

CHEMISORPTION OF HYDROGEN ON IRON SURFACES

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The adsorption of hydrogen on Fe(110), (100) and (111) single crystal planes has been studied by means of low energy diffraction (LEED), thermal desorption spectroscopy (TDS), work function measurements and ultraviolet photoelectron spectroscopy (UPS). Isotope exchange experiments revealed the atomic nature of all species held at the surface above 140 K. The chemisorption bond is characterized by a bonding level with an ionization energy of 5.6 eV below the Fermi energy as identified by UPS which is derived from coupling the H 1s state to the valence states of the metal. Initial adsorption energies of 26, 24 and 21 kcal/mole were derived for the (110), (100) and (111) planes, respectively. The work function decreases with Fe(110) by 95 mV, whereas total increases by 75 and 310 mV were determined for the (100) and (111) surfaces, respectively. At saturation the (110) and (100) planes reveal the existence of two desorption states, whereas three states are observed with Fe(111). Whereas Fe(100) and (111) reveal no variation of the LEED pattern a series of ordered overlayer structures, ranging from $c2 \times 2$ (or " 2×1 ") at $\theta = 1/2$ to 1×1 at $\theta = 1$, were observed with Fe(110). These structures can be interpreted in a straightforward manner in terms of subsequent filling of rows of adsorption sites along the [001]-surface direction whereby repulsive interactions are operating between particles in neighbouring rows. This model fits perfectly with the TDS data and enables the calibration of the absolute coverage ($\theta_{\text{sat}} = 1$, i.e. a 1:1 ratio of H:Fe surface atoms). The initial sticking coefficient on Fe(110) is $s_0 = 0.16$ and it was found that with this plane the variation of this quantity with coverage between $\theta = 0.1$ and 1 obeys a simple Langmuir type law for dissociative adsorption on two adjacent vacant sites, viz. $s = s_0 (1 - \theta)^2$.

1. Introduction

Despite the importance of hydrogen chemisorption on iron as a reactant in ammonia synthesis or the Fischer–Tropsch reaction surprisingly little systematic studies on this system were performed in the past. The reason is probably that the preparation of clean Fe surfaces is a very difficult task and almost all the work so

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far was performed with polycrystalline samples: Chornet and Coughlin [1] as well as Wedler and Borgmann [2] recorded thermal desorption spectra from Fe wires and evaporated films. The latter were also used in a ultraviolet photoelectron spectroscopy study by Yu et al. [3]. Quite recently Cavalier and Chornet [4] published results mainly on the H_2 - D_2 exchange reaction on Fe(110), (100) and (111) planes. To our knowledge this is so far the only report on studies with single-crystals in the literature which however were performed without any of the electron spectroscopic techniques for characterization of the chemical and structural state of the surfaces.

The present paper is concerned with the investigation of hydrogen chemisorption on clean (110), (100) and (111) single-crystal planes of iron by means of Auger spectroscopy, LEED, uv-photoelectron spectroscopy, thermal desorption spectroscopy and work function measurements. This combination of methods was successfully also applied in a previous study on the interaction of N_2 with the same Fe single crystal surfaces [5,6].

2. Experimental

Details of the experimental equipment, sample cleaning etc. may be found in earlier reports [5,7,8]. With the exception of the photoemission measurements all experiments were performed in the same apparatus equipped with a quadrupole mass spectrometer and facilities for LEED, Auger (AES) and work function ($\Delta\phi$) measurements by means of the vibrating condenser technique. The single crystal surfaces were carefully cleaned by elaborate argon ion bombardment and annealing cycles until the surface concentration of the most persistent contaminant carbon was suppressed to below a few percent of a monolayer and no further impurities were detectable by AES. Clean, well-annealed surfaces were characterized by bright and sharp diffraction spots in the LEED pattern, indicating a high degree of structural perfection.

High purity gases were admitted from glass bulbs into the vacuum chamber through UHV leak valves. The base pressure of the system was lower than 10^{-10} Torr. The composition of the residual gas atmosphere was continuously monitored with the mass spectrometer. Effects of other gases (CO) in the adsorption experiments were negligible.

3. Results

3.1. Fe(110)

Fig. 1 represents a series of thermal desorption spectra recorded with a heating rate of 7 K/sec from Fe(110) after H_2 exposures between 0.4 and 3500 L at 140 K.

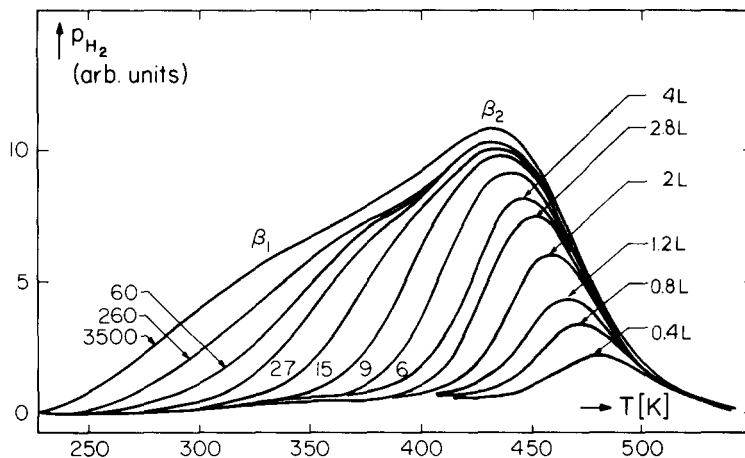


Fig. 1. Thermal desorption spectra from H/Fe(110) (exposures between 0.4 and 3500 L).

