

A LEED ANALYSIS OF THE (2×1) H-Ni(110) STRUCTURE

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A monolayer of H atoms adsorbed on Ni(110) below 180 K forms a (2×1) structure. The unit cell exhibits a glide symmetry plane and contains two adsorbed atoms. Based on a quantitative comparison between experimental and calculated LEED I/V spectra using standard R -factors the following structure was derived: On the clean Ni(110) surface the separation between the first two atomic layers, d_{12} , is contracted by $8.5\% \pm 1.5\%$ with respect to the bulk value; those between the second and third and the third and fourth layer, d_{23} and d_{34} , are expanded by $3.5\% \pm 1.5\%$ and $1\% \pm 1.5\%$, respectively – in agreement with recent other results. In the presence of the H adlayer the contraction of d_{12} is reduced to $4.5\% \pm 1.5\%$, while the expansion of d_{23} is not affected within the limits of accuracy. The third interlayer spacing d_{34} returns to its bulk value. The H atoms occupy threefold-coordinated sites formed by two Ni atoms from the first layer and one Ni atom from the second layer which confirms previous more qualitative conclusions based on He diffraction and vibrational spectroscopy. The bond lengths between H and its neighbouring Ni atoms were determined to be equal, namely 1.72 ± 0.1 Å.

The structure of adsorbate layers is of particular interest for the understanding of the energetics of the adsorption system; for the substrate–adsorbate interaction determining the local adsorption geometry as well as for the adsorbate–adsorbate interactions which govern the lateral distribution of the adparticles. Under these aspects the system H/Ni(110) [1] appears extremely promising because of its large number of ordered structures. At $T < 180$ K the adsorbed H atoms form a series of ordered lattice gas structures, which are completed with a (2×1) phase at $\theta = 1.0$ [2,3]. Above this coverage H_{ad} induces a reconstruction of the surface into domains of a (1×2) structure [4] which covers the entire surface at a saturation coverage of

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$\theta = 1.5$ [5]. At $T \geq 200$ K a local reconstruction into a one-dimensionally disordered phase starts already at rather low coverages [6]; it equally exhibits a (1×2) pattern.

The present work is concerned with a LEED structural analysis of the low temperature (2×1) phase at $\theta = 1.0$ (There is strong evidence that the derived local geometry of the adsorption site equally holds for all of the lattice gas phases at $\theta_{\text{H}} \leq 1.0$, e.g. by the coverage independent magnitudes of the adsorption energy, the frequency of the Ni-H vibration and the change in work function in this coverage range).

Before starting the analysis of the adsorbate covered system, also the structure of the clean Ni(110) surface was determined. A full account of the LEED structure analysis itself will be given elsewhere [7], in addition a similar analysis of the (1×2) reconstructed surface was reported recently [8].

The LEED pattern of the $(2 \times 1)\text{H}$ phase is characterized by a systematic extinction of the $(0, n/2)$ beams at normal incidence indicating the presence of a glide symmetry plane [9] and thus of two H atoms per unit cell [2]. Based on He diffraction experiments Rieder and Engel [2] proposed a structural model which is reproduced in fig. 1a and whereafter the adsorbed atoms form

