# Magnetism of Epitaxial fcc-Fe(100) Films on Cu(100) Investigated *in Situ* by Conversion-Electron Mössbauer Spectroscopy in Ultrahigh Vacuum

W. A. A. Macedo[a] and W. Keune

*Laboratorium für Angewandte Physik, Universität Duisburg, D-4100 Duisburg 1, Federal Republic of Germany*

(Received 13 November 1987)

Ultrathin films (10 to 17 monolayers) of fcc Fe(100) grown epitaxially on Cu(100) are unambiguously found to be paramagnetic at 295 K by $^{57}$Fe conversion-electron Mössbauer spectroscopy in UHV. Below $T_N = 65 \pm 5$ K, fcc-Fe films are magnetically ordered and show a small average hyperfine field, e.g., 1.1 T at 29 K for 10 monolayers, indicating a small atomic magnetic moment. This demonstrates that fcc Fe(100) stabilized at a lattice constant close to that of Cu has an antiferromagnetic ground state.

PACS numbers: 75.70.Ak, 75.50.Bb, 76.80.+y

The extreme volume dependence of the ground-state magnetic properties of bulk fcc ($\gamma$-)iron predicted by electronic band-structure calculations[1-7] has stimulated new theoretical and experimental activity recently. Since pure bulk fcc Fe only exists at high temperatures, fcc Fe must be stabilized down to very low temperatures either as small $\gamma$-Fe precipitates in a Cu matrix[8] or as thin epitaxial $\gamma$-Fe films on a Cu substrate.[9] While antiferromagnetism (AF) in $\gamma$-Fe precipitates with a small atomic magnetic moment of $\simeq 0.7\mu_B$ is generally accepted,[10,11] contradicting results on the type of magnetic order in epitaxial $\gamma$-Fe films have been reported. Ferromagnetism (FM) at 295 K has been inferred from magnetization measurements[12,13] on Cu-coated $\gamma$-Fe(111) films up to 80 Å thick. To the contrary, Mössbauer results[14-16] from Cu-coated $\gamma$-Fe(100), $\gamma$-Fe(110), and $\gamma$-Fe(111) films (18-25 Å thick) have demonstrated paramagnetism (PM) at 295 K and AF below $T_N \simeq 80$ K. In addition, polarized-neutron diffraction from Cu-coated fcc Fe epitaxied to Cu(100) and Rh(100) indicated no in-plane ferromagnetism at 300 K.[17] Recently, conflicting results of PM[18,19] and FM[20,21] at 295 K for uncoated epitaxial fcc-Fe films of up to several monolayers thickness in UHV have been reported. Electronic band-structure calculations indicate FM in a surface layer, but AF in the interior of the fcc Fe(100) film.[19] FM at the surface of fcc-Fe films has been observed experimentally.[19,22] For a fcc-Fe(100) bilayer on Cu(100), recent calculations[20] indicate strongly enhanced Fe magnetic moments and show the ferromagnetically coupled Fe bilayers at the Cu lattice constant have a lower total energy than antiferromagnetically coupled bilayers.

In this Letter we report the first *in situ* measurement of the local magnetic properties of ultrathin (10 to 17) monolayers (ML) fcc-($\gamma$-)Fe(100) films pseudomorphically grown on Cu(100) surfaces under UHV conditions. The purpose of our experiments is to investigate the magnetic hyperfine interaction and its temperature dependence in well-prepared and well-characterized fcc-Fe(100) films with the aim of solving the crucial conflict of *ferromagnetism* or *antiferromagnetism* in fcc-Fe films on Cu. Our films can be considered almost like bulk fcc Fe, since the electronic structure of 4-ML fcc Fe(100) has been found to be almost bulklike.[20] Using energy-differential $^{57}$Fe conversion-electron Mössbauer spectroscopy (DCEMS) in UHV we find unambiguously that uncoated (bulklike) fcc-Fe(100) films on Cu(100) are paramagnetic at 295 K and magnetically ordered below $T_N = 65 \pm 5$ K.

A review of the DCEMS method was given elsewhere.[23] *K* conversion electrons of 7.3 keV are emitted after deexcitation of $^{57}$Fe Mössbauer nuclei, and electrons leaving the sample surface are detected by use of an electron spectrometer[24,25] of 2.7% energy resolution. For the present experiment we have chosen $\theta = 75°$ ($\theta$ = angle between the selected electron emission direction and the sample surface normal) and a specrometer energy setting of 7.35 keV, implying $\phi = 42°$ between $\gamma$-ray direction and surface normal. Sample cooling by liquid helium is achieved by a UHV cold-finger-type flow cryostat. The system is equipped with a four-grid LEED optics for low-energy electron diffraction and retarding-field Auger-electron spectroscopy (AES). The base pressure of our UHV system was $2 \times 10^{-10}$ Torr. A $^{57}$Co Mössbauer source of $\simeq 100$ mCi activity (in Rh matrix) has been used.

