

## ADSORPTION AND DECOMPOSITION OF AMMONIA ON Fe(110)

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The interaction of  $\text{NH}_3$  with a Fe(110) surface was studied by means of LEED, AES, UPS, work function and thermal desorption measurements. Below room temperature non-dissociative adsorption takes place into two states with bond strengths of about 17 and 10 kcal/mole leading to the formation of a partially disordered overlayer with a maximum coverage of  $\theta = 1/6$  ( $\hat{=} 2.9 \times 10^{14}$  molecules/cm<sup>2</sup>) and a maximum work function decrease by 2.4 eV. The dipole moment of the adsorbate is independent of coverage (2.2 Debye) and even larger than that of the free  $\text{NH}_3$  molecule, which indicates that chemisorption is predominantly taking place through coupling of the N lone electron pair to the metal.  $\text{NH}_{3,\text{ad}}$  is characterized by valence ionization potentials of 6.7 and 11.2 eV below  $E_F$ . The adsorption kinetics follows a simple first-order rate law with an initial sticking coefficient  $S_0 = 0.16$ . At 350 K a stable surface intermediate characterized by ionization potentials of  $-5.2$  and  $-8.4$  eV and a  $2 \times 2$ -LEED pattern is formed which is identified with  $\text{NH}_{\text{ad}}$ . Above 400 K complete dissociation and desorption of  $\text{H}_2$  takes place. The remaining adsorbed N-atoms recombine and desorb as  $\text{N}_2$  only above 850 K. In contrast to the previously investigated Fe(111) plane adsorbed ammonia exhibits no isotopic exchange with adsorbed deuterium which is attributed to somewhat different rate constants of the consecutive steps of dissociation and recombination. This effect is also made responsible for the fact that with Fe(111) and (100) presumably  $\text{NH}_{2,\text{ad}}$  is observed as a transient intermediate, whereas with Fe(110)  $\text{NH}_{\text{ad}}$  may be isolated on the surface. Preadsorption of  $\text{N}_{\text{ad}}$  influences the adsorption energy and sticking coefficient of  $\text{NH}_3$ , but has no strong influence on the totally adsorbed amount.

### 1. Introduction

This work is an extension to the most densely packed (110) plane of Fe of previous investigations from our laboratory dealing with the interaction of ammonia with Fe(100) and (111) surfaces [1,2]. The general conclusion of these studies as well of those by other authors [3,4] was that  $\text{NH}_3$  adsorbs in the molecular form at low temperatures but dissociates upon warming to room temperature whereby at least one intermediate species (presumably  $\text{NH}_{2,\text{ad}}$ ) could be detected [1,2]. The behaviour of the Fe(110) surface turned out to be similar in many respects, but exhibits also distinct differences. Among others, it was possible to isolate an intermediate surface species which most probably is identified with  $\text{NH}_{\text{ad}}$  and which was

never observed so clearly with the other planes. In addition, the results confirm previous conclusions whereafter the kinetics of ammonia synthesis on iron is markedly influenced by the surface structure [5–7].

## 2. Experimental

Experimental details are described in previous publications [2,5,8]. The UPS measurements were performed within a separate apparatus [9] with He II radiation ( $h\nu = 40.8$  eV) and by data handling with a computer. For all the other experiments a UHV system was applied which was equipped with facilities for LEED, AES, thermal desorption and work function measurements. Ammonia was introduced through a capillary tube with its orifice about 1 cm in front of the sample surface. Cleaning of the surface was achieved by previously developed procedures [5,8].

## 3. Results

### 3.1. Ultraviolet photoelectron spectroscopy

A series of photoemission spectra ( $h\nu = 40.8$  eV) from an Fe(110) surface with different  $\text{NH}_3$  treatments at 175 K is reproduced in fig. 1a. The corresponding difference spectra are shown in fig. 1b. After an exposure of 4 L (corresponding to about 70% of the maximum coverage) two rather broad maxima outside the d-band range are observed which are centered at 6.7 and 11.2 eV below the Fermi level  $E_F$ . These features are rather similar (although not identical in energy, which is presumably due to different work functions) to those reported for Fe(111) and (100) [2] and are identified with states derived from the  $3a_1$  and  $1e$  levels of free  $\text{NH}_3$ , respectively. In contrast to the findings with Fe(111) and (100) in the present case the emission maxima are not broadening further with time, suggesting that the surface species remains stable under these conditions. This effect was ascribed to the continuously progressing partial dissociation of adsorbed ammonia with the other planes even at temperatures as low as 160 K.

No evidence is found from photoemission data for such a process to occur with the system  $\text{NH}_3/\text{Fe}(110)$  at 175 K, indicating a higher thermal stability with this plane. Even after warming to 240 K and recooling to 175 K in an ammonia atmosphere the same spectrum is obtained (curve c). The spectrum also remains unaffected by evacuation at 175 K, indicating that no appreciable desorption takes place at this temperature. This process is however practically completed after heating to 240 K as can be seen from curve d. If the sample is further warmed to 310 K in a residual  $\text{NH}_3$  atmosphere very weak emission maxima at  $-2$ ,  $-5.2$  and  $-8.4$  eV are discernible (curve e) which indicate that in this temperature range (partial) decomposition of  $\text{NH}_3$  starts. The first maximum at  $\approx 2$  eV below  $E_F$  was also observed

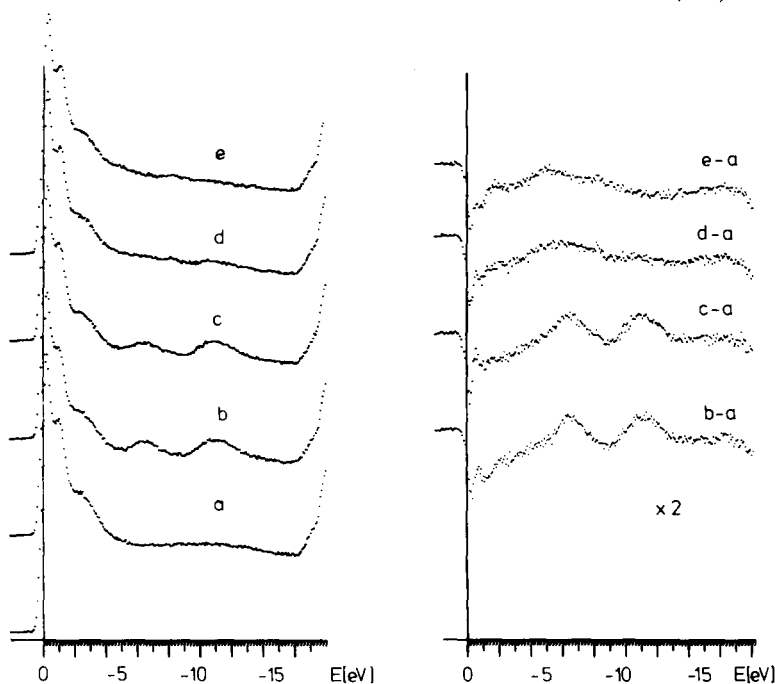


Fig. 1. Ultraviolet photoelectron spectra (left) and corresponding difference spectra (right) from a Fe(110) surface at different stages of interaction with  $\text{NH}_3$ . ( $h\nu = 40.8$  eV. The origin of the energy scale coincides with the Fermi level  $E_F$ .) Curve a: clean Fe(110) surface; b: after 4 L  $\text{NH}_3$  exposure at 175 K; c: after warming to 240 K and recooling to 175 K in an  $\text{NH}_3$  atmosphere; d: after warming to 240 K in vacuo; e: after warming to 310 K in an  $\text{NH}_3$  atmosphere.

with the other planes. Since it is located within the range of d-band emission where an interpretation is complicated it will not be considered in the further discussion.

