JOURNAL OF CATALYSIS 50, 519–529 (1977)

Interaction of Nitrogen with Iron Surfaces

II. Fe(110)[1]

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Received April 18, 1977; revised August 26, 1977

Previous work on the interaction of N_2 with Fe(100) and (111) single-crystal planes was extended to the most densely packed (110) face. The dissociative chemisorption proceeds even slower than with the two other planes and is associated with an activation energy of about 7 kcal/mole at low coverages. At 683 K the initial rates of adsorption have a ratio of about 60:3:1 for Fe(111):(100):(110). The activation energy for desorption is estimated to be about 56 kcal/mole and is thus slightly smaller than on Fe(100)(58 kcal/mole), but higher than on Fe(111) (51 kcal/mole). The formation of two ordered surface structures (I and II) was observed. Their unit cell vectors b_1, b_2 are related with the (unreconstructed) substrate lattice vectors a_1, a_2 through: $b_1 = 3a_1$, $b_2 = 2a_2$ (I) (which may also be designated as 2×3 structure), and $b_1 = 4a_1$, $b_2 = a_1 + 3a_2$ (II). Both phases appear with two equivalent domain orientations with the mirror plane along the [001] direction. Structure I appears at lower surface concentrations than structure II; however their kinetics of formation is also influenced by the concentration of dissolved nitrogen. It is most probably that these large unit cells reflect the reconstruction of the topmost layer of Fe atoms [as in the case of the (111) plane]. For both surface structures quasihexagonal arrangements of Fe atoms may be constructed the nearest-neighbor distances for which agree to within ±3% with those in the (111) plane of fcc Fe_4N. Thus the concept of the formation of "surface nitrides" is further supported. Dissolution of nitrogen atoms in the bulk again interferes with the surface processes.

1. INTRODUCTION

A preceding paper (*1*) was concerned with a detailed study of the interaction of N_2 with clean Fe(100) and (111) single-crystal surfaces using a whole variety of experimental techniques such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), thermal desorption spectroscopy (TDS), and work-function measurements. One of the main conclusions was that dissociative chemisorption causes reconstruction of the (111) plane whereas with Fe(100) a simple c2 × 2-overlayer structure was formed. This work was extended to the (110) (most densely packed) surface. It will be shown that the results fit well into the general scheme as developed for the other planes. In particular, surface reconstruction is suggested on the basis of LEED observations which support the idea of the formation of "surface nitrides" related to bulk Fe_4N.

2. EXPERIMENTAL

The experimental equipment, sample preparation and cleaning procedure, and performance of the experiments were identical to those applied in the previous work (*1, 2*). No UPS measurements were performed since the primary features of the present system are similar to those obtained with the other two planes. Since the rate of

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ISSN 0021-9517

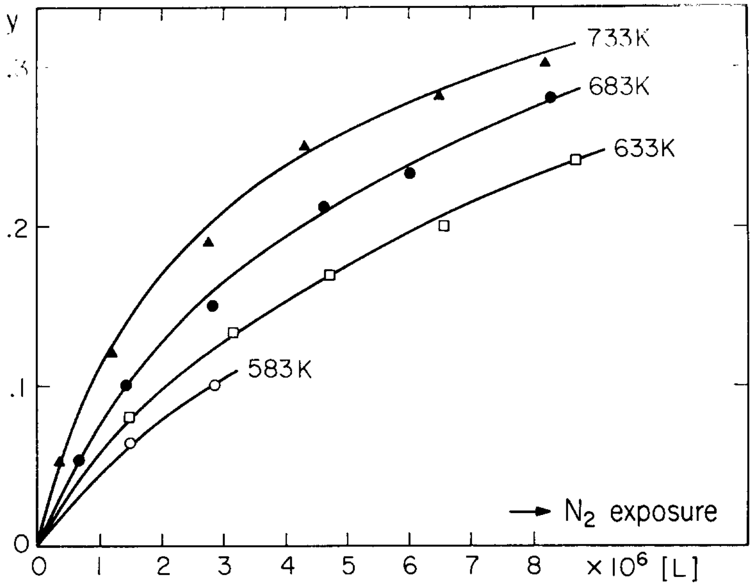

FIG. 1. Nitrogen chemisorption on Fe(110) at different temperatures as followed by recording the N:Fe Auger peak-height ratio y as a function of N_2 exposure.

chemisorption was even smaller than with Fe(100) and higher surface temperatures had to be applied, keeping the surface free from impurities became an even more serious problem than in the preceding study.