The highest exposure marks saturation of the adsorbed layer at this temperature. These spectra may be regarded as a superposition of 2 states, β_1 and β_2 , which are subsequently filled. The temperature maximum of the β_1 state is at about 340 K, whereas the β_2 -peak shifts towards lower temperatures with increasing coverage indicating second-order desorption kinetics. The β_2 state completely fills at an exposure of about 7 L and the area below the saturated β_2 peak is almost exactly 50% of the total area, that means that at saturation of the adsorbed layer both states exist with equal concentration on the surface.

For a second order desorption process with activation energy E_d the following relation holds [9]

$$E_d/RT^2 = (n_{\max}\nu/\alpha) \exp(-E_d/RT_{\max}),$$

where α the heating, ν the preexponential factor, T_{\max} the temperature of the peak maximum and

$$n_{\max}\alpha \int_{t_{\max}}^{\infty} p dt$$

the adsorbate concentration at T_{\max} . A plot of $\ln(n_{\max}T_{\max}^2)$ versus $1/T_{\max}$ should yield a straight line from whose slope E_d may be determined. Fig. 2 shows such an evaluation for the β_2 state whose desorption thus in fact may be considered to obey second-order kinetics. Its desorption energy is determined to $E_d(\beta_2) = 26 \pm 1$ kcal/mole and may be considered to remain independent of coverage until the β_2 state is completed. A similar analysis for the β_1 state fails because it cannot clearly be separated from the β_2 state. Since this state continuously emerges as a

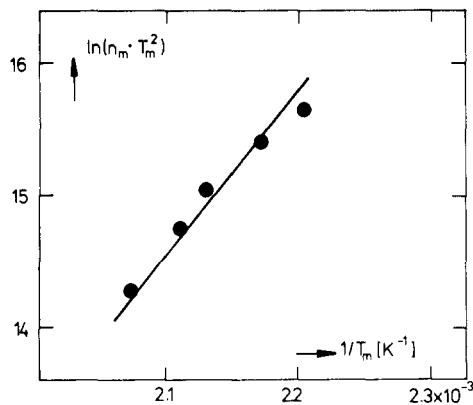


Fig. 2. Plot of $\ln(n_{\max} T_{\max}^2)$ for the β_2 state of H/Fe(110).

shoulder from the β_2 state its adsorption energy is at first obviously only slightly smaller ($\sim 1-2$ kcal/mole) but probably continuously decreases with increasing coverage.

The area below a flash desorption trace is proportional to the adsorbed amount n_s and the variation of this quantity with exposure as evaluated from the data of fig. 1 is plotted in fig. 3. It will become evident from the analysis of the LEED data that the saturation coverage $\theta_{\max} = 1$ (i.e., a 1:1 ratio of adsorbed hydrogen atoms and Fe atoms in the surface layer), or $n_{s,\max} = 1.7 \times 10^{15}$ H atoms/cm². Graphical differentiation of the curve of fig. 3 yields in the usual manner the sticking proba-

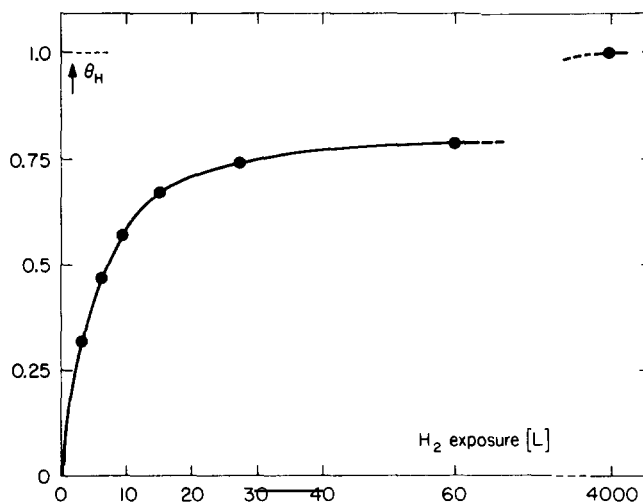


Fig. 3. H/Fe(110): variation of the coverage θ with H_2 exposure at 140 K.

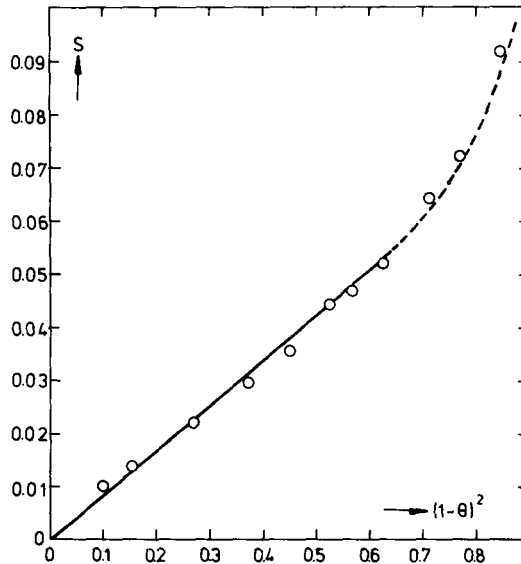


Fig. 4. H/Fe(110): variation of the sticking coefficient s at 140 K with $(1 - \theta)^2$.

bility. The initial sticking coefficient (extrapolated to $\theta = 0$) is thus evaluated to be $s_0 = 0.16$ at 140 K.

