Ferromagnetic Order in a Fe(110) Monolayer on W(110) by Mössbauer Spectroscopy

M. Przybylski[(a)] and U. Gradmann
Physikalisches Institut, Technische Universität Clausthal, D-3392 Clausthal-Zellerfeld,
Federal Republic of Germany

(Received 22 June 1987)

Ferromagnetic order in Fe(110) monolayers on W(110) was analyzed with the use of conversion-electron Mössbauer spectroscopy. The Ag-coated monolayer is ferromagnetic up to $T_C(1)=296$ K $=0.28T_C(\infty)$. The gross shape of $B_{hf}(T)$ resembles that of bulk material. $B_{hf}(0)$ is reduced to 11.9 ± 0.3 T. In the critical region 275 K $\leq T \leq$ 295 K, a continuous transition from a magnetic to a nonmagnetic component takes place. For the uncoated monolayer, the ground-state hyperfine field and Curie temperature are reduced to $B_{hf}(0)=10\pm1$ T and $T_C(1)=210$ K $=0.20T_C(\infty)$, respectively.

PACS numbers: 75.70.Ak, 75.30.Cr

Ferromagnetic order in a two-dimensional lattice has been a fascinating problem since Bloch[1] stated its absence for the isotropic Heisenberg model, which has been confirmed rigorously by Mermin and Wagner.[2] However, it had been shown before by Döring[3] that long-range ferromagnetic order can be triggered for the monolayer, too, by magnetic anisotropies.[4] As strong crystalline anisotropies are present in monolayers,[5] the physical problem is magnetic order in an anisotropic monolayer, not in the isotropic one. Furthermore, it has been shown recently by Yafet, Kwo, and Gyorgy[6] that the bare dipolar interactions can induce ferromagnetism in two dimensions.

For the ground state of the ferromagnetic monolayer, recent band-structure calculations[7-9] show a general trend for enhanced ground-state moments. For finite temperatures, magnetic order is predicted to react much more sensitively on anisotropies than in three dimensions,[3,4,6] and T_C should be lowered to less than half the bulk value,[10-13] in rough agreement with the mean-field argument[10] that T_C is proportional to the number of nearest neighbors. For comparison with these results, only a few experiments are available.

Ferromagnetic monolayers of Co(111) and of Ni_{48}-Fe_{52}(111), both in a matrix of Cu(111), were analyzed by torsion oscillation magnetometry.[14] Normalized Curie temperatures $T_C(1)/T_C(\infty)=0.21$ and 0.30, respectively, were in good agreement with theoretical predictions.[11] In both cases, J_s depended linearly on T, in a broad temperature range, and J_s was along the surface normal, as a result of strong surface-type anisotropies. Pescia *et al.*[15,16] used spin-polarized photoemission to show that monolayers of fcc Co and of fcc γ-Fe on Cu(100) are ferromagnetic up to 400 and 200 K, respectively. Farle and Baberschke[17] used electron-spin resonance to analyze a Gd monolayer on W(110), in the paramagnetic range. They found strong evidence for transition to ferromagnetism at a surprisingly high temperature, $T_C(1)T_C(\infty)=0.93$. In the present Letter, Mössbauer spectroscopy is used to give the first study of monolayer magnetism in bcc α-Fe. Recently stated ferromagnetism of the free Fe(110) monolayer on W(110)[18] at room temperature could not be confirmed.

Experiments were performed in a UHV system,[19,20] equipped for molecular-beam epitaxy, LEED, Auger-electron spectroscopy, and magnetic analysis *in situ* by conversion-electron Mössbauer spectroscopy (CEMS). Pure ^{57}Fe(110) films were prepared at $T_P=300$ K on clean W(110) surfaces. Film thickness was measured with use of a quartz-crystal monitor with an accuracy of 4% of one monolayer and is given by the number of bulk monolayers, D. In agreement with previous work,[21] the first two monolayers were pseudomorphic on W(110), thus each containing the material of 0.82 monolayers of bulk Fe(110) ($a_{Fe}=2.866$ Å, $a_W=3.165$ Å, $f_{Fe/W}=-9.4\%$). Monolayers were analyzed both coated by Ag and with free surface. For the following analysis, it is crucial to know whether the first monolayer is completed before the second one starts to grow. This question has been answered with use of CEMS, as will be discussed in detail elsewhere.[22] The method can be explained in Fig.

