

## ADSORPTION OF HYDROGEN ON PALLADIUM SINGLE CRYSTAL SURFACES

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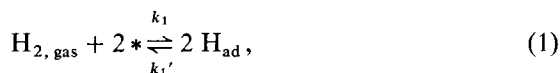
The adsorption of hydrogen on clean Pd(110) and Pd(111) surfaces as well as on a Pd(111) surface with regular step arrays was studied by means of LEED, thermal desorption spectroscopy and contact potential measurements. Adsorption in the bulk plays an important role but could be separated from the surface processes. With Pd(110) an ordered  $1 \times 2$  structure and with Pd(111) a  $1 \times 1$  structure was formed. Maximum work function increases of 0.36, 0.18 and 0.23 eV were determined with Pd(110), Pd(111) and the stepped surface, respectively, this quantity being influenced only by adsorbed hydrogen under the chosen conditions. The adsorption isotherms derived from contact potential data revealed that at low coverages  $\theta \propto \sqrt{p_{\text{H}_2}}$ , indicating atomic adsorption. Initial heats of  $\text{H}_2$  adsorption of 24.4 kcal/mole for Pd(110) and of 20.8 kcal/mole for Pd(111) were derived, in both cases  $E_{\text{ad}}$  being constant up to at least half the saturation coverage. With the stepped surface the adsorption energies coincide with those for Pd(111) at medium coverages, but increase with decreasing coverage by about 3 kcal/mole.  $\text{D}_2$  is adsorbed on Pd(110) with an initial adsorption energy of 22.8 kcal/mole.

### 1. Introduction

The hydrogen-palladium system was, owing to its unique bulk properties already the subject of numerous investigations. The processes on the surface are also of considerable importance if one remembers the high activity of Pd as a catalyst for hydrogenation reactions. However, only very limited data about the adsorption of hydrogen on palladium are available in the literature. Beeck<sup>1)</sup> determined the initial heat of adsorption on evaporated films as 26 kcal/mole. A similar value was obtained for supported Pd catalysts<sup>2)</sup>. Recently Aldag and Schmidt<sup>3)</sup> concluded from flash desorption experiments with a Pd wire, that three chemisorption states with energies of 22, 25 and 35 kcal/mole exist, the state with the highest adsorption energy being, however, only weakly present in their spectra. Suhrmann et al.<sup>4)</sup> concluded from measurements of the electrical resistivity of thin Pd films that adsorbed hydrogen is negatively charged, which would correspond to an increase of the work function.

A complicating factor with all adsorption studies arises from the fact that adsorbed hydrogen atoms may penetrate the phase boundary into the bulk.

The reaction scheme for the interaction of hydrogen with Pd was formulated by C. Wagner<sup>5)</sup> about 40 years ago as follows:



$\text{H}_{\text{Me}}$  denotes a hydrogen atom in the bulk,  $\text{H}_{\text{ad}}$  in the (atomic) chemisorbed state and  $*$  a free adsorption site.

We report on studies with Pd(110) and (111) single crystal planes where the main emphasis is directed towards the adsorption/desorption equilibrium (1), the subsequent step (2) however also playing an important role.

## 2. Experimental

The experiments were performed using an UHV system (base pressure  $\sim 10^{-10}$  Torr) with a four grid LEED optics (Varian) and an additional glancing angle electron gun for recording Auger electron spectra. The vacuum chamber was further equipped with a quadrupole mass spectrometer (Balzers QMG 111 A) for the measurement of flash desorption spectra and of the residual gas composition, and with a vibrating reference electrode. The latter consisted of oxidized tantalum and was used for measuring variations of the work function with an accuracy of about 3 mV by means of a self-compensating Kelvin method<sup>6)</sup>. A few control measurements were performed by the diode method using the LEED gun as electron source. Gases of high purity were introduced from glass bulbs through variable leak valves into the UHV chamber.

