

## Hydrogen-induced restructuring of close-packed metal surfaces: H/Ni(111) and H/Fe(110)

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We report that hydrogen can induce surface reconstructions by adsorption even on close-packed substrates. New low-energy electron-diffraction analyses for H/Ni(111) and H/Fe(110) show that consideration of reconstruction is essential for a convincing experiment-theory fit as well as for reliable determination of the adsorption site. There are two different types of reconstruction: Hydrogen pulls nickel atoms out of the surface but pushes iron atoms towards the bulk. These findings are mirrored by a different sign of work-function change for both systems and demonstrate the correlation between geometric and electronic structure.

Numerous surface structure determinations have demonstrated that the reconstruction of surfaces upon adsorption is more the rule than an exception. Nevertheless, close- or nearly-close-packed atomic arrangements as in hcp(0001), fcc(111), or bcc(110) metal surfaces were believed to be rather inert with respect to adsorption except for examples such as S/Fe(110).<sup>1</sup> However, recent detailed surface analyses by low-energy electron diffraction (LEED) have also shown that these surfaces can be induced to reconstruct quite considerably. So, for O/Ni(111) a substantial substrate reconstruction was found<sup>2</sup> and also molecules can modify the substrate structure.<sup>3</sup> In this paper we demonstrate that even hydrogen can cause a reconstruction of close-packed surfaces. Also, we show that weak superstructure spots are not a reliable indication of an unreconstructed substrate. But their intensity level can serve as an independent measure for the reconstruction amplitude. We demonstrate that only the full consideration of reconstruction allows for a reliable determination of the adsorption site and a convincing theory-experiment fit. We concentrate on the adsorption phases H/Ni(111) and H/Fe(110), which are of particular interest, for the following reasons.

(i) Earlier analyses assuming unreconstructed substrates exist for both systems, namely for  $(2 \times 2)$ -2H/Ni(111) (Ref. 4) and  $c(2 \times 2)$ H/Fe(110).<sup>5</sup> Although they were careful state-of-the-art studies, unsatisfactory theory-experiment agreement by today's standards resulted.

(ii) Hydrogen was always found in threefold-coordinated sites with comparable hydrogen-metal bond lengths. The work-function change, however, is different in sign, i.e.,  $\Delta\phi = +165 \text{ meV} > 0$  for H/Ni(111) (Ref. 4) and  $\Delta\phi = -85 \text{ meV} < 0$  for H/Fe(110).<sup>6</sup> So, different rearrangements of the charge distribution within the surface slab must exist which hardly can be understood when the local adsorption structure is of the same type.

(iii) The presence of an adsorbate-induced reconstruction is essential for a quantitative understanding of interactions between adatoms, particularly when it is indirect as in the case of hydrogen.<sup>7</sup>

(iv) Hydrogen adsorption systems show only weak superstructure spots which must be reliably measured in or-

der to retrieve adatom positions as well as local reconstructions from their intensities. Therefore, these structures are real challenges for modern LEED structure determination.

LEED data were taken for both clean and hydrogen-covered surfaces. Sample preparations followed procedures described in Refs. 8 and 9 reducing surface impurities as *S*, *P*, and *C* to less than 0.01 monolayers as checked by Auger-electron spectroscopy. Hydrogen was adsorbed from the gas phase with the Ni sample at 90 K and the Fe sample at 40 K. In both cases we observed a well-ordered  $2 \times 2$  superstructure with two adatoms in the unit cell. For Ni(111) this is the well-known structure for coverage  $\theta = 0.5$ ,<sup>10-13</sup> but the superstructure known until recently for Fe(110) at  $\theta = 0.5$  was  $c(2 \times 2)$ .<sup>4,14,15</sup> We have demonstrated in a recent paper<sup>9</sup> that both phases  $2 \times 2$  and  $c(2 \times 2)$  on Fe(110) transform into each other reversibly. The transition takes place at about 80 K leaving the intensity spectra of the centered superstructure spots practically unchanged. This was interpreted by the  $c(2 \times 2)$  phase being a locally disordered  $2 \times 2$ -2H phase in which hydrogen fluctuates between neighbored threefold-coordinated sites with the same local adsorption geometry.<sup>9</sup> We concentrate in the following on the well-ordered  $(2 \times 2)$ -2H phase for both substrates.

