Reconstruction of the clean and H covered “magnetic live surface layer” of Fe films grown on Cu(1 0 0)

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Received 11 November 2003; accepted for publication 9 June 2004
Available online 17 June 2004

Abstract
The surface of 6–7 monolayer thick fcc Fe films grown at room temperature on a Cu(1 0 0) substrate is characterized by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The STM images show a p4g(2×2) structure at 5 and 80 K, but not at 300 K. LEED, however, indicates an expansion of the interlayer distance and lateral distortions of similar magnitude both at 150 K and at 300 K. No evidence for a significant change of the surface structure is detected by a LEED spot profile analysis between 150 and 300 K. We attribute the apparent absence of the reconstruction in the STM images at 300 K to surface dynamics caused by domain boundary motion. The particular surface structure with bond angles and distances similar to bcc Fe suggests a driving force of the reconstruction which is similar to that operative in the fcc-to-bcc transition of bulk Fe. Dosing less than 5 L H2 decorates the p4g(2×2) surface reconstruction, while higher hydrogen doses transform the surface reconstruction to p(2×1).

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Keywords: Scanning tunneling microscopy; Low energy electron diffraction (LEED); Epitaxy; Surface relaxation and reconstruction; Magnetic phenomena (cyclotron resonance, phase transitions, etc.); Iron; Hydrogen atom; Chemisorption

1. Introduction
Ultrathin Fe films grown at room temperature on Cu(1 0 0) surfaces fascinate by their complex magnetic behavior, which includes two novel ferromagnetic phases. Since the relation between crystal structure and magnetic ordering of Fe is crucial for a deeper understanding of this important element, much effort is spent on determining the precise atomic structure of each of the new magnetic phases. Motivated by the two-γ phase hypothesis [1] and by first principles calculations [2,3], which suggest the stability of a ferromagnetic fcc phase with substantially increased volume, ultrathin Fe films on Cu(1 0 0) have been considered a model system of ferromagnetic fcc Fe for the past 15 years. This picture, however, has been corrected recently by the discovery of a bcc-like reconstruction in Fe films less than 5 monolayers (ML) thick [4,5], which provides a more conventional explanation for the ferromagnetism in these
films. The question concerning the origin of the surface ferromagnetism of 5–10 ML fcc films, however, remains open and is addressed in this article.

The good matching between the lattice constants of Cu (3.615 Å) and fcc Fe (≈3.58 Å at 300 K [6]) facilitates a comparatively stress free growth of fcc Fe on Cu(100). Three phases can be distinguished as a function of film thickness for films grown at room temperature [7,8]: Phase I, comprising the thickness range from the onset of ferromagnetism at 1–2 ML to 4 ML, is a commensurate bcc(110)-like reconstruction termed “nanomartensite” [4,5] with a Curie temperature \( T_C \) above room temperature and the magnetic moment oriented out-of-plane [7,8]. Phase II is fcc with a ferromagnetic surface and is described in detail below. Phase III are films more than \( \approx10 \) ML thick (critical thickness depending on film purity [7,9]) showing the incommensurate relaxed bcc(110) bulk structure, which, as expected, is ferromagnetic with the magnetic moment oriented in-plane.

This paper focuses on phase II in the thickness range from 5 to \( \approx10 \) ML. A ferromagnetic surface with perpendicular magnetization was found residing on top of the non-ferromagnetic deeper Fe layers [7,10] and accordingly was dubbed “magnetic live surface layer” [7]. There is a general consensus that the surface layer is non-ferromagnetic at room temperature. Man et al. [11] report a growth rate dependence of the Curie temperature with \( T_C \) ranging between 210 and 260 K for growth rates between 0.055 and 0.55 ML/min. Other published values for \( T_C \) (deposition rate) are 250 ± 20 K (0.5 ML/min) [8], 261 K (0.3 ML/min) [12], \( \approx270 \) K (1–2 ML/min) [7], or 280 K (0.2 ML/min) [13]. The bulk of these films shows a complex magnetic order with a critical temperature lower than that of the surface. While recent first principles calculations favor anti-ferromagnetically coupled bilayers [14,15], experimental results point to a spin density wave structure with a period of 2.4–2.7 times the thickness of a ML and a critical temperature below 200 K [8,16–18].

From the point of view of crystallographic structure, this phase fulfills the original goal to grow pseudomorphic fcc Fe films. This is true, however, only for the deeper layers, while the surface reconstructs [19–23], and it is only the surface which shows ferromagnetism [10]. Since initially the lateral atomic displacements of the reconstruction were not recognized [7], the magnetic moment was attributed to the interlayer spacing of the two topmost layers, which is substantially expanded with respect to the deeper layers of the films [7,20–23]. From the viewpoint of density functional theory, interlayer distances of an fcc-like Fe structure are indeed larger when the (bi-)layers couple ferromagnetically and smaller when coupling anti-ferromagnetically [15], although the calculated relative changes are around 1% or below [15] rather than 5% as observed.

Based on quantitative LEED-I/V studies near 100 K, a p2mg(2\times1) reconstruction of the topmost layer was proposed [20–23]. In this model, adjacent atomic rows are shifted in alternating directions with a displacement \( s_D \) relative to the fcc position of up to 0.16 (0.20) Å for 8 (6) ML films [21,23] (note the smaller values in Ref. [22]). This model is supported by an excellent Pendry \( R \)-factor of 0.11 (0.09). The reconstruction is most pronounced for 6 ML Fe films. For thicker films the superstructure spots in LEED images disappear because the long range order is lost [21,22], but the measured surface interlayer distances show an almost constant expansion of \( \approx5\% \) up to 10 ML thickness [7,21,22].

