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## Rapid Communications

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# Low-coverage ordered phases of hydrogen on Ni(110)

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Three new submonolayer phases of hydrogen on Ni(110) with periodicities $c(2\times6)$, $c(2\times4)$, and $c(2\times6)$ and respective coverages $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{2}{3}$ monolayers were observed and analyzed with the use of He-diffraction techniques. The corrugation functions provide a direct picture of the adatom configurations and give further insight into the interplay of adatom-substrate and adatom-adatom interactions at adsorbate densities up to one monolayer.

The observation and structural analysis of three new low-coverage phases of hydrogen on Ni(110), with use of He scattering, yields, together with the previously observed phases,[1,2] a surprising and fascinating picture of the coverage-dependent ordering of hydrogen adatoms in the range up to one monolayer (ML). Even at very low coverages, the hydrogens tend to form well-ordered and rather long zigzag chains along the close-packed Ni rows ($x$ direction); the lateral interaction of these rather stable chains is so long ranged, that at a coverage $\Theta=\frac{1}{3}$ ML they form a well-ordered $c(2\times6)$ phase with alternating zigzag and zagzig configurations at more than 10-Å distance, leaving two close-packed Ni rows between the rows covered with H chains adsorbate-free. At $\Theta=\frac{1}{2}$ ML, a (somewhat disordered) $c(2\times4)$ phase is observed; at this coverage most of the H chains have moved together to leave one Ni row in between adsorbate-free, whereby the zigzag and zagzig alternation is maintained. The next ordered structure corresponding to $\Theta=\frac{2}{3}$ is again a $c(2\times6)$; in this phase, two zigzag and two zagzig hydrogen chains alternate leaving one close-packed Ni row between them hydrogen-free. The fourth ordered structure corresponding to $\Theta=\frac{5}{6}$ ML has again $c(2\times6)$ periodicity[1,2]; the extra $\frac{1}{6}$ ML of adatoms goes into high-symmetry sites on the previously adsorbate-free Ni rows, thus forming a distorted hexagonal overlayer of adatoms; this is the only phase in which two inequivalent adsorption sites are occupied. It may be regarded as a precursor to the $(2\times1)$ phase with $\Theta=1$ ML, in which the adatoms also form a distorted hexagonal pattern by covering all close-packed Ni rows with parallel hydrogen zigzag chains.

In previous He-diffraction studies, three ordered hydrogen phases on Ni(110) with periodicities $c(2\times6)$, $(2\times1)$ (Refs. 1 and 2), and $(1\times2)$ (Refs. 2 and 3) were observed. The corrugation functions for the first two of these phases delivered a direct picture of the adsorbate configurations and allowed determination of the absolute coverages; they amount to $\frac{5}{6}$ ML for the $c(2\times6)$ and 1 ML for the $(2\times1)$ phase. Flash desorption measurements confirmed the relative coverages of these phases and yielded for the $(1\times2)$ phase $\Theta\approx1.5$ ML. The corrugation function of the $(1\times2)$ saturation phase did not yield a direct picture of the adatom locations[2] because of a reconstruction of the substrate[4,5] and a partial accommodation of hydrogen in subsurface layers.[2,6]

The motivation of the present work was to learn more about the interactions of the hydrogen adatoms with the substrate as well as among one another. Indeed, three further ordered hydrogen phases with periodicities $c(2\times6)$, $c(2\times4)$, and $c(2\times6)$ corresponding to lower coverages could be isolated (some evidence for the existence of a further ordered phase near a coverage of 0.7 ML was already presented in Ref. 2). None of these phases was seen with our retarding-field analyzer–low-energy-electron diffraction (LEED) system, but they have all been observed recently by Christmann *et al.*[7] using video-LEED techniques.

