Magnetic Order-Disorder Transition Mediated by a Temperature-Driven Structural Transformation

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Low energy electron diffraction and magneto-optical Kerr effect measurements were carried out in interleaved mode for epitaxially grown Fe/Cu(100) at temperature variation. What was believed to be a regular thermodynamic Curie transition in 4 monolayer Fe/Cu(100) is shown to be the result of a temperature-driven structural transformation. [S0031-9007(96)00446-2]

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The loss of spontaneous magnetization in ferromagnets with increasing temperature belongs to the class of thermodynamical second-order phase transitions. When the critical (Curie) temperature is approached thermal fluctuations of the spins overcompensate their aligning exchange interaction, and the ferromagnetic long-range order leading to the occurrence of the spontaneous magnetization disappears.

In this Letter we report on another kind of magnetic order-disorder transition, namely, a temperature-driven structural rearrangement in thin epitaxial Fe films on Cu(100), affecting the existence of ferromagnetism in the film. What was up to now believed to be the "normal" thermodynamically driven Curie transition in a 4 monolayer (ML) Fe film on Cu(100)—a loss of the long-range magnetic order above 330 K—is shown to be exclusively due to a crystalline restructuring occurring at that temperature and its consequences on the magnetic properties. The link between structure and magnetism in ferromagnets [and, in particular, in Fe/Cu(100)] is thus found to reveal itself in the new way.

Ultrathin Fe films on Cu(100) are characterized by a rather interesting structural and magnetic behavior as a function of coverage and growth temperature, which makes them one of the most frequently investigated objects in thin films magnetism [1–9]. Grown at room temperature, these films have a perpendicular orientation of the remanent magnetization that becomes in-plane after the fcc-bcc structural phase transition at a thickness around 11 ML [1]. The value of the remanent magnetization in the fcc Fe/Cu(100) is observed to be a nonmonotonous function of the Fe thickness: Up to a thickness of about 4 ML an almost linear increase of the magnetization takes place, whereas this value drops down at higher thicknesses and remains approximately constant between 5 and 10 ML [1–3]. This unusual behavior can be explained by considering that fcc Fe may assume several magnetic phases depending on the atomic volume V_a: At $V_a \approx 11.4$ Å^3 an antiferromagnetic phase exists, whereas ferromagnetic order can be expected at an enlarged atomic volume of 12.1 Å^3 [10,11]. The lattice constant of Cu (3.61 Å) exceeds that of fcc Fe (3.55–3.58 Å) by (1–2)%, thus leaving the epitaxial fcc film essentially unstable with respect to structural transformations. In this situation the vertical interlayer spacing $a_\perp$ is mainly affected. Detailed low-energy electron diffraction (LEED) investigations [3–6] using the tensor LEED technique to fit experimental $I(E)$ curves showed that the whole Fe film on Cu(100) assumes a tetragonally expanded fcc structure (fct) for $d \leq 4$ ML, characterized by an enlarged atomic volume of 12.1 Å^3 ($a_\perp \approx 1.87$ Å). At higher thicknesses only the top layers keep an enlarged value of $a_\perp$, whereas the bulk of the film relaxes into the undistorted (isotropic) fcc structure ($a_\perp \approx 1.78$ Å, $V_a \approx 11.4$ Å^3) [3]. This correlates with the observed drop of the remanent magnetization if one assumes that the ferromagnetism in the film is indeed related to an expanded interlayer spacing. This assumption was recently substantiated by conversion-electron Mössbauer spectroscopy experiments [8,9] which also showed that the isotropic fcc Fe, in fact, orders antiferromagnetically at low temperatures, in agreement [12] with the results of previous magneto-optical Kerr effect investigations [2].

Thus, thickness dependences of both the structural and magnetic properties of Fe/Cu(100) closely correlate with each other and are believed to be well understood. At the same time there is a definite lack of information on the temperature dependence of these properties. The questions, whether the structure of the Fe film remains stable against temperature variation and whether possible temperature-driven structural transformations are accompanied by some change of magnetic properties, are still open. In this Letter we answer both of these questions and present the results on the temperature dependence of the structural and magnetic properties of Fe/Cu(100) in the range of 120–400 K. For the sake of clarity and because of space constraints, we concentrate on the results for 3 and 4 ML Fe/Cu(100). A detailed data analysis for other thicknesses will be presented elsewhere.