Egawa et al. [19] investigated the clean surface as well as the influence of hydrogen adsorption at 90 K by LEED and thermal desorption spectroscopy (TDS). For 8 ML thick films, a p4g(2\times2) LEED pattern was observed after dosing 6 L hydrogen at 180 K. They found that even as-deposited films showed a small hydrogen desorption peak due to hydrogen adsorption from the residual gas at low temperatures but argue that also the hydrogen free surface is p4g(2\times2) reconstructed [19]. The proposed H adsorption sites are the short bridge sites of the rhomb-like configurations.

In a recent experiment Vollmer and Kirschner [24] studied the influence of the adsorption of small \( H_2 \) doses (3 L) on the magnetism of the films. While a significant effect on the structure was found in the transition regions around 5 ML and
around 10 ML thickness, there is little or no effect in the thickness range between 6 and 8 ML.

In this work we clarify the crystallography of the “magnetic live surface layer”. We investigated clean 6–7 ML films at temperatures between 5 and 300 K and the influence of hydrogen adsorption on the surface reconstruction using STM, a LEED spot profile analysis, and a quantitative LEED-I/V analysis. Section 2 lists the experimental and evaluation procedures. Section 3 focuses on the surface of clean films, while the influence of hydrogen on the surface reconstruction is presented in Section 4. The overall conclusions are discussed in Section 5.

2. Experimental

The STM measurements were done using a commercial low temperature (LT-) STM mounted inside a concentric liquid He and liquid N₂ bath cryostat and a room temperature (RT-) STM, both of which are operated with electrochemically etched W tips conditioned by sputtering with Ar⁺ under UHV conditions. Both STM systems are equipped with an Auger electron spectroscopy (AES) and a LEED system for analytical purposes. The LEED-I/V experiments were carried out in a third, magnetically shielded ultrahigh vacuum system, which includes an AES system as well.

The pressure during evaporation of the films in the preparation chambers is typically below 1×10⁻¹⁰ mbar, during measurement in the separate STM chamber of the RT-STM system and in the LEED-I/V system in the 10⁻¹¹ mbar range, and in the STM chamber of the LT system around 1×10⁻¹¹ mbar.

The Cu(1 0 0) single crystal was sputtered with 2 keV Ar⁺ ions and annealed at 600 K for about 10 min. The films were grown by evaporation from the tip of an Fe wire using an electron bombardment evaporator. The deposition rate of 0.5–1 ML/min was calibrated by a quartz microbalance. The Cu concentration in the surface of the 6–7 ML films is less than a few percent [25]. After deposition the film thickness was checked by quantitative AES [26]. The resulting accuracy of the film thickness is ±0.7 ML for 6–7 ML films.

In all experiments, hydrogen dosing was done by flooding the respective vacuum chamber to the desired pressure. The Langmuir dose unit (10⁻⁶ Torr s) used is based on the true pressure, which is the pressure measured by the ionization gauge multiplied by 1.8.

For the analysis of the surface reconstruction by LEED, temperature dependent data were acquired using a standard two-grid LEED system. This was done either by acquisition of LEED images at a fixed energy in dependence of temperature or by recording intensity versus energy (I/V) curves at different temperatures. In order to determine the film structure, the I/V curves were compared to simulated curves from a dynamic calculation of the electron scattering using the TensErLEED program package [27] on the basis of geometric information from our STM images. A more detailed description of our setup and evaluation procedures can be found in Ref. [28]. The error bars given in this paper were derived from Pendry’s variance [29], namely by varying a certain parameter away from the best-fit structure until the difference between the according R-factor gets larger than this variance. To reduce the computational effort, all other parameters were fixed to their best-fit value, i.e., no subsequent re-optimization was performed. This approach neglects the possibility of a strong coupling between parameters, however, and can lead to an underestimation of the error bars in such cases [30].

A spot profile analysis was performed to determine the temperature dependence of the surface reconstruction. The Gaussian width σ_{\text{instr}} of the nearly background free (1,1) beams (signal from adjacent terraces nearly in-phase) was used as the instrument width and subtracted from the measured Lorentzian width \( \xi_m \) to recover the true width \( \xi_t \) of the respective fractional order beam. This was done in an approximate fashion using an exponential weight of 1.5, which interpolates between 2, exact for Gaussians and 1, exact for Lorentzians; \( \xi_t = \xi_m - \sigma_{\text{instr}}^{1.5} \). The widths of the (1,1/2) and (1/2,1/2) spots are typically two to five times larger than the instrument width and were used to determine the average domain size of the reconstruction. Assuming uncorrelated anti-phase domain boundaries (of the type shown in Fig. 1), we
utilize the formulas for scattering from terraces with uncorrelated step edges in anti-phase condition [31]. The estimated domain size in units of the superstructure lattice constant is \(2 \left(\frac{1}{C_0} \exp \left(\frac{C_0}{n}\right)\right)\overline{C_0}\) [31], which simplifies to \(2 \frac{n}{C_0}\) for larger domain sizes. The normalized spot width \(\xi\) is defined by the Lorentzian \(\left[\frac{\xi^2 + (k - \pi n)^2}{C_1}\right]^{-1}\) with \(n = 1\) corresponding to the \((0, 1/2)\) vector in the LEED image.

Some of the atomically resolved STM images show inverse corrugation, i.e., the atom positions indicated by corrugation minima rather than maxima as intuitively expected. This is not unusual for the Fe surface and can be explained by the extremely low corrugation of the undisturbed Fe surface in the first place, and the complex tip–sample interactions, which are thought to enhance or even produce the (positive or negative) atomic contrast [32].