Fig. 4 shows a plot of $s(\theta)$ as a function of $(1 - \theta)^2$ which yields a straight line between 0 and 0.7 indicating that also the absorption process between $\theta = 0.15$ and 1 may be described by second-order kinetics. At coverages $\theta < 0.1$ the sticking probability increases considerably with decreasing θ . The physical origin of this effect is unclear and might even be caused by small concentrations of structural imperfections on the surface.

In order to elucidate the nature of the adsorbed species in some more detail a series of thermal desorption experiments following exposure to D₂ as well as to H₂ was performed: A clean surface was at first exposed at 345 K to 12 L H₂ leading to saturation of the β_2 state but keeping the β_1 -state empty. Subsequently the sample was cooled to 140 K and exposed to additional 200 L D₂. Thermal desorption spectra for H₂, HD and D₂ revealed that these species desorbed in proportional amounts from both β_1 and β_2 states indicating complete isotopic equilibration on the surface. This result further shows that particles initially adsorbed in the β_2 state do not remain fixed in distinct adsorption sites but rather that there is a complete transformation between both states suggesting that the β_1 state is not caused by filling of a second type of site but rather due to repulsive interactions between neighbouring adsorbed particles leading to an induced heterogeneity of the surface.

The Fe(110) surface was the only plane which showed the formation of ordered adsorbate structures. A series of LEED patterns corresponding to increasing H₂ exposure at 140 K is reproduced in fig. 5. After about 2 L weak extra spots of a $c2 \times 2$

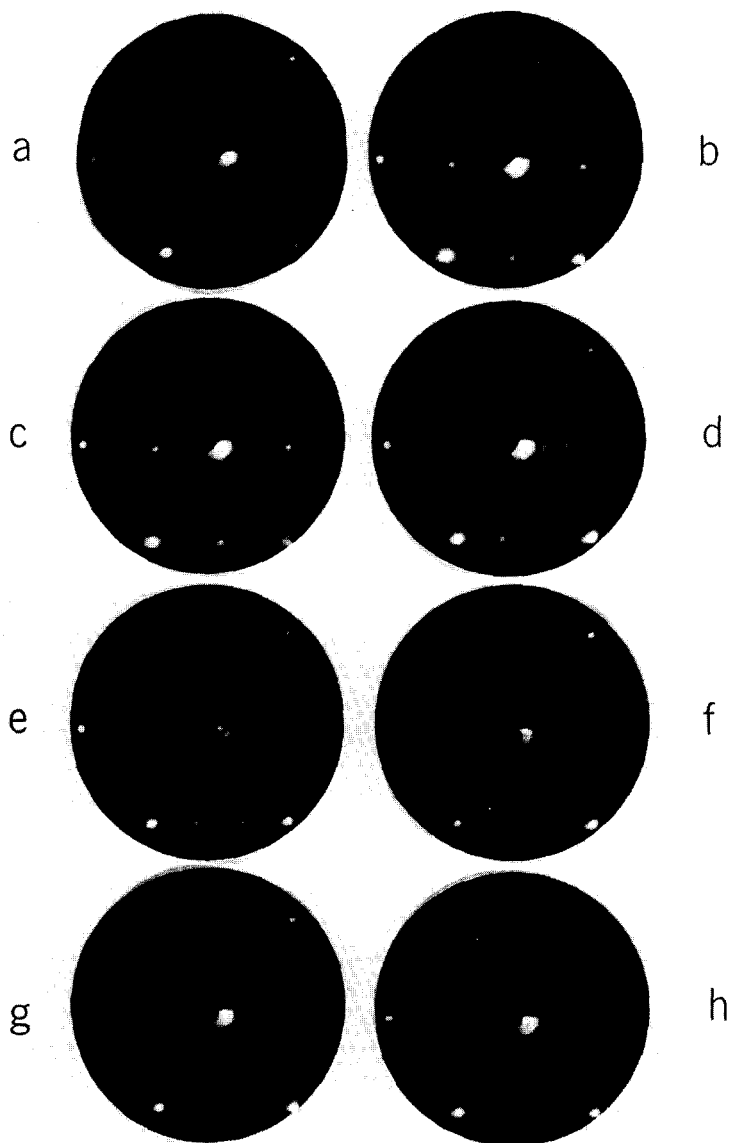


Fig. 5. LEED patterns from Fe(110) with increasing hydrogen exposure at 140 K ($U = 59$ eV): (a) 2.8 L; (b) 6 L; (c) 9 L; (d) 15 L; (e) 27 L; (f) 40 L; (g) 260 L; (h) 3500 L.

structure become visible (fig. 5a) which become brighter with increasing exposure and attain maximum intensity after about 7 L. The designation of this structure as $c2 \times 2$ refers to the unit cell vectors of the Fe(110) surface along the $[1\bar{1}1]$ and $[\bar{1}11]$ directions. If instead the $[1\bar{1}1]$ and $[001]$ axes of the substrate lattice are chosen as reference (see fig. 10a) then this structure has to be denoted by " 2×1 ". This latter nomenclature will be chosen in the following enabling a more convenient classification of the other structures.