3. RESULTS

3.1. *Auger Electron Spectroscopy*

Auger electron spectroscopy was used to follow the rate of nitrogen uptake. The ratio y of the Auger signal height at 380 eV (N) to that at 650 eV (Fe) served as a relative measure of the concentration in the surface region. As with the other planes, it was observed that dissolution of nitrogen atoms in the bulk and segregation from the bulk to the surface interferes with the process at the solid/gas interface. A similar pretreatment was therefore applied in order to obtain reproducible and comparable results: After prolonged interaction of the sample with N_2 at elevated temperatures adsorbed nitrogen was removed from the surface by brief argon ion sputtering and subsequent annealing at 650 K. The clean surface was then exposed to 4×10^{-4} Torr of N_2 for increasing times at various temperatures and the rate of chemisorption was monitored by recording Auger spectra after evacuation of the vacuum system.

It turned out that Fe(110) was the least reactive plane among the three surfaces studied and therefore even higher sample temperatures were necessary than with Fe(100). This fact increased the danger of surface contamination by segregation of bulk impurities. Since desorption starts above 750 K it was not reasonable to work beyond that temperature. Figure 1 shows the variation of y with exposure at different temperatures, demonstrating that under these conditions ($\leq 10^7$ L[3]) we were still far from saturation of the surface. Ths highest y value was about 0.6 and wae reached after a 3×10^7-L exposure around 700 K. Above this temperature bulk diffusion and the onset of desorption became important factors so that after a 3×10^7-L exposure even smaller y values were observed. An Auger ratio of $y = 0.6$

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[3] 1 L = 10^{-6} Torr × sec.

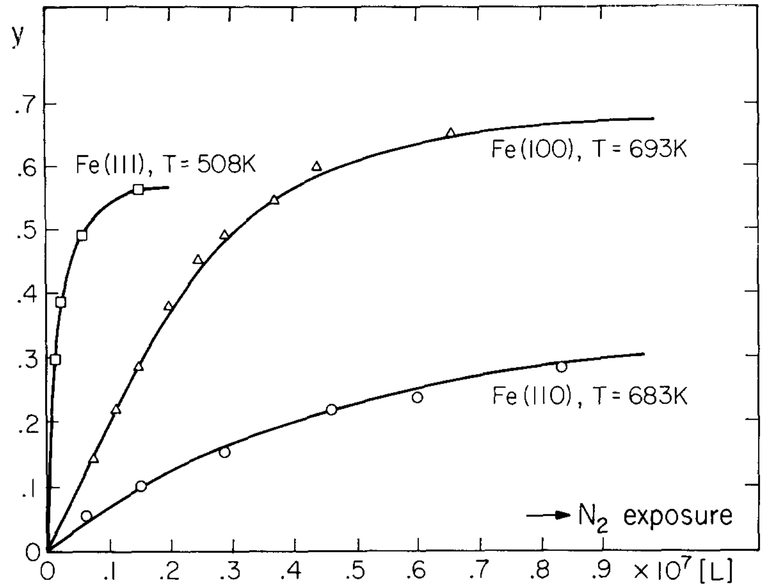

FIG. 2. Variation of the relative nitrogen surface concentration y with N_2 exposure on Fe(110), (100), and (111) planes. [With Fe(111) no data for higher temperatures are available.]

is comparable in magnitude with the saturation values obtained with the other planes. From the temperature dependence of the rate of adsorption an activation energy at low coverages of $E^*_{ad} = 7$ kcal/mole was derived. It is probable that this number increases at higher coverages as with the other planes, but in the present case insufficient experimental data were available for an evaluation. However, it seems that E^*_{ad} remains essentially constant up to $y = 0.25$, in contrast to the behavior of the (100) and (111) surfaces where the activation energy increases with coverage even for rather low surface concentrations.

A comparison of the rates of adsorption on the three planes is made in Fig. 2. Measurements with Fe(111) were only performed up to 508 K. However, since in this case the initial rate of adsorption is practically independent of temperature we concluded that the initial slope of this curve should be essentially the same even at a higher temperature of about 690 K. The initial rates of adsorption at this temperature have a ratio of about 60:3:1 for (111):(100):(110). At lower temperatures, this difference would of course become even more pronounced.

Besides the high-energy Auger transitions in the 650-eV region Fe also exhibits a peak at 46 eV ($M_{2,3}VV$) which [due to the energy dependence of the escape depth of slow electrons (*3*)] is more surface sensitive. It was observed that the intensity of this peak decreased by up to 30% with increasing nitrogen coverage, whereas that of the 650-eV transition remained essentially unchanged. This observation is considered to support the surface reconstruction model as discussed later.