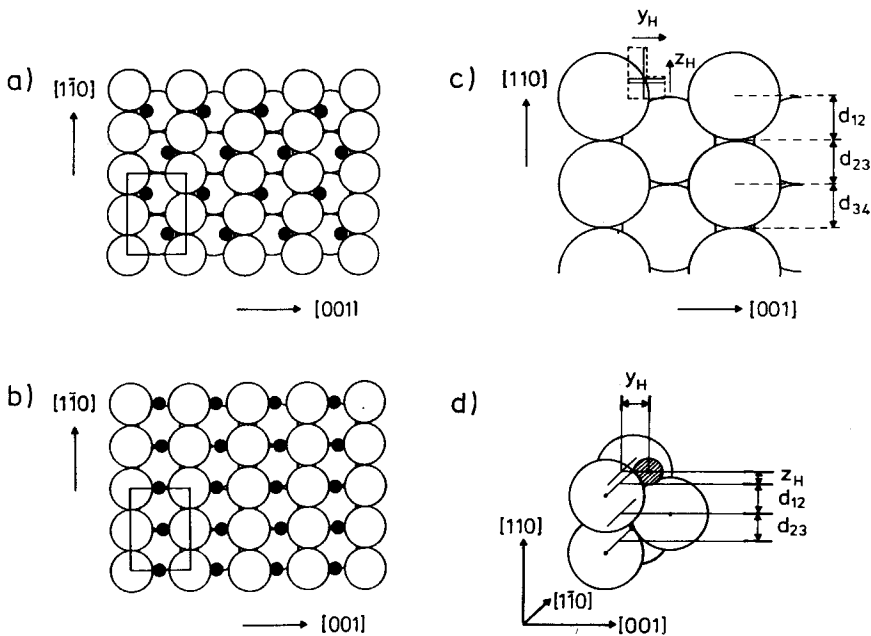


Fig. 1. Models of the $(2 \times 1)\text{H-Ni}(110)$ structure: (a) for H atoms on quasi-threefold sites, top view; (b) for H atoms on long-bridge sites, top view; (c) side view illustrating the structural parameters; (d) geometry of the local $\text{Ni}_3\text{-H}$ adsorption cluster.

zig-zag rows and occupy quasi-threefold sites. Recent vibrational spectroscopic data [10] were also interpreted in terms of this kind of local symmetry, in accord with theoretical predictions [11,12]. While there seems to be general agreement on the adsorption site, the situation is much less clear for the detailed geometry of the adsorption complex. This includes the Ni-H bond lengths and also the Ni-Ni interlayer spacings which might possibly be affected by the adsorbate [13]. This information is not accessible by techniques that essentially probe only the properties of the outermost atomic layer like He beam scattering.

Details for the experiments and sample preparation can be found elsewhere [3,7]. The $(2 \times 1)\text{H}$ phase was formed by exposing the clean Ni(110) surface to 0.8 L H_2 ($1 \text{ L} \cong 10^{-6} \text{ Torr s}$) at 120 K. The LEED intensity versus voltage (I/V) data were recorded by the use of a computer interfaced video system [14]. The direction of the incident primary beam was controlled by comparing the spectra from symmetrically equivalent beams (4 at normal incidence, 2 at oblique incidence along a symmetry plane), which procedure proved to be very sensitive towards small angular derivations. The polar angle was determined from the energy at which e.g. the (0, 1) beam in the normal incidence configuration had the same position on the LEED screen as the (0, 0) beam at oblique incidence. The final experimental data were obtained by averaging the I/V spectra from equivalent beams. For the structure analysis of the clean surface 10 nonequivalent beams were used at normal incidence, while for the (2×1) structure the data base was given by 3 (0) integer order and 3 (5) fractional order beams at normal (off normal) incidence.

The calculations were performed following standard procedures. For the clean and the adsorbate covered surface multiple scattering between the layers was calculated within the layer doubling scheme [15]. In the latter case the topmost layer of Ni atoms and the H atoms were treated as a combined layer, multiple scattering within this entity was calculated in angular momentum space. It was found that for distances $\leq 0.7 \text{ \AA}$ between these layers the calculation in momentum space is more efficient. The number of angular momentum components as well as the number of atoms within the unit cell were reduced by symmetry adapted functions, since the summation over symmetrically equivalent positions within the unit cell can be performed prior to matrix inversion [16]. In all calculations the first three interlayer spacings were varied systematically; for the calculations on the adsorbate covered surface also the lateral and vertical positions of the H atoms were freely selectable.