The effects of  $\text{NH}_3$  dissociation become more clearly evident from fig. 2 which reproduces spectra recorded after interaction at higher temperatures. Curve a was obtained after interaction of  $2 \times 10^{-8}$  Torr  $\text{NH}_3$  at 340 K for 200 s (= 4 L) and shows two additional maxima at 5.2 and 8.4 eV below  $E_F$ . These peaks are relatively narrow which indicates that these features are arising from a single surface species and are not due to composite contributions (as was the case with Fe(100) and (111) under comparable conditions). This species remains stable and can also not be pumped off at this temperature which would be the case with molecularly adsorbed  $\text{NH}_3$ . It has to be identified with a partly dissociated molecule of the type  $\text{NH}_x$  ( $x = 1$  or 2), and the later discussion will demonstrate that there is in fact great evidence for the formation of  $\text{NH}_{\text{ad}}$ .

Complete dissociation takes place upon further heating the sample to 500 K. As can be seen from curve b the spectrum now contains a pronounced peak at  $-4.9$  eV

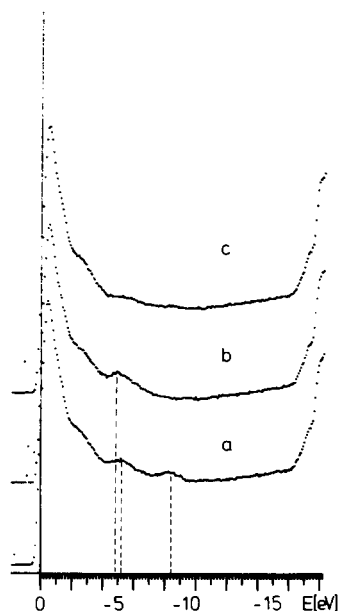


Fig. 2. Ultraviolet photoelectron spectra ( $h\nu = 40.8$  eV) from Fe(110). Curve a: after interaction of the clean surface with  $2 \times 10^{-8}$  Torr  $\text{NH}_3$  for 200 s at 340 K ( $\cong \text{NH}_{\text{ad}}$ ); b: after subsequent short heating to 500 K ( $\cong \text{N}_{\text{ad}}$ ); c: after subsequent heating to 950 K ( $\cong$  clean surface).

which is identified as with previous studies with  $\text{N}_{\text{ad}}$  [2,5]. It should be noted that adsorbed hydrogen atoms produced only a relatively weak maximum around 5–6 eV below  $E_{\text{F}}$  which is only discernible with He I-radiation ( $h\nu = 21.2$  eV), but not with He II as applied in the present measurements. In addition desorption of hydrogen will be completed at 500 K [10].

Curve c of fig. 2 was recorded after further increasing the temperature to 950 K and is identical with the spectrum of the clean Fe(110). At this temperature recombination of the adsorbed nitrogen atoms and desorption as  $\text{N}_2$  are completed [6].

If a clean Fe(110) surface is exposed to  $\text{NH}_3$  at 650 K only the spectrum characteristic for  $\text{N}_{\text{ad}}$  is observed, i.e. complete dissociation is so fast that the existence of an intermediate species is no longer discernible.

### 3.2. Auger electron spectroscopy

In the present context AES was mainly applied for an estimate of the nitrogen content of the surface. The relative N concentration was determined as in previous work through the peak height ratio  $y$  of the Auger signal from N at 380 eV to that of Fe at 650 eV. With Fe(100) adsorbed nitrogen atoms were observed to form a

c  $2 \times 2$ -LEED pattern which corresponds to  $\theta = 0.5$  or a surface density of  $n_N = 6 \times 10^{14} \text{ cm}^{-2}$ .

This concentration gave rise to  $y = 0.9$ . If no surface reconstruction occurs (as is the case with N/Fe(100) but also with  $\text{NH}_3$  adsorbed on Fe(110)) this correlation between  $n_s$  and  $y$  may reasonably well be applied for an estimate of the absolute N content of other systems.

With a Fe(110) surface saturated with adsorbed  $\text{NH}_3$  at 130 K  $y = 0.39$  was determined. It was checked with independent measurements that an electron beam will mainly cause dissociation of adsorbed  $\text{NH}_3$  molecules on the surface and only a minor amount of desorption of N-containing species, so that the N-concentration on the surface should not be markedly affected by electron bombardment. According to the just mentioned arguments  $y = 0.39$  correspond to a surface density  $n_N = 2.6 \times 10^{14} \text{ cm}^{-2}$ . Since the Fe(110) plane contains  $17 \times 10^{14}$  surface atoms per  $\text{cm}^2$ , this results in a saturation coverage with adsorbed  $\text{NH}_3$  molecules of  $\theta = 0.15$ . This number will be supported by the results of the LEED observations where a value  $\theta = 1/6$  was derived.

### 3.3. Thermal desorption

Fig. 3 shows a series of thermal desorption spectra for  $m/e = 17$  which were recorded with a heating rate of 9 K/s after different exposures of the Fe(110) surface to  $\text{NH}_3$  at 125 K. Calibration of the exposure was achieved by measuring the work function changes  $\Delta\phi$  prior to desorption which were then compared with corresponding  $\Delta\phi$ -values resulting from normal gas inlet into the vacuum system (i.e. not

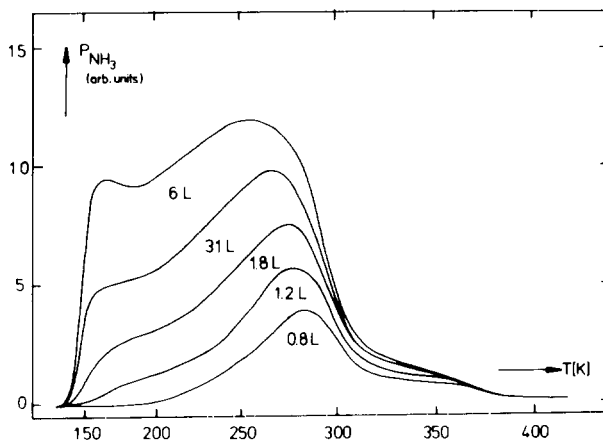


Fig. 3. Thermal desorption spectra for  $\text{NH}_3$  after exposing a clean Fe(110) surface to varying ammonia doses at 125 K. (Heating rate 9 K/s.)

through the capillary tube). In order to exclude possible contributions to the thermal desorption spectra from spurious amounts of H<sub>2</sub>O (which would also yield a signal at  $m/e = 17$  in the mass spectrometer) similar measurements were made for  $m/e = 16$  for which the contribution from NH<sub>3</sub> is (due to fragmentation in the ion source) of nearly the same magnitude as for  $m/e = 17$  whereas H<sub>2</sub>O would contribute very little to this mass. The spectra for  $m/e = 16$  look identical to those reproduced in fig. 3 so that interference by H<sub>2</sub>O desorption can be excluded.

The spectra show the formation of two desorption states,  $\beta_1$  and  $\beta_2$ , with peak temperatures at about 165 and 255 K. The  $\beta_2$ -peak shifts slightly to lower temperatures with increasing coverage which is ascribed to a slightly decreasing heat of adsorption, whereas the temperature of the  $\beta_1$ -state remains constant. It is suggested that desorption from both states follows first-order kinetics. By assuming a "normal" preexponential factor of  $10^{13} \text{ s}^{-1}$ , desorption energies of 10 and 17 kcal/mole for the  $\beta_1$ - and  $\beta_2$ -states, respectively, are estimated from the peak temperatures.

The areas below the thermal desorption traces are proportional to the corresponding NH<sub>3</sub> coverages and were evaluated in order to achieve a calibration of the respective  $\Delta\phi$ -values discussed in the next section. During heating an NH<sub>3</sub> covered surface, nearly complete desorption of this molecule and only negligible decomposition occurs. This becomes evident from AES measurements performed after desorption as well as from the UPS data described in section 3.1.