3.2 Thermal Desorption

The maximum of the N_2 thermal desorption spectra from the surface layer is about 60 K higher than with Fe(111) and about 20 K lower than with Fe(100). As a consequence there is some interference with contributions originating from the bulk as in the case of the (100) plane, whereas with Fe(111), due to the lower desorption temperature of the surface species, these two

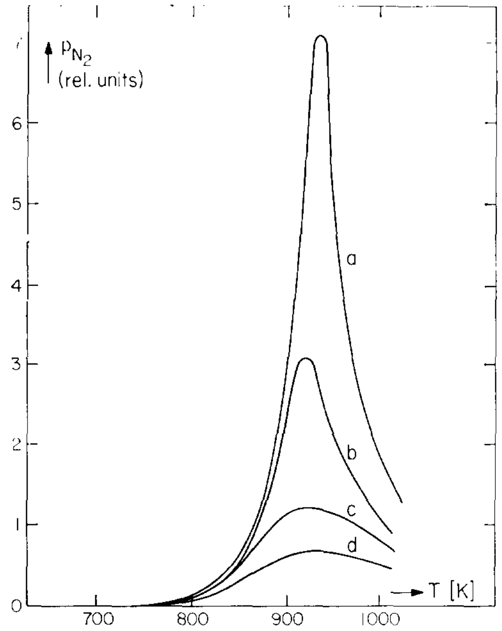

FIG. 3. Series of N_2 desorption spectra ($m/e = 30$) from a ^{15}N-covered Fe(110) surface. (a) $y = 0.48$; (b) $y = 0.35$; (c) $y = 0.21$; (d) $y = 0.13$.

contributions are well separated within the thermal desorption spectra.

In order to separate widely these effects from each other the following procedure was applied.

The surface was cleaned by Ar$^+$ ion bombardment and annealing at 630 K and subsequently was exposed to 8×10^{-4} Torr of $^{30}N_2$ at 670 K for various periods of time. The resulting surface concentrations were monitored by AES. Using this treatment the exchange reaction between bulk and surface could be largely suppressed so that $^{30}N_2$ desorption spectra reflect primarily the decomposition of the surface layer. A series of these spectra is reproduced in Fig. 3. These traces are characterized by a relatively narrow width at higher surface concentrations (~70 K) and exhibit peak maxima which occur at essentially constant temperature. It was further estimated that the contribution from "bulk" nitrogen to the high-temperature parts of these curves is, at most, in the order of about 5% of the totally desorbing amount.

Figure 4 is a plot of the relative amount m of N_2 desorbing from the surface region as derived from the areas below the thermal desorption traces, $m = \int p dt$, as a function of the Auger peak-height ratio y. The result is quite similar to that found with Fe(111). The ratio y/m does not remain constant but decreases with increasing concentration which is further evidence of the occurrence of surface reconstruction.

The combined use of $^{28}N_2$ and $^{30}N_2$ was further used to confirm the atomic nature of the surface species as well as to establish the occurrence of the exchange process: $N_{\mathrm{surf.}} \rightleftharpoons N_{\mathrm{bulk}}$. Exposing a clean surface at 680 K to a 1:1 mixture of $^{28}N_2$ and $^{30}N_2$ leads to the subsequent desorption of $^{29}N_2$. Analysis of the mass balance revealed that complete isotopic equilibration had occurred on the surface, as was also observed with the other planes.

If a freshly sputtered surface is exposed to $^{30}N_2$ after a brief annealing (leading to $y = 0.5$) subsequently recorded desorption spectra show the desorption of $^{29}N_2$ (Fig. 5 curve a). That means that a part of the ^{15}N from the surface region had been exchanged with the ^{14}N which had been

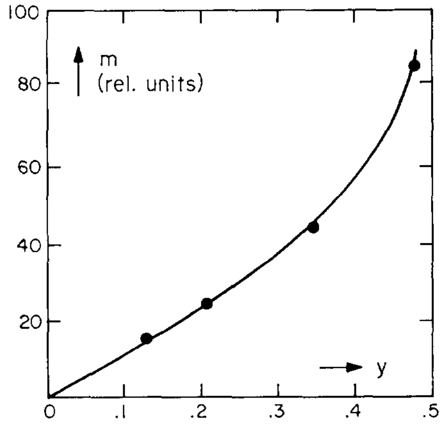

FIG. 4. Variation of the relative amount m of desorbing N_2 (as determined by $m = \int p dt$ from the thermal desorption spectra) with the N:Fe Auger peak-height ratio y.