For the deposition of Fe films, substrates of 600-Å-thick epitaxial Cu(100) films were prepared by electron-beam evaporation onto air-cleaved NaCl(100) crystals maintained at 320 °C. Subsequently, fcc-Fe films were obtained by evaporation of (95% enriched) $^{57}$Fe metal from a resistivity heated alumina crucible at a rate of 0.2 Å/min onto the Cu(100) surface which was held at 200 °C. The pressure during evaporation was better than $5 \times 10^{-10}$ Torr. Directly after Fe film preparation the contamination of the surface by impurities was recorded by AES: Traces of C, Cl, and S (and no traces of O) have been detected. Since, in the present study, we are *not* interested in magnetic properties of the *top-*

*most* surface layer of fcc-Fe films, but only in properties of the film interior, some surface contamination is of minor importance for the present problem.

The basis for pseudomorphic growth of fcc Fe on Cu is the similarity of lattice constants of Cu (3.615 Å at 295 K) and $\gamma$-Fe (3.588 Å at 293 K, extrapolated from bulk $\gamma$-Fe data[26] above 910 °C, or 3.5757 Å at 80 K measured for $\gamma$-Fe precipitates in Cu.[27] Figure 1 shows a $p(1\times1)$ LEED pattern of a 11-ML fcc-Fe film at 295 K which is typical for all of our $\gamma$-Fe films. The observed LEED pattern is identical to that of the underlying substrate film implying pseudomorphic growth of fcc Fe(100) on fcc Cu(100). There is no indication for a LEED pattern of bcc ($\alpha$-)iron.[13] Our LEED patterns for fcc Fe(100) are in agreement with those described in the literature for clean $\gamma$-Fe(100) surfaces.[16,18,21,28,29] fcc-Fe(100) films prepared under similar growth conditions (150–200 °C) closely follow the structure of bulk Cu,[26,29] and grow predominantly in a layer-by-layer mechanism.[29] Evidence for growth of flat Fe films is provided by our AES signal measured at 61 eV for Cu and 47 eV for Fe, and comparison with Fig. 2 of Ref. 22 obtained for atomically flat Fe(111) layers on Cu(111): The relative AES amplitude [relative to the bulk, and corrected for the 15% larger atomic area density of (111) planes as compared with (100) planes] was found to be less than 2% for the Cu signal and 97% for the Fe signal with our 10-ML Fe(100) film, indicating complete coverage of the Cu(100) substrate by Fe without significant island formation.

Figures 2(a) and 2(b) show typical DCEM spectra of 17 and 10 ML fcc Fe(100) at 295 K, respectively. These spectra could be least-squares fitted by Lorentzian lines, i.e., a main single line and a less intense (asymmetric) pair of quadrupole-split lines. The main single line has a linewidth (FWHM) of 0.31 mm $s^{-1}$ which is only slightly broader than the observed linewidth of the inner two lines of an $\alpha$-Fe calibration foil (e.g., 0.28 mm $s^{-1}$). The measured isomer shift of the single line (relative to $\alpha$-Fe at 295 K) of $-0.085(3)$ mm $s^{-1}$ for a 17-ML film and $-0.077(5)$ mm $s^{-1}$ for a 10-ML film is identical within error limits or very close to the isomer shift of paramagnetic fcc $\gamma$-Fe precipitates in a Cu matrix [e.g., $-0.088(3)$ mm $s^{-1}$ at 295 K (Refs. 14 and 16)]. This similarity provides clear evidence for *paramagnetism* of our fcc-Fe(100) films at 295 K. The complete absence (in Fig. 2) of spectral lines typical for $\alpha$-Fe indicates the absence of bcc Fe, in agreement with our LEED result.

The less intense quadrupole-split component in Figs. 2(a) and 2(b) has been attributed to Fe atoms with a certain number of Cu neighboring atoms and located at the Fe-Cu interface.[15] For the $\gamma$-Fe(100)/Cu(100) interface at 295 K, we obtain a quadrupole splitting $\Delta E_Q = \frac{1}{2}e^2qQ$ of 0.57(5) mm $s^{-1}$ and an isomer shift of $+0.02(2)$ mm $s^{-1}$ (relative to $\alpha$-Fe at 295 K), in fair agreement with values obtained on Cu-coated $\gamma$-Fe(100) films.[15] The intensity ratio $I_2/I_1$ of the two quadrupole lines obtained from computer fitting is $1.9\pm0.7$, with the intensity $I_2$ at more positive velocities. This asymmetry has been interpreted[15] in terms of a positive electric field gradient component $V_{zz}$ oriented preferentially perpendicular to or out of the film plane, in agreement with our observation.