In order to elucidate possible isotope exchange processes which could be regarded as evidence for transient dissociation and recombination of the adsorbed ammonia molecules the following experiments were performed:

(i) A clean surface was first exposed at 130 K to 4.5 L D<sub>2</sub> ( $\theta_D = 0.3$  [10]) and then to 6 L NH<sub>3</sub>. Subsequently thermal desorption was performed whereby the mass spectrometer was set to  $m/e = 18$  (NH<sub>2</sub>D). However no formation of NH<sub>2</sub>D could be observed. The same result was obtained with a higher concentration of preadsorbed D ( $\theta_D = 0.65$ ). In both cases only NH<sub>3</sub> came off the surface.

(ii) The surface was first exposed to 3 L D<sub>2</sub> at 130 K and then again to 6 L NH<sub>3</sub>. Now thermal desorption of HD ( $m/e = 3$ ) was followed. The amount of HD was rather small and only about 10% of the amount observed if the surface was exposed to 3 L D<sub>2</sub> and 4 L H<sub>2</sub>. That HD is formed at all in the case of coadsorption of D<sub>2</sub> and NH<sub>3</sub> is due to the fact that during increasing the temperature the latter molecule dissociates to a small extent into  $N_{ad} + H_{ad}$  as becomes evident from application of the other techniques.

The above findings differ clearly from those made with Fe(111) where under similar conditions the formation of small amounts of NH<sub>2</sub>D and even of very small concentrations of NHD<sub>2</sub> could be detected [2]. This indicates that with Fe(110) the probability for partial dissociation and subsequent recombination of adsorbed ammonia is considerably smaller.

If the clean surface is exposed to NH<sub>3</sub> at 340 K and subsequently heated up no ammonia desorption ( $m/e = 17$ ) is observed. According to the UPS measurements under these conditions complete dissociation into  $NH_x + (3-x)H_{ad}$  takes place

which obviously do not recombine into  $\text{NH}_3$  upon further increasing the temperature. By contrast  $\text{NH}_x$  decomposes further into  $\text{N}_{\text{ad}} + x\text{H}_{\text{ad}}$ . From the UPS measurements it became evident that this latter process is completed at 500 K, at which temperature the recombination of  $2\text{H}_{\text{ad}}$  and desorption of  $\text{H}_2$  takes place. Thermal desorption spectra for  $\text{H}_2$  could therefore probably yield some information on the rate-limiting step of the two consecutive reactions for  $\text{H}_2$  evolution from dissociation of  $\text{NH}_x$  (i.e.  $\text{NH}_x \rightarrow \text{N}_{\text{ad}} + x\text{H}_{\text{ad}}$ ,  $2\text{H}_{\text{ad}} \rightarrow \text{H}_2$ ) and on the maximum surface concentration of this species. For this purpose a clean surface was at first saturated with adsorbed hydrogen at 140 K. From previous studies [10] it is known that this is equivalent to a surface concentration of  $1.7 \times 10^{15}$  H-atoms per  $\text{cm}^2$ . The corresponding thermal desorption spectrum is reproduced in fig. 4 by curve a. In the next experiment the surface was exposed to  $\text{NH}_3$  at 340 K until no further change of the work function ( $\Delta\varphi = -0.6$  eV) occurred which was considered to indicate saturation of the surface with  $\text{NH}_x + (3-x)\text{H}_{\text{ad}}$ . Curve b in fig. 4 shows the subsequently recorded thermal desorption spectrum for  $\text{H}_2$ . Curve c was recorded after a smaller  $\text{NH}_3$ -exposure, characterized by  $\Delta\varphi = -0.23$  eV. After desorption of  $\text{H}_2$  the remaining surface concentrations of  $\text{N}_{\text{ad}}$  were monitored by AES, yielding values of  $y = 0.25$  and  $0.13$  for the two runs, respectively.

It is remarkable that curves b and c exhibit only a single desorption maximum. The peak temperature is shifted to slightly higher temperature ( $\approx 10$  K) as if  $\text{H}_2$  desorbs from a clean Fe(110) surface, and the high-temperature decrease of  $p_{\text{H}_2}$  occurs somewhat steeper. The whole process of  $\text{H}_2$  evolution occurs according to the following steps

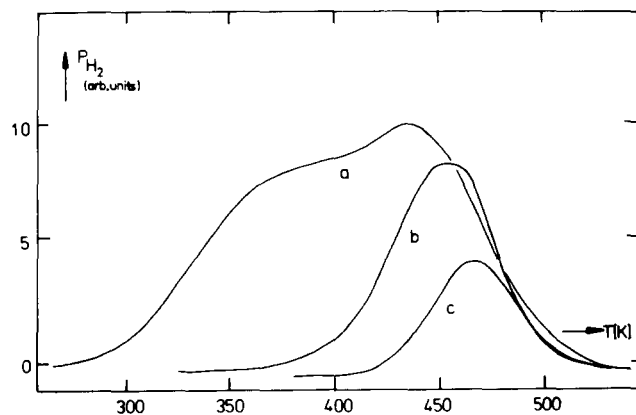


Fig. 4. Thermal desorption spectra for  $\text{H}_2$  from Fe(110). Curve a: after exposing a clean surface to  $\text{H}_2$  at 140 K up to saturation; b: after exposing a clean surface to  $\text{NH}_3$  at 340 K up to saturation, characterized by a work function change  $\Delta\varphi = -0.6$  eV; c: after exposing a clean surface to  $\text{NH}_3$  at 340 K up to  $\Delta\varphi = -0.23$  eV.



If step (3) would occur with a smaller rate than reaction (2), two maxima would be expected in the thermal desorption spectrum of  $\text{H}_2$ . The first one should practically coincide with that for  $\text{H}_2$  desorption from a clean Fe(110) plane (eventually slightly influenced by effects due to interactions between  $\text{H}_{\text{ad}}$  and the remaining  $\text{NH}_x$  species), and the second one should be determined by the activation energy of step (3) and should occur at a higher temperature. In fact such a behavior was not observed which indicates that dissociation of  $\text{NH}_x$  is faster than or comparable in rate with desorption of  $\text{H}_2$ . This conclusion will further be supported by results of work function measurements which indicate that dissociation of  $\text{NH}_x$  occurs in the temperature range of 400–450 K.

The area below curve b of fig. 4 is 37% of that from curve a. This corresponds to a concentration of  $6.3 \times 10^{14}$  H-atoms per  $\text{cm}^2$ . The corresponding N-concentration derived from  $y = 0.25$  is  $1.7 \times 10^{14}$   $\text{cm}^{-2}$  leading to a H : N ratio of 3.7 instead of 3. This result is quite satisfactory in view of the approximations underlying the quantitative analysis of the AES data. For curve b the resulting numbers are  $3.4 \times 10^{14}$  H-atoms/ $\text{cm}^2$  and  $0.9 \times 10^{14}$  N-atoms/ $\text{cm}^2$ . The peak temperature of curve b is slightly lower than that for curve a. This displacement is however too small to account for a simple second-order rate process which conclusion was confirmed by recording a whole series of thermal desorption spectra at various coverages. This is in contrast to hydrogen desorption from a clean Fe(110) surface where desorption follows second order kinetics [10] and indicates that in the present case the process is a composite one, i.e. that the steps  $\text{NH}_x \rightarrow \text{N}_{\text{ad}} + x\text{H}_{\text{ad}}$  (first-order) and  $2\text{H}_{\text{ad}} \rightarrow \text{H}_2$  (second-order) occur within the same temperature range.

From the  $\text{NH}_3$  exposure necessary for the formation of a certain  $\text{NH}_x$ -concentration at 340 K (as derived from the  $\text{H}_2$ -thermal desorption and N-Auger data) a rough estimate for the reaction probability for the step  $\text{NH}_3 \rightarrow \text{NH}_x + (3 - x)\text{H}_{\text{ad}}$  at this temperature was made, yielding a value of about  $0.2 \pm 0.1$ . This is of the same order of magnitude as the initial sticking coefficient for adsorption of  $\text{NH}_3$  at low temperatures as outlined in section 3.4.

