

Adsorption of Hydrogen on a Nickel (100) Surface

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Dedicated to Professor Dr. Drs. h. c. G.-M. Schwab on the occasion of his 80th birthday

The adsorption of hydrogen on a clean Ni(100) single crystal surface was studied in UHV between 120 K and 500 K means of LEED, thermal desorption spectroscopy and work function measurements. H₂ chemisorption occurs in two atomic states β_1 and β_2 with maximum desorption rates (at saturation) at 318 K and 348 K. The activation energy for desorption was determined to be $20 (\pm 2)$ kcal/mole for the β_1 -state and $23 (\pm 1)$ kcal/mole for the β_2 -state, in excellent agreement with previous results. Saturation at 120 K corresponds to a coverage of $0.9 (\pm 20\%)$.

The initial sticking probability is $0.06 (\pm 0.01)$ and the rate of adsorption follows second order kinetics. No additional LEED spots arose from the H overlayer, indicating the absence of long-range order even at 120 K. The work function results clearly show the existence of two different binding states: Whereas the β_2 -population gives rise to a linear increase by 100 meV (at 120 K) the β_1 -state leads to a decrease of $\Delta\phi$ to a final value of 30–40 meV.

I. Introduction

Although numerous studies on the chemisorption of hydrogen on Ni single crystal faces have been performed during the past decade there is still some disagreement concerning e.g. the saturation density of the chemisorbed hydrogen, the binding energy as a function of coverage or the kinetic data such as sticking probability or frequency factor. Since all these quantities are strongly affected not only by surface contaminants like carbon or sulfur but to a large extent also by crystallographic defects, special care has to be taken in the course of hydrogen adsorption experiments in order to get representative results which might serve as a proper basis for theoretical chemisorption calculations of the nickel-hydrogen system.

Regarding previous investigations on Ni(100)/hydrogen mainly three papers [1, 2, 3] have to be mentioned. Lapujoulade and Neil [1] used thermal desorption techniques. An extensive work was done in our own laboratory [2] with LEED, thermal and laser-induced desorption, and electron energy loss- and work function ($\Delta\phi$)-measurements. Whereas Lapujoulade and Neil [1] report on a saturation density of 3.3×10^{14} H atoms/cm² (at room temperature) which corresponds only to a coverage* of $\theta = 0.2$, we got evidence for a higher coverage at room temperature which was estimated to be in

the range of $\theta = 0.4$ – 0.5 . However, good agreement was found with respect to the desorption energy which in both studies resulted to be 23 kcal/mole for the β_2 -state. Quite recently Andersson [3] re-examined the system Ni(100)/H₂ by means of LEED, $\Delta\phi$ - and high resolution electron energy loss measurements whereby the temperature range was extended down to 200 K.

Interesting results arose from this study: A very weak and transient LEED extra pattern from the adsorbed hydrogen was observed at temperatures below 250 K, whereas the $\Delta\phi$ -data revealed good agreement with our previous (room temperature) work on this system. The features of the loss experiments which are described in more detail in the discussion section were interpreted by assuming a fourfold hollow site for the location of the hydrogen atom on the Ni(100) plane and, furthermore, gave clear evidence for the atomic adsorption mechanism.

The paper presented here combines thermal desorption and $\Delta\phi$ -data obtained at fairly low temperatures with the results of previous work [1, 2] and may (together with the study of Andersson [3]) lead to a still better understanding of the chemisorption mechanism of hydrogen on a nickel single crystal surface, the nature of the bonding and the interaction forces between the adsorbed particles coming into play at higher surface coverages.

II. Experimental

The Ni sample was prepared by cutting a circular slice (front area of about 0.47 cm², thickness

* The coverage θ is defined throughout this paper as the ratio of the number of adsorbed particles (H-atoms) over the number of substrate atoms in the topmost layer.