The experiments were performed with the apparatus described previously[2,3] with the use of He energies between 40 and 75 meV and beam-velocity spreads around 10%. The sample was kept at 100 K during hydrogen adsorption and He-diffraction measurements. Small dosage steps of 0.01 L ( 1 L $=10^{-6}$ torr sec) were used in order to isolate the ordered phases as well as possible, since small extra amounts of hydrogen deteriorated the diffraction patterns rapidly. Typical experimental in-plane and out-of-plane diffraction scans of the two new $c(2\times6)$ phases are shown as solid lines in Figs. 1 and 2. The doses for which the optimum diffraction spectra of the first $c(2\times6)$, the $c(2\times4)$, and the second $c(2\times6)$ were obtained amount to 0.15, 0.24, and 0.33 L, respectively. Although some disorder was present in all cases manifesting itself in broader peaks than expected from the velocity spread, the $c(2\times N)$ periodicity ($N=4,6$) is clearly visible in all phases: only $(m,g/N)$ and $(u/2,u/N)$ beams have nonzero intensities [$m$ denotes any integer number, and $g$ and $u$ denote even and odd integers, respectively; the indices refer to the unit cell of the clean Ni(110) surface]. Initially, the $c(2\times4)$ was not accepted as an ordered phase, as the fractional beams were all very broad; however, as this phase was clearly observed with LEED at 130 K,[7] in further He experiments it could be obtained with better order by warming the sample to 130 K. Analyses of beam intensities to obtain the best-fit corrugations were performed for all new phases on the basis of the corrugated hard-wall model with use of the eikonal approximation,[8] which works very well because of the small maximum corrugation amplitude in all cases. Incoming angles larger than 40° were not used to avoid influences due to the softness and the attractive well of the He-surface potential.[9] The analyses were performed by use of a general Fourier ansatz for the corrugation compatible with the surface symmetry, and by exploring the magnitude of about ten Fourier coefficients to obtain optimum agreement with the experimental intensities. Note that with this procedure the analysis is not dependent on any model assumptions of the adsorbate structures; the best-fit corrugations immediately reflect the adatom configurations. The best-fit coefficients for all submonolayer phases are

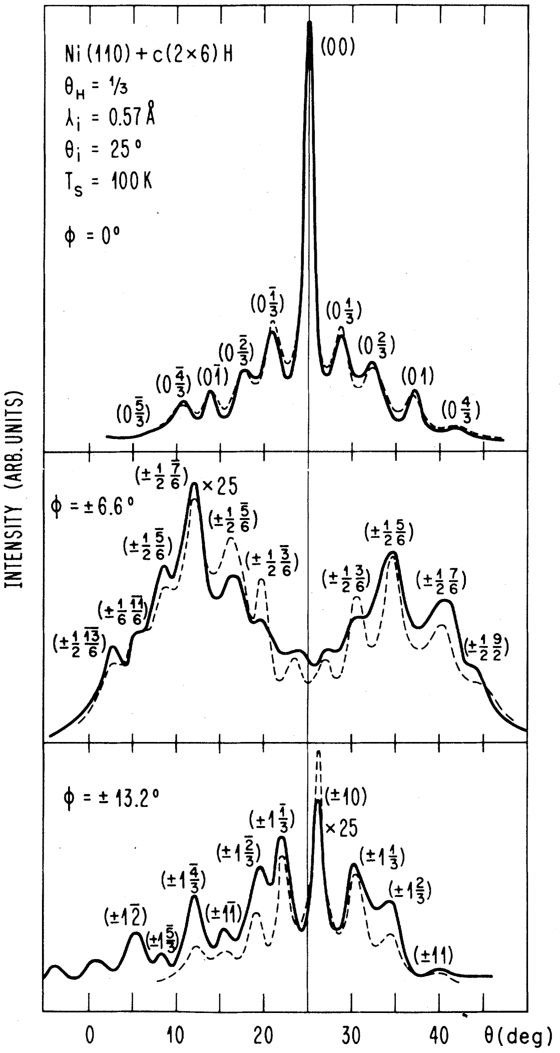

FIG. 1. Typical in-plane and out-of-plane He-diffraction spectra for the low-coverage $c(2\times6)$ phase of hydrogen on Ni(110). The diffraction peaks are indexed according to the unit cell of the substrate ($a_1=2.49$ Å, $a_2=3.52$ Å). The best-fit spectra are shown by the dotted lines.

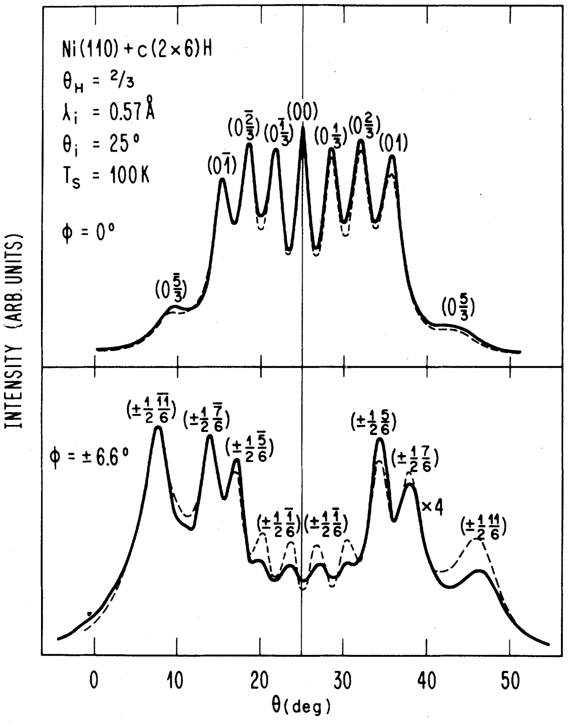

FIG. 2. Same as Fig. 1 for the medium coverage $c(2\times6)$ phase of hydrogen on Ni(110).