Beyond 7 L additional spots of a " 3×1 " structure appear (fig. 5c) and increase in intensity whereas those from the " 2×1 " structure gradually disappear (figs. 5d and e). Above about 20 L the spots of the " 3×1 " structure become streaky and all "extra" features of the LEED pattern loose continuously in intensity until after very high exposures (leading to saturation of the adsorbate layers) only the diffraction spots from the substrate lattice remain, indicating the formation of a true 1×1 structure. After exposures beyond about 40 L sometimes some modulation of the intensity of the diffraction streaks in the reciprocal lattice could be observed indicating the formation of 4×1 , 5×1 , etc. periodicities within certain regions of the surface.

If the surface was exposed to 8 L H_2 at 345 K the LEED pattern showed only very weak additional spots from the " 2×1 " structure which however became very much brighter if the sample was subsequently cooled in vacuo to 140 K. This observation suggests that at elevated temperature considerable disorder in the adsorbate layer exists, an effect which presumably also may serve to interpret the somewhat complex findings with regards to the measurements of the work function variation.

In contrast to the behavior of the other planes hydrogen adsorption on Fe(110) was observed to *decrease* its work function as shown in fig. 6 for continuous expo-

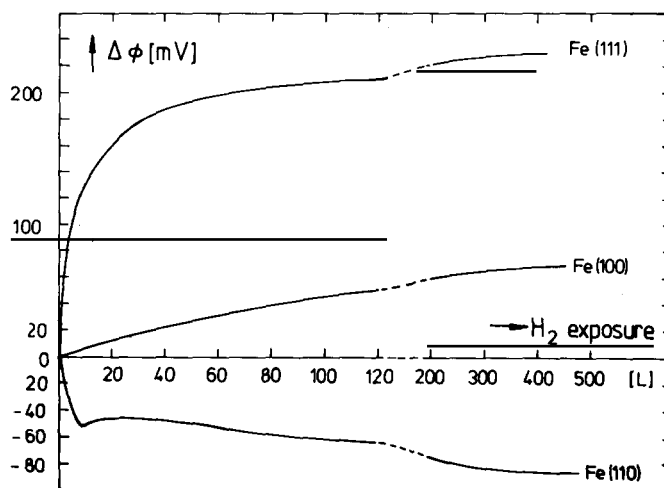


Fig. 6. Variation of the work function $\Delta\phi$ of Fe(110), (100) and (111) surfaces with hydrogen exposure at 140 K.

sure at 140 K. This curve exhibits a small minimum around the exposure where the β_2 state is completed and subsequently continuously further decreases to a saturation value of $\Delta\phi = -85 (\pm 5)$ mV. Filling of the β_2 state under these conditions was characterized by $\Delta\phi = -55$ mV. If instead the β_2 state was filled at 345 K (leading to only rather weak extra spots of the “ 2×1 ” structure as outline above) the work function change was only -25 mV. Subsequent lowering of the temperature to 140 K caused $\Delta\phi$ to change to -65 mV which is almost the same value obtained if the exposure was performed at this low temperature. These findings together with the corresponding LEED observations suggest that partial disordering of the β_2 state ($\hat{=}$ “ 2×1 ” structure) at higher temperature is accompanied with a lowering of the effective dipole moment of the adsorbed particles. Since the total $\Delta\phi$ variation due to ordered filling the β_2 state is 60 mV and that of the β_1 state only 30 mV it has to be concluded that particles of the former kind exhibit a considerably larger dipole moment than the adsorbates at saturation since the population of both states is equal. It is believed that the $\beta_2 \rightarrow \beta_1$ transformation upon increasing the exposure beyond that necessary for completion of the β_2 state is also responsible for the occurrence of the $\Delta\phi$ minimum although a quantitative interpretation cannot yet be offered.

3.2. Fe(100)

In analogy to fig. 1 thermal desorption spectra from a hydrogen covered Fe(100) surface are reproduced in figs. 7a and b. Exposure was again performed at 140 K. Again two states, β_1 and β_2 , are discernible whose populations however are not equal but exhibit a ratio of about 4:1. Fig. 7b again indicates a continuous shift of the β_2 peak towards lower temperature with increasing coverage, however a quantitative analysis in terms of second-order kinetics revealed not to be useful since soon also the β_1 state starts to be occupied and thus overlaps. Instead only an estimate of the desorption energy of the β_2 state was made from its peak temperature at saturation (400 K) leading to $E_d(\beta_2) \approx 24$ kcal/mole.

The shift of the β_1 peak with temperature is too small to account for second-order desorption kinetics of this state. Instead it is probable that the kinetics follow a first-order rate law with the desorption energy decreasing somewhat with decreasing coverage. The relatively narrow-half-width of this state at saturation is remarkable whose desorption energy is estimated to be about $E_d(\beta_1) \approx 18$ kcal/mole.

Since in this case no calibration of the absolute coverage via the observation of ordered adsorbate structures was possible also the initial sticking probability could not be determined.

Thermal desorption spectra taken after exposure to H₂ and D₂ revealed HD desorption and complete isotopic mixing as found with the other planes.