The samples were cylindrical slices of about 6 mm diameter and 2 mm thickness which were prepared from a Pd single crystal rod (99.999% purity, Metals Research) after proper X-ray orientation by means of spark erosion. The surfaces were subsequently mechanically polished and spot-welded between two parallel running thin W wires which themselves were fixed to vertical Mo rods. The crystal was heated by a current passing through the tungsten wires. The sample temperature was measured by a fine Pt/Pt Rh thermocouple spot-welded to the backside of the crystal which was mounted together with its holder on the axis of a manipulator.

Impurities present on the surface after evacuation and bakeout of the UHV chamber were removed by prolonged argon ion bombardment (energy 400 eV) and subsequent annealing. The main contaminants were S and C, as usual. The determination of small amounts of carbon at the surface by

means of Auger electron spectroscopy was somewhat complicated by the fact that the C peak at 275 eV nearly coincides with a Pd transition at 282 eV. It was found however that the variation  $\Delta\phi$  of the work function caused by hydrogen adsorption is influenced markedly by the presence of traces of surface impurities. The cleaning procedure was always continued until maximum and completely reproducible values of  $\Delta\phi$  were attained. With such surfaces no further contaminants could be detected by AES and the LEED patterns exhibited sharp diffraction spots from the substrate lattices.

### 3. Results

#### 3.1. Pd(110) SURFACE

Adsorption of hydrogen at room temperature at a Pd(110) surface leads initially to the formation of additional streaks in the LEED pattern in [01] direction between the substrate spots. After a longer  $H_2$  exposure these streaks had contracted to "extra" spots of a  $1 \times 2$  structure whose diffraction pattern is shown in fig. 1 together with that from the clean surface. This sequence was reversed by mild heat treatment in vacuo. The "extra" spots elongated into streaks which finally disappeared completely. Quite similar variations of the LEED pattern were also observed after hydrogen absorption on a Ni(110) surface<sup>6, 7</sup>). More detailed studies revealed however that the adsorption kinetics and isotherms in the two cases differ considerably<sup>8</sup>).

If the adsorbed hydrogen was removed from the surface by annealing for a short time at about 100°C, the  $1 \times 2$  structure reappeared shortly after cooling the crystal in UHV. This was not due to readsorption from the

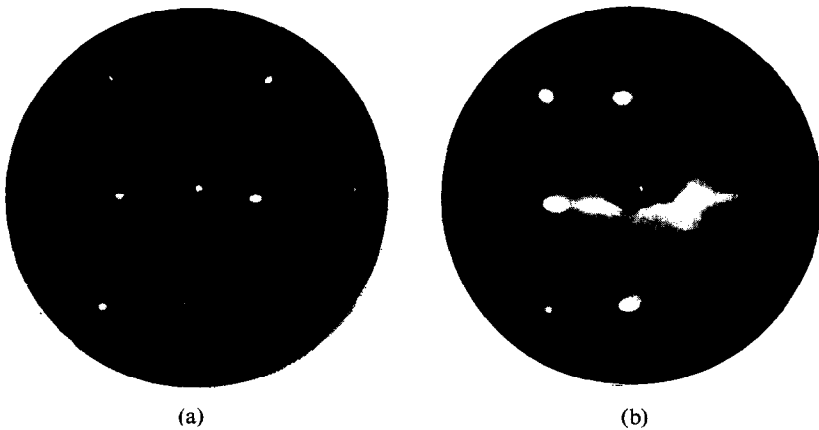


Fig. 1. LEED patterns from Pd(110). (a) Clean surface; (b)  $1 \times 2$  structure after completing the adsorbed hydrogen layer.

residual gas atmosphere, but by back-diffusion of hydrogen dissolved in the bulk to the surface.