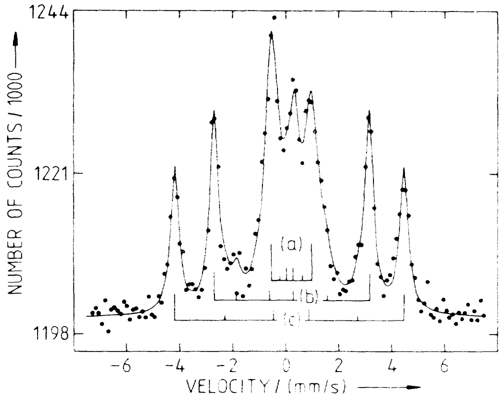

FIG. 1. Mössbauer spectrum, taken at 295 K, of a Fe(110) film on W(110), consisting of 1.09 bulk monolayers, coated by Ag, W(110)/Fe(1.09 ML)/Ag.

1, which shows the CEMS spectrum measured at 295 K, of a probe W(110)/Fe(1.09 ML)/Ag [$D = 1.09$ bulk monolayers (ML) ^{57}Fe on W, coated by Ag], prepared at $T_P = 300$ K.

The spectrum consists of three components (a), (b), and (c) with clearly distinct hyperfine fields of 5, 18, and 27 T, respectively. Component (a) can be attributed to monolayer patches, components (b) and (c), which are of equal intensity, to the first and the second layer of double-layer patches. Their intensities, being proportional to ($D - 0.82$ ML), follow a straightforward layer-by-layer growth model, which thus clearly is established for $T_P = 300$ K.[22] Accordingly, samples W(110)/Fe(0.82 ML)/Ag and W(110)/Fe(0.82 ML)/-(0.82 bulk monolayers coated by Ag or uncoated, respectively), when prepared at 300 K, can be taken as true pseudomorphic monolayers, in the limits of $D = 0.82 \pm 0.04$.

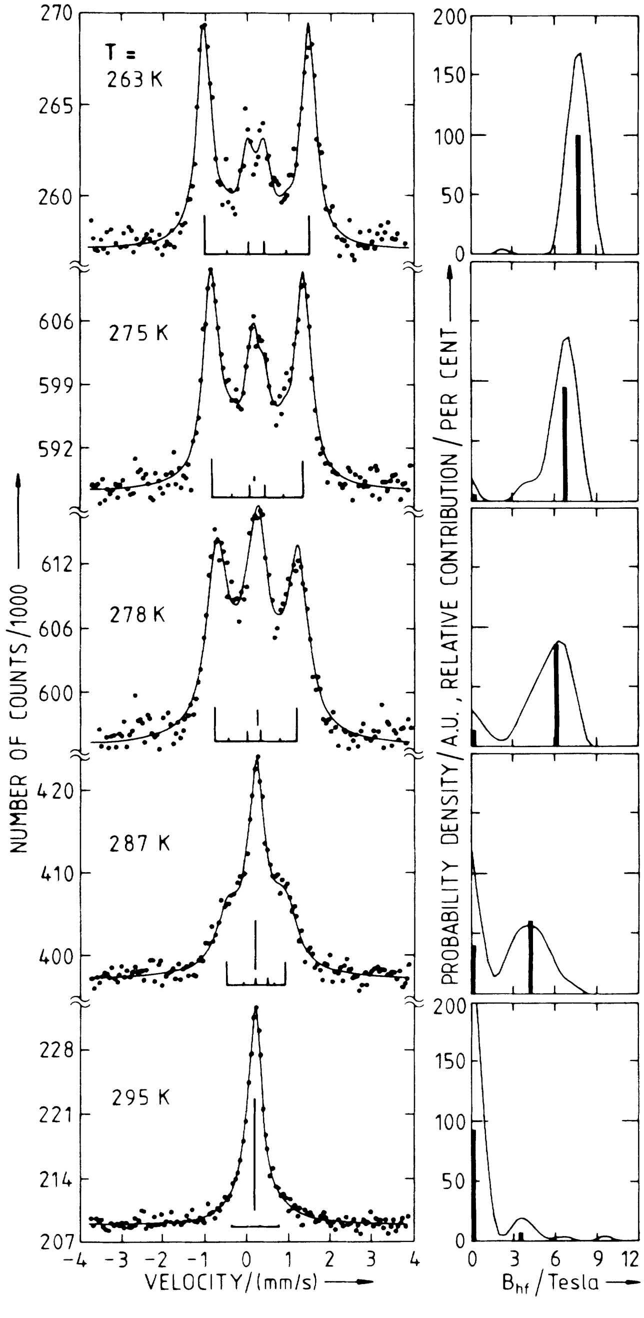

FIG. 2. Mössbauer spectra of a pseudomorphic Fe(110) monolayer coated by Ag, W(110)/Fe(0.82 ML)/Ag, measured at the given temperatures (left side). Probability density for hyperfine field distribution and relative contribution vs B_{hf} for a two-component fit, respectively (right side).