Up to 8 phase shifts were used to calculate scattering within the muffin-tins representing the Ni atoms, they were derived from a Ni potential communicated by Moruzzi [17]. For the H atoms a muffin-tin potential was constructed from a fictitious H crystal with an atomic radius of 0.53 \AA (1 a.u.) by symmetrizing the overlap between neighbouring atoms. This approximation

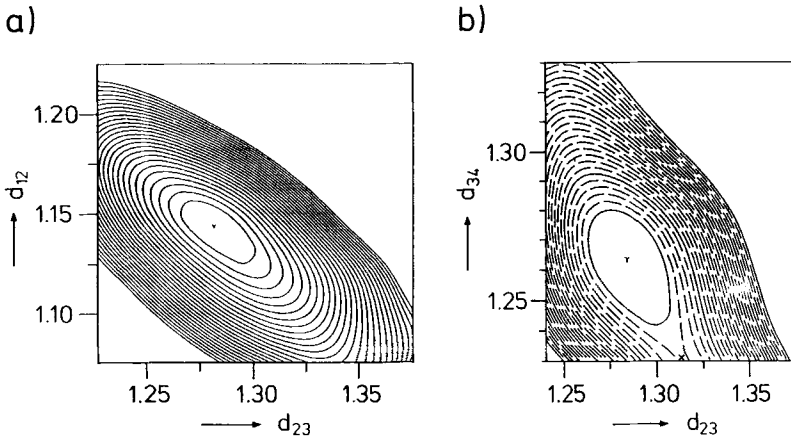


Fig. 2. (Pendry) R -Factor contour plot of the clean Ni(110) surface as a function of the first two (a) and the second and third (b) interlayer spacings.

had previously been successfully applied in a structural analysis of the H/Fe(110) system [18]. The real part of the inner potential was optimized for comparison with experimental data according to a theoretical function proposed by Hedin and Lundqvist [19], yielding $V_{or} = -1.2 - 93/(E + 13)^{1/2}$ eV. For the imaginary part we choose $V_{or} = 0.85(E + V_{or})^{1/3}$; thermal vibrations were accounted for by a Debye temperature of 450 K for all Ni and the H atoms. (The introduction of a reduced Debye temperature for the surface metal atoms was found not to affect either the optimum structure or the magnitude of the R -factor [20].) The agreement between experimental and calculated I/V spectra is expressed in terms of R -factors as introduced by Zanazzi and Jona (R_{ZJ}) [21] and Pendry (R_P) [22], respectively.

On the clean surface the calculations were performed for the energy range 40–390 eV, varying the spacing d_{12} , d_{23} and d_{34} between the layers marked by the indices. Both R -factors yield their minimum for almost identical structural parameters; $d_{12} = 1.14$ Å, $d_{23} = 1.29$ Å and $d_{34} = 1.26$ Å. Contour plots of the Pendry R -factor are reproduced in fig. 2. The minimum values – averaged over all beams – were $R_P = 0.20$ and $R_{ZJ} = 0.04$, which is generally considered to represent excellent agreement. From a statistical analysis the error bars were estimated to ± 0.02 Å. Compared to the bulk interlayer separation of 1.246 Å these data indicate a contraction of $8.5\% \pm 1.5\%$ between the topmost two layers followed by an expansion of $3.5\% \pm 1.5\%$ and $1\% \pm 1.5\%$ between the subsequent three layers. These data compare well with the results of three other LEED studies on this surface [23–25] as listed in table 1.

Table 1
Contraction/expansion of the separation between two subsequent layers

$d_{12}(\%)$	$d_{23}(\%)$	$d_{34}(\%)$	Ref.
-8.4 ± 0.8	$+3.1 \pm 1.0$		[23]
-9.8 ± 1.8	$+3.8 \pm 1.8$		[24]
-8.7 ± 1.5	$+3.0 \pm 0.6$	-0.5 ± 0.7	[25]
-8.5 ± 1.5	$+3.5 \pm 1.5$	$+1.0 \pm 1.5$	This work

An oscillatory behaviour in the interlayer spacing has been reported so far for several surfaces [26]. It has recently been explained in a simple electrostatic model as a general surface effect, which is, however, most strongly present on “open” surfaces due to their smaller interlayer distances [27].