A significant problem of the experiments is the avoidance of inadvertent H contamination from the residual gas. \(\text{H}_2\) adsorbs at temperatures below 300 K with a high sticking coefficient and can modify the surface reconstruction (see Section 4). According to our estimate of the initial sticking probability of \(\text{H}_2\) molecules \((\approx 1/10)\), 5% \(\text{H}\) coverage corresponds to a dose of about 2 h at \(5 \times 10^{-11}\) mbar partial \(\text{H}_2\) pressure. Extrapolation of our LEED data to zero coverage, however, suggests that this unavoidable amount is irrelevant for our conclusions.

3. Reconstruction of the clean surface

3.1. STM at 5, 80, and 300 K

The STM image in Fig. 1a shows the surface of a 7 ML film grown at room temperature and imaged at 5 K with the atoms appearing as corrugation minima (inverse corrugation, cf. Section 2). Due to the low residual pressure inside the cryostat, contamination by residual \(\text{H}_2\) gas is negligible (below 5%). The grayscale-inverted enlargement
and the schematic below (Fig. 1b and d) show the atoms arranging in a pattern of rotated squares and rhombi characteristic for reconstructions with p4g(2×2) symmetry. The analysis of the atomic positions shown in Fig. 1c reveals the long range order of the reconstruction at 5 K. The criteria for distinguishing square-like and rhomb-like configurations is the ratio of the two diagonals of each quadrangle. The threshold ratio is set to 1.20, the arithmetic center of the range bounded by the values for the ideal fcc(100) and bcc(110) lattice, 1 and √2, respectively. The average diagonal ratio of the rhomb-like quadrangles in the STM image is 1.25 corresponding to a bond angle of 70°176. The p4g(2×2) reconstruction may also be interpreted as a zigzag deformation of the atomic rows in both lateral dimensions (peak-to-peak amplitude 2sD ≈ 0.4 Å, displacement from the fcc site in ⟨100⟩ direction ≈ 0.3 Å). Towards the left edge of the image in Fig. 1a and in the center of Fig. 1b a domain boundary can be seen, which is an anti-phase defect in the zigzag deformation of the horizontal atom rows and shows a local (2×1) structure.

At somewhat higher but still low temperatures the character of the reconstruction changes slightly. The STM images in Fig. 2a and b show two films similarly prepared compared to that shown in Fig. 1 but imaged at 80 K. While at 5 K the entire surface is p4g(2×2) reconstructed, at 80 K also apparently (2×1) reconstructed areas and even unreconstructed areas can be seen. The largest observable distortion relative to the fcc lattice, however, shows again bcc-like bond angles of ≈ 70°. Note that the surface region shown in Fig. 2b borders to a rare bcc-like nanocrystal (2–3 nm wide, cf. Section 5) on the left edge of the image, which appears very bright because of the large volume expansion of the multilayer reconstruction there (surface elevation ≈ 1 Å [33]).

The weakening of the reconstruction in the 80 K images may be interpreted as a precursor of the apparent total disappearance of the reconstruction in STM images at 300 K (Fig. 2c). Besides a few point defects, presumably due to residual Cu from the substrate, the 300 K images show the ideal fcc(100) square lattice. The LEED data, presented in the next sections, however, show that the disappearance of the reconstruction in the STM images does not correctly reflect the surface state, but is a consequence of the surface dynamics at 300 K.

3.2. Temperature dependent LEED between 150 and 300 K

The p4g(2×2) reconstruction seems to disappear in STM images somewhere between 80 and 300 K. If this is indeed the case, it should be visible in the temperature dependence of the fractional order LEED spots. Since the (1/2,1/2) spots are too weak on the clean surface, only the (1,1/2) LEED spots can be used for this analysis.

Fig. 3a shows the temperature dependence of the (1,1/2) fractional order LEED spot profiles while cooling the sample from 300 to 150 K. When looking at the data in direction of increasing temperature, the measured signal appears to drop by a factor of 3. This decrease, however, is continuous and mainly due to the uncorrelated thermal motion of the surface atoms (Debye–Waller factor for a Debye temperature of about 300 K). To monitor the temperature dependence of the surface reconstruction in a more quantitative way, the total (1,1/2) spot intensity is determined by integrating either over the entire Brillouin zone using Lorentzian curve fits to a line section through the spots or alternatively but less precise over a smaller circular area around the spot directly in the image. The Debye–Waller factor is removed by taking the ratio of the fractional order spots and any of the integer order spots, here the (1,1) type. The resulting intensity ratio I1,1/1 decreases less than 30% over the considered temperature range of 150–290 K (Fig. 3b), indicating that the reconstruction remains intact up to 290 K. It should be mentioned that the Debye–Waller factor correction used can only be an approximation. Multiple scattering effects may result in different effective Debye temperatures for every beam. In the present case, however, the estimated error of ±15% for a ±20% variation of the beam-dependent Debye temperature is acceptable.

The domain size estimated from the spot width (see Section 2) is quite small, about 6–7 lattice constants at 150 K in this case, but only weakly
temperature dependent. The preparation dependence of the domain size is stronger, presumably due to different island densities, which depend on the flatness of the underlying Cu surface, film thickness, and surface purity. The domain size shown here is representative of typical films, although domain sizes twice as large have been encountered occasionally.