Finally again some isotope exchange experiments were performed: A clean Fe(110) surface at 140 K was exposed to  $\text{H}_2$  and  $\text{D}_2$  in a way which caused about equal coverages of both atomic species,  $\theta_{\text{D}} \approx 0.30$ ,  $\theta_{\text{H}} \approx 0.25$ . The total coverage corresponds just to complete filling of the  $\beta_2$ -state [10]. Curve a of fig. 5 shows the resulting desorption spectrum for HD, i.e.  $m/e = 3$ , which is caused by complete isotopic equilibration within the adlayer. For the next experiment the surface was first

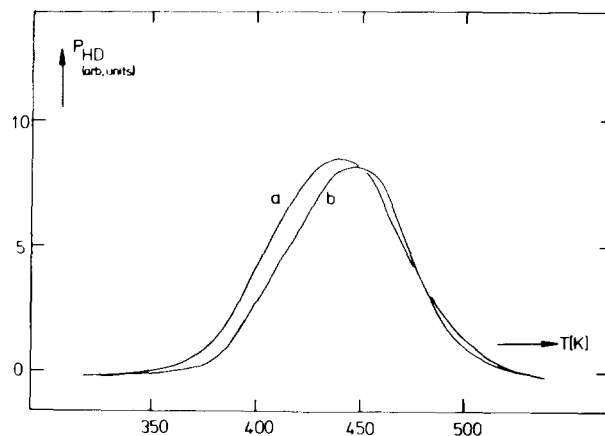


Fig. 5. Thermal desorption spectra for HD from Fe(110). Curve a: after exposing a clean surface at 140 K to H<sub>2</sub> and D<sub>2</sub> up to partial coverages  $\theta_H = 0.25$  and  $\theta_D = 0.30$ ; b: after exposing a clean surface at 140 K to D<sub>2</sub> up to  $\theta_D = 0.30$  and subsequent warming up to 340 K and exposure to NH<sub>3</sub>.

exposed to 3.5 L D<sub>2</sub> (yielding  $\theta_D \approx 0.3$ ) at 140 K and then warmed up to 340 K and exposed to NH<sub>3</sub>. The amount of H<sub>ad</sub> released from the latter was equal to  $\theta_H \approx 0.25$  as derived from the N-concentration built up on the surface. The resulting desorption spectrum for HD is reproduced by curve b of fig. 5 whose area is about 90% of that from curve a. This indicates that also in this case practically complete isotopic mixing occurs and excludes the possibility of direct H<sub>2</sub> formation through reactions of the type  $2 \text{NH}_{ad} \rightarrow 2 \text{N}_{ad} + \text{H}_2$  or  $\text{NH}_{2,ad} \rightarrow \text{N}_{ad} + \text{H}_2$ .

### 3.4. Work function changes

As can be seen from fig. 6, curve a, the work function of a Fe(110) surface decreases continuously with increasing NH<sub>3</sub> exposure at 120 K until after about 15 L a saturation value of  $\Delta\varphi = -2.4$  eV is reached. Calibration of  $\Delta\varphi$  against the adsorbed amount was achieved by comparing  $\Delta\varphi$ -values with the areas below the corresponding thermal desorption traces. As can be seen from fig. 7 a linear correlation between both quantities nearly up to saturation is found, i.e.  $\Delta\varphi \approx \theta$ . This result is somewhat surprising since in view of the high dipole moment of the adsorbate complex depolarization effects would have been expected. Since according to the analysis of the LEED and AES data the saturation coverage is  $\theta_{\text{max}} = 1/6$  the work function change can be used as a convenient means for monitoring the absolute NH<sub>3</sub> coverage, provided that the temperature (< 180 K) is low enough so that decomposition of ammonia can be excluded.

By converting  $\Delta\varphi$  into  $\theta$ -values and from curve a of fig. 6 the sticking coefficient of NH<sub>3</sub> at 120 K as a function of the coverage was evaluated. Fig. 8, curve a, shows a plot of the resulting data as a function of  $1 - \theta/\theta_{\text{max}}$ . The initial sticking coefficient

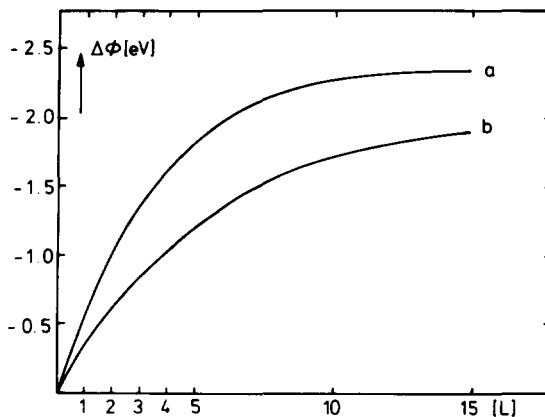


Fig. 6. Work function change,  $\Delta\phi$ , as a function of  $\text{NH}_3$  exposure at 120 K. Curve a: starting with a clean Fe(110) surface; b: starting with a surface partially precovered with  $N_{\text{ad}}(\gamma = 0.6)$ .

cient at  $\theta \rightarrow 0$  results to be  $s_0 = 0.16$ . The straight line indicates that the adsorption kinetics may be well described by a first-order Langmuir model.

If the temperature of a surface nearly saturated with adsorbed  $\text{NH}_3$  ( $\Delta\phi = -2.17$  eV) is continuously increased (0.5 K/s) the work function is also continuously rising as shown by fig. 9, curve a. Two processes may be distinguished. First the work function changes strongly between 140 and 340 K which according to the thermal desorption data is caused by desorption of  $\text{NH}_3$ . The arrow in fig. 9 indicates the temperature at which this process will be certainly finished. Due to the lower heating rate with the present experiments  $\Delta\phi$  exhibits a break already at about 280 K from where on this quantity remains practically constant up to 400 K. Within this tem-

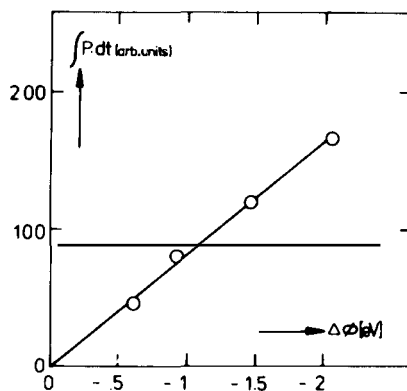


Fig. 7. Variation of the relative amount of adsorbed  $\text{NH}_3$  (as derived from the areas below the thermal desorption spectra  $\int p dt$ ) with the corresponding work function change  $\Delta\phi$ .

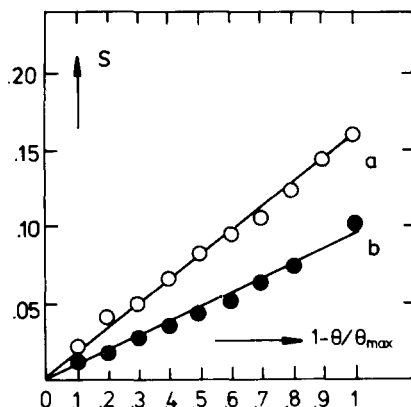


Fig. 8. Adsorption kinetics: Variation of the sticking coefficient for  $\text{NH}_3$  adsorption at 120 K with  $1 - \theta/\theta_{\max}$ . Curve a: initially clean surface; b: surface precovered with  $\text{N}_{\text{ad}}$  ( $\gamma = 0.6$ ).

perature range a small concentration of the reaction intermediate,  $\text{NH}_x$ , is stable on the surface and starts to decompose around 400 K. This latter process will be accompanied by desorption of  $\text{H}_2$  and is completed at about 450 K. A small amount of adsorbed N atoms remains on the surface, giving rise to a relative Auger signal  $\gamma = 0.05$  and to a work function which is nearly identical with that of the clean surface.