Such effects were even more pronounced with the thermal desorption experiments. In this type of experiment the crystal was heated at a rate of about  $20^\circ\text{C}/\text{sec}$  in UHV. The chamber was continuously pumped and the variations of the partial pressures due to desorbing gases were recorded with the quadrupole mass filter. A series of spectra taken after different hydrogen exposures of the surface is shown in fig. 2. After an  $\text{H}_2$  exposure of 1 Langmuir ( $1 \text{ L} = 10^{-6} \text{ Torr sec}$ ) only a single desorption peak appears which in-

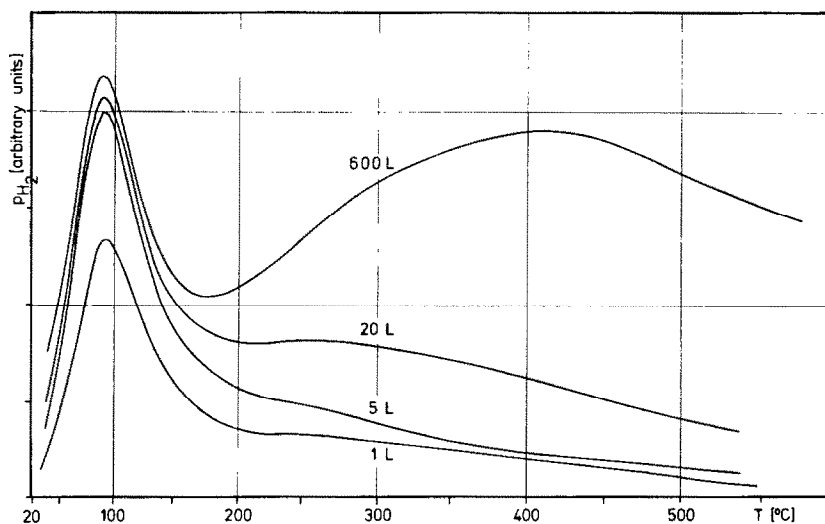


Fig. 2. Thermal desorption spectra from a Pd(110) surface after different hydrogen exposures.

creases in size with increasing exposure up to  $\sim 5 \text{ L}$ , but remains constant with still greater exposures. However a second broad desorption peak develops whose maximum is shifted towards higher temperatures with increasing exposure. The first peak arises from adsorbed hydrogen whereas the broad second peak is attributed to desorption of a species which was originally absorbed in the bulk. This statement is supported by the following observations: After hydrogen from the first state was thermally desorbed, only the substrate lattice spots were visible in the LEED pattern and the work function (see below) decreased to the initial value of the clean surface. If such a sample rests in UHV at room temperature for a few minutes the adsorbed layer is filled up again by hydrogen back diffusing from the bulk, meaning that the work function increases and a subsequently recorded thermal desorption spectrum again exhibits the first peak at  $100^\circ\text{C}$ .

The position and the shape of the second peak are strongly influenced by the history of the sample. The peak becomes more flat and is shifted towards higher temperatures if the period of time between H<sub>2</sub> exposure and thermal desorption is increased. This is interpreted as a more uniform distribution of the dissolved hydrogen to deeper layers. From the known bulk diffusion coefficient at 25 °C<sup>19</sup>) it follows that H atoms diffuse into the bulk a mean distance of about 0.2 mm within 1000 sec.

From the temperature of the first peak the mean energy of activation  $E^*$  for desorption of the hydrogen from the adsorbed state may be derived<sup>9</sup>). If a coverage  $\theta = \frac{1}{2}$  ( $\cong 4.7 \times 10^{14}$  atoms/cm<sup>2</sup>), a frequency factor  $\nu = 8 \times 10^{-2}$  cm<sup>2</sup>/particles sec, and second order desorption kinetics are assumed, then from the heating rate (17.4 K/sec) and the temperature of the pressure maximum (368 K) a value  $E^* = 23$  kcal/mole is obtained, which agrees well with the adsorption energies derived from the adsorption isotherms as described below. The numerical value of  $\nu$  was suggested from results of more detailed investigations with the system Ni(100)/H<sub>2</sub><sup>10</sup>), but variations of  $\nu$  and  $\theta$  over a wide range would only be of minor influence for the resulting value of  $E^*$ .

The electron work function  $\phi$  of the Pd(110) surface increased by 0.36 eV under the influence of a hydrogen atmosphere (with pressures up to 10<sup>-5</sup> Torr). It was demonstrated that dissolved hydrogen does not contribute to a measurable extent to the variation of the work function  $\Delta\phi$ ; therefore this quantity could be used as a measure of the surface concentration of adsorbed particles. From detailed measurements with H<sub>2</sub>/Ni<sup>10,11</sup>) it is known that for these systems  $\Delta\phi$  is almost completely proportional to the coverage  $\theta$  up to at least half the saturation coverage.