The measurements of structural and magnetic properties were carried out in an interleaved mode to exclude irreversibility effects. The magnetic properties were probed using the magneto-optical Kerr effect (MOKE) by registering hysteresis loops in the polar geometry. The loops had a square shape except for the region of the Curie transition where a pronounced change of the loop shape was observed. The maximum magnetic field applied $H_{\max}$ was 250 Oe which allowed us to reach the saturation magnetization over most of the temperatures and thicknesses covered (for $4.5 \leq d \leq 10$ ML coercivity at low temperatures exceeded $H_{\max}$). Conclusions on the crystalline structure of the Fe films were drawn from a kinematic analysis of LEED $I(E)$ curves for the (00) diffraction beam. Such curves often show a periodic (as a function of $\sqrt{E}$) sequence of intensity maxima that result from constructive interference, whenever the vertical interlayer spacing corresponds to an integer multiple of the electron wave length [13]. Such a sequence $S(E)$ thus represents a kind of fingerprint for a certain structural phase in the system under investigation. Moreover, it is possible to evaluate (in the kinematic approximation) the corresponding average vertical interlayer spacing, what is especially beneficial in a system where the magnetic properties are determined by this parameter.

The iron films were epitaxially deposited on a Cu(100) single crystal kept at room temperature. The deposition rate was varied between 0.3 and 0.6 ML/min and the pressure during the evaporation was always below 2×10^{-8} Pa. The growth process was monitored and controlled *in situ* by medium energy electron diffraction (MEED), the typical behavior for the specular beam [1] being reproduced in our experiments. This procedure and additional Auger electron spectroscopy (AES) measurements allowed a thickness determination with an accuracy of 0.2 ML.

The $I(E)$ curves for the (00) LEED beam in fcc Fe/Cu(100) ($d < 11$ ML) reveal two periodic (as a function of $\sqrt{E}$) sequences of maxima. The corresponding values of $a_\perp$ (1.8 and 1.9 Å) and the comparison with the case of clean Cu(100) both show that the observed sequences, which we will address as $S_{\mathrm{fcc}}(E)$ and $S_{\mathrm{fct}}(E)$, correspond to the isotropic and tetragonally expanded fcc Fe structures, respectively.

The $I(E)$ curves collected at temperatures of about 160 K [which are typical for previous LEED investigations on Fe/Cu(100) [3–6]] provide the same d dependence for the structure of the fcc Fe films as the previous investigations. The characters of the $I(E)$ curves at $d \leq 4$ ML (the lowest curve in Fig. 1 is typical) and at $4.5 \leq d \leq 10$ ML (the topmost curve in Fig. 1 is typical) are different, manifesting the transition from the completely tetragonally expanded fcc lattice of Fe to a structure with only the topmost layers expanded. At $d \leq 4$ ML $S_{\mathrm{fct}}(E)$ dominates, whereas the intensity of the sequence observed at higher energies decreases with increasing d, which allows us to associate the latter sequence with the substrate. Because of the same value of $a_\perp$ (1.8 Å), this sequence is practically indistinguishable from $S_{\mathrm{fcc}}(E)$. At $4.5 \leq d \leq 10$ ML $S_{\mathrm{fcc}}(E)$ becomes dominating, whereas the maxima corresponding to the expanded phase are observed in the $I(E)$ curves only at low energies. They may therefore be associated with low-energy electrons having a small escape length, which suggests that the expansion really takes place only in the upper layers of the film. It should also be noted that these maxima are slightly shifted to higher energies as compared with the ones in $S_{\mathrm{fct}}(E)$ at $d \leq 4$ ML ($a_\perp$ changed to 1.85 Å).