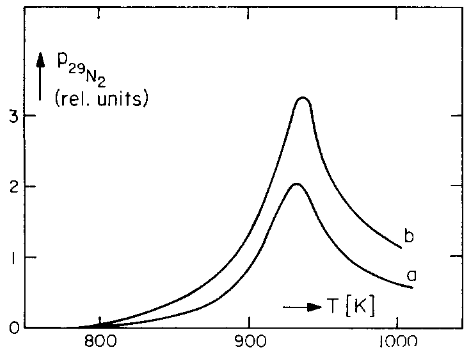

FIG. 5. $^{29}N_2$ desorption spectra demonstrating the occurrence of exchange between surface and bulk nitrogen. (For explanation see text.)

stored in the bulk. In a further experiment the ^{14}N concentration of the bulk was first increased by exposing the sample at 680 K for 36 h to 8×10^{-4} Torr of $^{28}N_2$. Subsequently, the surface was cleaned and exposed to $^{30}N_2$ as above (i.e., again to $y = 0.5$). Thermal desorption of $^{29}N_2$ (curve b in Fig. 5) after this treatment showed an appreciably larger amount of this species desorbing from the surface, as expected.

3.3 Low-Energy Electron Diffraction

A series of LEED patterns corresponding to various nitrogen surface concentrations is reproduced in Fig. 6. At a first glance these patterns appear to be rather complex, but a detailed inspection reveals the formation of two different long-range periodicities: (a) Structure I is formed first (Fig. 6a,b) and can be designed as a 2×3 struc-

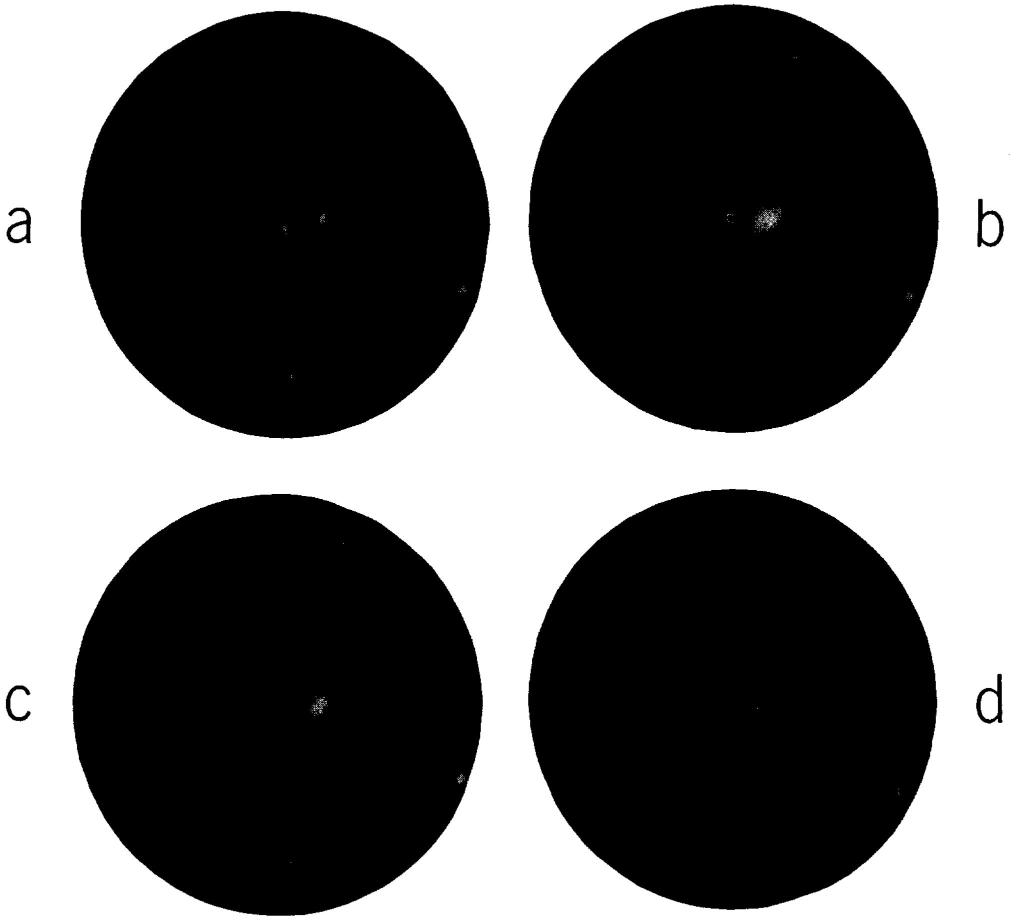

FIG. 6. LEED patterns from Fe(110) after interaction with N_2. (a) $y = 0.25$; (b) $y = 0.3$; (c) $y = 0.4$; (d) $y = 0.6$.