Curve b shows the result of a similar measurement with a smaller initial  $\text{NH}_3$ -coverage which is characterized by  $\Delta\varphi = -1.2$  eV. Desorption of  $\text{NH}_3$  starts now at a somewhat higher temperature which is in accordance with the TDS data. The pla-

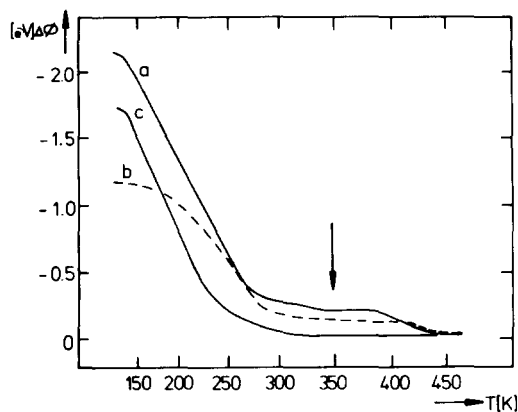


Fig. 9. Variation of the work function change,  $\Delta\varphi$ , with temperature upon continuously increasing the sample temperature (0.5 K/s). Curve a: clean surface almost saturated with adsorbed  $\text{NH}_3$  at 140 K ( $\Delta\varphi = -2.17$  eV); b: clean surface only partially covered with  $\text{NH}_{3,\text{ad}}$  ( $\Delta\varphi = -1.20$  eV); c: surface precovered with  $\text{N}_{\text{ad}}$  ( $\gamma = 0.6$ ,  $\Delta\varphi = -1.75$  eV).

teau exhibits a smaller work function change than before, indicating that now also the concentration of  $\text{NH}_x$  is lower. If a clean surface is exposed to  $2 \times 10^{-7}$  Torr  $\text{NH}_3$  at 345 K a stationary decrease of the work function by 0.70 eV is reached, which increases slightly to  $\Delta\phi = -0.65$  eV upon pumping off the  $\text{NH}_3$  atmosphere. This latter effect is ascribed to desorption of  $\text{NH}_3$  which will be present on the surface with a small concentration in a reversible adsorption–desorption equilibrium under these conditions of pressure and temperature. Since it is known from the other measurements that such a treatment will cause the exclusive formation of an  $\text{NH}_x$ -adlayer,  $\Delta\phi = -0.65$  eV is regarded as the work function change caused by this species present with its saturation concentration.

Fig. 10, curve a, shows the variation of  $\Delta\phi$  with time if a surface which is saturated with  $\text{NH}_x$  at 340 K ( $\Delta\phi = -0.65$  eV) is heated in vacuo within 40 s to a constant new temperature of 440 K. The work function increases rather rapidly and reaches after about 1 min nearly the value of the clean surface after which time it slightly decreases again by about 0.05 eV. At the end of this experiment the relative N-concentration of the surface was determined to be  $y = 0.22$ , the LEED pattern exhibited diffraction spots as observed previously after dissociative  $\text{N}_2$  chemisorption [6]. If the same experiment is performed in a  $\text{NH}_3$ -atmosphere of  $2 \times 10^{-7}$  Torr curve b of fig. 10 results. The work function increases again nearly to the value of the clean surface. Afterwards, however, it decreases to a considerably lower value than in the preceding experiment. After 90 min  $\Delta\phi = -0.15$  eV and  $y = 0.4$  were recorded.

The explanation is as follows: At 440 K  $\text{NH}_x$  dissociates and  $\text{H}_2$  is desorbing whereby the work function increases. The remaining atomic nitrogen causes a recon-

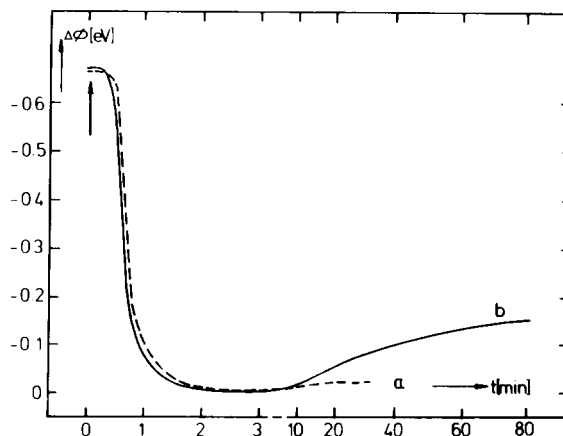


Fig. 10. Variation of the work function change,  $\Delta\phi$ , with time after increasing the temperature of a surface saturated with  $\text{NH}_{\text{ad}}$  from 340 K to 440 K within 40 s. Curve a: heating in vacuo; b: heating in an atmosphere of  $2 \times 10^{-7}$  Torr  $\text{NH}_3$ .

struction of the surface [6] which has a lower work function than the non-reconstructed plane. This transformation causes the slow decrease of  $\Delta\varphi$  beyond the maximum in curve a. With curve b the additional continuous decomposition of  $\text{NH}_3$  causes a still higher surface concentration of atomic nitrogen which enhances the surface reconstruction further and therefore a lower  $\Delta\varphi$  is reached in the end. Dissociative chemisorption of  $\text{N}_2$  itself causes a lowering of the work function by 0.16 eV at  $y = 0.6$ .

If once  $\text{NH}_3$  is dissociated at 340 K into  $\text{NH}_x + (3-x)\text{H}_{\text{ad}}$  this process cannot be reversed. If the sample is cooled down to 120 K  $\Delta\varphi$  remains constant at  $-0.65$  eV. If  $\text{NH}_{3,\text{ad}}$  had been formed the work function should be lowered further due to the high negative dipole moment of this adsorbate complex.

Some interaction between  $\text{NH}_x$  and  $\text{H}_{\text{ad}}$  could however be observed at 340 K. A surface precovered with  $\text{NH}_x$  ( $\Delta\varphi = -0.28$  eV) was exposed at this temperature to a  $\text{H}_2$  atmosphere of  $2 \times 10^{-4}$  Torr for 10 min. After evacuation the work function had slightly increased by 0.03 eV. Since hydrogen adsorption itself lowers the work function of Fe(110) [10] this effect can only be caused by partial removal of  $\text{NH}_x$  through the reaction  $\text{NH}_x + (3-x)\text{H}_{\text{ad}} \rightarrow \text{NH}_3$  ( $\text{NH}_3$  will desorb at this temperature). This qualitative observation gives some indication how the formation of ammonia may proceed via the reaction intermediate if the  $\text{H}_2$  partial pressure is high enough in order to shift the equilibrium into the other direction.

### 3.5. Low energy electron diffraction (LEED)

Interaction of  $\text{NH}_3$  with Fe(110) was observed to form ordered surface structures which is in contrast to the observations made with Fe(100) and Fe(111). If a clean Fe(110) surface is exposed to ammonia at 120 K weak additional features appear in the LEED pattern after 1 L and attain maximum intensity after about 15 L. According to the TDS and  $\Delta\varphi$ -measurements this exposure marks the saturation coverage. Even then the quality of the diffraction pattern is relatively poor (indicating imperfect order) so that only a schematic sketch is reproduced in fig. 11. The diffraction

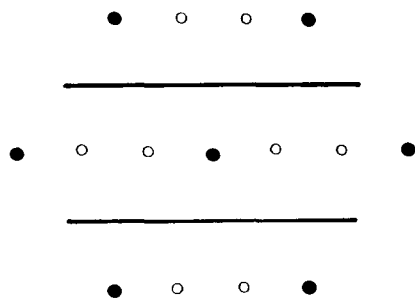


Fig. 11. Sketch of the LEED pattern observed after  $\text{NH}_3$  adsorption at 120 K. Dark circles: substrate lattice spots; open circles and streaks: features arising from the adsorbate overlayer.

pattern consists of third-order "extra" spots between the substrate spots in  $\langle 111 \rangle$ -direction and half-order streaks and can therefore be designed as " $2 \times 3$ "-structure. The formation of the streaks indicates partial disorder of the overlayer structure. Diffraction patterns of this type were first described and analyzed by Gerlach and Rhodin for the adsorption of alkali metals on Ni(110) [11]. A structure model will be presented in the discussion section. It is assumed that the "unit cell" of this partly disordered structure contains only *one* adsorbed  $\text{NH}_3$  molecule which is supported by the following arguments:

(i) The van der Waals-diameter ( $2.07 \text{ \AA}$ ) is rather large and therefore the presence of a second particle within the unit cell is rather unlikely. This will become evident from an inspection of the structure model shown in fig. 14.