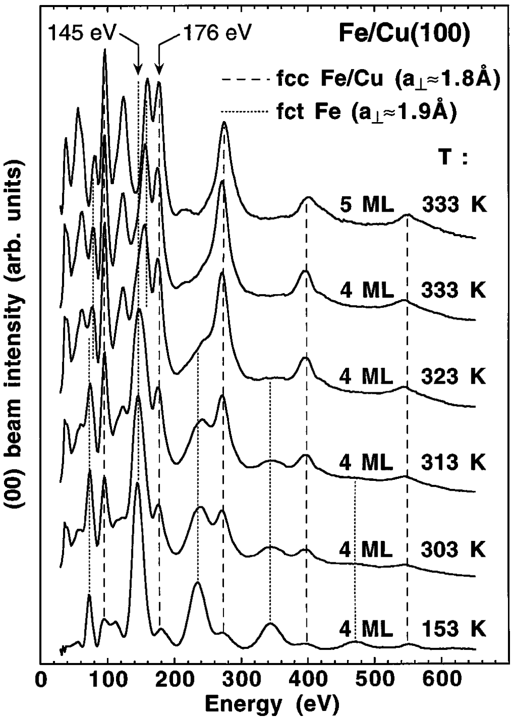

FIG. 1. Intensity vs energy dependence of the LEED (00) beam for 4 ML Fe as well as for 5 ML Fe (topmost curve) on Cu(100) measured at various temperatures during heating. The curves were taken with an angle of incidence of 6° in the (100) mirror plane of the substrate. Two periodic sequences of maxima [$S_{\mathrm{fcc}}(E)$ and $S_{\mathrm{fct}}(E)$] corresponding to the fcc and fct structures of Fe on Cu(100) are traced by vertical dashed and dotted lines, respectively. $S_{\mathrm{fcc}}(E)$ overlaps with an analogous sequence for Cu(100). $S_{\mathrm{fct}}(E)$ observed at lower temperatures disappears completely between 313 and 333 K, and a new sequence slightly shifted to higher energies with respect to the previous values for $S_{\mathrm{fct}}(E)$ appears. At $d = 5$ ML the character of the $I(E)$ curve does not change upon heating from 153 to 333 K.

Varying the temperature results in a change of the relative weights of $S_{\mathrm{fcc}}(E)$ and $S_{\mathrm{fct}}(E)$ in the $I(E)$ curves; relative intensities of the peaks at higher and lower kinetic energy within the sequences also change slightly. Nevertheless, the character of the curves remains the same except for the case of 4 ML (Fig. 1). The corresponding $I(E)$ curve changes dramatically upon heating, the most abrupt changes occurring between 313 and 333 K. On the one hand, $S_{\mathrm{fcc}}(E)$ becomes dominant. On the other hand, $S_{\mathrm{fct}}(E)$ observed at lower temperatures disappears completely, and a new sequence, slightly shifted to higher energies with respect to the previous values for $S_{\mathrm{fct}}(E)$, appears. The maxima in this new sequence are observed only at low energies and are characterized by the same positions as the ones in $S_{\mathrm{fct}}(E)$ at $4.5 \leq d \leq 10$ ML. Thus, the $I(E)$ curve for the 4 ML film becomes exactly the same as that for the films with $4.5 \leq d \leq 10$ ML, which is also clearly seen from the direct comparison of the $I(E)$ curves for the 4 and 5 ML films at 333 K in Fig. 1. From this it follows that the 4 ML film at $T = 333$ K assumes a similar structure as the 5–9 ML films, namely, an fcc structure in the bulk of the film and fct in the topmost layers.

Such a drastic structural transformation is also found to affect the magnetic properties of the 4 ML film. This is illustrated by Fig. 2 which represents the main result of this Letter. In Fig. 2 the ratio of the intensities of the $I(E)$ peak at ≈145 eV (I_{145}) in $S_{\mathrm{fct}}(E)$ and that at ≈176 eV (I_{176}) in $S_{\mathrm{fcc}}(E)$ as well as the saturation magnetization (M_{sat}) are presented as a function of temperature. The latter was increased from 150 to 343 K and then decreased to 190 K by steps of 5–30 K. Comparison of these two plots shows that they are practically identical; the same curve can be used [dashed line in Figs. 2(a) and 2(b)] to fit both experimental curves. The ratio $I_{145}(\mathrm{fct})/I_{176}(\mathrm{fcc})$ reveals a relation between the fct and fcc phases in the bulk of the Fe film. The peaks at ≈145 and ≈176 eV were chosen because of their intensity. If another pair of the $I(E)$ peaks is taken, the corresponding ratio behaves in the same way: it decreases slowly during heating to 313 K and then drops fast between 313 and 333 K.

