reconstruction and the adsorption geometry, when not too many atoms surrounding the adatom are involved in the reconstruction process. Otherwise, it can become impossible to decide whether a special feature in the intensity spectra comes from hydrogen or from the reconstruction cluster, and then the safe determination of the adsorption site might become impossible. Perhaps the system investigated in most detail is H/Rh(110) for which the adsorption site and substrate reconstruction were determined for various coverages (see [3] and references therein). Again hydrogen seeks for sites with maximum coordination and thus occupies three-fold coordinated sites offered jointly by first and second layer substrate atoms. In a detailed LEED analysis of e.g. the Rh(110)-(1 × 3)-H phase it could be shown that not only immediately coordinated substrate atoms are displaced, but also second nearest neighbours move [10]. Nevertheless, the induced displacements quickly die away with increasing distance from the adatom. However, with increasing coverage the substrate reconstruction clusters more and more overlap and additional to the occurrence of a local reconstruction also the average interlayer distances change. Of course this effect is largest when at full coverage all displacements add up. We will address this case next.

3. Full Coverage Adsorption: Vertical and Lateral Layer Relaxations

When full coverage with one (or more) hydrogen atom(s) per substrate layer atom adsorbed is achieved and the bulk-like (1 × 1) LEED pattern reappears, symmetry inhibits

the appearance of surface reconstructions. Of course, the chemical influence of the adatoms must still be active whereby, however, the local vertical atomic shifts add up to modified interlayer distances (vertical layer relaxation). Lateral displacements either cancel each other or may lead, at least in principle, to registry shifts of layers (lateral relaxation). The vertical layer relaxation has been determined in numerous cases and was found to be always in the sense of a derelaxation, i.e. contractions or expansions of interlayer distances of the clean surface are weakened or even completely removed. Obviously, hydrogen adatoms in a way act as to restore the surface bonds which had been broken during the creation of the surface. So, e.g. for Rh(110)-(1 × 1)-2 H, the clean surface relaxations $\Delta d_{12}/d_0 = -6.9\%$, $\Delta d_{23}/d_0 = +1.9\%$ are reduced to values -1.3% and $+0.2\%$, respectively [3, 11]. This demonstrates that the electronic influence of hydrogen extends down to the second to third layer. However, it seems also to be limited to that range as obvious from investigations of the clean and fully hydrogen covered $\text{Mo}_{75}\text{Re}_{25}(100)$ surface. In this exceptional case the multilayer relaxation of the clean surface extends as deep as to the sixth layer. By hydrogen adsorption only the top two layer spacings are modified ($\Delta d_{12}/d_0 = -11.9\% \rightarrow -0.9\%$, $\Delta d_{23}/d_0 = +5.1\% \rightarrow +1.4\%$) whilst deeper layer distances remain practically unaffected [12].

In principle the locally induced atomic displacements could also add up to produce a lateral relaxation of layers, i.e. a registry shift. Indeed this was reported to happen for W(110)-(1 × 1)-H by Chung et al. [13] with the top tungsten layer shifted in $[\bar{1}\bar{1}0]$ direction. For the sample used this shift direction was believed to be favoured over the symmetrically equivalent opposite direction by the presence of surface steps. The conclusion for the lateral relaxation was drawn from the lift of degeneracy of beams which are identical for the clean surface due to the existence of a mirror plane. Hydrogen was believed to reside in bridge sites, so that the break of symmetry could not come from mere hydrogen scattering. However, a new LEED analysis shows that this exactly is the misleading assumption [14]. Our group finds that hydrogen adsorbs in three-