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~ 1 mm) from a bulk single crystal (99.999% purity, purchased by Metals Research Corp.) after x-ray orientation to within ± 0.5 degrees. The front face was mechanically polished to a mirrorlike finish and carefully cleaned with acetone and distilled water. The crystal was fixed between two parallel-running 0.25 mm tungsten wires and mounted via two 1 mm Au rods to the 360° rotatable manipulator. The sample temperature was measured by means of a chromel-alumel thermocouple spot-welded on the rear of the crystal. A stabilized D.C. power supply (Rohde & Schwarz) served for heating the sample up to 1500 K, cooling down to 120 K could be achieved by a liquid nitrogen cooling coil device. Thermal desorption experiments could be performed by using a temperature programmer which allowed a linear heating rate of the sample between 100 K and 1000 K [4]; usually a heating rate of 10 K s^{-1} was applied.

The studies were carried out in a 120 L stainless steel system (Varian) with a base pressure of less than 10^{-8} Pa. The apparatus contained facilities for low energy electron diffraction (LEED) and Auger electron spectroscopy with the LEED optics serving as an energy analyser, a quadrupole mass spectrometer for flash desorption studies (Balzers) and a self-compensating Kelvin capacitor device for measuring work function changes of the sample. Details of the latter method have been described elsewhere [5].

High purity gases could be admitted to the system via bakeable leak valves. The total gas pressure was measured with an ionisation gauge (Bayard-Alpert type) which also served for a calibration of the mass spectrometer. The pressure data were corrected with respect to hydrogen by means of the manufacturer's gauge conversion factor.

After mounting the crystal in the UHV system the surface was precleaned by a single oxidation/reduction treatment at 1300 K. The main contaminants were sulfur and carbon. In the course of the experiments it became soon evident that the most effective cleaning was obtained by repeated Argon ion bombardment and subsequent annealing cycles rather than by further oxidation/reduction procedures, since the admission of O_2 to the system resulted in a considerable increase of the CO background pressure. In order to avoid any carbon formation due to CO dissociation on the sample surface the LEED electron and the Auger electron

excitation beam currents were kept below $1 \mu\text{A}$ and $10 \mu\text{A}$, respectively.

The LEED pattern of the clean Ni(100) surface exhibited sharp and bright diffraction spots with very low background intensity indicating a high degree of crystallographic order.

III. Results

1. LEED

The adsorption of hydrogen on a clean and well annealed Ni(100) surface was studied at different gas exposures ranging from 0.1 L up to 100 L ($1 \text{ L} = 1.333 \times 10^{-4} \text{ Pa} \cdot \text{sec}$) and at temperatures between 120 K and 400 K. However, in any case attempts to observe "extra spots" in the diffraction pattern failed. Sometimes very faint additional features could be found which however remained on the surface even at temperatures above the hydrogen desorption maximum and, therefore, have to be attributed to carbon contamination. At very high hydrogen coverages the background LEED intensity slightly increases indicating a disordered H phase or a hydrogen induced change of the overall surface reflectivity for low energy electrons.

2. Thermal Desorption Spectroscopy (TDS)

During the present experiments it became soon evident that hydrogen adsorbs in two different binding states depending on the H surface concentration. The state with the lower binding energy, however, only forms a relatively weakly held chemisorption complex although it is still an atomic state. In order to get a hydrogen saturated surface it was therefore necessary to perform the adsorption prior to the thermal desorption at the lowest attainable temperatures ($\sim 120 \text{ K}$). A completely linear and reproducible heating rate (10 K sec^{-1}) was used during the experiments with the ion pump being slightly throttled. Separate measurements performed under pressure conditions very similar to that of the hydrogen adsorption study yielded a time constant τ for the pumping speed of the recipient of about $242 (\pm 10) \text{ msec}$. The effective volume of the system was estimated to be $V = 100 (\pm 10)$ liters and the active sample area A was 0.47 cm^2 . These data provide (notwithstanding the inaccuracy concerned with the absolute pressure calibration of the ion gauge) the determination of

the number of adsorbed (or desorbed) particles, n_{ad} , by a numerical integration of the desorption curve according to the expression:

$$n_{ad} = \frac{V}{A k T \tau} \int_0^{\infty} p dt. \quad (1)$$

Because of the fairly large uncertainties in the determination of the system parameters the absolute coverage data are accurate only to within 20%. However, the relative degree of coverage, $\Theta = \Theta/\Theta_{max}$, could be evaluated from the desorption spectra much more precisely.