3.3. LEED-I/V analysis at 150 and 300 K

It is known from previous LEED-I/V results [7,20–23] obtained at low temperatures that the topmost interlayer spacing is expanded by \( \approx 5\% \). A separate kinematic analysis of LEED-I/V-spectra, however, indicates a similar expansion also at 300 K [34]. Therefore, we performed a dynamic

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**Fig. 2.** (a) STM image of a 6.4 ML film imaged at 80 K (−0.6 mV, 10 nA) with atoms visible as corrugation minima (dark) and its square-and-rhomb segmentation shown directly below (threshold diagonal ratio 1.15). (b) STM image of 7 ML thick film similar to (a) but showing atoms as corrugation maxima (−0.5 mV, 1.5 nA). In both cases the surface is not evenly reconstructed, although the bond angles reach again \( \approx 70^\circ \) in areas showing maximum reconstruction amplitude. (c) STM image of a 7 ML film imaged at 300 K (−1 mV, 1 nA) lacking any visible reconstruction.
LEED-I/V analysis both at 150 and 300 K (Table 1). Being aware of the high density of domain boundaries, we used a domain (phase) mixing approach based on an incoherent superposition of $p2mg(2 \times 1)$ and $p4g(2 \times 2)$ scattering intensities. Both phases are related in the sense that they are characterized by a zigzag deformation in one or both lateral dimensions, respectively, described by a displacement amplitude $s_D$, or equivalently the peak-to-peak amplitude $2 \times s_D$ (Fig. 4). The $p4g(2 \times 2)$ reconstruction may also show a vertical buckling $b_2$ in the second layer below the surface since the atoms below the square- and rhomb-like arrangements may relax differently. For all calculations, however, the buckling is very small. All interlayer distances of the 6 ML film are used as free parameters, although only the two topmost interlayer distances of the $(2 \times 2)$ and $(2 \times 1)$ domains are assigned independent parameters, $d_{12}^{(2 \times 1)}$, $d_{12}^{(2 \times 2)}$, $d_{23}^{(2 \times 1)}$, and $d_{23}^{(2 \times 2)}$. The remaining interlayer distances $d_{34-6Cu}$ of both phases are coupled.

The 150 K results were obtained using four integer spots and three fractional order spots of the $(1,1/2)$ type (each averaged over all symmetrically equivalent spots) but not the $(1/2,1/2)$ type spots, which are virtually invisible on the clean surface and can be seen only after adsorption of small amounts of $H_2$ (cf. Section 4). The sum of the energy ranges of these seven $I/V$ curves used for the fitting procedure is 1100 eV. The Pendry $R$-factor [29] shows a significant improvement from 0.13 and 0.15 for the pure $p4g(2 \times 2)$ and $p2mg(2 \times 1)$ models, respectively, to 0.11 for a $p4g(2 \times 2)$ model with a 30% admixture of a weakly distorted $(2 \times 1)$ phase. This result is quite compelling as the corresponding structural parameters correctly reflect the proportionality of in-plane distortion to interlayer expansion: The $(2 \times 1)$ phase, which can be related to the domain boundaries is weakly reconstructed and is consequently only about 2% expanded, while the dominant $p4g(2 \times 2)$ phase is strongly reconstructed reaching almost the lateral displacement observed by STM at 5 and 80 K ($\sim 0.3$ Å in $(100)$ direction) and shows a 6% interlayer expansion. This correlation is just that expected for a hard-sphere model assuming bcc-Fe interatomic distances (cf. Fig. 4).

For the quantitative LEED analysis at 300 K, the thermal vibrations of the topmost layers were introduced as free fit parameters for a calculation using a $(1 \times 1)$ surface model, and the result (18/13/10 pm RMS amplitude for the surface, subsurface, and bulk layers) was used for the more detailed $p2mg(2 \times 1)$ and $p4g(2 \times 2)$ structural models. These vibration amplitudes correspond to a surface Debye temperature of $T_D \sim 270$ K, which is
in good agreement with the \( T_D \sim 300 \) K corresponding to the Debye–Waller factor obtained from the analysis of the temperature dependent intensity data. Due to the weak fractional order spots at 300 K, the quantitative calculations for this temperature are based on four integer spots only (total energy range 745 eV). Therefore, the 300 K evaluation is not very significant with respect to whether a pure \((1/2,1/2)\) or mixed phase is present. The lowest Pendry \( R \)-factor, however, is obtained again for a mixed phase with a similar \( \text{p}4\overline{g}(2\times2) \) fraction and surface interlayer expansion as those measured at 150 K. Note that while the accuracy of the 300 K values for the in-plane displacements is rather low, the value for the surface interlayer expansion is accurate (cf. error bars in Table 1). The result is in agreement with the LEED spot profile analysis, which does not show any abrupt change of the surface structure between 150 and 300 K.

To check for consistency, our results may be compared with previous LEED-I/V work based on a pure \( \text{p}2\text{mg}(2\times1) \) phase. If assuming a pure \( \text{p}2\text{mg}(2\times1) \) phase we obtain \( s_{\text{p}} = 0.14 \) A, \( d_{12} = 1.89 \) A, \( d_{23} = 1.80 \) A with \( R_p = 0.15 \) at 150 K for a 6 ML film. This is in acceptable agreement with \( s_{\text{p}} = 0.20 \) A, \( d_{12} = 1.87 \) A, \( d_{23} = 1.78 \) A and \( R_p = 0.11 \) at 90 K for 6 ML films in Refs. [21,23].

### 4. Influence of hydrogen on the surface reconstruction

To analyze whether hydrogen induces, stabilizes, or even destabilizes the \( \text{p}4\overline{g}(2\times2) \) reconstruction of the clean film surface, the integrated \((1/2,1/2)\) and \((1/2,1)\) LEED spot intensities have been measured in dependence of the molecular hydrogen dose at a temperature of 140 K for 7 ML films. The intensity curves shown in Fig. 5a and b...
are circular integrals in the LEED image, which have been averaged over equivalent spots and background corrected by subtracting the average brightness around each LEED spot. The two different experiments show different degrees of surface order, which is visible in the different widths of the superstructure spots.