Extended spectra between 90 and 400 K were measured for one special sample W(110)/Fe(0.82 ML)/Ag. Spectra in the critical region 263 K $\le T \le$ 295 K are shown on the left side of Fig. 2. They were fitted by the superposition of one six-line Zeeman component and one single line, as indicated by the fingerprints (left side) or alternatively by hyperfine field B_{hf}, and relative contribution (right side). This fit is justified by an alternative fit using a continuous hyperfine-field distribution, shown for comparison, which clearly confirms the two-component structure of the spectra. The spectrum for $T = 263$ K is representative for all low-temperature spectra $T \le 263$ K, in that they could be fitted by one single six-line component, with intensity ratios $I_1{:}I_2{:}I_3{:} = (2.7 \pm 0.3){:}(0.2 \pm 0.1){:}1$ near the theoretical ratio 3:0.14:1 for the present geometry (grazing incidence near [001], with $\mathbf{J}_s$ along [$1\bar{1}0$]). Figure 3 shows hyperfine field B_{hf} of the magnetic component (open circles), mean hyperfine $\bar{B}_{hf}$ (filled circles), and relative contribution p_{single} of the single line (crosses) versus T. For low temperatures, $B_{hf} = \bar{B}_{hf}$ decreases with increasing T in a similar way as in bulk material. In the critical region, however, a con-

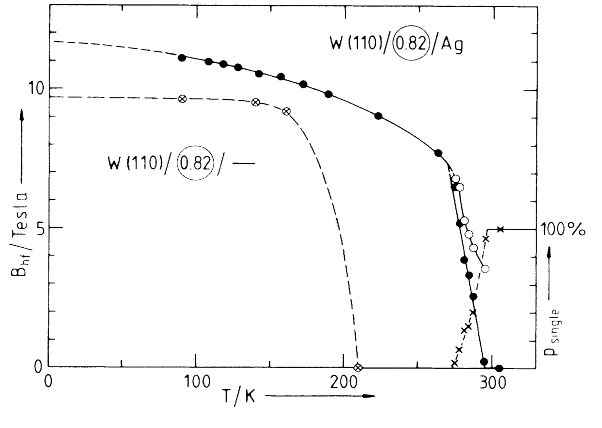

FIG. 3. Magnetic hyperfine fields $B_{hf}(T)$ vs temperature for pseudomorphic Fe(110) monolayers on W(110). Mean values $\bar{B}_{hf}$ (filled circles) and B_{hf} for the magnetic component (open circles) for the Ag-coated layer [W(110)/Fe(0.82 ML)/Ag]. B_{hf} from extrapolation and $T_C(1)$ from thermal scan for the uncoated monolayer (circled crosses).

tinuous transition from the six-line to the single-line component takes place. Note the finite value of B_{hf} near the critical temperature, $T_C(1) = 296 \pm 1$ K, which can be taken both from the disappearance of B_{hf} and from the approach to $p_{\mathrm{single}} = 1$. Measurements with further samples W(110)/Fe(0.82 ML)/Ag confirmed the results with respect to B_{hf} of the main component, in the limits of accuracy.

Some experiments were done with the uncoated monolayer. They are complicated by residual gas adsorption, even at 3×10^{-11} Torr. Separate preparations had to be done for each temperature, and $B_{\mathrm{hf}}(T)$ of the free (pseudomorphic) monolayer had to be determined by extrapolation to the time just after preparation, as was done previously for the surface of $D = 21$ ML films.[19] Some results are included in Fig. 3. In addition, we determined the Curie temperature of the free monolayer by thermal scanning at a fixed source velocity, as shown in Fig. 4 for $D = 0.82$ ML. The resulting Curie temperature $T_C(1) = 210$ K of the uncoated monolayer is included in Fig. 3. It is remarkable that this $T_C(1)$, the Curie temperature of the monolayer component, was nearly independent of the mean film thickness. For $D = 1.0$, we measured $T_C(1) = 214$ K by the same method! The gross shape of $B_{\mathrm{hf}}(T)$ is the same as for the Ag-coated monolayer. In the paramagnetic state $T > 210$ K, the uncoated monolayer shows a quadrupole doublet, in contrast to the Ag-coated monolayer, which shows a single line above $T_C(1) = 296$ K. This reflects the lower symmetry of surface atoms in comparison with interface atoms.