A set of thermal desorption curves taken from a Ni(100) sample initially kept at 150 K is reproduced in Figure 1. Parameter is the hydrogen exposure in Langmuirs. Two different binding states are clearly discernible which will be labeled as β_1 and β_2 . The saturation of the β_2 -state is completed at about 6–8 L H_2 exposure, whereas β_1 is filled at hydrogen exposures of more than 100 L. At least the β_2 -maximum exhibits a shift to lower temperatures when the hydrogen coverage is increased indicating a second-order rate process. The maximum desorp-

tion rates (at saturation) occur at 318 K (β_1 -state) and 348 K (β_2 -state).

2.1. The Activation Energy of Desorption

Provided that the activation energy E^* for the desorption reaction (which for non-activated adsorption is equal to the adsorption energy E_{ad}) is independent of the coverage Θ , the simple Redhead evaluation method [6] may be used well for a determination of E^* . It has turned out from equilibrium measurements [2] that E_{ad} is almost coverage-independent up to H surface concentrations of about $\Theta = 0.4$ –0.5. According to Redhead the 2nd order desorption process can then be described by the expression:

$$T_m^2 n_{max} = \frac{\beta E^*}{\nu R} \cdot \exp\left(\frac{E^*}{R T_m}\right) \quad (2)$$

(T_m = temperature of the desorption maximum, $n_{max} = \frac{V}{A k T \tau} \int_{t_{max}}^{\infty} P dt$, ν = frequency factor, $\beta = dT/dt$ = heating rate).

A plot of $\ln(2 n_{max} T_m^2)$ versus T_m^{-1} is shown in Figure 2. The data points can be fitted well over an appreciable coverage range by a straight line. Its slope yields an activation energy E^* for the β_2 -state of about 23 (± 1) kcal/mole = 96 kJoule/mole. A similar treatment for the β_1 -state yields an activation energy $E_{\beta_1}^*$ of about 20 (± 2) kcal/mole = 84 kJoule/mole. The saturation of the β_2 -state is attained at $\Theta = 0.4$ –0.5 (± 0.1) whereas a further increase of the surface hydrogen concentration leads to adsorption into the β_1 -state. However it

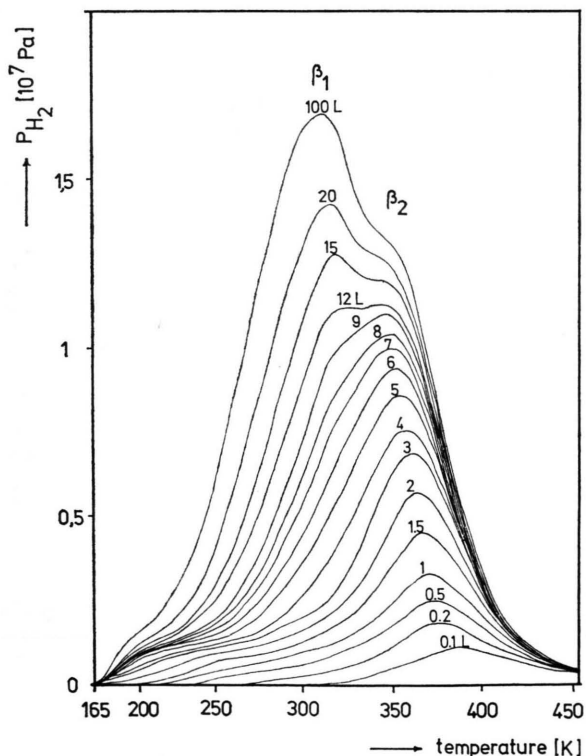


Fig. 1. Thermal desorption spectra for the β_1 and β_2 states of H_2 on a Nickel(100) surface, Parameter is the exposure (L).