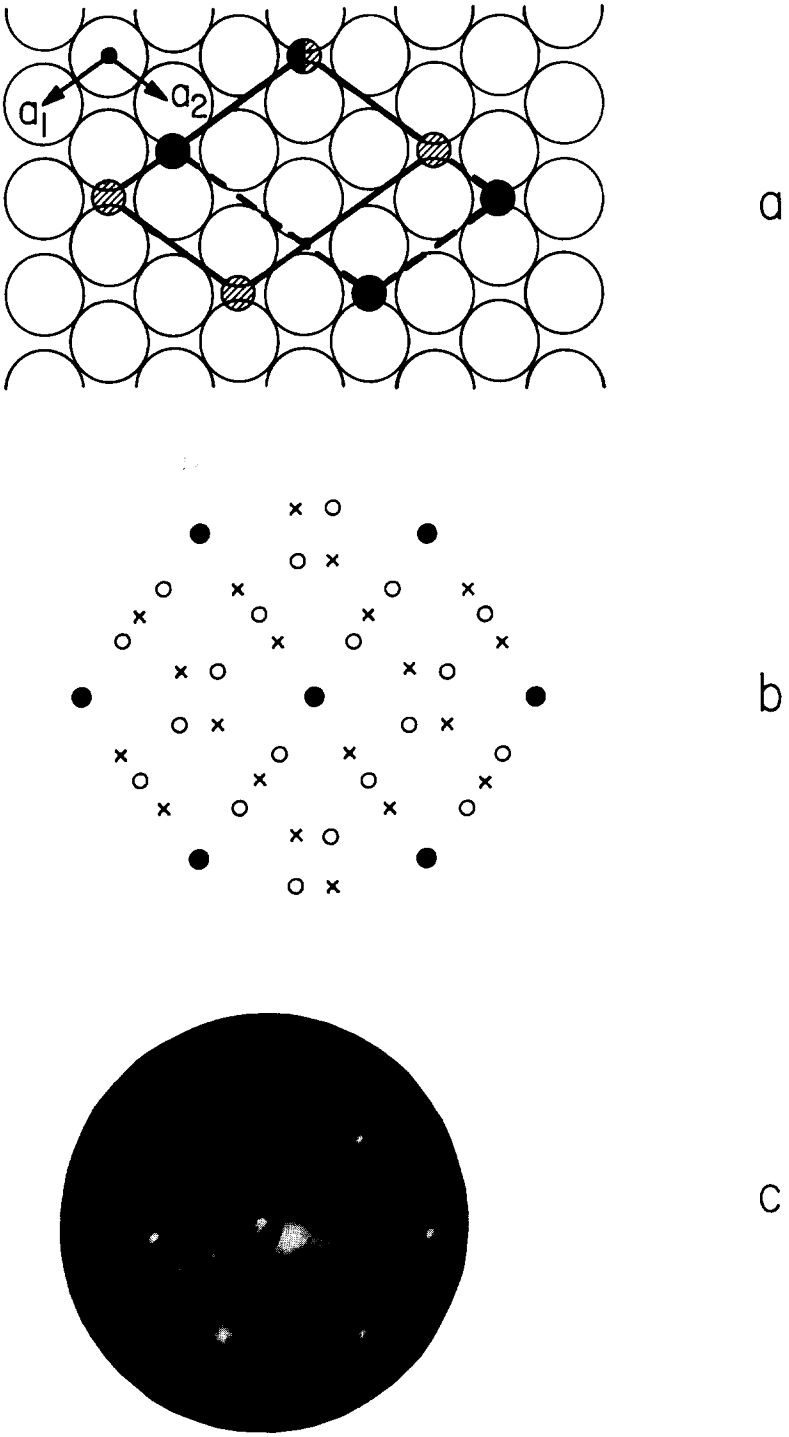

FIG. 7. Structure I. (a) Unit cells of both domain orientations. (b) Constructed reciprocal lattice: (●) substrate lattice [unreconstructed Fe(110); (○ and ×) reciprocal lattice points from both domain orientations from the surface structure. (c) Corresponding LEED pattern ($U = 120$ V).