A coincidence between the temperature behavior of M_{sat} and the ratio $I(\mathrm{fct})/I(\mathrm{fcc})$ indicates that the ferromagnetic long-range order in the 4 ML film is not destroyed by the usual thermodynamic way, but by the temperature-driven structural transformation. An observed irreversibility of the ferromagnetic-paramagnetic transition also supports this conclusion, pointing towards an activated process. For the thicker Fe films ($d \geq 4.5$ ML) the limitation of the fct structure only to the upper layers is energetically more favorable than an overall fct structure. The corresponding reduction of the elastic energy in the film should then overcompensate the increase of the interfacial energy. Additionally, some energy barrier between two different structural states can exist and must then be overcome. At a fixed thickness, the temperature affects both the balance between elastic and interfacial energies and the probability to overcome the effective barrier. If such a barrier really exists and the depth of the potential minima on its opposite sides is different, a temperature irreversibility of the structural transition can be expected. Such an irreversibility is, in fact, observed in Fig. 2(a): the 4 ML film turns into the new structural state after heating and keeps this new structure even during subsequent cooling. The onset of the ferromagnetic long-range order occurs then at $T \approx 270–280$ K [Fig. 2(b)], which is the typical Curie temperature for the Fe film with fcc structure expanded only in the topmost layers [1]. The initial fct structure with $a_\perp = 1.9$ Å ($a_\perp$ for the fct structure changes to 1.85 Å after the structural transition) appears in the same temperature range [Fig. 2(b)]; two different fct structures ($a_\perp = 1.85$ and 1.9 Å) and the fcc structure coexist in a rather extended range of temperatures. Only after cooling down to temperatures $T_{\min}$ of about 120–180 K the system slowly returns to the initial structural state and to the full magnetization. The time scale of this process depends on the cooling procedure and $T_{\min}$, and varies from 20–30 min to some hours.

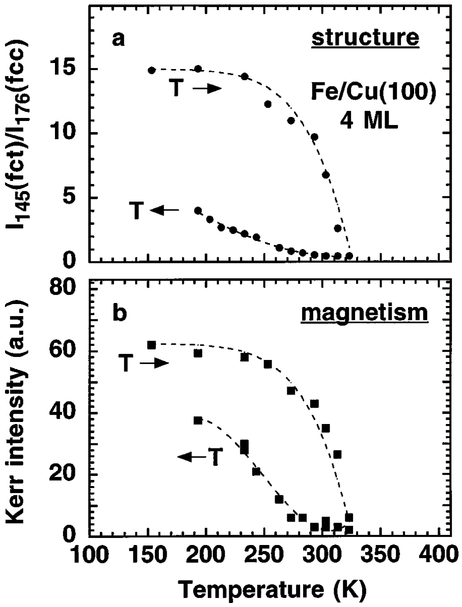

FIG. 2. The ratio of the intensity of the peaks at 145 and 176 eV (marked in Fig. 1) in the $I(E)$ curves for the (00) beam (a) as well as saturation magnetization (b) for 4 ML Fe/Cu(100) during heating and cooling of the sample (indicated by arrows) at the order-disorder magnetic transition. The peaks at 145 and 176 eV belong to the periodical sequences of maxima corresponding to fct and fcc Fe, respectively. Dashed lines serve as a guide to the eye. The identical dashed line is used to trace the temperature dependence of both the ratio I_{145}/I_{176} in (a) and the saturation magnetization in (b) during heating.