LEED intensities were taken from a four-grid back view optics by use of a video camera. Its electronic signal is evaluated under computer control as described in detail elsewhere.<sup>16,17</sup> For H/Ni(111) data were taken at 90 K, for H/Fe(110) at 40 K; both sets at normal incidence of the primary electron beam. An image intensifier camera was used since all extra spot intensities were less than 10% of substrate spot signals. However, most extra spots were clearly visible up to energies of more than 400 eV indicating that they do not arise from hydrogen scattering only.

Intensity analyses were carried out by full dynamical calculations using standard LEED programs.<sup>18,19</sup> The parameter space was scanned by testing equidistant values of parameters independently in a physically reasonable range. A maximum of eight phase shifts ( $J_{\text{max}} = 7$ ) was used for all elements. They were tempera-

ture corrected using Debye temperatures  $\Theta_D = 440$  K for Ni and  $\Theta_D = 467$  K for Fe. The Debye temperature for hydrogen was chosen in a way to produce the same vibrational amplitudes for the adatoms and the substrate atoms. This procedure has proved to be successful in other analyses with hydrogen as an adsorbate.<sup>20</sup> Layer diffraction matrices were calculated by matrix inversion. The hydrogen-covered top substrate layer was treated as a composite layer. Layers were stacked by the layer doubling method<sup>18,19</sup> and electron attenuation was simulated by an imaginary part of the inner potential,  $V_{oi} = -5$  eV. For the theory-experiment fit the Pendry  $R$  factor<sup>21</sup> was applied. The analyses of the clean surfaces reproduced earlier results [Ni,<sup>17,22-24</sup> Fe (Ref. 25)] showing that both surfaces are bulk terminated within the limits of error ( $\pm 1\%$  of the layer distance). The Pendry  $R$  factors of  $R_p = 0.16$  for Ni(111) and  $R_p = 0.14$  for Fe(110) are convincing.

As a starting point for the analysis of  $(2 \times 2)$ -2H/Ni(111) we took the best-fit model of the earlier LEED analysis by Christmann *et al.*<sup>4</sup> These authors favored a honeycomblike structure with hydrogen adsorbed in both fcc and hcp threefold-coordinated sites according to Fig. 1(a). As this model was also confirmed by helium scattering,<sup>26</sup> other than threefold-coordinated sites were not tested in our analysis. However, on an unreconstructed substrate our theory-experiment fit varying the first three interlayer spacings was of poor quality. Quantitatively, this is mirrored by a Pendry  $R$  factor of  $R_p = 0.53$  as averaged over three substrate and five half-order spots and a total energy range of 977 eV. Inspection of the spectra shows that calculated intensities decay much faster with energy than experimental data as shown in Fig. 2(a) for a selected beam. Moreover, the calculated ratio of energy averaged intensities of fractional order spots relative to that of substrate spots is only  $\nu = 1.4\%$  while the experimental value is  $\nu = 3.2\%$ . This suggests the presence of a substrate reconstruction. Therefore, we allowed the three hydrogen-coordinated nickel atoms in

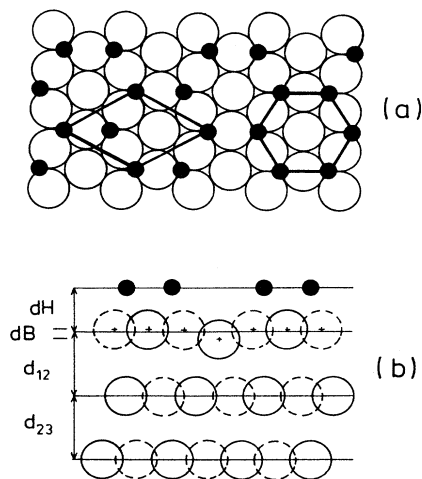


FIG. 1. Structural model for  $(2 \times 2)$ -2H/Ni(111) in the top (a) and side (b) views.