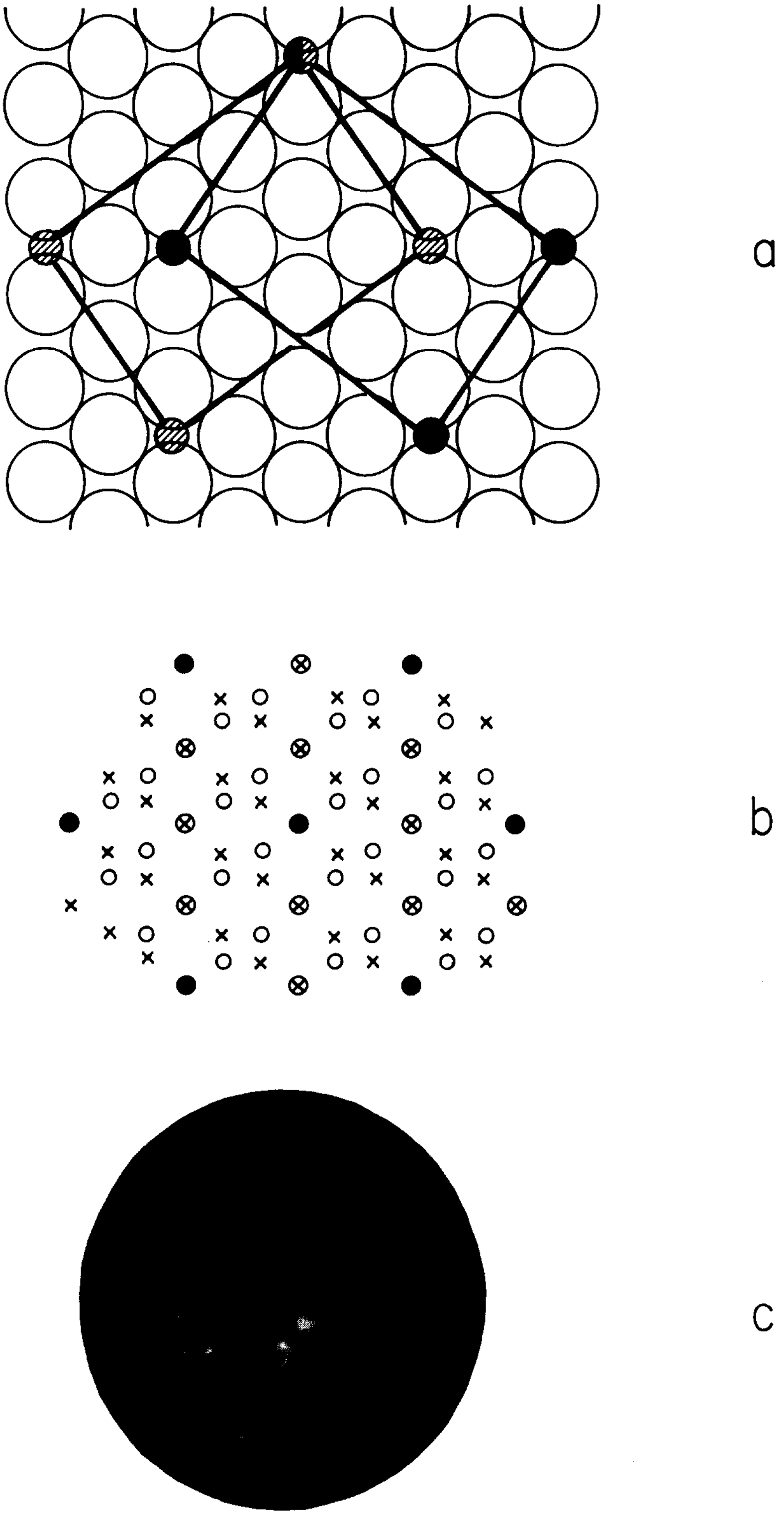

FIG. 8. Structure II. (a) Unit cells of both domain orientations. (b) Constructed reciprocal lattice. (c) Corresponding LEED pattern ($U = 94$ V).

ture. Its unit cell vectors (b_1, b_2) refer to those of the substrate lattice (a_1, a_2) through $b_1 = 3a_1$, $b_2 = 2a_2$, as shown by Fig. 7a. The symmetry of the surface demands the formation of a second equivalent domain orientation with $b_1 = 2a_1$, $b_2 = 3a_2$ with a mirror plane along the [001] direction. The constructed reciprocal lattice points for both domain orientations are drawn in Fig. 7b and have to be compared with the observed corresponding diffraction pattern as reproduced in Fig. 7c.

(b) Structure II (Fig. 6d) is characterized by a larger unit cell with vectors $b_1 = 4a_1$, $b_2 = a_1 + 3a_2$ (first domain orientation) and $b_1 = 3a_1 + a_2$, $b_2 = 4a_2$ (second domain orientation) as shown in Fig. 8a. This is obviously no longer a "simple" surface structure which may be related to the substrate structure through Wood's nomenclature (*4*) since the angle between a_1 and a_2 differs from that between b_1 and b_2. The corresponding reciprocal lattice (including multiple diffraction spots) is reproduced in Fig. 8b and is identical to the observed LEED pattern (Fig. 8c).