No appearance of additional LEED spots was observed over the whole range of coverages. It is assumed that no long-range order of the adsorbed layer is established at the attainable temperatures. Since the hydrogen atom is a rather weak scatterer a

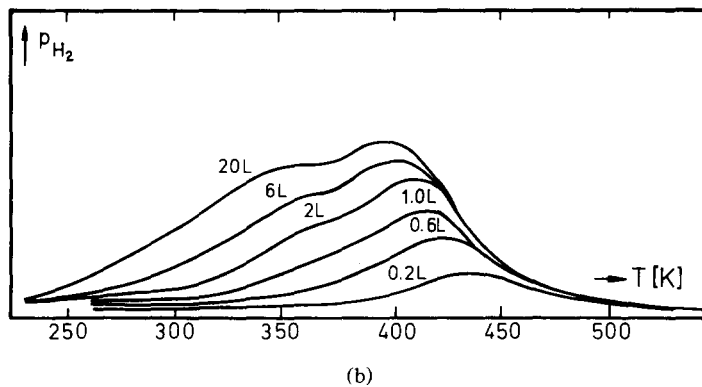
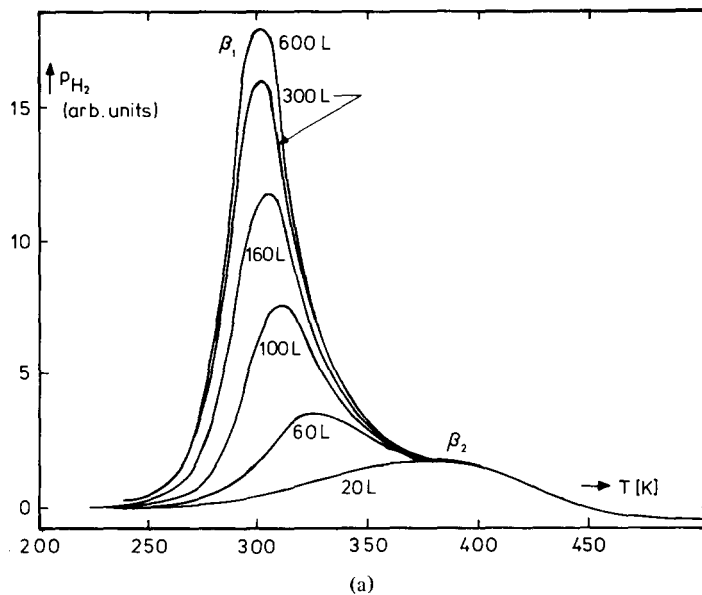


Fig. 7. Thermal desorption spectra from H/Fe(100): (a) exposures between 20 and 600 L; (b) exposures between 0.2 and 20 L.

disordered overlayer would presumably not cause any appreciable variation of the intensities of the substrate lattice spots as well as of the background brightness.

The variation of the work function upon exposing a Fe(100) plane at 140 K to hydrogen is included in fig. 6. $\Delta\phi$ increases continuously to a saturation value of +75 mV. No differences between the β_1 and the β_2 states were discernible.

Fig. 8. shows ultraviolet photoelectron spectra ($h\nu = 40.8$ eV) from a clean (curve a) and a hydrogen covered Fe(100) surface (curve b) as well as the difference

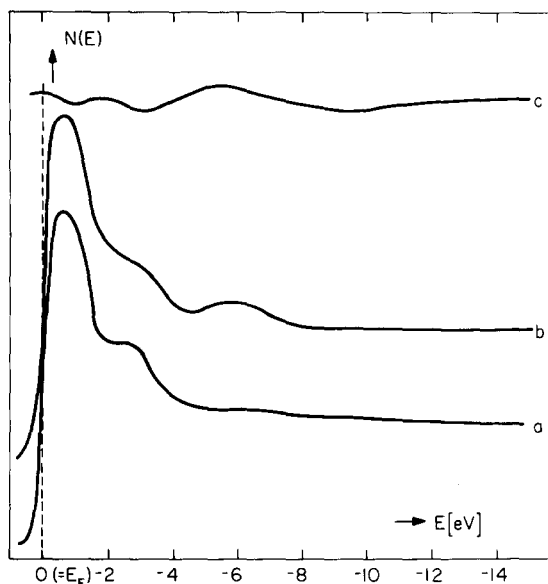


Fig. 8. Ultraviolet photoelectron spectra ($h\nu = 40.8$ eV) from Fe(100): (a) clean surface; (b) after saturation with adsorbed hydrogen; (c) difference spectrum.

spectrum (b-a), i.e. the variation of the spectrum caused by H₂ adsorption. The Fe d-band extends from 0 to about 5 eV below the Fermi level E_F . Besides some slight modification of the emission from the d-band hydrogen adsorption causes the appearance of a relatively broad maximum centered at about 5.6 eV below E_F .

3.3. Fe(111)

Fig. 9 shows a series of thermal desorption spectra from Fe(111) exposed to various doses of H₂ at 135 K. The essential difference to the other planes is that

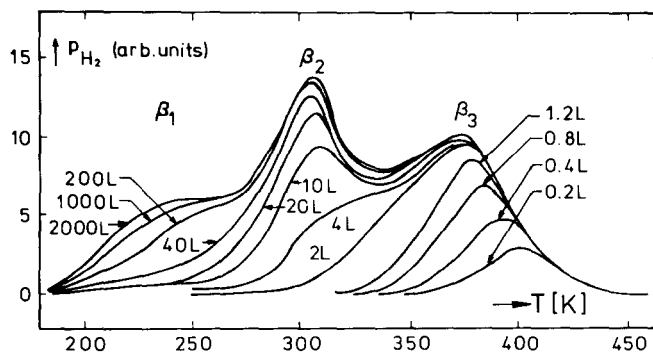


Fig. 9. Thermal desorption spectra from H/Fe(111).

now three desorption states, β_1 , β_2 and β_3 , appear. These states are filled successively.

A second-order plot for the desorption kinetics of the β_3 state yields its desorption energy to $E_d(\beta_3) = 21$ kcal/mole. Desorption energies for the other two states are estimated to be $E_d(\beta_2) = 18$ kcal/mole and $E_d(\beta_1) = 13$ kcal/mole.