At least for not too large values of  $\theta$  such a proportionality may also be assumed in our case. Since bulk diffusion is coupled to the adsorption/desorption equilibrium, relatively long periods of time were necessary until, at given values of  $p_{H_2}$  and  $T$ , the stationary state of the surface coverage was reached and  $\Delta\phi$  remained constant. (As indicated by the results of the flash desorption and LEED experiments the binding energy and the structure of the adsorbed layer is not influenced by the presence of dissolved hydrogen). If the concentration  $[H_{Me}]$  of hydrogen atoms in a layer just below the surface is in a steady state, then it follows from eqs. (1) and (2):

$$\frac{d[H_{Me}]}{dt} = 0 = k_2 [H_{ad}] - k'_2 [H_{Me}] [*], \quad (3)$$

$$\begin{aligned} \frac{d[H_{ad}]}{dt} = 0 &= k_1 p_{H_2} [*]^2 - k'_1 [H_{ad}]^2 - k_2 [H_{ad}] + k'_2 [H_{Me}] [*] \\ &= k_1 p_{H_2} [*]^2 - k'_1 [H_{ad}]^2. \end{aligned} \quad (4)$$

That means in this case measuring  $[H_{ad}]$  (through  $\Delta\phi$ ) leads to a description of the adsorption/desorption equilibrium alone; under steady-state conditions  $[H_{ad}] = f(p_{H_2}, T)$ . A series of such adsorption isotherms using  $\Delta\phi$  as a measure for  $[H_{ad}]$  is shown in fig. 3, from which the isosteric heat of adsorption as a function of coverage (i.e.  $\Delta\phi$ ) may be evaluated using the Clausius-Clapeyron equation:

$$\left[ \frac{d \ln p}{d(1/T)} \right]_{\theta = \text{const}} = - \frac{E_{ad}}{R} \quad (5)$$

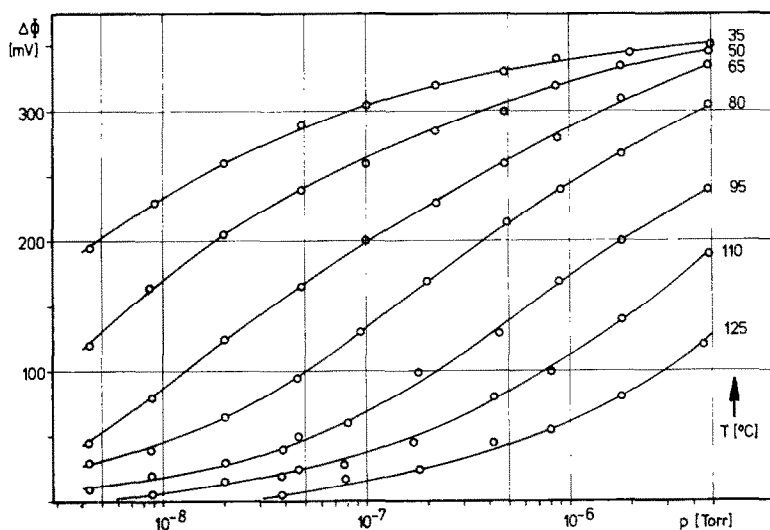


Fig. 3. Adsorption isotherms ( $\Delta\phi$  versus pressure) for hydrogen adsorption on Pd(110).