Figure 6a shows that at rather low nitrogen surface concentrations the LEED pattern contains elongated spots of structure I. This indicates an island growth mechanism with at first anisotropic dimensions, i.e., the domains grow at first preferentially in the direction of their shorter periodicity. [The width of LEED spots is inversely proportional to the degree of long-range order in the regarded direction (*10*). Note also that the LEED pattern cannot yield information on the question whether the "extra" spots are caused by Fe or N atoms without analysis of the intensities.]

With increasing nitrogen concentrations these "extra" spots become sharper due to growth of the islands in both directions and finally they gradually disappear at the expense of the emerging pattern from structure II. (Figure 6c shows a superposition of LEED spots from both structures.) Above $y > 0.4$ only structure II was observed. However, the formation of both phases was not a unique function of the N surface concentration but was also influenced by the content of the bulk in the subsurface region. If the latter was high the structures were formed at smaller y values, e.g., structure II might already appear at $y = 0.25$. This result suggests that we are not dealing with simple overlayer structures which may be associated with definite coverages but rather that interaction with N_2 causes a structural transformation of the Fe atoms at the surface. It is remarkable that [as in the case of Fe(111)] removal of the nitrogen by desorption leads to a complete restoration of the initial (nonreconstructed) surface periodicity.

4. DISCUSSION

The present results must be discussed in connection with the conclusions drawn for the (100) and (111) surfaces (*1*), and we believe that a relatively closed and consistent general picture will be reached.

(i) With all three planes above room temperature only atomic chemisorption is observed. In the present case this conclusion is confirmed by the isotopic exchange experiments and by the close analogy of the kinetics and energetics of adsorption and desorption with those observed with the two other planes where more direct evidence was reached by ultraviolet photoelectron spectroscopy. Hints for the formation of a molecularly adsorbed species were only obtained at rather low temperatures and relatively high pressures. With Fe(110) the work function decreases by about 15 mV at 4×10^{-4} Torr of N_2 and 120 K in a manner similar to that of the (111) plane. It is suggested that chemisorbed N atoms are slightly negatively charged, whereas adsorbed N_2 molecules are associated with a very small positive charge, in agreement with earlier work with evaporated Fe films (*11*).

(ii) The initial activation energies for adsorption were found to be about 7, 5, and 0 kcal/mole for Fe(110), (100), and (111), respectively. Consequently, chemisorption of nitrogen proceeds at the lowest rate on the most densely packed (110) plane. If this step is in fact rate determining in ammonia synthesis this plane would be the least active; the rate at 683 K is about 60-fold smaller than that on Fe(111).

(iii) The thermal desorption spectrum exhibits a rather narrow peak the maximum temperature of which is essentially independent of coverage. Both observations suggest that desorption is a first-order rate process from a surface with coverage-independent adsorption energy. This result is somewhat surprising in view of the fact that two different surface structures were observed, but it closely resembles the behavior of the (111) plane where a single narrow TDS peak was also observed despite the occurrence of a whole series of complicated LEED patterns. It has to be concluded that the effective metal–nitrogen bond strengths (and therefore also the structures) are very similar for the different phases. Using the TDS peak temperatures [930 K for Fe(110), 850 K for Fe(111)] and assuming first-order desorption kinetics with a "normal" frequency factor of 10^{13} $\sec^{-1}$, activation energies for desorption [E^*_d = 57 kcal/mole for (110) and 52 kcal/mole for (111)] are derived using Redhead's (*5*) formula. If these numbers are used to evaluate the half-widths of the TDS traces according to a procedure as outlined by Edwards (*6*) a value of about 70 K is attained for first-order desorption kinetics which agrees reasonably well with the findings for the (110) and (111) planes, whereas 100 K would be predicted for second-order desorption kinetics. In contrast, with Fe(100) the thermal desorption peaks are considerably broader (130 K) and shift toward lower temperature with increasing coverage, although a detailed analysis again suggests a first-order rather than second-order desorption process, the desorption energy presumably varying with coverage. The mean desorption energy from Fe(100) was estimated to be about 58 kcal/mole. The essential difference between Fe(100) and the other two planes consists in the structure: With Fe(111) and (110) there is strong evidence for surface reconstruction with formation of "surface nitrides," whereas there is no indication of such a process with Fe(100) where the c2 × 2-overlayer structure, although closely related to the (002) plane of Fe_4N resembles more a "regular" adsorption system.

Combining the activation energies for adsorption with those for desorption the following adsorption energies are deduced: (110) 50, (100) 53, and (111) 52 kcal/mole. These values are suprisingly similar keeping in mind that adsorption and desorption are complex processes involving [at least for the (110) and (111) planes] not only the formation or breaking of M–N bonds but also changes in the metal–metal bonds associated with the surface reconstruction. It is suspected that several effects counterbalance each other so properly that nearly equal "effective" adsorption energies result.