HD desorption spectra after exposure to H₂ + D₂ revealed as with the other planes complete isotopic mixing of the three states and suggests again that the adsorbed species is in all states atomic hydrogen.

Fig. 6 contains data on the variation of the work function of the Fe(111) surface as a function of hydrogen exposure at 140 K. $\Delta\phi$ increases continuously to a value of about 240 mV. However this number does not represent the possible maximum variation as becomes evident from the following experiments: if the surface is exposed to 500 L H₂ at 210 K $\Delta\phi$ increases by 275 mV. Subsequent cooling to 140 K in an H₂ atmosphere of 10⁻⁶ Torr (completion of the β_1 state) causes a further increase by 35 mV to a maximum $\Delta\phi = 310$ mV. Obviously all three states exhibit the same sign of the dipole moment, i.e. contribute to the work function increase. If the temperature of this sample (i.e. with $\Delta\phi = 310$) is raised the work function decreases continuously due to successive desorption. If, however, the surface saturated a priori at 140 K ($\Delta\phi = 240$ mV) is heated, the work function at first increases by about 30 mV, passes through a maximum at about 200 K and then drops continuously.

This effect is interpreted as follows: if a Fe(111) plane is exposed to H₂ at 140 K the mobility of the adsorbed hydrogen atoms is restricted so that no equilibrium configuration (connected with $\Delta\phi = 310$ mV) is attained. Sufficiently high mobility is reached at about 200 K so that warming of the sample causes a work function increase parallel to the continuous decreases due to the onset of desorption thus giving rise to the observed (transient) $\Delta\phi$ maximum.

As with Fe(100) also the (111) surface exhibited no visible change of the LEED pattern throughout the whole range of coverages.

The uv photoemission spectrum from the clean Fe(111) surface as well as its variation by hydrogen adsorption (appearance of a new maximum at 5.6 eV below E_F) are quite similar to the results with the Fe(100) plane so that a reproduction of these data is omitted.

4. Discussion

The isotopic mixing experiments strongly indicate that in all cases hydrogen adsorbs dissociatively and has a high enough mobility in order to enable complete isotope equilibration. The observation of an additional maximum in the photoemission spectrum at about 6 eV below the Fermi level is in agreement with the findings by Yu et al. [3] and with the observation of similar effects after hydrogen adsorption on Ni and Pd surfaces [10]. This feature is attributed to a bonding chemisorp-

tion orbital created by coupling the H 1s level to the metallic valence states [10]. The bond is obviously mainly covalent which manifests itself also in the small work function changes which indicate only minor net charge transfer effects between adsorbate and substrate. The strength of the M–H bond (as evaluated from the adsorption energies) varies between 65 kcal/mole (for Fe(110)) and 62 kcal/mole (for Fe(111)) and is thus again quite similar to the values for other transition metals such as nickel [11].

The probably most spectacular result is the observation of a sequence of ordered overlayer structures with the (110) plane. Since the hydrogen atom is a weak scatterer for low energy electrons so far only few examples are known where hydrogen adsorption causes the appearance of additional LEED spots, e.g. W(100) [12], the (110) planes of Ni [13] and Pd [14], and Ni(111) [15]. Whereas with the H/Ni(110) system there is some evidence that the diffraction spots are mainly caused by a reconstruction of the topmost layer [16] this possibility can almost certainly be ruled for the densely packed Ni(111) plane on the basis of current analysis of LEED intensity data [15]. It is believed that the situation with Fe(110) is similar to that with Ni(111), i.e. that no surface reconstruction occurs and that the “extra” LEED spots reflect the periodicity of the adsorbate layer. The interpretation of the “ 2×1 ” structure is straightforward: Its unit cell obviously contains a single H atom which is tentatively placed in a location as reproduced in fig. 10a. (Of course, the determination of the adsorption site is only possible by analysis of the LEED intensities which is planned for the future.) This structure has a coverage $\theta = 1/2$ and corresponds to completion of the β_2 state in the thermal desorption

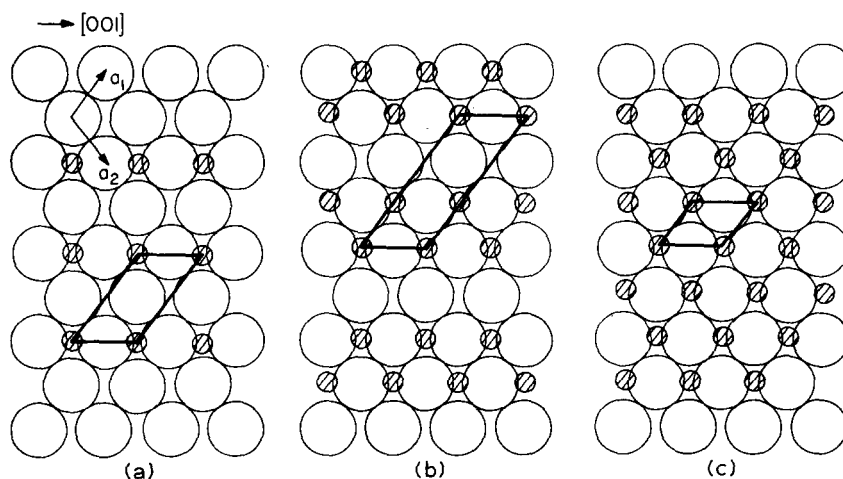


Fig. 10. Possible structure models for the configuration of adsorbed H atoms in the ordered overlayers on Fe(110). (a) $\theta = 1/2$, “ 2×1 ” structure; (b) $\theta = 2/3$, “ 3×1 ” structure; (c) $\theta = 1$, 1×1 structure.

spectra. Since this state contains 50% of the total amount adsorbed at saturation the latter obviously corresponds to $\theta = 1$ and is on the other hand characterized by the continuous disappearance of the LEED "extra" spots, i.e. the formation of a 1×1 -structure (fig. 10c). Thus these two sets of independent data fit nicely together.