From the relative spectral area of the interface lines

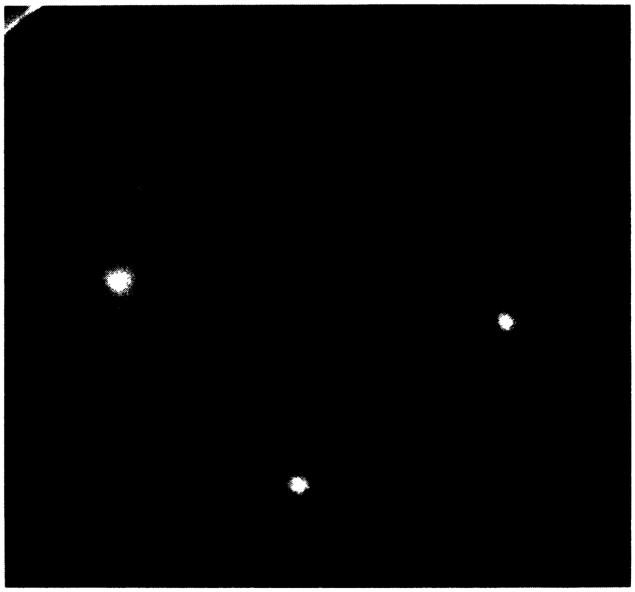

FIG. 1. $p(1\times1)$ LEED pattern of 11-ML fcc Fe(100) on Cu(100) at 78-eV electron energy. [A (11) spot of the quadratic diffraction pattern is hidden by the sample holder.]

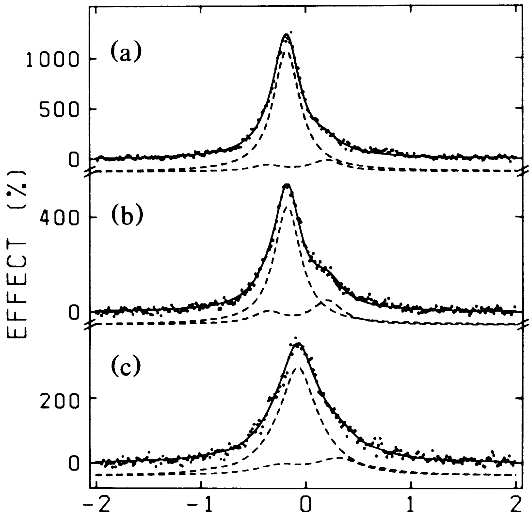

FIG. 2. DCEM spectra from fcc-Fe(100) films on Cu(100) for (a) 17-ML Fe at 295 K, (b) 10-ML Fe at 295 K, and (c) 10-ML Fe at 29 K.

the width of the interface can be estimated. The relative area of the interface component amounts to 13.6% of the total area for a 17-ML $\gamma$-Fe(100) film and increases to a value of 25.5% for the thinner 10-ML $\gamma$-Fe film [Figs. 2(a) and 2(b)]. By using the Monte Carlo computed weight function[30] (probability of electron escape and detection as a function of escape depth) for our experimental DCEMS arrangement, we can estimate from the measured spectral areas that the interface involves 3.8 atomic layers for the 17-ML $\gamma$-Fe film, and 3.3 atomic layers for the 10-ML $\gamma$-Fe film, i.e., an about constant number of atomic layers independent of $\gamma$-Fe film thickness. This indicates that the $\gamma$-Fe/Cu interface is by no means sharp despite the rather low substrate temperature (200 °C) chosen in order to minimize interdiffusion.[29] Obviously, for all our films a constant amount of 3 to 4 atomic layers forms an alloyed interface region. Thus the observed quadrupole-split subspectrum is a mean spectrum averaged over an about 3.5-ML-thick interface, implying that an electric field gradient is still observable up to the third or fourth interfacial atomic layer.

Clear evidence for magnetic ordering of our fcc Fe(100) films is provided by a drastic broadening of the $\gamma$-Fe line at lower temperatures, e.g., at 29 K for 10-ML $\gamma$-Fe(100) [Fig. 2(c)]. This observation is analogous to the case of $\gamma$-Fe precipitates in Cu below their Néel temperature where a reduction of temperature leads to increasing line broadening due to an increasing degree of antiferromagnetic ordering.[11] The antiferromagnetic state in $\gamma$-Fe is indicated by a line broadening only, since the magnetic hyperfine-field saturation value (~2.4 T for large precipitates) is of the order of the nature linewidth due to a small Fe atomic moment, and thus the full six-line Zeeman pattern cannot be resolved.[11,14,15] The similarities in the low-temperature spectra of $\gamma$-Fe precipitates and of our $\gamma$-Fe(100) films suggest that antiferromagnetic ordering occurred also for the latter. The spectrum shown in Fig. 2(c) was least-squares fitted as a hyperfine-field distribution for the $\gamma$-Fe component, plus a Lorentzian quadrupole pair for the interface component. The average hyperfine field of the $\gamma$-Fe film obtained from this fit is 1.1 T at 29 K which is of similar magnitude as that of antiferromagnetic $\gamma$-Fe precipitates in Cu at that temperature. The observed difference in the $\gamma$-Fe isomer shift between the 29 K and the 295-K spectra (0.099 mm $s^{-1}$) is a thermal red shift.