The maximum temperature to which the 4 ML film was heated (343 K) is significantly lower than that for the onset of interdiffusion (410 K [14]). Nevertheless, if some influence of this process on the structure would take place at lower temperatures, it should reveal itself in the same way not only in the 4 ML film but also in 3 ML, where the onset of interdiffusion occurs at even lower temperature [14,15]. The dependences of M_{sat} and I_{145}/I_{176} on T for the 3 ML film are depicted in Figs. 3(a) and 3(b), respectively, the same scaling as in Fig. 2 being used. The ratio I_{145}/I_{176} in Fig. 3(a) decreases slowly with increasing temperature, but has in no way the same behavior as M_{sat} and shows no abrupt changes between 313 and 333 K (as it occurs in the 4 ML film) or in the region of the Curie transition at ≈365 K. If the structure of the 3 ML film is, however, to some extent affected by the temperature, corresponding changes are not as dramatic as in the 4 ML film and do not significantly influence the magnetic properties. The reversibility of both dependences in Figs. 3(a) and 3(b) supports this conclusion. The observed structural and magnetic transitions are, in fact, characteristic *only* for the 4 ML film, which seems to be structurally unstable

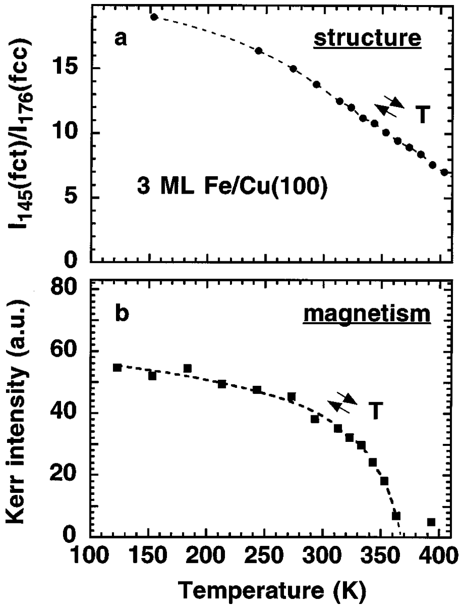

FIG. 3. The ratio of the intensity of the peaks at 145 and 176 eV in the $I(E)$ curves for the (00) beam (a) as well as saturation magnetization (b) for 3 ML Fe/Cu(100) during heating and cooling of the sample (indicated by arrows) at the Curie transition. The peaks at 145 and 176 eV belong to the periodical sequences of maxima corresponding to fct and fcc Fe, respectively. Dashed lines represent a guide to the eye. The same scales as in Figs. 2(a) and 2(b) are used in (a) and (b), respectively.

because of the competition of the elastic and interfacial energies. Just increasing the thickness by 0.5 ML or heating up to 333 K is sufficient to force the film into the new structural and magnetic state.

Our finding explains a curiosity in the thickness dependence of the Curie temperature T_c of Fe/Cu(001) the attentive reader of Ref. [1] may have come across. Generally, in magnetic thin film systems the Curie temperature increases with increasing film thicknesses as a result of the scaling law [16], as long as the whole film is magnetic and no other properties of the system (structure, morphology, composition) are changed. What was observed instead by Thomassen *et al.* [1] (and exactly reproduced by us) is a monotonous increase of T_c with film thickness up to about 3 ML and a distinct decrease of T_c at 4 ML. This is difficult to understand, because the structural phase transition from the entirely tetragonally expanded fcc structure to that expanded only in the topmost layers was thought to occur at higher thicknesses, as judged by the behavior of the remanent magnetization extrapolated to 0 K. This unusual behavior was not discussed by the authors, and we provide evidence that indeed an important property of the system, namely, the structure, is altered already at 4 ML thickness by temperature variation. By extrapolating the $T_c(d)$ dependence in Fe/Cu(100) from the range below 3 ML to $d = 4$ ML, the thermodynamical Curie temperature of the 4 ML film can be estimated to be approximately 460 K. But before the thermodynamical Curie transition can occur, a structural rearrangement takes place. The new structure which the 4 ML film assumes at $T \geq 333$ K also possesses ferromagnetic properties, but the corresponding Curie temperature ($\approx$270 K) is significantly lower than 333 K. As soon as the structural transformation takes place, the film happens to be above T_c for this particular system and consequently becomes paramagnetic.

In conclusion, we have for the first time observed a magnetic order-disorder transition mediated by a structural transformation. The temperature-driven structural rearrangement in 4 ML Fe films on Cu(100) was shown to lead to a breakdown of the ferromagnetic long-range order. Two factors are of importance for the existence of this phenomena, namely, the strong dependence of the magnetic properties of Fe on the atomic volume and the structural instability of fcc Fe on Cu(100).

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