The " 3×1 " structure is fully developed after about 15L which by using the coverage versus exposure calibration of fig. 3 corresponds to $\theta \approx 2/3$. Thus it is clear that its unit cell has to contain two H atoms which, if placed into identical positions, give rise to the structure model drawn in fig. 10b. Obviously the adsorbed particles prefer to stay in rows along the [001] direction which persists also at even higher coverages giving rise to the observed streak formation in the LEED patterns. So we have to assume some attraction between neighbouring atoms in [001] direction but repulsion between parallel neighbouring rows, otherwise no " 2×1 " structure would be formed. Since the " 3×1 " structure contains the adsorbed atoms in this less favorable configuration its formation should manifest itself in a decrease of the adsorption energy. This is exactly what is observed since after completion of the β_2 state the β_1 state with its lower desorption temperature continuously emerges in the thermal desorption spectra. The pairwise repulsive interaction energy between nearest neighbors in the $[\bar{1}\bar{1}1]$ direction is estimated to be of the order of about 1 kcal/mole. It is interesting to notice that the transition " 2×1 " \rightarrow " 3×1 " is not characterized by a uniform mixing of singly and doubly spaced rows. This would cause a continuous splitting of the half-order beams [17] as was for example observed with the O/Ni(110) system [18]. Instead a superposition of spots from both periodicities is observed (fig. 5) and with increasing coverage the intensities from those of the " 3×1 " structure grow up whereas the spots of the " 2×1 " structure gradually disappear. That means the existence of a two-phase region with islands (with diameters exceeding the coherence width of the electron beam, i.e. about 100 Å) of both structures coexisting on the surface. A similar example is found with the O/Cu(110) system where islands of 2×1 and $c6 \times 2$ structures may coexist and grow on the expense of each other with variation of the total coverage [19].

Beyond $\theta = 2/3$ the still empty rows on the surface will gradually be occupied. At a coverage $\theta = 1 - 1/n$ on the average every n th row will be empty causing sometimes the observation of diffuse " 4×1 ", " 5×1 ", ... patterns. In fact the periodicity is then given by the *empty* rows. Since, however, no real long-range order over such very large distances exists the diffraction pattern exhibits more or less uniform streaks. Finally at saturation all adsorption sites will be filled leading to the observed 1×1 structure with identical periodicities of overlayer and substrate lattices.

The interactions between adparticles in neighboring rows not only cause a decrease of the adsorption energy but are obviously also responsible for the nonlinear variation of the work function change with coverage as well as for the temperature effects observed with $\Delta\phi$. At 140 K $\Delta\phi$ decreases continuously with increasing exposure to -55 mV until the " 2×1 " structure is completed indicating constant dipole moments for the adsorbate complexes in this configuration. Since at $\theta = 1$ the total work function change is only $\Delta\phi = -85$ mV it follows that the adsorbate di-

pole moment at saturation is about 30% smaller than within the “ 2×1 ” structure. This effect is probably due to mutual depolarization since the distance between neighboring adsorbates in the $[1\bar{1}1]$ direction (2.48 Å) is smaller than that in $[001]$ direction (2.86 Å). This could also qualitatively account for the $\Delta\phi$ minimum in a similar way as it is observed with systems involving adsorption of alkali metals [20].

If adsorption takes place at 345 K the work function change at $\theta = 1/2$ was considerably smaller than at low temperatures and the LEED pattern indicated a high degree of disorder. Obviously the higher temperature favours the high mobility and the tendency for random distribution of the adsorbed particles which would explain both observations.

All observed effects are quite reversible and exhibit no indication for hysteresis thus making it highly improbable that partial dissolution of hydrogen atoms into the bulk plays any role. Although this possibility cannot completely be ruled out, it has to be stated that all observations may be interpreted in a straightforward manner without such an assumption.

With Fe(100) and (111) it is not possible to identify the different desorption states with particular configurations on the surface since the LEED patterns do not reveal any evidence for long-range order. However in the case of the Fe(100) plane it is believed that the formation of the β_1 state is also due to repulsive interactions between adsorbed particles although it is unclear why the relative population of the β_2 state is so small compared with that of the β_1 state.

The situation is somewhat different with the (111) surface. The unit cell of this plane is rather large and exhibits various possibilities of high symmetry adsorption sites. The work function measurements indicate that the dipole moments are a function of coverage and adsorption temperature which – as in the case of Fe(110) – might be due to depolarization effects but which however might also be caused by the occupation of different adsorption sites. The occurrence of *three* adsorption states (in contrast to only two states with Fe(110) and (100) surfaces) point into the same direction. However, these suggestions remain speculative as long as no structural information is available.