The simultaneous increase of both the (1,1/2) and (1/2,1/2) fractional order spots up to a hydrogen dose of 5 L shows that in the initial adsorption phase the adsorbed hydrogen does not change the $p4g(2 \times 2)$ symmetry of the surface reconstruction. This supports the model suggested by Egawa et al. [19], who hypothesized a decoration of the rhomb-like arrangements of the $p4g(2 \times 2)$ reconstruction by H atoms adsorbing at the short bridge site.

While imaging of this phase by STM was not particularly successful, the LEED-I/V analysis of a 6 ML film after dosing of 13 L molecular hydrogen unambiguously favors the $p4g(2 \times 2)$-H model with a Pendry $R$-factor of 0.12 (H at bridge site, Table 1). A $p2mg(2 \times 1)$-H model yields a significantly worse Pendry $R$-factor of 0.25. The H$_2$ dose used (13 L) is somewhat higher than would be necessary to maximize the (1/2,1/2)-beam intensity (5 L), but this is irrelevant considering the much smaller sticking coefficient of hydrogen on the completed $p4g(2 \times 2)$-H phase (see below). $I/V$ curves of four integer order spots, three (1,1/2) type fractional order spots, and one (1/2,1/2) type fractional order spot, covering a total energy range of 1425 eV, were used. In addition to the parameters used for the clean surface, the height of the H atoms above the Fe surface atoms is introduced as a free parameter. Various H locations in the $p4g(2 \times 2)$ reconstruction were tested including the square fourfold-hollow site, the two equivalent threefold sites of each rhomb with 50% occupation probability, and the short bridge site of the rhomb. The
resulting $R$-factors indicate only a weak preference for the rhomb sites (short bridge $R_p = 0.119$, threefold $R_p = 0.123$) with respect to the square sites ($R_p = 0.124$) or total absence of H ($R_p = 0.129$). Since Pendry’s variance is 0.021 in this case, an error bar for the height of the H atom above the surface metal atoms cannot be determined, although the resulting Fe–H bond length of 1.75 Å is realistic. The small $R$-factor differences are due to the low sensitivity of LEED to the H position.

The temperature dependent spot profile analysis of the (1/2,1/2) spots (Fig. 6) does not show a significant difference to the clean surface, besides the onset of recombinative H$_2$ desorption around 280 K (cf. desorption peaks at 290–350 K in a TDS experiment [19]) which causes the abrupt decrease of the integrated intensity at 280 K. A similar analysis of the (1,1/2) spots of the H covered surface shows exactly the same temperature dependence. A coverage dependent spot profile analysis of the (1,1/2) spots (Fig. 7) shows that the effect of the adsorption of $\approx$2 L of hydrogen on the domain size is also rather small causing an increase of the domain size equivalent to cooling the film by 50–100 K. The strong dependence of the intensity on the coverage is analyzed in detail towards the end of this section.

Significantly larger H$_2$ doses transform the surface structure. Fig. 8 shows the topography of a 6.4 ML thin Fe Film grown at room temperature and exposed to 100 L hydrogen at 80 K. As a
result, the surface shows a reconstruction with $(2 \times 1)$ symmetry interspersed with a few areas that appear brighter, less reconstructed, and show remnants of the $p4g(2 \times 2)$ phase. The lateral atomic displacement of the $(2 \times 1)$ reconstruction visible in the STM image is $s_D \approx 0.35$ Å, which corresponds to a zigzag deformation with a bond angle of about 75$^\circ$, the same as observed for the bcc-like $(n \times 1)$, $n = 4–6$, multilayer reconstructions in sub-5 ML films [4].

To interpret the STM image, it is necessary to realize that this is a system where the $(2 \times 1)$ surface reconstruction of the metal atoms and a slightly different $(2 \times 1)$ adsorption superstructure are mixed. The bright surface strip marked by the dashed line in Fig. 8a is apparently $(2 \times 1)$ reconstructed just as the adjacent darker areas. A closer inspection, however, reveals that this must be a domain boundary in the H superstructure on top of a homogeneously reconstructed metal surface. The difference between the left and right side is not visible in the metal atom positions (corrugation maxima) but in the location of the dark spots in between (corrugation minima) as shown in the image details in Fig. 8b. The rhomb-like hollow sites are distinctly asymmetric indicating H atoms in one of the two threefold hollow sites. On a single-domain surface such an asymmetry would not be significant because it can also be due to an

Fig. 6. Temperature dependence of $(1/2,1/2)$ LEED spots measured at 119 eV on a 6 ML film after adsorption of about 1.5 L molecular hydrogen. (a) Intensity line profiles (130–260 K) and corresponding LEED image (130 K) with profile line and circular integration area indicated. (b) Integrated $(1/2,1/2)$ intensity either from the area under the Lorentzian curve fits (○) or determined by direct integration of the spot intensity in the LEED image (—). All intensity values are normalized to the intensity of the $(1,-1)$ integer order spot in order to compensate for the Debye–Waller factor. The behavior is similar to that of the $(1,1/2)$ spots of this surface (not shown) and that of the clean surface shown in Fig. 3, although the domain size of this particular film is larger (with and without hydrogen). Note that the peak intensity drop in (a) appears to be larger than that of the $(1,1/2)$ spots in Fig. 3 because the temperature dependent blurring of the LEED spot is two-dimensional in this case but one-dimensional for the $(1,1/2)$ spots.

Fig. 7. H$_2$ dose dependence of $(1,1/2)$ LEED spots measured at 119 eV on a 6 ML film. The domain size (○) is estimated from the width of the spots (details in Section 2) and increases slightly up to a hydrogen dose of about 2 L, where it levels out. According to our Langmuir adsorption model (see text), 2 L correspond to more than 50% filling of the $p4g(2 \times 2)$-H structure. The integrated intensity values (○, area under Lorentzian curve fits) are similar to those shown in Fig. 5a and b but differ by the integration method.
asymmetric STM tip. In the present case, however, the asymmetry is mirrored when passing the domain boundary. The model resulting from these symmetry considerations (cf. Fig. 5c) is consistent with H adsorption experiments on the bcc Fe(1 1 0) surface, which is structurally similar to our reconstructed fcc Fe surface and also shows H adsorbing at threefold hollow sites [35,36].