The results are given in fig. 4 together with values which were derived from analogous measurements with  $D_2$ . In both cases  $E_{ad}$  is constant up to about half the maximum value of  $\Delta\phi$ . The initial heat of  $H_2$  adsorption  $E_{ad, H_2}^0 = 24.4$  kcal/mole is about 1.5 kcal/mole larger than that for adsorption of  $D_2$ ,  $E_{ad, D_2}^0 = 22.8$  kcal/mole. Although the absolute values for  $E_{ad}$  might be erroneous within  $\pm 1$  kcal/mole, the difference between  $E_{ad, H_2}$  and  $E_{ad, D_2}$  is clearly evident from fig. 4. If hydrogen adsorption is dissociative as formulated by eq. (1) then it is predicted that  $[H_{ad}] \propto \sqrt{p_{H_2}}$  at low coverages, provided that within this region  $E_{ad}$  is independent of coverage which in fact is demonstrated by fig. 4. Some of the adsorption isotherms are plotted in fig. 5 in a double logarithmic scale. Up to about  $\Delta\phi \approx 100$  mV straight lines are obtained whose slopes are exactly  $\frac{1}{2}$ . This gives strong evidence that hydrogen is in fact adsorbed in the atomic state.

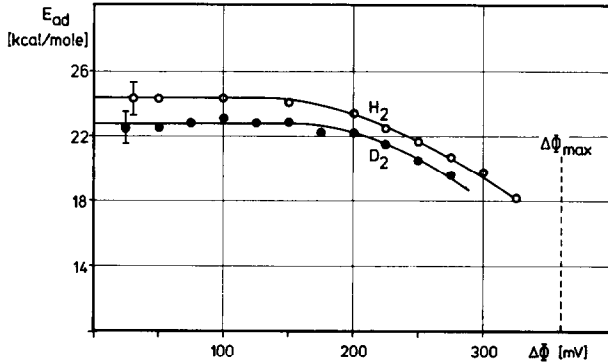


Fig. 4. Isosteric heats of adsorption of  $H_2$  (○) and  $D_2$  (●) on Pd(110) as a function of the work function change.

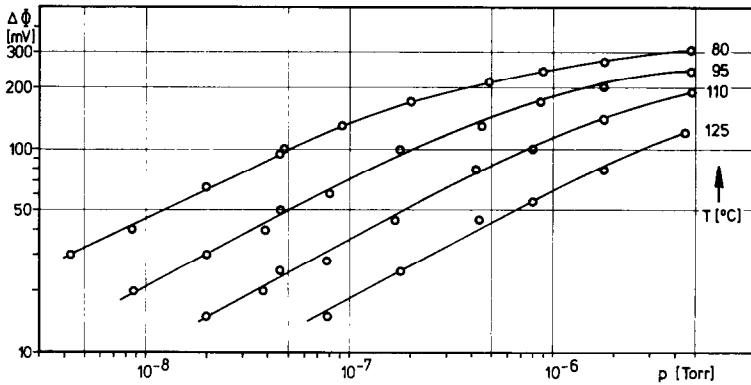


Fig. 5. Double logarithmic plot ( $\log \Delta\phi$  versus  $\log p_{H_2}$ ) of the adsorption isotherms for  $H_2$ /Pd(110).

### 3.2. Pd(111) SURFACE

After interaction of hydrogen with a Pd(111) surface no additional diffraction spots in the LEED pattern were visible. A detailed analysis of the LEED intensities<sup>11)</sup> lead however to the conclusion that the adsorbed hydrogen layer causes appreciable variations in the intensity/voltage ( $I/V$ ) curves and that in this case a "true"  $1 \times 1$  structure is formed.

The results of thermal desorption measurements were similar to that with the Pd(110) surface, namely a peak below 100°C and a further increase of the pressure around 400°C, the latter being again attributed to the desorption of initially dissolved hydrogen. There is some evidence that the rate of dissolution and depth of penetration depend on the surface orientation, but such effects were not studied in detail.

The work function of the Pd(111) surface increases only by 0.18 eV, which

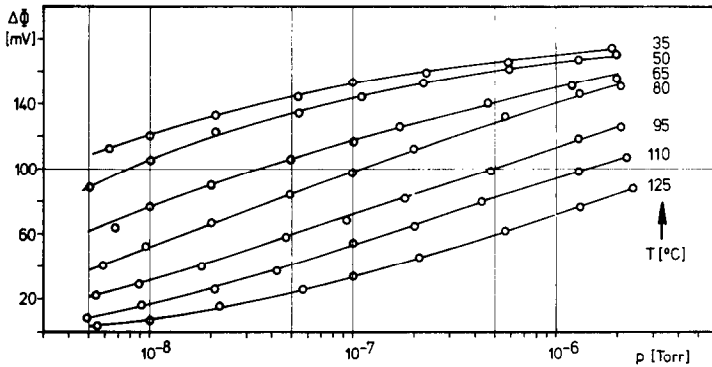


Fig. 6. Adsorption isotherms for hydrogen adsorption on Pd(111).