Comparison of the three planes with each other reveals that the initial adsorption energies decrease in the order $(110) > (100) > (111)$ which is just opposite from what would be expected from a simple picture which relates the strength of the chemisorption bond with the degree of “saturation” of the valencies of the surface atoms (i.e. their coordination numbers). It is interesting to notice that Cavalier and Chornet [4] in their study on the H_2/D_2 exchanges reaction found the same sequence for the reactivity of the different single crystal surfaces.

Only limited comparison of the present results is possible with those from previous studies with polycrystalline materials: During the last two decades to our knowledge the only measurements on the variation of the work function were performed in 1962 by Suhrmann et al. [21] with evaporated films. These authors reported a total increase by 250 mV which would correspond to the value obtained with the (111) plane. However, it cannot be assumed that this plane predominates with eva-

porated films. Keeping in mind the difficulties in preparing clean iron surfaces and that the work function is very sensitively influenced by the adsorption of impurities from the residual gas atmosphere suggests that these earlier data are not representative for pure hydrogen adsorption on a clean Fe surface. The observation that with the most densely packed plane H₂ adsorption – in contrast to the other planes – causes even a decrease of the work function is probably surprising but by no means singular: Similar observations were recently made with the hydrogen/platinum system [22].

Earlier measurements of the initial heats of adsorption revealed values up to 39 kcal/mole [23]. More recent data are considerably lower and are closer to those found in the present study: Chornet and Coughlin [1] determined an isotheric heat of adsorption of 21 kcal/mole at low coverage with an Fe wire. Wedler and Borgmann [24] quote so far unpublished results of calorimetric measurements with evaporated Fe films whereafter at medium coverages E_{ad} drops steplike from 23 to 18 kcal/mole. They also concluded that at saturation $\theta = 1$ (i.e. H:Fe = 1:1) is reached which agrees with the present findings with the Fe(110) plane. The same authors also published thermal desorption spectra from evaporated Fe films exhibiting at first the filling of a β_2 state with a temperature maximum (at saturation) at 430 K and subsequently the growth of a second state (β_1) with no clearly resolved maximum at about 350 K but with desorption already starting at 250 K. This agrees fairly well with the present results for Fe(110). However even if the total area of a polycrystalline surface would contain in addition minor fractions of (100) and (111) planes a superposition of the corresponding contributions to the total thermal desorption spectrum would yield a desorption trace essentially identical to those reported by Wedler and Borgmann [2].

Chornet and Coughlin [1] derived an initial sticking coefficient of 0.05 with a Fe wire. The variation of s with θ revealed to be rather complex in this work. Adsorption kinetics on Fe(111) appears to be “normal” although no further analysis is made. The behavior of the (110) surface is surprisingly simple: The linear variation of s with $(1 - \theta)^2$ (see fig. 4) over a wide range of coverages has to be interpreted in terms of adsorption of the H₂ molecules at two adjacent empty adsorption sites which is rather plausible in view of the derived structural properties of this system.

Finally it should be mentioned that Cavalier and Chornet [4] concluded in their H₂ – D₂ exchange study that besides adsorption also dissolution of hydrogen in the bulk may take place and participate in the surface reactions. However, it is reported that no evidence for such an effect was obtained for exposures smaller than 3×10^6 L at 294 K. Such exposures would exceed those applied in the present work by several orders of magnitude and in fact from the present results there is no indication for the possible existence of appreciable amounts of dissolved hydrogen atoms interfering with the processes at the surface.

Interesting analogies are found if the present results are compared with those for the extensively studied H/W systems:

With W(110) two binding states (β_1 and β_2) with equal population, differing in

desorption energy by about 6 kcal/mole were observed [25]. A saturation coverage of 1 was derived [25,26] as in the present case and Tamm and Schmidt [25] suggested the formation of a 1×1 structure with the adsorbed hydrogen atoms in the same locations as shown in fig. 10. However, there are no LEED data available which would indicate long-range periodicities similar to those observed in the present work. In contrast to the (100) and (111) planes H_2 adsorption on W(110) causes a decrease of the work function [27], as in the present case. Agreement also exists with regard to the rate of adsorption being proportional to $(1 - \theta)^2$ [27] and to second-order desorption kinetics [25,27].

The shape of the thermal desorption spectra from H/W(100) [28] is similar to those obtained with Fe(100), although the $\beta_1 : \beta_2$ ratio of 2:1 is not achieved in the present case. Completion of the β_2 state is associated with a $c2 \times 2$ structure [29], whereas no ordered overlayers were observed in the present case. The saturation coverage was found to be $\theta_{\max} = 2$ [26] and on the basis of vibrational spectra Froitzheim et al. [30] recently concluded that at saturation all the H atoms are located in bridge positions, whereas the β_2 state is characterized by the occupation of on-top sites. Whether similar conclusions are justified for Fe(100) is however questionable as long as no further structural information is available.

W(111) exhibits *three* β -states [25,31] like Fe(111). (In addition, a γ state desorbing around 100 K was observed which could have not been detected with the present system since the lowest attainable temperature was only about 130 K.) It was argued in a similar way that this higher complexity is presumably caused by the fact that this plane exposes surface atoms with different coordination [25,27,31].

However, there are also differences: With W the heats of adsorption decrease in the order (111) > (110) \sim (100), whereas with Fe the sequence (110) > (100) > (111) was found. The work function change is larger on W(100) than on W(111) which is again reverse to the behavior of Fe. The similarities in the shapes of the thermal desorption spectra, however, suggest that similar principles are operating with both bcc metals regarding the energetic aspects of different adsorption sites and of the interactions between adsorbed hydrogen atoms.

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