For the adsorbate covered surface the analysis was split up into three steps: The calculated I/V curves of the integral order beams turned out to be rather insensitive with respect to the position of the H atoms, which had also been observed for the ordered H_{ad} structures on Fe(110) [18] and reflects the low scattering power of the H atoms. Therefore the Ni–Ni spacings could be determined independently just from the integral order beams in a first approximation. In turn the position of the H atoms was determined from the I/V data of the fractional order beams only using the previously determined Ni–Ni interlayer spacings. Due to the relatively independent effects of the structural parameters of Ni atoms and H atoms, respectively, the process of finding the minimum R -factor in the multi-dimensional space has been simplified in this way. Finally all positions were optimized independently using the entire data set.

Due to the length of the computation and the negligible intensity of the extra beams at high energies the energy range for the calculations on the H-covered surface was limited to 40–180 eV. The best R -factors – $R_p = 0.27$, $R_{Zl} = 0.17$ – were obtained for the following substrate geometry (fig. 3a): $d_{12} = 1.19 \pm 0.02 \text{ \AA}$, $d_{23} = 1.31 \pm 0.02 \text{ \AA}$ and $d_{33} = 1.25 \text{ \AA}$ (at its bulk value of 1.246 \AA). For comparison with the respective values of the clean surface it was verified before that the reduction of the energy range does not affect the position of the R -factor minimum. Then the adsorbate induced changes of the oscillatory lattice distortion are as follows: The contraction in d_{12} is reduced from 8.5% to 4.5%, the expansion of d_{23} is even increased from 3.5% to 5% and d_{34} (1% expansion) has returned to its bulk value. While the variations of d_{23} and d_{34} may be considered as within the error limits of this analysis, this is certainly not the case for d_{12} . A reduction of the oscillatory distortion of the surface near interlayer spacings in the presence of an adsorbate – as observed here – agrees well with the general experience on the effect of an adsorbate layer upon the structure of a metal substrate, they tend to (partially) offset the lattice distortions caused by the truncation of the bulk [26]. This effect is

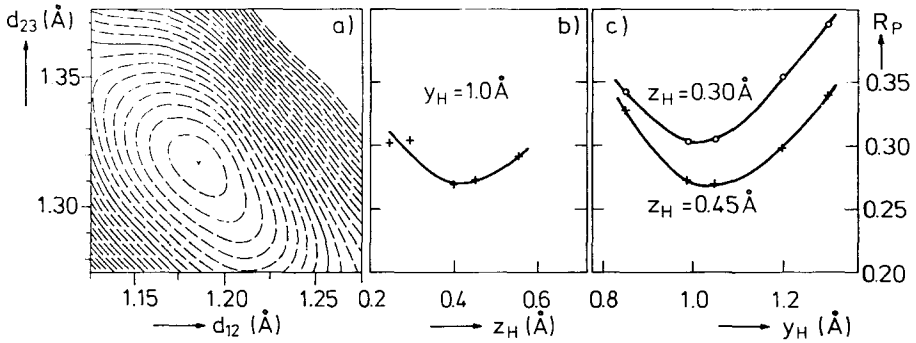


Fig. 3. (Pendry) R -Factor dependence of the $(2 \times 1)\text{H-Ni}(110)$ structure upon variation of one or two structural parameters, while the remaining ones are kept close to their optimized value: (a) contour plot of the first two Ni-Ni interlayer spacings ($y_H = 1.0$ Å, $z_H = 0.3$ Å); (b), (c) R -factors as a function of the vertical (z) and lateral (y) displacement of the H atoms as defined in fig. 1c ($d_{12} = 1.175$ Å, $d_{23} = 1.32$ Å, $d_{34} = 1.246$ Å $\hat{=}$ bulk value).

especially pronounced on surfaces with strong distortions already in their clean state and can even lead to a sign reversal of the oscillatory distortion [13,26]. The predominant effect of the adsorbate on the topmost interlayer spacing is plausible already on the basis of a local bond picture, a similar behaviour has been reported recently for H adlayers on Pd(110) [20] and Cu(110) [29].