(ii) The Auger data described in section 2.2 yield a saturation coverage of  $\theta = 0.15$ , which is in rather good agreement with the value of  $\theta_{\text{max}} = 1/6$  derived from the size of the adsorbate unit cell provided that the latter contains just one particle. That ammonia is in fact present on the surface in its undissociated form under these conditions is evident from the results of the other techniques, mainly from UPS. The LEED pattern from the adsorbed ammonia layer is relatively easily distorted by the influence of the electron beam causing a transformation into the pattern characteristic for the  $\text{NH}_x$  species which will now be described.

Longer exposure of a clean surface to  $\text{NH}_3$  at 340 K leads to the formation of a well-developed  $2 \times 2$ -structure in the LEED pattern as reproduced in fig. 12. This structure is obviously caused by the  $\text{NH}_x$  species which will be build up on the sur-

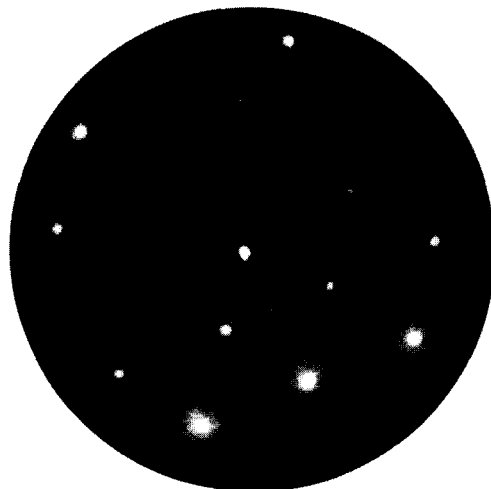


Fig. 12. LEED pattern from a  $2 \times 2$ -structure formed by the interaction of  $\text{NH}_3$  with Fe(110) at 340 K. ( $U = 70 \text{ eV}$ .)

face under these conditions, there are however several arguments against an interpretation in terms of a simple ordered overlayer:

(i) The formation of sharp "extra" spots was not directly correlated with the increase of the surface concentration of the  $\text{NH}_x$ -species but depended on the duration of annealing at 340 K. In fact maximum intensity was reached only after about 2 h which indicates the operation of a slow activated process at this temperature, whereas saturation with  $\text{NH}_x$  was reached after a few minutes. Surface diffusion of  $\text{NH}_x$  can hardly account for this effect.

(ii) A  $2 \times 2$ -overlayer needs at least a coverage  $\theta = 0.25$  (namely if the unit cell contains a single particle). The maximum coverage with  $\text{NH}_x$  as determined by AES and TDS was however only of the order  $\theta = 0.1$ . It is therefore suggested that the observed  $2 \times 2$ -pattern arises from a reconstruction of the surface which is initiated by the presence of  $\text{NH}_x$ . Surface reconstruction of Fe(110) occurs also with adsorbed N atoms, presumably assisted by the strong metal–nitrogen bond [6]. Since the strength of the Fe– $\text{NH}_{\text{ad}}$  bond is estimated to be of the order of 100 kcal/mole [2] a similar effect appears to be plausible in the present case, although a reasonable structure model may not yet be offered.

If the surface exhibiting the  $2 \times 2$ -LEED pattern is further heated to 400 K it transforms into the N–I-structure described previously [6]. This process proceeds parallel to the complete dissociation of  $\text{NH}_x$  and desorption of  $\text{H}_2$ . Further increase of the temperature to 500 K causes the appearance of diffraction spots from the N–II-structure [6]. The same sequence of patterns is observed if the clean surface is exposed to  $\text{NH}_3$  at  $T > 400$  K. Heating to 950 K leads to the desorption of  $\text{N}_2$  and the LEED pattern of the clean, unreconstructed Fe(110) plane is restored.

### 3.6. Experiments with a surface precovered by atomic nitrogen

Since it cannot be excluded a priori that the catalytic synthesis of ammonia proceeds under steady-state conditions on Fe surfaces exhibiting an appreciable concentration of chemisorbed nitrogen a series of experiments with N-precovered surfaces was performed. For this purpose the sample was first exposed to  $\text{NH}_3$  at 400 K until the desired concentration of N atoms (as monitored by AES) was built up. The latter show up in the photoemission spectrum as a peak at  $-4.9$  eV (see section 3.1). Upon additional exposure to  $\text{NH}_3$  at 190 K new maxima, centered at  $-7.1$  and  $-11.3$  eV, appear which have to be ascribed to molecularly adsorbed ammonia. These additional features disappear completely upon warming to 300 K due to desorption of  $\text{NH}_3$ . The UPS difference spectrum shows clearly that the surface concentration of  $\text{N}_{\text{ad}}$  did not further increase during this procedure. This indicates that preadsorbed nitrogen inhibits the dissociation of adsorbed ammonia in a similar manner as observed previously with Fe(100) and Fe(111) [2].

Fig. 13a–c show different series of thermal desorption spectra for  $\text{NH}_3$  which was adsorbed at 125 K on surfaces precovered with various amounts of atomic nitrogen (as characterized by the AES  $\gamma$ -values). In fig. 13a three desorption states,

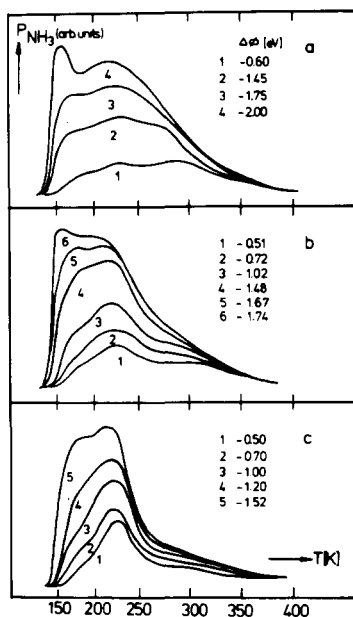


Fig. 13. Thermal desorption spectra for  $\text{NH}_3$  after exposing Fe(110) surfaces with varying concentrations of preadsorbed nitrogen to ammonia at 125 K. (a)  $y = 0.45$ ; (b)  $y = 0.55$ ; (c)  $y = 0.65$ .

$\beta'_1$ ,  $\beta'_2$  and  $\beta'_3$  are discernible. The population of the latter decreases with increasing N-concentration as can be seen from fig. 13b and 13c. This observation together with the fact that the peak temperature of the  $\beta'_3$ -state nearly coincides with that of the  $\beta_2$ -state of the clean surface (see fig. 3) suggests that this state arises from  $\text{NH}_3$  molecules which are adsorbed on the still bare and unreconstructed parts of the surface. Similar arguments presumably apply for the  $\beta'_1$ -state which coincides with the  $\beta_1$ -state of the clean surface.