(iv) Beside desorption kinetics there is further evidence for surface reconstruction with the present system based on arguments similar to those used in the case of Fe(111): (a) The LEED patterns reveal the formation of complex structures with rather large unit cells which cannot be reconciled with simple overlayer geometrics [in contrast to Fe(100)]. The observation that, in both cases, the existence of a certain surface structure is not solely a function of coverage but is also influenced by the history of the sample (i.e., the subsurface nitrogen concentration) as well as by kinetic parameters such as annealing temperature suggests the operation of nucleation phenomena. This again points toward the growth of new phases rather than the formation of simple adsorbate

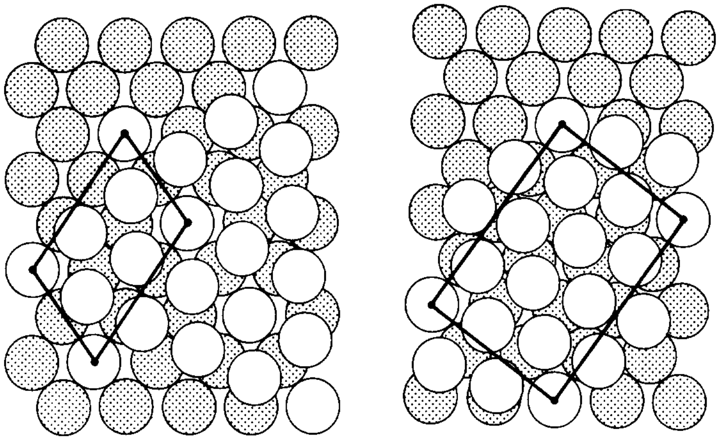
a b

FIG. 9. Possible configurations of Fe atoms (open circles) on the Fe(110) substrate plane (dotted circles). No locations of the nitrogen atoms are drawn. (a) Structure I; (b) structure II.

layers. (b) The Auger peak height ratio y is not proportional to the desorbing amount of N_2, $m = \int p dt$, as derived from the thermal desorption spectra. As discussed in detail in Ref. (*1*) this effect can be explained by assuming that the N atoms are not only located on top of the surface but to some extent also below the topmost layer of Fe atoms.

(v) The close similarities of the desorption energies of the N/Fe(100) and (111) systems with the activation energy of decomposition of Fe_4N was previously considered as support for the proposed surface structures which were closely related to the configurations of Fe atoms in the (002) and (111) planes of fcc Fe_4N (*1*). If the same argument is applied in the present case, it is again possible to construct arrangements of Fe atoms on the unreconstructed surface which would cause the observed LEED patterns and which, on the other hand, are rather similar to the atomic configuration in the (111) plane of Fe_4N. (a) Figure 9a shows the proposed geometry of Fe atoms in structure I, forming a hexagonal array with nearest-neighbor distances of 2.85 Å. [In Fe_4N this distance would be 2.68 Å (*7*)]. The density of Fe atoms in this layer would be 1.43×10^{15} cm^{-2}. The vectors of the primitive unit cell of this structure c_1, c_2 would be related to those of the substrate lattice through $c_1 = 6/5a_1 + 3/5a_2$, $c_2 = 4/5a_1 + 3/5a_2$. (b) A model for structure II is reproduced in Fig. 9b. This, in fact, is no longer an exact hexagonal arrangement. The nearest-neighbor distances (2.64 and 2.71 Å) differ slightly from each other but agree very closely with the value for Fe_4N. The primitive unit cell vectors may be written as $c_1 = 9/11a_1 - 5/11a_2$; $c_2 = 3/11a_1 + 13/11a_2$. The density of Fe atoms in this layer is 1.57×10^{15} cm^{-2}.

No positions for the nitrogen atoms (which presumably will be located in threefold-coordinated sites as in Fe_4N) are drawn in Fig. 9 since even their absolute concentrations are not known. In addition we may once more only speculate on the thickness of the "surface-nitride" phase which in the case of Fe(111) was assumed to involve Fe atoms from two layers. The atomic densities of the structures proposed for the N/Fe(110) systems would be about 20% smaller than with the unreconstructed Fe(110) plane which implies considerable movement of the remaining atoms if for example they are not built in in a second layer. However, the occurrence of appreciable mass transport on Fe surfaces during decomposition of ammonia is a well known fact and was recently directly observed by scanning electron microscopy by Löffler and Schmidt (*8*). Also in the course of the present investigations irreversible faceting as a consequence of NH_3 interaction at higher temperatures was observed by LEED (*9*). The restoration of the initial unreconstructed substrate structure after desorption of N_2 from Fe(110) and Fe(111) could be regarded as some kind of epitaxial growth.

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