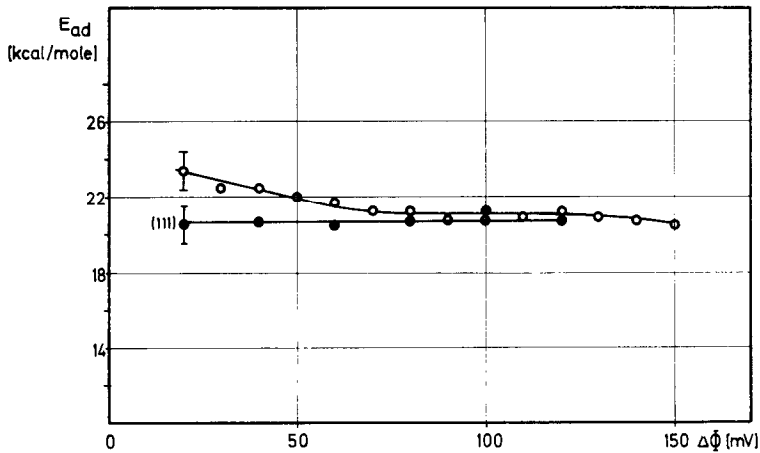


Fig. 7. Isothermic heat of  $H_2$  adsorption on Pd(111) (●) and on a (111) surface with regular steps arrays (○) as a function of  $\Delta\phi$ .

is about half the maximum value attained with Pd(110). A series of adsorption isotherms is reproduced in fig. 6, from which the isothermic heat of adsorption was again derived. As can be seen from fig. 7 within the covered region up to  $\Delta\phi = 130$  mV,  $E_{ad} = 21 \pm 1$  kcal/mole is constant. At still higher coverages the uncertainties of the evaluation become too large.

A double logarithmic plot of the adsorption isotherms again leads to straight lines at low coverages with slope  $\frac{1}{2}$ , meaning that on Pd(111) also hydrogen adsorbs dissociatively.

### 3.3. STEPPED Pd(111) SURFACE

Recently Somorjai and his coworkers<sup>20</sup>) observed interesting adsorption properties of high index platinum surfaces. These surfaces were shown to

consist of low index terraces of constant width linked by monoatomic steps.

A high index palladium surface was prepared by cutting a (111) plane with a deviation of  $6.5 \pm 0.5^\circ$ . In Somorjai's nomenclature this would correspond to a Pd(S)-[9(111)  $\times$  (111)] surface, indicating terraces with (111) orientation, 9 atomic rows in width, separated by monoatomic steps also with (111) orientation. The LEED pattern showed the characteristic splitting of the spots into doublets, although some portions of the surface exhibited other step orientations leading to the existence of domains. The main purpose was to investigate, whether the adsorptive properties of such a stepped surface differ markedly from that of a low index (111) surface.

The work function of the stepped surface increased after hydrogen adsorption by about 0.23 eV as compared with 0.18 eV with the (111) surface. This higher value is ascribed to the presence of more "open" surface atoms as in the case of a (110) plane, where  $\Delta\phi = 0.36$  eV was found.

From the adsorption isotherms again the isosteric heat of adsorption was evaluated. The result is drawn in fig. 7 together with the values for the (111) surface. As can be seen, at medium coverages the values of both surfaces nearly coincide. At small coverages, however, for the (111) surface  $E_{ad}$  remains at the same constant value, whereas with the stepped surface it increases with decreasing coverage and nearly reaches the value found for the (110) plane. This phenomena is obviously caused by the presence of surface atoms at steps which exhibit a somewhat stronger bond with the H atoms. Such atoms might well play the role of "active centers" in catalytic reactions, but their effect on hydrogen adsorption is not fundamentally different from that of the low index (111) plane.