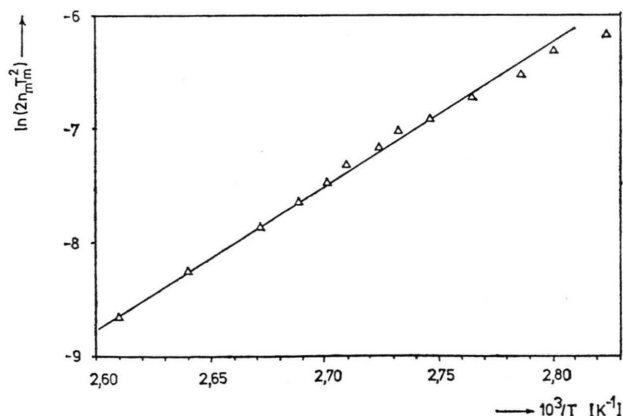


Fig. 2. Second order plot according to Redhead [6] of $\ln(2 n_m T_m^2)$ versus $1/T$.

should be mentioned that the population of the β_1 and β_2 -states does not occur completely sequentially, there is some adsorption into β_1 even before β_2 is completely filled. This feature can be seen clearly from an inspection of Figure 1. Both states consist of atomic hydrogen as is evident from $\text{H}_2\text{-D}_2$ -exchange experiments. A comparison of the areas $\int p \, dt$ of the β_1 and β_2 states at saturation reveals a slightly higher population for the β_1 -state; the total adsorbed amount is determined by Eq. (1) to $1.48 \times 10^{15} (\pm 20\%)$ H-atoms/cm² which corresponds to a Θ of about 0.9. Therefore a saturation density of 1 H-atom per Ni surface atom seems to be a reasonable assumption.

2.2. The Adsorption and Desorption Kinetics

The desorption trace sequence of Fig. 1 may be used for a determination of the kinetics of the adsorption as well as of the desorption process. By comparing the amount of gas exposed to the sample at a constant temperature with that actually adsorbed (for which the integral $\int p \, dt$ of the desorption traces can be taken as a measure) the integral sticking probability s^* as a function of the coverage Θ can be evaluated. The only prerequisite is the knowledge of the system parameters, as can be seen from Eq. (3):

$$s^*(\Theta) = \frac{V(2\pi m kT)^{1/2}}{A kT \tau} \left(\frac{\int p \, dt}{\text{exposure}(L)} \right). \quad (3)$$

From a subsequent graphical differentiation the more commonly used "differential" sticking probability $s(\Theta)$ can be obtained which is reproduced in Figure 3. Whereas at very small hydrogen coverages (less than $0.01 \Theta_{\max}$) the initial sticking coefficient s_0 seems to be considerably high (in the order of 0.1) a further exposure of the sample leads to a strong decrease of s to values around 0.06 which appear to be more representative for the clean and well-ordered Ni(100) face. The observed initial sticking probability of 0.1, however, may be attributed to some kind of preferred adsorption on surface defects. It will be shown in the discussion section that hydrogen gas as an adsorptive appears to be an extremely sensitive tool for detecting surface defects, for just the sticking probability is strongly affected. The $s(\Theta)$ dependence of Fig. 3 may be fitted quite well by a function

$$s(\Theta) = s_0(1 - \Theta/\Theta_{\max})^2$$

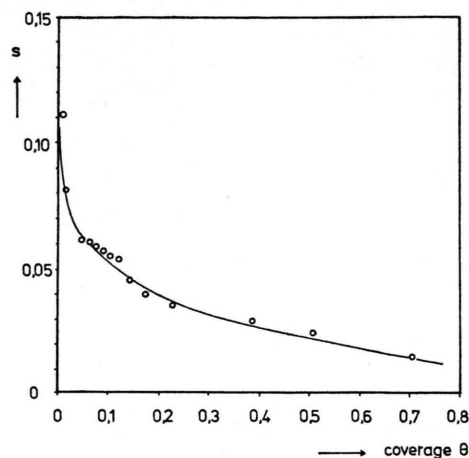


Fig. 3. Sticking probability for $\text{H}_2/\text{Ni}(100)$: $s(\Theta)$ versus Θ .