The  $\beta'_2$ -state on the other hand is identified with adsorption on sites which are formed by the reconstructed "surface nitride" phase. Its desorption energy is estimated to be around 13 kcal/mole. The work function change revealed again to be proportional to the total amount of adsorbed  $\text{NH}_3$  and can therefore serve as a measure for this quantity. Subsequent exposure to  $\text{D}_2$  and  $\text{NH}_3$  at 130 K did not lead to any measurably  $\text{NH}_2\text{D}$  evolution during thermal desorption. There is therefore no indication for intermediate dissociation and recombination of adsorbed ammonia, in agreement with the findings with the clean surface.

Curve c of fig. 9 shows the variation of the work function with temperature if a N-precovered surface ( $y = 0.6$ ) was initially exposed to  $\text{NH}_3$  at 140 K. In contrast to the findings with the clean surface  $\Delta\phi$  reaches its initial value at 300 K indicating complete desorption of  $\text{NH}_3$  without any intermediate dissociation.

Curve b of fig. 6 shows the variation of the work function with  $\text{NH}_3$  exposure at 120 K if the experiment is started with a surface precovered by nitrogen ( $\nu = 0.6$ ). The maximum variation is  $\Delta\varphi = -1.9$  eV. If it is assumed that the dipole moment of adsorbed  $\text{NH}_3$  is unaffected by the presence of preadsorbed nitrogen (which is supported by the proportionality between  $\Delta\varphi$  and  $\text{NH}_3$  coverage) then this result means that the adsorbed amount is somewhat smaller than on a clean surface. Analysis of fig. 6, curve b, then yields an initial sticking coefficient  $s_0 = 0.10$  which is markedly smaller than with the clean surface. A plot of  $s$  versus  $(1 - \theta/\theta_{\text{max}})$  yields again a straight line as shown by curve b of fig. 8.

## 4. Discussion

### 4.1. Adsorption of $\text{NH}_3$

$\text{NH}_3$  is molecularly adsorbed on a clean Fe(110) surface at low temperatures in a manner similar to that reported for the (100) and (111) planes [2]. Gaseous  $\text{NH}_3$  exhibits a photoelectron spectrum with two bands centred at  $-11$  eV and  $-17$  eV with respect to the vacuum level which are identified with  $3a_1$  (= N lone pair) and  $1e$  (= N–H bond) levels, respectively [12].

If the work function of clean Fe ( $\approx 5$  eV) is taken into account these maxima will be located at about  $-6$  and  $-12$  eV on an energy scale which refers to the Fermi level of iron. The peak observed with adsorbed  $\text{NH}_3$  at  $-11.2$  eV arises clearly from ionisation of the N–H bonds ( $1e$  levels) which are believed to be only slightly influenced by the formation of the chemisorption bond. The “relaxation shift” is – in contrast to other adsorption systems – rather small which is ascribed to the fact that in the present case the adsorbate complex exhibits a rather high negative dipole moment [13]. The second peak observed with adsorbed  $\text{NH}_3$  is located at  $-6.7$  eV and arises from a chemisorption state derived from coupling the lone electron pair at the N-atom ( $3a_1$  level) to the metal. The separation between both maxima is only 4.5 eV in the adsorbed state as compared with 6 eV with gaseous  $\text{NH}_3$  molecules. A similar effect was already observed with the other Fe planes and is ascribed (at least in part) to the lowering of the  $3a_1$ -level due to formation of the chemisorption bond.

The adsorbed ammonia layer forms a partly disordered structure of a type as first described by Gerlach and Rhodin [11] for the case of alkali metal adsorption on Ni(110). Following the analysis presented by the authors a structure model is proposed as shown in fig. 14. This model takes account of the arguments given in sections 3.2 and 3.5 whereafter the maximum  $\text{NH}_3$  coverage as estimated from AES data as well as the effective area occupied by an  $\text{NH}_3$  molecule allow only for a single adsorbed particle within the overlayer unit cell.

As can be seen from fig. 14 the  $\text{NH}_3$  molecules are located within every third row formed by the  $\langle 111 \rangle$ -direction whereby every second site is occupied. The interaction between neighboring rows of  $\text{NH}_3$  molecules is too weak so that these are shifted

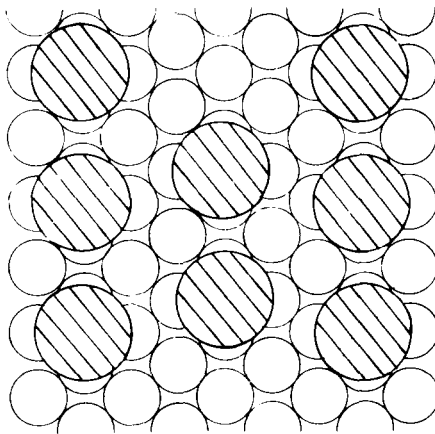


Fig. 14. Structure model for  $\text{NH}_3$  (large hatched circles) adsorbed on a Fe(110) surface (small open circles).

randomly with respect to each other giving rise to the streaks in the diffraction pattern. The total coverage of such an arrangement is  $\theta = 1/6$ , corresponding to a density of adparticles  $n_s = 2.9 \times 10^{14} \text{ cm}^{-2}$  which is in agreement with the estimate derived from the AES data. The exact geometry of the adsorption sites can of course only be obtained from a dynamical analysis of the LEED data. Since, however, with many other adsorption systems highly coordinated sites are occupied such an assumption appears also to be justified in the present case.

The initial adsorption energy is estimated from the  $\beta_2$ -peak of the thermal desorption spectra to be about 17 kcal/mole, indicating weak chemisorption whose order of magnitude can be qualitatively accounted for by coupling of the N lone electron pair of  $\text{NH}_3$  to the metal. It is assumed that the rather large dipole moment of the adsorbate causes in addition an appreciable electrostatic contribution to the bond energy. With increasing coverage the adsorption energy decreases as becomes evident by the formation of the  $\beta_1$ -state in the thermal desorption spectrum with an effective adsorption energy of about 10 kcal/mole. This effect is ascribed to repulsive interactions between neighboring  $\text{NH}_3$  molecules. Since both states strongly overlap in the TDS traces a determination of their relative populations becomes questionable and therefore any more detailed conclusions on the nature of these interactions remain speculative. An estimate of the dipole-dipole forces on the basis of the proposed structure model and of the measured work function change reveals that this effect cannot account for the full amount of the repulsive energy. Instead it has to be assumed that in addition indirect interactions (via the metal's valence electrons) come into play, although such an effect does not reflect itself in the UPS and  $\Delta\phi$ -data.

From the data presented by fig. 8 it follows the kinetics of adsorption follows a rather simple law: The rate of adsorption varies proportional to  $1 - \theta/\theta_{\max}$  and obeys therefore first-order kinetics within a simple Langmuir-type model. That means, there is no need for assuming the existence of a weakly held precursor state, but if a  $\text{NH}_3$  molecule strikes from the gas phase a free adsorption site it will be adsorbed with a probability equal to the initial sticking coefficient ( $s_0 = 0.16$ ), otherwise it is reflected. Within such a model it appears also quite reasonable why  $s_0$  is not equal to unity since obviously only a limited range of all possible orientations of the impinging  $\text{NH}_3$  molecules will lead to a collision with the surface which enables the formation of the chemisorption bond during the time of interaction.

It was found that the work function of Fe(110) decreases linearly with  $\text{NH}_3$  coverage until at saturation ( $n_s = 2.9 \times 10^{14} \text{ cm}^{-2}$ )  $\Delta\varphi = 2.4 \text{ eV}$  is reached. From these data the dipole moment of the adsorbate complex,  $\mu_s$ , is easily derived through

$$\mu_s = \epsilon_0 \Delta\varphi / n_s ,$$

where  $\epsilon_0 = 8.85 \times 10^{-14} \text{ A} \cdot \text{s}/\text{V} \cdot \text{cm}$  (note that  $1 \text{ A} \cdot \text{s} \cdot \text{cm} = 3 \times 10^{27} \text{ Debye}$ ). It results that  $\mu_s = 2.2 \text{ Debye}$ , which is even larger than the dipole moment of the free  $\text{NH}_3$  molecule ( $\mu = 1.47 \text{ Debye}$  [14]).