TABLE I. Best-fit Fourier coefficients in Å for the submonolayer adsorption phases observed for hydrogen on Ni(110). The indices in brackets refer to the extended unit cell of the adsorbate phases; they have to be multiplied by ($\frac{1}{2}$, $1/N$) to relate them to the unit cell of the clean Ni(110) surface. The values are averages obtained for several different diffraction spectra.

| H phase $c(2\times N)$ | $D(02)$ | $D(04)$ | $D(06)$ | $D(11)$ | $D(13)$ | $D(15)$ | $D(17)$ | $D(20)$ | $D(22)$ |
|---|---|---|---|---|---|---|---|---|---|
| $c(2\times 6)$ $(\Theta=\frac{1}{3})$ | 0.085 | 0.105 | 0.09 | | 0.03 | 0.035 | | −0.045 | |
| $c(2\times 4)$ $(\Theta=\frac{1}{2})$ | −0.12 | 0.04 | | 0.055 | −0.06 | | | −0.03 | 0.02 |
| $c(2\times 6)$ $(\Theta=\frac{2}{3})$ | 0.07 | −0.09 | −0.14 | −0.05 | | 0.07 | 0.04 | | |
| $c(2\times 6)$ $(\Theta=\frac{5}{6})$ | 0.09 | −0.12 | −0.09 | | 0.03 | −0.06 | | | |

given in Table I. Best-fit spectra for the two new $c(2\times 6)$ phases are shown as dashed lines in Figs. 1 and 2.

The best-fit corrugations of the two new $c(2\times 6)$ phases are shown in Fig. 3 together with hard-sphere models of the adsorbate structures. The adatom configurations can be inferred directly from the corrugations: each of the pronounced maxima corresponds to a H atom. The $c(2\times 6)$ phase corresponding to the lower converage shows zigzag chains along each third close-packed Ni row, whereby zigzag and zagzig configurations alternate, thus giving rise to the $c(2\times 6)$ periodicity. In the other new $c(2\times 6)$ phase, the zigzag and zagzig chains are simply doubled [Fig. 3(b)]. In the $c(2\times 4)$ phase occurring between the two $c(2\times 6)$ zigzag and zagzig H chains lie along each second Ni row leaving all other Ni rows empty. Determination of the absolute coverages of all phases is simply made by dividing the number of substrate atoms by the number of adatoms, and yields $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{2}{3}$ ML in reasonable agreement with flash desorption data, from which $\Theta=0.3$–$0.4$ ML for the first $c(2\times 6)$, around 0.5 ML for the $c(2\times 4)$, and 0.6–0.7 ML for the second $c(2\times 6)$ were expected.[1,2] Based on the above results, very recently Christmann *et al.*[7] were able to confirm the adatom configurations of the low-coverage H phases by performing LEED *I*-*V* measurements and kinematical calculations.

In accordance with the results of Refs. 10 and 11, the hydrogen adatoms are plotted in Fig. 3 to adsorb at places slightly shifted from the twofold-coordinated

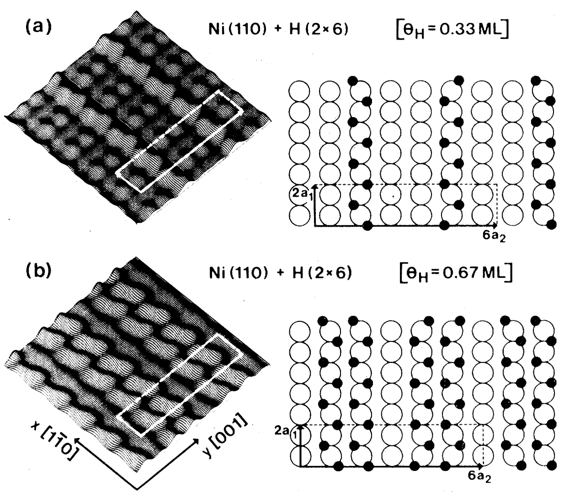

FIG. 3. Best-fit corrugation functions (left side) and hard-sphere models (right side) of the $c(2\times 6)$ phases of hydrogen on Ni(100): (a) $\Theta=\frac{1}{3}$; (b) $\Theta=\frac{2}{3}$ ML. Note that the corrugations yield a direct picture of the adsorbate configurations: every pronounced hill corresponds to a H atom. The alternation of hydrogen zigzag and zagzig chains along the close-packed Ni rows is clearly visible. The corrugations are expanded by a factor of 5 in the vertical direction. At $\Theta=\frac{1}{2}$ ML, a $c(2\times 4)$ phase forms, in which every second close-packed Ni row is covered with alternating hydrogen zigzag and zagzig chains. The total corrugation amplitude is ~0.25 Å for all phases. For the corrugations of the $c(2\times 6)$ with $\Theta=\frac{5}{6}$ ML and the $(2\times 1)$, see Refs. 1 and 2. In the models, the small circles denote H and the large ones Ni atoms.