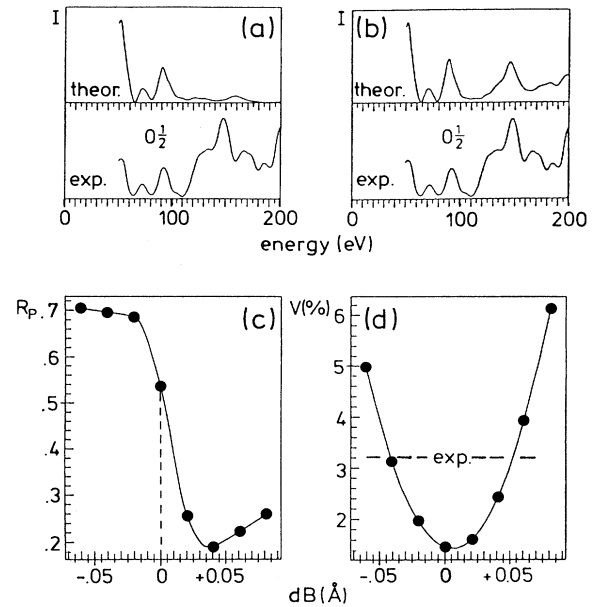


FIG. 2. Best-fit spectra for the  $0\frac{1}{2}$  beam for the Ni(111) substrate unreconstructed (a) and reconstructed (b). In (c) the  $R$ -factor dependence on the buckling amplitude  $dB$  is shown and (d) displays the behavior of the quantity  $\nu$  (see text).

the unit mesh to move vertically relative to the uncoordinated atom. This causes a buckling in the top substrate layer [Fig. 1(b)] which makes the theory-experiment fit improve dramatically when the three nickel atoms are lifted by the buckling amplitude  $dB = 0.04$  Å. The corresponding decrease of the  $R$  factor from  $R_p = 0.53$  to  $R_p = 0.19$  is displayed in Fig. 2(c) together with a best-fit spectrum in Fig. 2(b). As demonstrated in Fig. 2(d) the buckling brings the intensity ratio  $\nu$  very near to the experimental value. Additional lateral displacements in the top substrate layer lead to no further improvement. In view of the low  $R$  factor reconstructive movements in the second substrate layer were not considered. The overall best-fit values for the parameters given in Fig. 1(b) are  $dH = 0.98 \pm 0.08$  Å,  $dB = 0.04 \pm 0.02$  Å,  $d_{12} = 2.03 \pm 0.03$  Å ( $\Delta d_{12}/d_0 = 0 \pm 1.5\%$ ), and  $d_{23} = 2.05 \pm 0.05$  Å ( $\Delta d_{23}/d_0 = 1 \pm 2.5\%$ ). Layer distances refer to the center-of-mass planes. The H-Ni bond length is  $L_{H-Ni} = 1.73$  Å entailing a radius of hydrogen  $r_H = 0.49$  Å. The error limits result from the variance of the Pendry  $R$  factor<sup>21</sup> and are comparably large ( $\pm 0.08$  Å) for the weakly scattering hydrogen atom.

As a starting point for the analysis of  $(2 \times 2)$ -2H/Fe(110) we used threefold-coordinated adsorption sites as determined by Moritz *et al.*<sup>5</sup> for the  $c(2 \times 2)$  phase. The latter transforms to the  $(2 \times 2)$ -2H phase by displacement of every second hydrogen atom to its neighboring threefold-coordinated site as displayed in Fig. 3(a) (for more details see Ref. 9). This new phase is a distorted honeycomblike arrangement similar to the case H/Ni. In contrast to the latter, however, there are two subsets of superstructure spots for H/Fe which differ markedly in average intensity. The noncentered spots are extreme-

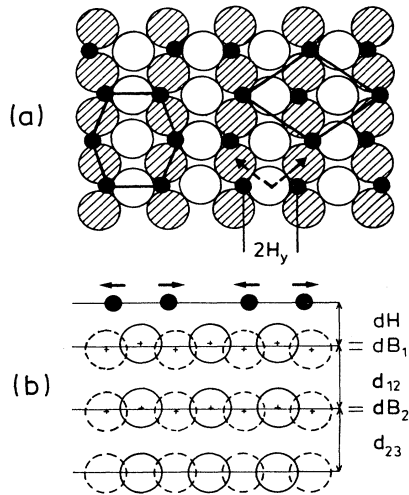


FIG. 3. Structural model of  $(2 \times 2)$ -2H/Fe(110) in the top (a) and side (b) views.

ly weak as expected from pure hydrogen scattering. The major part of superstructure intensities is carried by the centered spots with  $v = 4.7\%$ . This is a value much too high to be due to hydrogen scattering only and points at a hydrogen-induced substrate reconstruction of  $c(2 \times 2)$  type. Therefore we allowed—in a first step—for a buckling of the first substrate layer as described in Fig. 3(b). In view of the mobility of hydrogen leading to a phase transition at 80 K also a displacement of the adatom off the threefold-coordinated site was allowed [Fig. 3(b)]. As a result we get for the best fit a displacement of 0.18 Å towards the twofold-coordinated bridge site ( $H_y = 1.70$  Å). We took this shift as an indication that only the strongly hydrogen-coordinated iron atoms [hatched in Fig. 3(a)] are induced to rearrange. Various models with ideal bridge sites did not succeed to match the experiment. The new configuration implies essentially a  $c(2 \times 2)$  reconstruction of the substrate. The weakly coordinated iron atoms could also be affected though by a smaller amount. A corresponding additional but weaker buckling between iron atoms left unshaded in Fig. 3(a) would result, but we did not check for such an additional reconstruction. A respective increase of the intensity level of noncentered superstructure spots was not observed.