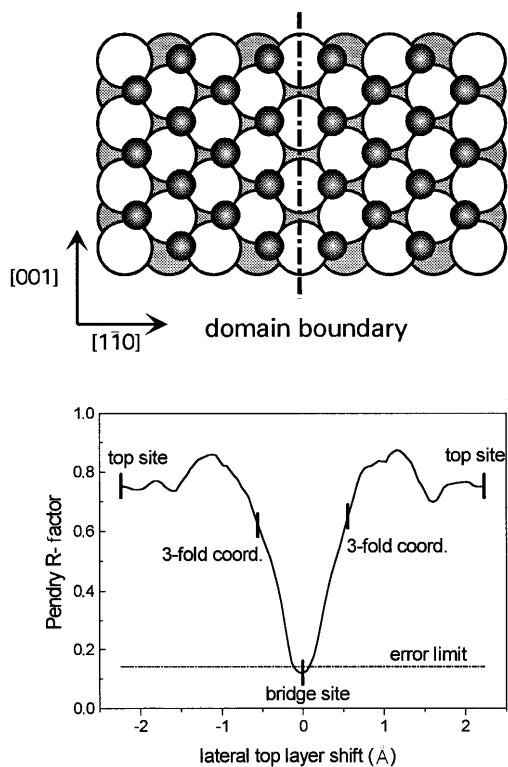


Fig. 2. Top: Two domains of the adsorption structure of W(110)-(1 × 1)-H in on-top view. Small circles stand for H-atoms, large circles for W-atoms of the first (white) and second (hatched) substrate layer. Bottom: Dependence of the Pendry R -factor on the lateral shift displacement of the top layer of tungsten (with adatoms being fixed within the top layer)

fold coordinated sites (Fig. 2 top), and this by its own breaks the mirror plane symmetry of the clean surface. In fact we can show that this scattering contribution is sufficient to explain the asymmetry of beam intensities observed by Chung et al. [13] when only one of two equivalent domains is predominant as was assumed. In our experiments both types of symmetrically equivalent domains (see Fig. 2, top) were present with equal weight. This was evident from identical $I(E)$ spectra of the mentioned beams for the clean as well as for the hydrogen covered surface.

The main outcome of our analysis of H/W(110) is the complete absence of a registry shift of the top tungsten layer. The R -factor minimum ($R_P = 0.12$) develops exactly for the bulk lateral position of the layer and the statistical error of the analysis discards any lateral shift larger than 0.1 \AA (Fig. 2, bottom). As usual, however, the first interlayer distance contraction of the clean surface ($\Delta d_{12}/d_0 = -3.1\%$) is reduced (to -1.7%). Our results are nicely and quantitatively corroborated by very recent density functional theory (DFT) calculations [14, 15] which within the limits of error produce the same structural parameters as LEED, in particular exclude any substantial registry shift. So, to our knowledge there is no case where hydrogen adsorption induces a registry shift in a bulk-like terminated substrate. However, it will be shown within the next section, that a registry shift already present in the clean surface (which, however, is a rare case, too) can be modified by adsorbed hydrogen atoms.

4. Strong Hydrogen Induced Reconstructions

In a few cases hydrogen adsorption on transition metal surfaces was observed to induce LEED superstructure spots with unusually high intensities even at energies extending to several hundreds of eV. Because of the weak scattering strength of hydrogen, these features are a clear indication of a substantial substrate reconstruction. In this case it is practically impossible to determine the hydrogen adsorption geometry on the reconstructed substrate because also the extra spot intensities are highly dominated by the substrate scattering *and* because the reconstruction extends deeper into the surface with many substrate atoms involved. As a consequence of the latter point a slight misadjustment of the large number of geometrical parameters for substrate atoms easily simulates the weak contribution of hydrogen. This is different from the above discussed (1×1) phases, where the integer order spot intensities are also dominated by the substrate: In this case the substrate structure is simple with only a few parameters as interlayer distances (or registry shifts) to be determined and so the adsorption site usually can be retrieved, too. In the case of a heavy reconstruction, however, one must be satisfied with the determination of the reconstruction leaving the adsorption site unknown.

The strong reconstruction induced arises either by substantial displacements of some substrate atoms, i.e. larger than about 0.1 \AA , or by a complete removal of them. The only safely known example of the latter case is the hydrogen induced missing row reconstruction of Fe(211) [15]. This case is additionally interesting because the clean Fe(211) surface to our knowledge is the only surface known which exhibits a registry shift of the top layer (about 0.2 \AA) [15, 16]. This is illustrated on the left of Fig. 3 and might indicate that the surface has a tendency to reconstruct. In fact, by hydrogen adsorption and thermal activation above 200 K, a (1×2) pattern with bright extra spots develops [17, 18]. The intensity analysis [15] – neglecting hydrogen scattering by the above discussed reasons – retrieves a missing row reconstruction with every second atomic row removed