The proposed H adsorption structures and the reconstruction of the clean surface may be put into perspective by a quantitative evaluation of the H\textsubscript{2} dose dependence of the fractional order LEED beams. The result obtained by fitting a simple analytic form to our data sets displayed in Fig. 5 is a third independent source of information, besides STM and LEED-I/V data, regarding the surface structure. We assume Langmuir adsorption, characterized by a sticking probability proportional to the number of free sites (first order) or to its square (second order). The dissociative hydrogen adsorption suggests a second order adsorption law, \( \theta_L(D,S) = DS/(1 + DS) \) (with dose D and initial sticking coefficient S) though lacking the details of the adsorption process, at least the initial process may also follow a first order law, \( \theta_L(D,S) = 1 - \exp(-DS) \). For the purpose of this discussion, however, the details of the adsorption are rather insignificant.

Already before any hydrogen is adsorbed, the clean surface shows a certain initial (1 1/2) and

Fig. 8. (a) STM image of a 6.4 ML film after exposure to \( \sim 100 \) L molecular hydrogen at 80 K (\( \sim 55 \) mV, 10 nA). Most of the surface is (2\( \times \)1) reconstructed. The areas which appear brighter, presumably due to a locally lower H coverage, occasionally show remnants of the p4g(2\( \times \)2) structure (see image detail). (b) The image details of the (2\( \times \)1) structure reveal the asymmetry of the hollow sites. The corrugation minima are located in one of the two triangular halves of the rhombi rather than in their center, indicating H occupation of the threefold coordinated hollow sites. This symmetry breaking generates two H domains on top of the underlying metal reconstruction, which are separated by a domain boundary indicated by the dashed line.
(1/2,1/2) scattering amplitude, \(q_{1/2}^{1/2}\) and \(q_{1/2}^{1/2}\), respectively. We assume that the changes in scattering amplitude are approximately proportional to the H coverage. These amplitude changes are mainly due to H-induced displacements of the metal atoms. The weak scattering by the H atoms themselves is neglected. Adsorption of hydrogen at the rhomb sites of the \(p4g(2\times2)\) reconstruction with an initial sticking coefficient \(S_0\) increases both the (1,1/2) and (1/2,1/2) amplitudes. Subsequent, much slower occupation of the remaining sites and the transformation to the \(p(2\times1)\) structure leads to an extinction of the (1/2,1/2) beams but further increases the (1,1/2) amplitude (scaled by a factor of 0.5). The corresponding sticking parameter \(S_{1/2}\) of this second process is defined as the sticking coefficient on the completed \(p4g(2\times2)\)-H structure at half coverage. By definition, the second adsorption process depends on the completion of the first process. Considering the very different sticking coefficients, however, this causal constraint is ignored in our simplified approach and the total coverage written as simple sum, \(\Theta = \Theta_L(d,S_0)/2 + \Theta_L(d,S_{1/2})/2\), and the dose dependent intensities as

\[
I_{\frac{1}{2}}(D) = \left[ q_{1/2}^{1/2} + (1 - q_{1/2}^{1/2}) \Theta_L(D,S_0) + f\Theta_L(D,S_1) \right]^2,
\]

\[
I_{\frac{1}{2}z}(D) = \left[ q_{1/2}^{1/2} + (1 - q_{1/2}^{1/2}) \Theta_L(D,S_0) - \Theta_L(D,S_1) \right]^2.
\]

In these functions, \(\Theta_L\) may either refer to a first or second order Langmuir adsorption law. The respective curve fits shown in Fig. 5 provide an estimate for the initial scattering amplitudes, \(q_{1/2}^{1/2} \sim 0.6\) and \(q_{1/2}^{1/2} \leq 0.2\). This shows in accordance to the STM images that also the clean surface has a significant scattering amplitude [at least for the (1,1/2) beams] of more than half its maximum value. The rather small initial (1/2,1/2) amplitude is discussed in Section 5. The accuracy of the resulting initial sticking probabilities of H atoms is good and depends on the assumed order of the process and the true final coverage (here assumed \(\Theta = 1\)). Nevertheless their orders of magnitude, \(S_0 \sim 1/10\) and \(S_{1/2} \sim 1/1000\)–1/100, respectively, can be estimated.

### 5. Discussion

The STM and LEED data provide compelling evidence that the clean surface is \(p4g(2\times2)\) reconstructed with a preparation dependent degree of disorder (domain size). The temperature dependence of the fractional order intensity, after correcting for the Debye–Waller factor, is weak and continuous, which shows that the surface is reconstructed up to 300 K. While H\(_2\) adsorption initially proceeds by a decoration of the \(p4g(2\times2)\) superstructure (with H most likely at bridge or threefold hollow sites of the rhombi), doses of more than 5 L convert the superstructure to a \(p(2\times1)\)-H reconstruction with H occupying threefold hollow sites. We would like to point out the similarity of both the \(p4g(2\times2)\) and the \(p(2\times1)\)-H surface structure to the nanomartensitic \((n \times 1)\) multilayer structures found in films less than 5 ML thick [4]. All are characterized by zigzag deformations of the fcc(100) lattice with wavelengths between 2 and 6 surface lattice constants. The \(p4g(2\times2)\) reconstruction differs only by showing this zigzag deformation in both lateral dimensions.