sites towards threefold coordination. The structure visible in the corrugation of Fig. 3(a) between the hydrogen chains suggests that the corrugation of the Ni substrate is also visible. It would mean, however, that the H adatoms are located in shifted on-top sites obtained by moving all adatoms by $a_1/2$ in the $x$ direction from the positions shown in the model of Fig. 3(a). The small structure in Fig. 3(a) may be simply an artifact due to the flatness of the substrate corrugation visible in those parts of the surface which are adsorbate-free (as is well known, flat parts require a very large number of Fourier coefficients to be described properly). However, also in calculations where every H adatom was described by a Gaussian hill, slightly better fits were obtained for both the first $c(2\times 6)$ and the $c(2\times 4)$ with the phase of the substrate corrugation compatible with the shifted on-top sites. The shifted on-top location is highly unlikely according to the theoretical work of Hamann[10] and Muscat,[11] as well as in view of the threefold-coordinated H sites observed on Ni(111).[12] From the presently available accuracy of the He-diffraction data, no decision as to the actual H location should be made and, as long as no dynamical LEED $I$-$V$ analyses are available, the theoretical results of Refs. 10 and 11 should be trusted.

Zigzag chains of hydrogen adatoms along the close-packed Ni rows on the (110) surface have been found also for the previously reported $c(2\times 6)$ and $(2\times 1)$ phases with coverages of $\frac{5}{6}$ and 1 ML, respectively.[1,2] The corrugation of the new $c(2\times 6)$ phase corresponding to $\Theta=\frac{1}{3}$ ML yields the new information that rather long and obviously well-ordered chains of hydrogen atoms form along the close-packed Ni rows even at very low coverages. It can be concluded that there is a strongly anisotropic interaction among the hydrogens favoring the buildup of rather stable zigzag chains along the close-packed Ni rows. Obviously, the H chains form the most important structural element on this surface. It is astonishing that the lateral interaction of the hydrogen chains is so long ranged that they order over a distance of 10.56 Å in forming the lowest coverage $c(2\times 6)$ phase, whereby they prefer the zigzag and zagzig alternation in the submonolayer range.

Another interesting feature is the following: the $c(2\times 4)$ phase formed at 100 K shows very broad fractional order beams which may indicate some remnant $c(2\times 6)$ patches on the surface. Thus the transition from the $c(2\times 6)$ with $\Theta=\frac{1}{3}$ to that with $\frac{2}{3}$ ML seems to take place mostly via a compression of the lowest-coverage ordered structure in the $y$ direction by 33% to give rise to the $c(2\times 4)$ phase with $\Theta=\frac{1}{2}$ ML, but in some parts by maintaining the $c(2\times 6)$ periodicity by pinning down H chains in the immediate neighborhood of the initial chains so that the phase with $\Theta=\frac{2}{3}$ ML is built up directly. The transition from the first $c(2\times 6)$ to a clean $c(2\times 4)$ phase is facilitated at higher temperatures. In this connection, it should be noted that all three new phases show a reversible order-disorder transition at about 160 K.

The third ordered $c(2\times 6)$ phase with $\Theta=\frac{5}{6}$ ML forms with the additional adatoms accommodated in the energetically less favorable twofold-coordinated sites.[1,2] This phase appears to be a necessary intermediate for the transition to the $(2\times 1)$ in which every close-packed (Ni) row is covered with a hydrogen zigzag chain ($\Theta=1$ ML), in contrast to the submonolayer phases where there is always an alternation of zigzag with zagzig chains; in the $(2\times 1)$ phase all chains are parallel.[1,2] Thus, for the transition to the $(2\times 1)$, half of the hydrogen chains have to move in the $x$ direction by an amount $a_1$. This is obviously facilitated by the formation of the distorted hexagonal close-packed arrangement in the $c(2\times 6)$ phase with $\Theta=\frac{5}{6}$, which must be simply compressed slightly along $y$ to form the $(2\times 1)$ arrangement. The peculiar coverage-dependent ordering of H on Ni(110) and the special role of the hydrogen zigzag chains are underlined by the observation that, on the chemically similar Pd(110), no ordered submonolayer phases of H are observed; on this surface, $(2\times 1)$ islands appear to form at very low coverages which grow with increasing $\Theta$.[13]

## ACKNOWLEDGMENTS

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