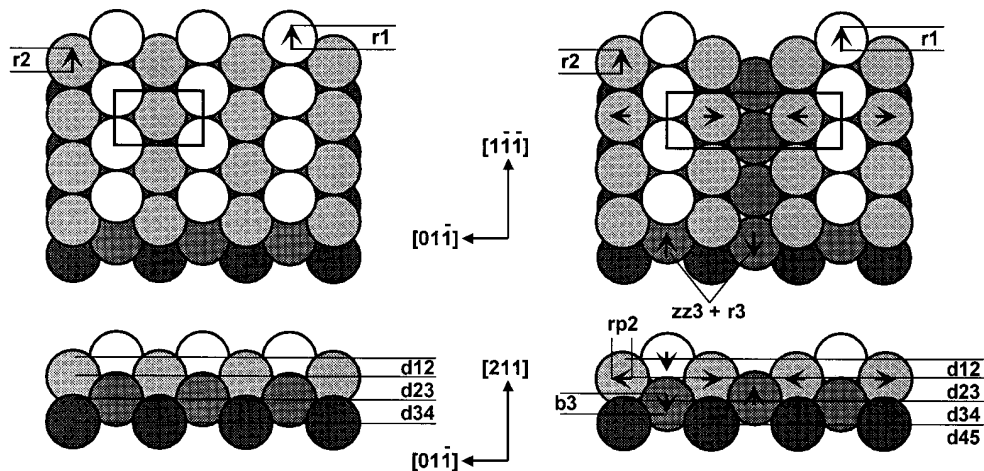


Fig. 3. Surface models of Fe(211) in the clean phase (left) and in the (1×2) missing row reconstructed phase as induced by hydrogen adsorption (right) [15]. The darker the hatching, the deeper the atomic layer

(see right-hand side of Fig. 3). Additionally, the registry shift of the remaining top layer is slightly reduced. In the second layer some row pairing and in the third layer some buckling is induced. Displacements in deeper layers were not detected which again demonstrates that the electronic activity of hydrogen extends and is restricted to about the first two or three layers.

Adsorption of hydrogen on a surface already reconstructed when clean is an interesting case, too. Hydrogen might be able to lift this reconstruction or to make the surface switch to a different type of reconstruction. Both cases happen with hydrogen adsorption on W(100) at full and medium coverage, respectively. The clean surface exhibits a $c(2 \times 2)$ reconstruction with a zig-zag like arrangement of surface atoms (Fig. 4, left)

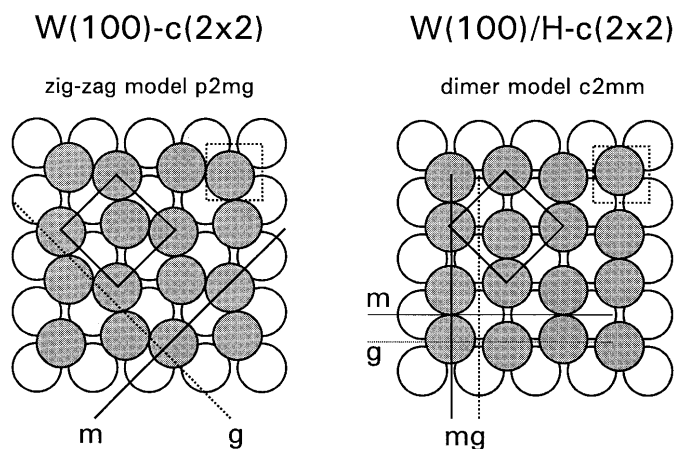


Fig. 4. Left: Zig-zag model of the (2×2) reconstruction of clean W(100). Right: Dimer model of the (2×2) reconstruction of hydrogen covered W(100). Hatched (white) circles represent first (second) layer atoms

due to diagonal atomic displacements [19] of slightly more than 0.2 \AA as determined by X-ray [20] and LEED [21] structure determinations. By adsorption of half a monolayer of hydrogen the $c(2 \times 2)$ diffraction pattern remains, but the intensity spectra change [21]. Their analysis retrieves a switch of the reconstruction type to a dimer-like arrangement as displayed on the right of Fig. 4. The amplitude of the atomic displacements relative to bulk positions remains practically the same, i.e. about 0.2 \AA [21]. This again produces extra spot intensities large enough to inhibit the safe determination of the hydrogen adsorption site. With increasing coverage superstructure spots fade away and eventually an unreconstructed (1×1) -2 H phase results. For this the determination of the substrate derelaxation and of the hydrogen adsorption site (here bridge site) is again possible [22] as described above.