The presence of surface steps had a pronounced effect on the absorption of hydrogen, which however was not studied in more detail.

#### 4. Discussion

Although the solubility of hydrogen is unique with palladium, the adsorption of hydrogen on this metal is not very different from the behaviour of other transition metals e.g. nickel<sup>8</sup>). The shape of the adsorption isotherms at low coverage has to be interpreted that in this region  $\theta \propto \sqrt{p_H}$  and therefore hydrogen is adsorbed in the atomic state, the recombination reaction  $2H_{ad} \rightarrow H_2$  being rate-determining for the desorption process. Similar conclusions were drawn by Aldag and Schmidt<sup>3</sup>) on the basis of their flash desorption data.

The observed increase of the work function indicates a net electron transfer from the metal to the adsorbed H atom. If one compares merely the ionization energy ( $I = 13.6$  eV) and the electron affinity ( $A = 0.7$  eV) of H with the

work function of Pd ( $\varphi \approx 5$  eV) a more or less neutral adsorbed state would be predicted. Measurements of the electron density in the bulk  $\beta$ -Pd/H by means of photoelectron spectroscopy<sup>12)</sup> indicated the formation of hydrogen-induced energy states centered at about 5.4 eV below the Fermi level. The results of APW calculations suggested that in  $\beta$ -Pd/H hydrogen is more electronegative than Pd. Since it may be assumed that for the adsorbed state the situation is not completely different these findings would explain the formation of a negatively charged adsorbed hydrogen layer.

Dissolved hydrogen atoms are located at octahedral interstices<sup>13)</sup> and similar sites might also be preferred for adsorption. LEED intensity measurements with the system H/Pd(111) revealed that an ordered adsorbed  $1 \times 1$  structure is formed<sup>10)</sup>. If it is assumed that a single H atom is contained within the unit cell this structure would correspond to a coverage  $\theta=1$ . Aldag and Schmidt<sup>9)</sup> concluded from their flash desorption data with a Pd wire the maximum coverage was 0.95. Since a polycrystalline surface consists predominately from the most densely packed planes this result may be regarded as being representative for the (111) plane, thus supporting the above assumed value  $\theta=1$ . A structure model for the arrangement of adsorbed H atoms on a Pd(111) surface as shown in fig. 8 is thus suggested.

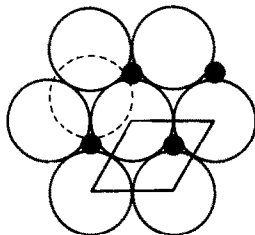


Fig. 8. Structure model for the arrangement of hydrogen atoms adsorbed on Pd(111) ( $1 \times 1$  structure).

Such a structure model was also proposed by Weinberg and Merrill<sup>14)</sup> for the atomic adsorption of hydrogen on Pt(111). However the formation of a further transient  $2 \times \sqrt{3}$  structure due to a molecular adsorption state was discussed for the latter system. In our case we failed to show the existence of such a phase in spite of detailed efforts. Dissociative adsorption of  $H_2$  on Pd(111) obviously occurs with no or only very small activation energy. This is also supported by the relatively high sticking coefficient for the formation of  $H_{ad}$  which was estimated to be between 0.1 and 0.2.

The derivation of a structure model for the system Pd(110)/ $H_2$  appears to be more problematic. The unit cell of the  $1 \times 2$  structure is considerably larger than that of the  $1 \times 1$  structure on Pd(111). If again only a single H atom is

assumed to be within the unit cell the surface concentration of  $H_{ad}$  would be smaller by about a factor of 3 as compared with Pd(111), although the change of the work function is twice as large on Pd(110) than on Pd(111). It is therefore felt that for the  $1 \times 2$ -Pd(110) structure more than one H atom is contained in the unit cell, but of course this problem may only be solved after a determination of the absolute coverage.