For the interpretation of $B_{\mathrm{hf}}(T)$ in Fig. 3, we use the generally accepted assumption that the thermal structure of B_{hf} equals that of the magnetization, in contrast to the local structure, which can be quite different near surfaces.[19,23] The gross features of $B_{\mathrm{hf}}(T)$ are the following:

(1) The shape of $B_{\mathrm{hf}}(T)$ surprisingly resembles that for bulk material, in contrast to monolayers of Co and NiFe(111) on Cu(111)[14] and of γ-Fe on Cu(100),[16] where a linear decrease of the magnetization was observed. Supposedly this is connected with the direction of magnetization, which was along the surface normal for the latter cases, caused by surface anisotropy, whereas it remains in the plane for the present monolayer. A similar phenomenon was observed in connection with magnetization switching in oligatomic NiFe(111) films.[14]

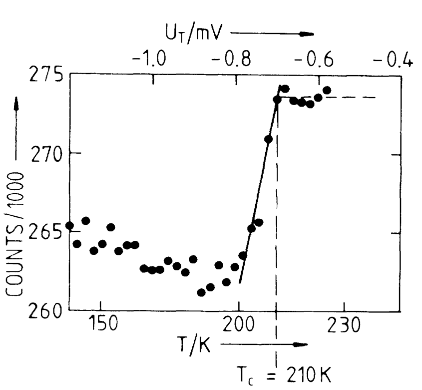

FIG. 4. Thermal scan at $v = \pm 0.15$ mm s for an uncoated pseudomorphic Fe monolayer, W(110)/Fe(0.82 ML)/-.

(2) In the low-temperature region, fitting and extrapolation to $T = 0$ is problematic for the Ag-coated layer. Following spin-wave arguments,[3,14] one might try a linear extrapolation, resulting in $B_{\mathrm{hf}}(0) = 12.0$ T. On the other hand, one may try a $T^{3/2}$ fit, in the spirit of the general bulklike behavior. Such a fit, using 90 K $\leq T \leq$ 172 K, is included in Fig. 3, resulting in $B_{\mathrm{hf}}(0) = 11.7$ T. Summarizing, $B_{\mathrm{hf}}(0) = 11.9 \pm 0.3$ T can be taken as a reliable result for the Ag-coated monolayer. For the free monolayer, only a rough estimate $B_{\mathrm{hf}}(0) = 10 \pm 1$ T is possible. The small difference in $B_{\mathrm{hf}}(0)$ between the free and the Ag-coated monolayer is in accordance with the situation at the free and the Ag-coated surface.[19] Measurements below 90 K are required.

(3) The Curie temperatures, $T_C(1) = 296\ \mathrm{K} = 0.28 \times T_C(\infty)$ for the Ag-coated and $T_C(1) = 210\ \mathrm{K} = 0.20 \times T_C(\infty)$ for the free surface, are in qualitative agreement with a high-temperature series expansion estimate,[11] which gives $T_C(1) = 0.46 T_C(\infty)$ for $S = 2$ and the present geometry.

(4) A narrow critical region between 270 K and $T_C = 296$ K is sharply separated from the low-temperature region. Apparently, a qualitative change of thermal decrease occurs near 270 K. Above 270 K, the mean hyperfine field $\bar{B}_{\mathrm{hf}}$, which can be taken as a measure of the mean magnetization, is proportional to $T_C - T$, which formally can be described by a critical exponent $\beta = 1.0$. The key property is given by the gradual transition of intensity from a magnetic component to a nonmagnetic single line in combination with a steep decrease of B_{hf} of the magnetic component to a finite value of 3.5 T when extrapolated to T_C. It might be connected with a nucleation from surface steps, in a similar way as has been observed in the $(7 \times 7) \leftrightarrow (1 \times 1)$ transition on Si(111),[24] which therefore has been claimed to be of first order. An alternative interpretation in terms of a superparamagnetic collapse can definitely be excluded for the free monolayer, where the LEED pattern clearly establishes the translational symmetry, and the independence of $T_C(1)$ on D up to $D = 1$ ML shows the intrinsic, microscopic nature of the transition. For the Ag-coated monolayer, one might speculate whether the translational symmetry might have been disturbed by periodic incorporation of Ag from the coating into the pseudomorphically strained Fe(110) monolayer, resulting in 10×10 atoms Fe-monolayer patches, separated or weakly coupled by Ag rows. Several arguments contradict this superparamagnetic interpretation. (a) A rough estimate of the blocking temperature, from known surface