5. Conclusion

The above examples, which are representative for the various structural features of hydrogen adsorption, have demonstrated that hydrogen always modifies the substrate structure when adsorbed on a transition metal. The modifications are often faint, with atomic displacements of a few $1/100 \text{ \AA}$ only, but can also become substantial with displacements $>0.1 \text{ \AA}$ and/or even removal of surface atoms. In any case the displacements die away quickly with increasing distance to the adatom. In the full coverage regime they add up to modify the layer relaxation. However, only changes of vertical layer distances towards a bulk-like terminated surface are observed and – up to now – no lateral relaxations (registry shifts), except when already existing for the clean surface. This indicates that at full coverage hydrogen in a way acts to restore the truncated surface bonds. In case of weak reconstructions the hydrogen adsorption site can be determined in addition to the reconstruction, at least if the latter involves not too many atoms. The adsorption site is also accessible for (1×1) phases, e.g. at full coverage. In all cases observed, hydrogen tends to occupy high symmetry adsorption sites, as three-fold coordinated sites on f.c.c.(111), (110), (311) and b.c.c.(110) surfaces and bridge sites on b.c.c.(100) surfaces. The reactivity of hydrogen seems to extend and to be limited down to the second to third substrate layer as judged from the displacements induced. Additional to the geometric reconstruction there obviously is also a redistribution of charges which can heavily affect the magnitude and even the sign of the work function change induced by hydrogen adsorption.

Acknowledgements The authors want to honour Prof. Klaus Müller †, who initiated much of the work whose results have been presented in this paper. Also, the authors gratefully acknowledge financial support through Deutsche Forschungsgemeinschaft (DFG).

References

- [1] NIST Surface Structure Database 2.0 (1995), Nat. Inst. Stand. Technol., Gaithersbury (USA).
- [2] K. H. RIEDER, Surface Rev. Letters **1**, 51(1994).
- [3] K. HEINZ and L. HAMMER, Z. Phys. Chem., in press.
- [4] K. CHRISTMANN, R. J. BEHM, G. ERTL, M. A. VAN HOVE, and W. H. WEINBERG, J. chem. Phys. **70**, 4168 (1979).
- [5] L. HAMMER, H. LANDSKRON, W. NICHTL-PECHER, A. FRICKE, K. HEINZ, and K. MÜLLER, Phys. Rev. B **47**, 15969 (1993).

- [6] J. B. PENDRY, *J. Phys. C* **13**, 937 (1980).
- [7] W. NICHTL-PECHER, J. GOSSMANN, L. HAMMER, K. HEINZ, and K. MÜLLER, *J. Vacuum Sci. Technol. A* **10**, 501 (1992).
- [8] W. MORITZ, R. IMBIHL, R. J. BEHM, G. ERTL, and T. MATSUSHIMA, *J. Chem. Phys.* **83**, 1959 (1985).
- [9] F. BOSZO, G. ERTL, M. GRUNZE, and M. WEISS, *Appl. Surface Sci.* **1**, 103 (1977).
- [10] K. HEINZ, *Rep. Progr. Phys.* **58**, 637 (1995).
- [11] W. NICHTL, N. BICKEL, L. HAMMER, K. HEINZ, and K. MÜLLER, *Surface Sci.* **188**, L729 (1987).
- [12] L. HAMMER, M. KOTTCKE, K. HEINZ, K. MÜLLER, and D. M. ZEHNER, *Surface Rev. Letters*, in press.
- [13] J. W. CHUNG, S. C. YING, and P. J. ESTRUP, *Phys. Rev. Letters* **56**, 749 (1986).
- [14] L. HAMMER, M. ARNOLD, K. HEINZ, B. KOHLER, and M. SCHEFFLER, *Phys. Rev. Letters*, submitted.
- [15] E. HASSOLD, U. LÖFFLER, R. SCHMIEDL, M. GRUND, L. HAMMER, K. HEINZ, and K. MÜLLER, *Surface Sci.* **326**, 93 (1995).
- [16] J. SOLOKOV, H. D. SHIH, U. BARDI, F. JONA, and P. M. MARCUS, *J. Phys. C* **17**, 371 (1984).
- [17] R. SCHMIEDL, W. NICHTL-PECHER, K. HEINZ, K. MÜLLER, and K. CHRISTMANN, *Surface Sci.* **235**, 186 (1990).
- [18] R. SCHMIEDL, W. NICHTL-PECHER, L. HAMMER, K. HEINZ, and K. MÜLLER, *Surface Sci.* **324**, 289 (1995).
- [19] M. K. DEBE and D. A. KING, *Surface Sci.* **81**, 193 (1979).
- [20] M. S. ALTMANN, P. J. ESTRUP, and I. K. ROBINSON, *Phys. Rev. B* **38**, 5211 (1988).
- [21] G. SCHMIDT, H. ZAGEL, H. LANDSKRON, K. HEINZ, K. MÜLLER, and J. B. PENDRY, *Surface Sci.* **271**, 416 (1992).
- [22] M. A. PASSLER, B. W. LEE, and A. IGNATIEV, *Surface Sci.* **150**, 263 (1985).