This result supports the proposed mechanism of the chemisorption bond, whereafter through coupling of the nitrogen atom to the metal electronic charge is transferred from the N lone electron pair to the metal (in a similar manner as with CO chemisorption) thus increasing the effective dipole moment of the adsorbate.

#### 4.2. Surface intermediates

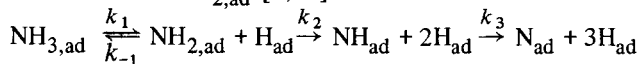
As was observed with Fe(111) and (100) [2] and also in the present case,  $\text{NH}_3$  decomposes completely at elevated temperatures and leads to the formation of  $\text{N}_2$  and  $\text{H}_2$ . These species come off the surface at practically the same temperatures at which they desorb if the surface was previously exposed to these compounds [6,10] so that not the decomposition of  $\text{NH}_3$  or its  $\text{NH}_x$ -fragments but recombination of the atoms is suggested as being the rate-limiting steps. As will be discussed below, this statement is however not completely correct for the hydrogen evolution.

$\text{N}_{\text{ad}}$  is the only species existing on the surface above 500 K since all H-containing compounds ( $\text{H}_2$  and  $\text{NH}_3$ ) desorb below this temperature. Atomically adsorbed nitrogen is easily identified from the UPS data which exhibit at this stage a single peak outside the d-band region at 4.9 eV below  $E_{\text{F}}$  which is in accordance with previous studies [2,6] identified with chemisorption levels derived from coupling the N2p-states to the metal. In addition, the LEED and  $\Delta\varphi$ -data are completely consistent with this conclusion.

Interestingly, a well-defined other surface intermediate may be formed and identified during the decomposition of  $\text{NH}_3$  on the surface. Under properly chosen conditions (i.e. exposure to gaseous  $\text{NH}_3$  at 340 K) obviously reaction step (1) as formulated in section 3.3 namely  $\text{NH}_{3,\text{ad}} \rightarrow \text{NH}_{x,\text{ad}} + (3-x)\text{H}_{\text{ad}}$ , is completed whereas

the consecutive steps of further decomposition and desorption are still too slow, so that such a mixed overlayer is build up. Unfortunately recombination of the split of H-atoms to  $H_2$  and further decomposition of the  $NH_x$ -species take place at quite similar temperatures, so that the  $H_2$ -desorption spectrum exhibits only a single peak. If the dissociation of  $NH_x$  would have been the slower step the  $H_2$  desorption spectrum would exhibit two peaks from whose relative populations the stoichiometry of the  $NH_x$ -species could easily be derived. Since this is not the case other arguments are needed for its identification and characterization which are partly based on a comparison with the findings obtained with other Fe planes: Intermediate stages during the dissociation of  $NH_3$  were also observed with Fe(111) and (100), although in these cases a complete isolation was never possible but only a superposition of features arising from different species. Partial dissociation of  $NH_3$  lead to the appearance of an additional maximum at about 9.5 eV below  $E_F$  in the photoelectron spectrum [2].

Quite similar observations were recently made by Grunze [15] during the interaction of  $N_2H_4$  with Fe(111). Arguments were presented that this species is to be identified with  $NH_{2,ad}$  [2,15] which means that in the reaction sequence



$k_1 > k_2$  and  $k_3 > k_2$ , i.e.  $NH_{2,ad}$  will accumulate on the surface (at properly chosen temperatures), whereas once  $NH_{ad}$  is formed it rapidly decomposes further. In addition it was observed that  $NH_{2,ad}$  could recombine with adsorbed hydrogen (or deuterium) atoms giving rise to a  $\beta_3$ -state in the desorption spectrum of ammonia at about 350 K. That means that the reaction steps  $k_2$  and  $k_{-1}$  exhibit comparable rates. The behaviour of Fe(110) is qualitatively different: The thermal desorption spectra for  $NH_3$  exhibit only a very slight indication for a  $\beta_3$ -state desorbing above room temperature. Consequently also no evidence for an H/D-isotope exchange with the desorbing ammonia was found. This result suggests that  $k_{-1}$ , is so slow that no H/D-exchange with ammonia is observed. This conclusion means that with Fe(110) the species  $NH_{ad}$  is built up on the surface for which additional support is given from the following points:

(i) The UPS spectrum of this species is characterized by two peaks at 5.2 and 8.4 eV below  $E_F$  whose small half-width indicates that in fact only a single species (apart from  $H_{ad}$  whose UPS intensity at  $\approx 5$  eV is rather low) is present on the surface. With Fe(100) and (111) the transient species ( $NH_{2,ad}$ ) exhibited maxima at 6 and 9.5 eV. Even if one takes into account that with Fe(110) also the  $NH_3$ -induced peaks are located closer to the Fermi level by 0.6 eV (which is ascribed to the higher work function of this plane) there still remains a difference of 0.5 eV between the 9.5 eV peak on Fe(111) and that at 8.4 eV on Fe(110), indicating that these features belong in fact to different species. As outlined previously [2] photoelectron spectra from free  $NH_2$  and  $NH$  radicals are not available. One can think of a comparison with spectra of  $N_2H_4$  and  $N_2H_2$  but the spectra of these compounds are relatively similar [16,17] so that no decision on the basis of the "fingerprint" approach may be

made. In addition, Grunze [15] has recently demonstrated that the photoelectron spectrum of hydrazine adsorbed on  $N_2H_4$  differs appreciably from those of its dissociation products.

(ii) Current studies on the system  $NH_3/Fe(110)$  by means of secondary ion mass spectroscopy (SIMS) [18] revealed the predominant release of the  $NH_3^+$ -ion if the sample was exposed to  $NH_3$  at 130 K. This observation is in agreement with the present findings whereafter under these conditions ammonia is non-dissociatively adsorbed. If the same experiment is performed above room temperature the predominant species recorded is  $NH^+$  which is identified with the species  $NH_x$  discussed in the present study. Even if the possible complications connected with the interpretation of SIMS data are taken into account this result seems to clearly indicate that the surface intermediate under discussion is in fact adsorbed NH.

It is interesting to note that Melton and Emmett [19] observed the transient occurrence of N and NH in the gas phase if an iron filament was suddenly flashed in an  $NH_3$  atmosphere from 350 to 1270 K which points towards the existence of the same surface species as concluded from the present work.

The transient  $\Delta\phi$ -measurements reproduced in figs. 9 and 10 indicate that  $NH_{ad}$  dissociates on the surface around 400 K at which temperature also recombination and desorption of hydrogen starts. This is the reason why the thermal spectra for  $H_2$  exhibit only a single (predominantly desorption limited) maximum (fig. 5). The dissociation energy of free NH is about 75 kcal/mole [14], but the activation energy for this process in the adsorbed state is certainly markedly smaller due to the energy gained by the formation of  $M-N_{ad}$  and  $M-H_{ad}$  bonds as discussed previously [2]. The complete isotopic equilibration of the hydrogen coming off the surface clearly demonstrates that no intramolecular formation of  $H_2$  from either  $NH_{3,ad}$  or  $NH_{2,ad}$  is taking place but that instead the H-atoms are first split-off individually to form  $H_{ad}$ -species.

Although  $NH_{ad}(+H_{ad})$  causes the formation of LEED "extra" spots no structural model can be offered since, from the arguments presented in section 3.5, the surface is believed to be reconstructed under these conditions. For the same reason no basis for a discussion of the associated work function change in terms of the dipole moment of the adsorbate complex is seen. All that can be said is that the sign of  $\Delta\phi$  is in the expected direction.

### Acknowledgement

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