anisotropies,[25] results in 60 K, by far too low in comparison with the experiment. (b) The width of the transition is much narrower than ever observed in standard superparamagnetic systems.[26] (c) In standard superparamagnetic systems[26] the rise of the single line is not connected with a strong decrease of B_{hf} of the magnetic components, as in our case. (d) It has been shown that the first monolayer remains pseudomorphic in a thick Fe(110) film on W(110) [27]; it can then hardly be expected that pseudomorphism is released by Ag. Summarizing, the transition, in our opinion, is not superparamagnetic. Final experimental decision with use of magnetometry is in preparation.

(5) There is only apparent contradiction to the statement of Kurzawa *et al.*[18] on ferromagnetism at room temperature for a free Fe(110) monolayer on W(110) of "2±0.2 Å." 2.2 Å equals $D=1.1$ ML (1.34 pseudomorphic layers), roughly the situation of Fig. 1. Half of the atoms then are in double-layer patches ferromagnetic at room temperature; apparently it is this double-layer magnetism which has been seen in the experiment.[18]

Summarizing, we have shown that the combination of Mössbauer spectroscopy with modern sophisticated methods of epitaxial growth forms an excellent method for the experimental analysis of monolayer magnetism. Fe(110) monolayers on W(110), whether uncoated or coated by Ag, are ferromagnetic with $T_C(1)=210$ and 296 K, respectively. New phenomena observed in the critical region remain to be analyzed.

Discussions with J. Korecki are gratefully acknowledged. This work was supported by the Stiftung Volkswagenwerk.

---

[a] Permanent address: Department of Solid State Physics, Institute of Metallurgy, Academy of Mining and Metallurgy, PL-30-059 Crakow, Poland.

[1] F. Bloch, Z. Phys. **49**, 619 (1928).
[2] N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).
[3] W. Döring, Z. Phys. A **16**, 1008 (1961).
[4] J. A. Davis, J. Appl. Phys. **36**, 3520 (1965).
[5] U. Gradmann, J. Magn. Magn. Mater. **54–57**, 733 (1986).
[6] Y. Yafet, J. Kwo, and E. M. Gyorgy, Phys. Rev. B **33**, 6519 (1986).
[7] J. Noffke and L. Fritsche, J. Phys. C **14**, 89 (1981).
[8] C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985).
[9] R. H. Victora and L. M. Falicov, Phys. Rev. B **28**, 5232 (1983).
[10] L. Valenta, Phys. Status Solidi **2**, 112 (1962).
[11] H. E. Stanley and F. A. Kaplan, Phys. Rev. Lett. **17**, 913 (1966).
[12] W. Brodkorb and W. Haubenreisser, Phys. Status Solidi **16**, 577 (1966).
[13] H. Hasegawa, Surf. Sci. **182**, 591 (1987).
[14] U. Gradmann, Appl. Phys. **3**, 161 (1974).
[15] D. Pescia, G. Zampieri, M. Stampanoni, G. L. Bona, R. F. Willis, and F. Meier, Phys. Rev. Lett. **58**, 933 (1987).
[16] D. Pescia, M. Stampanoni, G. L. Bona, A. Vaterlaus, R. F. Willis, and F. Meier, Phys. Rev. Lett. **58**, 2126 (1987).
[17] M. Farle and K. Baberschke, Phys. Rev. Lett. **58**, 511 (1987).
[18] R. Kurzawa, K. P. Kämper, W. Schmitt, and G. Güntherodt, Solid State Commun. **60**, 777 (1986).
[19] J. Korecki and U. Gradmann, Phys. Rev. Lett. **55**, 2491 (1985).
[20] J. Korecki and U. Gradmann, Hyperfine Interact. **28**, 931 (1986).
[21] U. Gradmann and G. Waller, Surf. Sci. **116**, 539 (1982).
[22] M. Przybylski and U. Gradmann, to be published.
[23] S. Ohnishi, M. Weinert, and A. J. Freeman, Phys. Rev. B **30**, 36 (1984).
[24] W. Telieps and E. Bauer, Surf. Sci. **162**, 163 (1985).
[25] U. Gradmann, J. Korecki, and G. Waller, Appl. Phys. A **39**, 101 (1986).
[26] K. Krop, J. Korecki, J. Zukrowski, and W. Karas, Int. J. Magn. **6**, 19 (1974).
[27] M. Przybylski and U. Gradmann, to be published.