Most of the calculations were performed for an adsorbate geometry as suggested by the He diffraction results and as illustrated in more detail in fig. 1a. The positions of the H atoms within the surface plane – defined by the lateral displacement (y_H) with respect to the close packed rows of Ni atoms in $[\bar{1}10]$ direction and the distance perpendicular to the surface (z_H) – were varied systematically; the total range is indicated in fig. 1c. In a first survey adsorption sites with rather large values for z_H were tested, following Hamann's predictions [28]. The poor agreement between theory and experiment, reflected by R -factors (for fractional order beams only) around $R_P = 0.8$, made these positions very improbable. Getting closer to the surface layer improved the R -factor of these beams significantly while very close to the topmost Ni plane or even below that this trend was reversed again (fig. 3b). At z -spacings of $z_H = 0.30$ Å and $z_H = 0.45$ Å the lateral displacement was then varied systematically. The effect upon the R -factor is depicted in fig. 3c. The minimum R -factor (over all beams) determined this way reaches values of $R_P = 0.27$ for $y_H = 1.1 \pm 0.1$ Å and $z_H = 0.41 \pm 0.1$ Å. As described above, the Ni-Ni interlayer spacings were finally tested again for this particular structure and were found to be still close to their former optimum position (which was determined for a slightly different H position).

Test calculations for H atoms adsorbed in “long-bridge” sites as shown in fig. 1b and also for a lateral zig-zag displacement of the metal atoms along the $[1\bar{1}0]$ rows in the topmost layer (in that case vertical displacements are not possible for symmetry reasons) could exclude both structural elements, from their I/V characteristics as well as from the total intensities of their fractional order beams [20]. We have not tested asymmetric adsorption sites (p1g1 symmetry), located between the “threefold-hollow” and the “long-bridge” site, because they appear highly improbable in terms of energetic considerations as discussed below.

If the y , z coordinates of the H atom are converted into Ni–H bond lengths to the three neighbouring Ni atoms, equal values of $1.72 \pm 0.1 \text{ \AA}$ result, i.e. the H atom is indeed adsorbed at a threefold site formed by two Ni atoms from the topmost layer and one Ni atom from the layer underneath (fig. 1d). Using the bulk value of 1.246 \AA for the atomic radius of the Ni atoms we obtain $r_{\text{H}} = 0.47 \pm 0.1 \text{ \AA}$ for the effective radius of the H atom. The resulting minimum R -factor – averaged over all beams, i.e. including the integer order beams which are dominated by the Ni lattice – is much better than the one obtained recently for H/Fe(110) [18] or the kind of visual agreement obtained for H/Ni(111) [30]. It is felt that further improvement would have to be sought in the non-structural parameters of the H atoms, which would, however, presumably not affect the structural data.

The lateral displacements derived by Rieder and Engel from their He diffraction data – $y_{\text{H}} = 0.9 \pm 0.1 \text{ \AA}$ – agrees well with the one determined here [2]. These authors had also suggested (without being able to provide definitive proof) that the vertical displacement of the atoms amounts to a value that gives rise to bonding in threefold sites with essentially equivalent Ni–H bond lengths, quite in contrast to Hamann who had postulated the position of the H atom to be much higher [28]. This latter statement was based on calculations for the corrugation of the He scattering potential derived from the total charge density [31] in comparison with experimental data from Rieder and Engel [2]. The Ni–Ni interlayer spacing was neither considered as a variable parameter nor would it be accessible for evaluation from those experiments. In recent careful vibrational studies it was concluded that within the $(2 \times 1)\text{H}$ phase – and also for the other lattice gas phases – only one type of adsorption site is occupied [10]. The two observed frequencies 71 and 131 meV, which are similar to the data found for Ni(111) [32], were assigned to symmetric and asymmetric stretch frequencies of H atoms attached to a site with threefold coordination. From their angular dependent intensities an inclination of this site with respect to the surface plane was concluded. Based on a nearest neighbour force constant model a Ni–H bond length of 1.53 \AA was derived, which is in reasonable agreement with the actual bond length (1.72 \AA) in view of the underlying crude approximation.