The STM measurements at 300 K, which lack any visible reconstruction, and the LEED results can be reconciled by assuming that the STM measures the center of mass of rapidly moving atoms by averaging the atom position on a microsecond time scale, while the scattering of electrons measured in a LEED experiment occurs on a much shorter time scale. Therefore, the motion of domain boundaries is irrelevant for the LEED diffraction pattern, while it can diminish the apparent reconstruction in STM images (Fig. 9). The temperature dependent size of the domains causing the observed weakly temperature dependent broadening of the fractional order spots can only be due to creation of new domain boundaries. Therefore the domain boundaries are likely to be mobile since the barriers for their motion should be smaller than those for their generation.

Originally, it was not clear whether the macroscopic magnetization of the “magnetic live surface layer” disappears around 250 K because of a structural or because of a magnetic transition, i.e.,
whether the transition temperature is really a Curie temperature. It is an important result of our experiments that the crystallographic surface structure of the reconstructed fcc Fe films does not change abruptly in the temperature range near the Curie temperature of the films. Therefore the sudden loss of macroscopic magnetization is primarily due to spin disorder. The preparation dependent high density of defects (domain boundaries) of the surface reconstruction, however, may shift $T_C$ slightly, causing the spread of the observed Curie temperatures between 210 and 280 K (see Section 1).

Prior to this work, the magnetization, its out-of-plane orientation, and the increased interlayer distance were interpreted in terms of a ferromagnetic fcc structure. Such a commensurate fcc-like structure would be characterized both by an increased interlayer distance and an increased interatomic distance between Fe atoms of adjacent monolayers, i.e., the surface interlayer spacing would increase to release a “magnetic stress”. The quantitative LEED data (Table I, Fig. 4), however, show a clear correlation of the surface interlayer distance and the lateral atomic displacements of the surface Fe atoms. This displacement requires a simultaneous upward movement of the surface atoms if constant interatomic distances between an Fe atom on the surface and its nearest neighbors in the subsurface monolayer are assumed. In fact, we find that this interatomic distance measured on the clean (H covered) surface, $d_{NN,12} = 2.49 (2.45)$ Å, is even smaller than that of fcc Fe ($\sim 2.53$ Å [6]) and almost equals that of the bcc phase of bulk Fe (2.48 Å). This combination of bcc-like interatomic distances and bcc(1 1 0)-like configurations (four atoms of rhomb plus subsurface atom) points towards a common driving force of the surface reconstruction of ultrathin fcc films and the fcc-to-bcc transition of bulk Fe: The formation of atomic arrangements, which are less densely packed (bcc volume is $\approx 2\%$ larger) but show smaller interatomic distances (bcc interatomic distances are $\approx 2\%$ smaller) than the fcc Fe lattice. Therefore, it is almost inevitable to link the ferromagnetic ordering of the surface layer to its strong reconstruction. The apparent contradiction that the reconstruction is stable also above the Curie temperature of the films can be resolved by considering another characteristic of (bulk bcc) Fe: According to current understanding, the spin-split band structure does not collapse at $T_C$ but persists to much higher temperatures [37–41]. As a consequence, the large energy gain from the ferromagnetic exchange interaction, which stabilizes the bcc with respect to the fcc structure (cf., e.g., [42]), does not vanish at $T_C$ and the bcc structure remains stable even above its Curie temperature of 1040 K [39]. Analogously, it can be expected that the surface reconstruction of the ultrathin films, even if it is stabilized by...
ferromagnetic exchange, remains intact above its Curie temperature of \( \sim 250 \) K.

Supporting our conclusions, recent first principles calculations [43,44] show that the surface reconstruction of 6 ML films and the nanomartensitic bcc-like reconstruction of the 2–4 ML films are indeed the ground states of these films and have the same driving force. The characteristic bond angles of the reconstruction found in this calculation are about 76° both for the multilayer reconstruction (4 ML film) and the surface reconstruction (6 ML film). Note that the 6 ML calculation was done for a p2mg(2\( \times \)1) reconstruction, virtually identical to the (2\( \times \)1)-H phase found by us but different to the p4g(2\( \times \)2) seen by us on the clean surface. Given the structural similarity, however, the total energy difference between these two phases is probably quite small.

The absolute value of the magnetization of the topmost surface layers is difficult to measure. However, the 5–10 ML thick films may be compared to the bulk-like magnetized [10,45] 2–4 ML thick films: (1) Spin-polarized metastable He deexcitation spectroscopy at \( \sim 190 \) K shows a virtually constant spin polarization of the vacuum interface regardless whether 2–4 or 5–7 ML thick films are considered [46]. (2) Two-photon photoemission spectroscopy of the lowest image potential state at 90 K suggests a slightly increasing spin splitting (\( \sim 50–70 \) meV) with decreasing thickness in the thickness range between 2 and 7 ML [47]. (3) Inverse photoemission (IPE) shows a 4sp-related peak in spectra of films between 2 and 8 ML thickness about 4 eV above the Fermi edge [37].

The corresponding spin splitting of 0.9 eV has been measured only for 6 ML films by means of spin-polarized IPE [48,49] and is comparable to the expected value for the 4sp-bands of bcc Fe in this energy range. Calculations of bcc(110) slabs indicate a spin splitting of the sp-bands which is about 2/3 of that of the d-bands [50,51], i.e., \( \sim 1.2 \) eV if referenced to the IPE result of 1.8 eV for the spin splitting of d-band transitions measured on thick bcc-Fe films [37].