As displayed in Fig. 4(a) the  $R$  factor decreases dramatically with increasing buckling with a minimum near  $dB = 0.02$  Å. We notice that hydrogen-coordinated substrate atoms are now pushed towards the bulk rather than lifted as in the case H/Ni. The relative average intensity of centered spots increases to 2.3% which, however, is still below the experimental value (4.7%). Therefore, we allowed for some additional buckling reconstruction in the second substrate layer as displayed in Fig. 3(b), too. Simultaneous optimization of all parameters brings the relative fractional order beam intensities near the experimental value. The theory-experiment fit improves mirrored by  $R_p = 0.23$  as indicated by the open circle in Fig. 4(a). The best-fit parameters by analysis of five half-order and three substrate spots in a total energy range of 974 eV are  $dH = 1.11 \pm 0.2$  Å,  $H_y = 1.70 \pm 0.33$

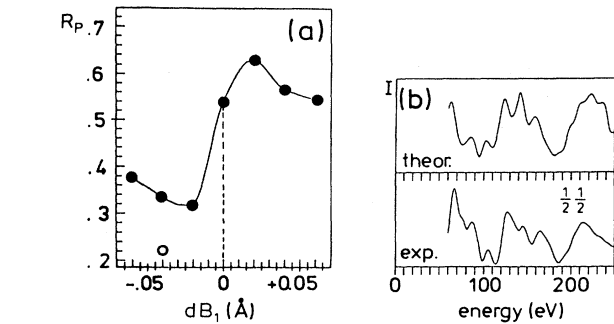


FIG. 4. (a) Dependence of the  $R$  factor on the buckling of the top Fe layer. The open circle results with additional buckling of the second layer. In (b) the best fit for the  $\frac{1}{2} \frac{1}{2}$  beam is shown.

Å,  $dB_1 = 0.04 \pm 0.025$  Å,  $dB_2 = 0.02 \pm 0.015$  Å,  $d_{12} = 2.03 \pm 0.04$  Å ( $\Delta d_{12}/d_0 = 0 \pm 2\%$ ),  $d_{23} = 2.05 \pm 0.06$  Å ( $\Delta d_{23}/d_0 = 1 \pm 3\%$ ). The H-Fe bond length is  $L_{H-Fe} = 1.84$  Å entailing a hydrogen radius  $r_H = 0.58$  Å. The quality of the fit is demonstrated in Fig. 4(b) for a selected beam.

In conclusion, we have demonstrated that hydrogen can induce substrate reconstructions even in the case of close-packed surfaces. The reconstructions are different for Ni(111) and Fe(110): For Ni(111) the hydrogen-coordinated atoms are pulled out of the surface while for Fe(110) they are pushed towards the bulk. This behavior is mirrored by a different sign of hydrogen-induced work-function change for both phases. Obviously, the surface charge redistributions responsible for the work-function changes are strongly correlated to the different atomic rearrangements in the surfaces. Also, this seems to be important for a quantitative understanding of the hydrogen-hydrogen interaction which is believed to proceed via the substrate.<sup>7</sup> For Ni(111) the reconstruction is concentrated at the top layer as the low  $R$  factor leaves no room for any substantial second layer reconstruction, though the latter was not explicitly tested. For the slightly more open Fe(110) surface reconstruction proceeds to the second layer with smaller amplitude. Hydrogen resides in ideal threefold-coordinated sites on Ni(111), while on Fe(110) there is a tendency to shift towards twofold-coordinated sites though the shift detected is within the limits of error. This effect might be a precursor of the structural transition  $(2 \times 2)$ -2H  $\rightleftharpoons$   $c(2 \times 2)$  occurring at about 80 K.<sup>9</sup> On the whole our analysis demonstrates the accuracy and potential of modern LEED structure determination. Only proper consideration of substrate reconstructions makes the determination of adatom sites reliable and the structure analysis convincing.

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