Applying an embedded cluster model Muscat found the threefold coordi-

nated site to be energetically most favourable [11], the Ni-H bond length of 1.64 Å he derived is in good agreement with our result. Calculation on the full adiabatic potential energy surface of the H/Ni(110) system, which were performed by Nordlander et al. [12] following the "effective medium" scheme [33], resulted in a very smooth potential along the troughs of the (110) surface with minima at the quasi-threefold and the long-bridge sites, respectively. The latter, however, can be clearly ruled out on the basis of the present analysis. Apparently single H atoms are strongly delocalized and only at higher coverages attractive (indirect) H-H interactions between neighbouring H atoms across a Ni atom [10] force them into the localized adsorption sites which then gives rise to long range order. Moreover the vibrational frequencies predicted by this model for H atoms adsorbed on threefold sites agree well with the experimental data [10].

The atomic radius $r_{\text{H}} = 0.47 \text{ \AA}$ is comparable to the values found in a recent LEED analysis of H structures on Fe(110) [18], and in a neutron diffraction study on a cluster compound $\text{H}_3\text{Ni}_4\text{Cp}_4$ [34]. In all of these cases the H atoms are threefold coordinated reflecting a general tendency of small atomic adsorbates to occupy highly coordinated adsorption sites [26]. On Ni(111) and Pd(110), where also threefold sites are occupied in the $(2 \times 2)\text{H}$ and $(2 \times 1)\text{H}$ structures, respectively, the atomic radius of hydrogen had been determined by LEED to $r_{\text{H}} = 0.6 \pm 0.1 \text{ \AA}$ [30,20]. Considering the error limits in the determination of the position of the H atoms and the similarities in adsorption characteristics, these values are still regarded as representative of a basically uniform H_{ad} species rather than to reflect changes in the chemical nature of the adsorbate.

In summary it is felt that the structure of the $(2 \times 1)\text{H}$ phase, which in its local bonding geometry is assumed to be representative of all of the H_{ad}

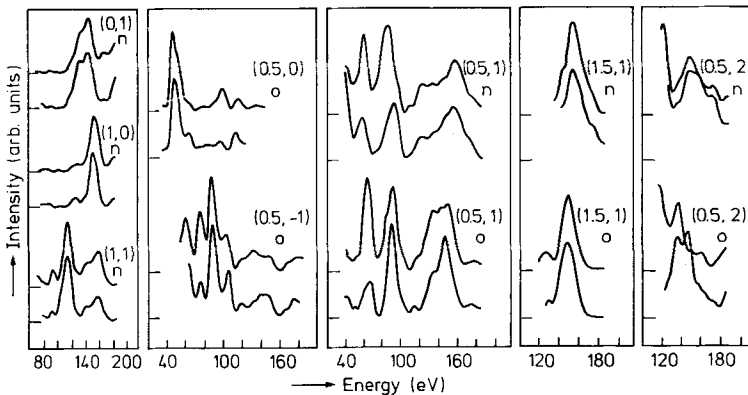


Fig. 4. Experimental and calculated (best model) I/V curves of the $(2 \times 1)\text{H-Ni}(110)$ structure (n: normal incidence, o: oblique incidence, $\theta = 6^\circ$, $\varphi = 90^\circ$).

lattice gas phases on Ni(110), has now been solved and that the information obtained by various methods (both experimentally and theoretically) yields a coherent picture. In addition the good agreement between calculated and experimental I/V curves also for the fractional order beams (fig. 4) unambiguously confirms the ability of an ordered H adlayer to produce such LEED spots, without any detectable reconstruction of the surface. The interaction between substrate and adsorbate leads to slight changes of the two topmost interlayer spacings with a tendency to return to bulk values. The Ni-H bond length ($1.72 \pm 0.1 \text{ \AA}$) is equal for all three neighbored Ni atoms in the threefold coordinated, inclined sites and leads to an effective radius of $r_H = 0.47 \text{ \AA}$.

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