It is remarkable that the same  $1 \times 2$  structure of Pd(110) was also found previously for hydrogen adsorbed on Ni(110)<sup>7</sup>). In the latter case the findings were formerly regarded as a strong support for the concept of "reconstructive" adsorption, i.e. the occurrence of displacements of the surface atoms. The present results yield no further indication for the validity of such a view. Measurements with Pd(111) and Ni(100) surfaces<sup>10</sup>), however, revealed that considerable variations of the LEED intensities after hydrogen adsorption may occur in those cases where no "extra" LEED spots appear and where displacements of surface atoms may be excluded.

The measurements with Pd(110) revealed that the adsorption energy for  $D_2$  is about 1.5 kcal/mole smaller than for  $H_2$ . The dissociation energies  $D$  of  $H_2$  (103.22 kcal/mole) and  $D_2$  (105.02 kcal/mole)<sup>15</sup>) differ by 1.8 kcal/mole. This indicates that the isotope effect is mainly due to the difference of the zero point energies of the free  $H_2$  and  $D_2$  molecules which would imply rather low values for the frequencies of hydrogen vibrations in the adsorbed state. We are not aware of any infrared data for hydrogen adsorbed on Pd, but some measurements were made with the Pt/H system. Primet et al.<sup>16</sup>) attributed a band at  $2120 \text{ cm}^{-1}$  to the Pt-H stretching vibration; with adsorbed deuterium they found a value of  $1520 \text{ cm}^{-1}$ . We thus calculate a difference of the zero point energies between Pt- $H_{ad}$  and Pt- $D_{ad}$  of 0.85 kcal/mole. The energy difference  $(D_{H_2} - 2E_{M-H}) - (D_{D_2} - 2E_{M-D}) = E_{ad, H_2} - E_{ad, D_2}$  is thus predicted to be in the order of only about 0.1 kcal/mole which is not in agreement with the present results for palladium.

An estimate for the frequencies of vibrations of H and D dissolved in Pd was made by Wicke and Nernst<sup>18</sup>). From the desorption entropies they evaluated  $\tilde{\nu}_H \approx 410 \text{ cm}^{-1}$  and  $\tilde{\nu}_D \approx 280 \text{ cm}^{-1}$ . Assuming these values also as representative for adsorbed species we calculate for the difference of the adsorption energies  $E_{ad, H_2} - E_{ad, D_2} = 1.4 \text{ kcal/mole}$  which is very close to the experimental result.

A somewhat smaller value of 0.85 kcal/mole was derived by Wicke and Nernst<sup>18</sup>) for the difference of the desorption enthalpies of dissolved  $H_2$  and  $D_2$ .

The adsorption energies for  $H_2$  on Pd(110) and Pd(111) differ by 3.5 kcal/mole, i.e. by about 15%. A similar result has been found with  $H_2$  adsorption on Ni<sup>8</sup>) and with CO adsorption on Pd<sup>17</sup>). It seems as if the "struc-

tural" factor in chemisorption is generally not of fundamental importance. However the experiments with the stepped surface demonstrate nicely the effect of structural imperfections on the adsorption energies.

It was possible to separate the adsorption of hydrogen from its absorption in the bulk, although the latter plays an important role for attaining steady-state conditions. Adsorption with  $E_{ad} > 20$  kcal/mole is energetically strongly favoured over dissolution in the bulk [ $E \approx 9$  kcal/mole<sup>18</sup>]. Therefore the surface will be occupied by hydrogen atoms back-diffusing from the bulk, and penetration of hydrogen into the bulk as well as diffusion through Pd are strongly influenced by the nature of the adsorbate phase. The equilibrium atomic ratio H/Pd in the bulk is predicted to be negligibly small under the pressure and temperature conditions used with our experiments<sup>18</sup>). However the observed shifts of the Bragg maxima in the LEED intensity-voltage curves from Pd(111)<sup>11</sup>) were interpreted as being caused by a slight expansion ( $\sim 2\%$ ) of the Pd lattice within the topmost few atomic layers. Thus it may be concluded that the concentration of dissolved H atoms is probably somewhat enhanced within the layers just below the surface. On the other hand the experiments revealed that the adsorptive properties of the surface (i.e. structure and binding energies of the adsorbate phase) are not influenced to any measurable extent by the presence of hydrogen atoms in the bulk.

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