thus exhibiting second-order kinetics as one would expect for a non-activated atomic chemisorption process. The overall kinetics of desorption (which is assumed to be of second-order as well) is phenomenologically described by the Wigner-Polanyi Equation (4):

$$\frac{dn_{\text{ad}}}{dt} = \nu_{(n)} n_{\text{ad}}^x \exp\left(-\frac{E^*(n)}{RT}\right) \quad (4)$$

(with $x = 2$ for 2nd order).

Assuming coverage-independent values for ν and E^* and using Redhead's formula (2) the intercept of a logarithmic plot of $T_m^2 2n_{\max}$ over T^{-1} :

$$Y_0 = \ln(\beta E^*/R\nu) \quad (5)$$

contains the frequency factor ν which can be separated, if E^* and the heating rate β are known. With $E^* = 23$ kcal/mole and $\beta = 10$ K sec⁻¹ a value for ν of $3 \text{ cm}^2 \text{ sec}^{-1} \text{ H-atom}^{-1}$ is calculated which, however, can be erroneous within one order of magnitude.

3. Work Function

In Fig. 4 the observed work function change $\Delta\phi$ is reported when a Ni(100) crystal is exposed to a constant flux of hydrogen gas; the temperature of the sample was kept at 150 K. A fairly steep increase up to 6–7 Langmuirs is followed by a maximum at about 96 meV and a much slower decrease down to values of about 30–40 meV at saturation. The $\Delta\phi$ -coverage dependence can be constructed by means of a proper calibration of the

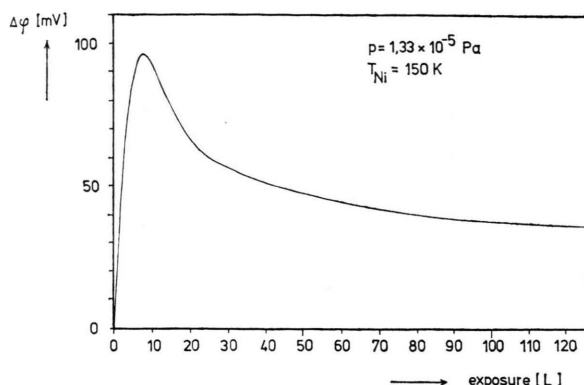


Fig. 4. Work function change $\Delta\varphi$ for $\text{H}_2/\text{Ni}(100)$ against the hydrogen exposure (L).

individual $\Delta\varphi$ -value against the corresponding desorption peak area. The relation $\Delta\varphi(\theta)$ is shown in Figure 5. At first a quite linear increase of $\Delta\varphi$ is observed until the β_2 -state is almost filled indicating a slightly negatively polarized adsorbate layer. Then $\Delta\varphi$ passes through a broad maximum at $\theta \approx 0.5 (\pm 0.1)$ before further uptake of hydrogen leads to adsorption into the β_1 -state thereby lowering the work function again. From thermal desorption experiments it was established that the population of the β_2 -state is responsible for the initial increase whereas hydrogen chemisorption