Another important magnetism-related quantity, which may be related to the geometric structure of the films, is the direction of the magnetization. Films grown below 250 K are in-plane magnetized if more than 5 ML thick [8,52]. To explain the out-of-plane magnetization of the 2–10 ML films grown at 300 K, we adopt the view presented by Thomassen et al. [7]: The magnetization direction is determined mainly by the surface component of the magnetocrystalline anisotropy. Shape anisotropy, which causes the in-plane magnetization of thicker bcc films (cf., e.g., Ref. [53]), cannot develop since the effectively magnetized film is only 2 ML thick even if the entire film is 5–10 ML thick. We further know that the 2–4 ML films exhibit a “nanomartensitic” bcc-like structure [4], which is a strongly strained, out-of-plane magnetized bcc-like phase. Since the atomic surface density and the local atomic arrangement of the 2–4 ML films and the 5–10 ML films is very similar, it is not surprising that the p4g(2\( \times \)2) surface reconstruction of the 5–10 ML films is also out-of-plane magnetized.

Two minor structural details of the 5–10 ML films and their surface reconstruction remain to be addressed: (A) Based on the LEED data it might appear that it is the H adsorption which causes the p4g(2\( \times \)2) reconstruction since the (1/2,1/2) spots are virtually invisible on the clean surface but become visible after adsorption of small amounts of H. H atoms themselves are clearly far too weak scatters to cause such a multiplication of the intensity and this increase can only be due to the influence of the H atoms on the Fe atom positions. On the other hand, STM and quantitative LEED clearly show that the reconstruction is a characteristic of the clean surface. There are two reasons for this apparent contradiction: First, the (1/2,1/2) intensity, i.e., the square of the structure factor for the (1/2,1/2) beam for a strictly lateral p4g(2\( \times \)2) reconstruction without vertical buckling, increases (for small displacements) with the fourth power of the in-plane atom displacement and is less than a tenth of that of the (1,1/2) spots even for large displacements. In other words, the (1/2,1/2) intensity caused by in-plane displacements is extremely weak and even a small increase of the lateral reconstruction amplitude or a very small c(2\( \times \)2)-like subsurface buckling can increase the intensity above the minimum signal to noise ratio of our video detection system. Second, the large dispersion of the LEED spots, which is one-dimensional for the (1,1/2) spots but two-dimen-
sional for the (1/2,1/2) spots blurs the intensity of the (1/2,1/2) spots much more strongly. This effect can be seen in Fig. 5b where the (1/2,1/2) spots are nearly invisible even with H adsorbed, while the (1,1/2) spots can still be clearly seen.

(B) STM images of 6 ML films acquired at 300 K also show a small amount of nanocrystals ("needle crystals"), characterized by a 9% strained bcc(1 1 0) structure [5,33]. These nanocrystals are the precursors of the incommensurate, relaxed bcc phase III (see Section 1) and grow in size when cooling the film to, e.g., 80 K [5,54]. The ferromagnetism of the 5–10 ML thick films, however, cannot be explained by these nanocrystals, whose density can fluctuate between less than 1% and up to 10% and more for different preparations, while the magnetization, according to several published experiments (e.g., Refs. [7,8,22,24,52]), does not vary significantly.

Finally we would like to discuss briefly the difference of our results to previous LEED-I/V analyses [21,23], which is subtle but significant. In the previous work the possibility of a p4g(2×2) phase was, to our knowledge, not included. Therefore even the largest lateral displacement vectors (s_D = 0.16–0.2 A [21,23]) obtained for a pure p2mg(2×1) model lead to surface bond angles of only 81–83°, which are still closer to the 90° angles of the fcc lattice. On the other hand, the displacement vector for the p4g(2×2) phase of our domain mixing model, 0.14 × √2 = 0.20 A, is at least as long and rotated by 45° and results in bond angles of about 77.5°, which is closer to the bcc angle of 70.5°, changing the physical interpretation from a magnetically expanded fcc-like surface bilayer to a reconstruction with purely reconstruction-caused interlayer expansion. In addition, our 5 and 80 K STM images demonstrate that the ideal ground state structure shows even larger displacements with bond angles almost equal to those of the perfect bcc structure (cf. Section 3.1).

6. Summary

The surface structure of 6–7 ML Fe films grown on Cu(1 0 0) at room temperature was studied in dependence of temperature by means of STM and LEED. The surface is reconstructed between 5 and 300 K. STM shows large p4g(2×2) domains at 5 K. The inhomogeneity of the reconstruction in the 80 K STM images and their apparent disappearance in the 300 K images can be rationalized by the presence of mobile domain boundaries, which suppress the visibility of the reconstruction in STM images but not in LEED experiments.

It is an important conclusion that the ferromagnetism of the surface is not related to the fcc phase, but to the strong surface reconstruction, which contains atom configurations closely resembling the local atomic arrangement of the bcc bulk phase. The increased surface interlayer distance can be entirely explained on the basis of a hard-sphere model with a bcc-like Fe atom diameter, which is smaller than that of the non-ferromagnetic fcc Fe phase. This suggests that the surface reconstruction of ultrathin fcc Fe films on Cu(1 0 0) and the fcc-to-bcc transition of bulk Fe have a common origin, which is the preference to form a ferromagnetic phase that is less densely packed and shows smaller interatomic distances than the fcc lattice.

Dissociative adsorption of hydrogen occurs with a high initial sticking probability of the order of 1/10. Up to 5 L hydrogen decorates the p4g(2×2) superstructure with the hydrogen atoms most likely adsorbing at the short bridge or threefold coordinated sites of the rhombi. Significantly higher hydrogen doses cause a transformation to a p(2×1)-H surface reconstruction with the hydrogen atoms adsorbing at the threefold coordinated sites.

Acknowledgements

We gratefully acknowledge support by the “Fonds zur Förderung der Wissenschaftlichen Forschung” (Austrian Science Fund) under the Start program Y75.

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