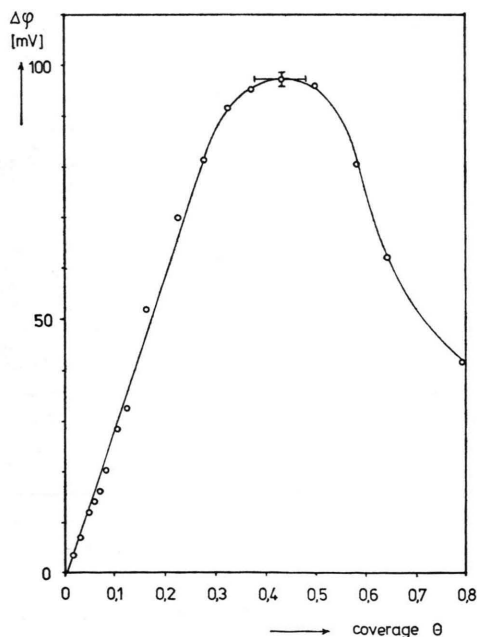


Fig. 5. Work function change $\Delta\varphi$ for $\text{H}_2/\text{Ni}(100)$ as a function of the absolute coverage θ .

into β_1 causes the reversal of the sign and the decay of $\Delta\varphi$.

The quantitative correlation between $\Delta\varphi$ and the concentration of adsorbed particles n_{ad} allows a determination of the initial dipole moment of the hydrogen-nickel surface complex using the simple electrostatic theory via the Helmholtz Equation (6) [7]:

$$\Delta\varphi = 4\pi n_{\text{ad}} \mu_0 f^* \quad (6)$$

[with μ_0 = initial dipole moment, f^* = conversion factor = $(4\pi\epsilon_0)^{-1}$, $\Delta\varphi$ = work function change (eV)].

μ_0 turns out to be 0.049 Debye, a value which is in very good agreement with that found for the adsorption complex of the hydrogen/nickel(111) system [8]. This relatively small number of μ_0 suggests that an almost negligible charge transfer is associated with the formation of the Ni—H bond.

IV. Discussion

Most of the previous studies on the adsorption of hydrogen on nickel single crystal surfaces which are reported in the literature have been performed at room temperature. From the present work it is again confirmed that hydrogen chemisorbs on a Ni(100) surface with a considerably high initial adsorption energy E_{ad}^0 indicating that a dissociation process takes place prior to the chemisorption. By taking into account the enthalpy of dissociation of an H_2 molecule ($E_{\text{diss}} = 103.2$ kcal/mole = 432 kJoule/mole) the experimental value of $E_{\text{ad}} = 23$ kcal/mole = 96 kJoule/mole can be used to determine the energy of 63 kcal/mole (= 2.73 eV) for the Ni—H bond. So far our results reported here do not deviate from that of previous studies [1, 2], there is in fact excellent agreement concerning the value of E_{ad}^0 which was reported by Lapujoulade and Neil [1] to be 23.1 kcal/mole and by Christmann et al. [2] to be 22.6 kcal/mole.

However, since the desorption rate into the gas phase as well as the surface diffusion are activated processes which depend strongly on the temperature, the fairly high temperature of 293 K (thermal energy = 25 meV) may cause mainly two important effects: i) the rate of desorption dn/dt may become appreciably high with the consequence that (at the usually employed pressures) the H surface equilibrium concentration always remains small and does

in no case exceed half a monolayer of hydrogen atoms. ii) The remaining hydrogen atoms on the surface may exhibit a fairly high mobility with a small residence time on a fixed adsorption site. This may possibly prevent the formation of an ordered adsorbate phase especially in those cases where the interaction energy between adsorbed particles is small. An effect of this kind has recently been observed with the nickel(111)/hydrogen system [9] where LEED "extra" spots caused by an ordered overlayer were visible only below room temperature. In general, a lower temperature of the metal surface offers the possibility of observing new experimental features.

Mutual interactions between the adsorbed particles can arise, if a sufficiently high density of H atoms is attained. Furthermore, the mean residence time of an adsorbed particle on a surface site becomes appreciable. A high surface concentration therefore has important consequences concerning the energetics of the chemisorption process. In the case of Ni(100)/H, two atomic binding states β_1 and β_2 separated by an energy difference of about 2–3 kcal/mole appear. This is by no means a feature characteristic for the Ni(100)/H system only but has been observed for a number of transition metal-hydrogen systems, e.g. for Ni(111)/H [10], Pd(111)/H [11], Pt(111)/H [12] or Ru(0001)/H [13]. A possible explanation for the occurrence of two binding states could be an *a priori* heterogeneity of the Ni(100) surface. This, however, seems to be less likely, for even at saturation each unit mesh of the surface lattice can offer one equivalent most favorable adsorption site for a hydrogen atom. Therefore the other alternative seems to be more plausible: For coverages $\Theta > 0.5$ obviously energetic heterogeneity is induced by mutual long-range interactions between the adsorbed atoms. As has been shown by Grimley and Torrini [14] for the W(100)/H system indirect interaction forces (even with oscillatory character) can act through the metal substrate over a range up to four lattice constants. Surprisingly, these forces do not depend directly on the strength of the chemisorption bond and can be attractive or repulsive with typical energies between 1 and 3 kcal/mole. Direct interactions between neighboring H atoms (e.g. dipole-dipole-repulsion forces or orbital overlap) should not be of any significance, for even at saturation (which has been determined to be 1 H atom per

1 Ni surface atom) the H–H distance is still large compared with the diameter of the H atom. Thus we explain the β_1 and β_2 state by the operation of indirect repulsive interactions, very similar to the Ni(111)/H system [8, 10]. However, there exists one important difference between the (100) and (111) surface: Whereas the latter system exhibited a well ordered hydrogen overlayer at temperatures below 273 K, this phenomenon could not be observed for the (100) face, even not at 120 K. Doyen [15] has calculated adsorption energy profiles for hydrogen chemisorption on different transition metal surfaces. It turned out for the Ni(100) plane that a fairly smooth energy surface (with small minima in the fourfold coordinated hollow positions) should facilitate surface diffusion, whereas in the case of the Ni(111) face a more pronounced energetic structure provided somewhat higher activation barriers for a diffusion of the hydrogen atoms. However, the quite recent work by Andersson [3] should not be concealed in this context. Andersson succeeded in preparing a somewhat ordered hydrogen chemisorption phase on a Ni(100) face at temperatures below 250 K. The (very faint and transient) quasiordered $p(2 \times 2)$ -H LEED superstructure was correlated with a quarter of a monolayer of surface hydrogen atoms ($\Theta = 1/4$); the saturation coverage suggested by Andersson was half that we found for the same surface. No reason can be offered, at the moment, for the rather considerable deviations concerning LEED-structure and saturation coverage. It should be noted, however, that even small amounts of carbon impurities can change the adsorption kinetics as well as the total adsorbed amount.

From high-resolution electron energy loss measurements Andersson [3] got very interesting information about the nature of the adsorbed species and its geometric location on the surface. For H₂, D₂ and HD adsorption, vibrational losses at 74 and 52 eV were observed, i.e. within the experimental accuracy the same energies for HD as for H₂ and D₂ separately. This is again a strong indication for the dissociative character of the hydrogen adsorption. The observed vibrational loss energy agrees well with that of a semiempirical calculation of a H atom located in the Ni(100) center site (van der Avoird [16]) and also with the results of Doyen [15] mentioned above. Recent model calculations by Wang [17] based on the

density functional formalism also favour the four-fold hollow as an adsorption site.

The two-state character of the H adsorption manifests itself also in our work function results which clearly exhibit two ranges: From $\Theta = 0$ up to $\Theta = 0.5$ an almost linear increase of $\Delta\varphi$ is observed indicating a negatively polarized hydrogen species. The maximum value of 96 meV, however is only less than two thirds of that found at room temperature [2]. Beyond $\Theta = 0.5$ a reversal of the sign appears, which has to be attributed to the positively polarized β_1 species. As some portions of the β_1 -“sites” are filled even below $\Theta = 0.5$ (see Fig. 1) a superposition of both positively and negatively polarized dipoles leads to the reduced $\Delta\varphi$ -maximum observed in the experiment. Again, there is some disagreement with the results of Andersson [3] who reported on a continuous increase of $\Delta\varphi$ up to 170 meV (which is identical to that we found in a previous room temperature study [2]) and without any evidence for a reversal of sign at higher coverages. A plausible explanation could perhaps be given, if it is taken into account that Andersson could only reach half a monolayer coverage and possibly might not have seen the β_1 species at all.

An important second aspect is concerned with the adsorption and the desorption kinetics. The state of cleanliness and/or the crystallographic order of the surface region may produce striking differences influencing mainly the kinetics of adsorption, e.g. the initial sticking probability s_0 . Nickel (100) surfaces prepared in the usual manner (argon sputtering for cleaning and subsequent annealing at 700 K) showed a sticking coefficient s_0 of about 0.1–0.15; surfaces which were not annealed carefully exhibited an even higher s_0 -value, whereas a very extensive cleaning and annealing procedure of the sample led to the s_0 and $s(\Theta)$ dependence shown in Figure 3. These results and conclusions are in very good agreement with recent H adsorption studies on Ni(111) faces [10] and on stepped platinum(111) samples [18]. It should be mentioned in this context that striking effects of this kind have never been observed with carbon monoxide or oxygen adsorption on various Ni or Pd surfaces. It is therefore assumed that the very small hydrogen atom (or molecule) “feels” foreign atoms as well as crystallographic disorder very sensitively. Thus in general the kinetics is more

strongly influenced than the energetics of a chemisorption process, although adsorption e.g. on a kink site may exhibit a somewhat higher adsorption energy as could be shown for the Pt(111)/H system [12, 18]. Evidence for this phenomenon had been given also for Ni surfaces in an previous study [2]; at that time, however, the data points reflecting the high initial adsorption energy had been regarded as an artifact and therefore were omitted from the graphs. Our recent measurements, however, support the idea that these results reflect just a non-negligible defect concentration of the surfaces in question. The absolute s_0 -value of our present work (which agrees well with the number of 0.06 of Lapujoulade and Neil [1]) is considerably lower than that we found in our previous study [2] for Ni(100) and again supports our statement concerning the role of the surface defects.

The overall second order kinetics of the adsorption/desorption process clearly reflects the atomic mechanism of the H chemisorption without any evidence for a precursor state, again in good agreement with Lapujoulade and Neil [1].

Some difficulties, however, may arise from an inspection of the preexponential factor ν of the desorption reaction. From a simple Redhead evaluation we arrived at $\nu = 3(\pm 50\%) \text{ cm}^2 \text{ H-atom}^{-1} \text{ sec}^{-1}$, a value which is fairly high and points into the direction of an immobile hydrogen surface layer. In our previous room temperature study [2] we estimated a ν of about $8 \times 10^{-2} \text{ cm}^2 \text{ H-atom}^{-1} \cdot \text{sec}^{-1}$ with some evidence for a slightly restricted mobility of the H-atoms; Lapujoulade and Neil [1] report on a ν of $2.5 \times 10^{-1} \text{ cm}^2 \text{ H-atom}^{-1} \text{ sec}^{-1}$ which is also pretty high. Our value for ν suggests that at lower temperatures ($T < 200 \text{ K}$) the surface diffusion is inhibited to a large extent. This would be in agreement with previous field emission experiments [19] of H on Ni tips whereafter the onset of hydrogen surface diffusion was found to occur around 250 K. On the other hand the lack of a well-ordered adsorbate phase (there are no or only very weak LEED “extra” patterns) can only be explained by either very weak H–H interactions or a quite high surface mobility of the adsorbate. Further careful LEED experiments including intensity/voltage measurements are planned for the near future which hopefully will give more insight into the nature of the hydrogen adsorbate phase at low temperatures.

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