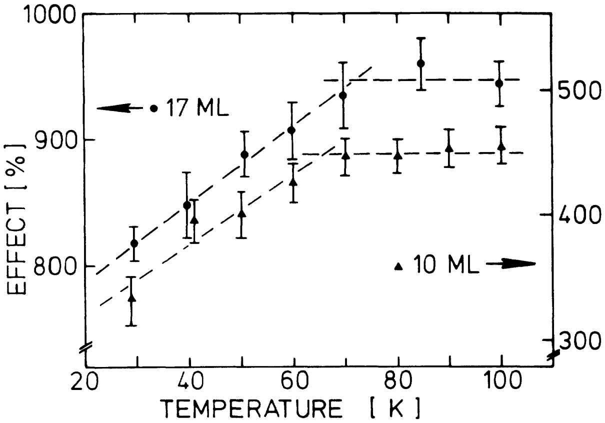

FIG. 3. fcc-Fe line intensity (peak intensity) vs temperature for 10- (triangles) and 17-ML (circles) fcc Fe(100) on Cu(100).

The magnetic transition temperature has been determined by the "thermal scan" method. The result (corrected for the small thermal red shift) indicates a drastic drop of the $\gamma$-Fe peak intensity due to magnetic ordering at $T_N = 65 \pm 5$ K (Fig. 3). Note that the same $T_N$ value is observed for 10- and 17-ML fcc Fe. This proves that $T_N$ is not a superparamagnetic blocking temperature, and that our Fe films do *not* consist in superparamagnetic islands, because the superparamagnetic relaxation frequency (and thus the blocking temperature) would strongly depend on island size, i.e., on film thickness. Our observed $T_N$ value is in very good agreement with the Néel temperature of larger $\gamma$-Fe precipitates in Cu ($T_N = 67$ K),[11] thus strongly supporting the concept of antiferromagnetism in bulklike fcc Fe(100) films on Cu(100).

Recent LEED studies[26,29] seem to indicate that "annealed" fcc Fe/Cu(100) films (prepared at 150–200 °C, as in our case) closely follow the structure of bulk Cu (within ±0.05 Å), while fcc-Fe films prepared at 295 K ("unannealed") show a thickness-dependent variation of the Fe interlayer spacings[26] up to 6–7-ML Fe where the spacing approaches that of bulk Cu. If we consider this effect, together with the calculated extreme volume dependence of magnetic properties of fcc Fe,[1-7] FM reported recently[20,21] for unannealed ultrathin (thickness $\lesssim 4$ ML) fcc-Fe(100) films is most likely related to their expanded interlayer spacings. On the other hand, PM at 295 K was reported in fairly thick (bulklike) fcc-Fe(100) films[18,19] (thickness $\gtrsim 8$ ML), in agreement with the present result. Since higher preparation temperatures are required in the latter cases, the observed interdiffusion within 3–4 ML at the interface might destroy the interlayer expansion within that region, thus destroying ferromagnetism of that part of the film and leaving paramagnetism (at 295 K) of an alloyed interface and of the remaining pure (bulklike) part of the Fe film.

In summary, our *in situ* investigation of 10- and 17-ML epitaxial (bulklike) pure fcc-Fe(100) films with a structure close to that of Cu gives clear evidence for paramagnetism at 295 K, and strongly suggests antiferromagnetism at low temperature in low-moment (bulk) fcc Fe, in agreement with calculations by Kübler.[3] Thus, our result contradicts previous reports of purported ferromagnetism at 295 K in equally thick (bulklike) pure fcc-Fe films on Cu.[12,13]

We wish to thank W. Kiauka for helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

---

[a] Permanent address: Centro de Desenvolvimento da Tecnólogia Nuclear, 30.000 Belo Horizonte, Brazil.

[1] O. K. Anderson, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollár, Physica (Amsterdam) **86–88B**, 249 (1977).

[2] D. G. Pettifor and D. M. Roy, Solid State Commun. **27**, 677 (1978).

[3] J. Kübler, Phys. Lett. **81A**, 81 (1981).

[4] D. Bagayoko and J. Callaway, Phys. Rev. B **28**, 5419 (1983).

[5] C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[6] F. J. Pinski, J. Staunton, B. L. Gyorffy, D. D. Johnson, and G. M. Stocks, Phys. Rev. Lett. **56**, 2096 (1986).

[7] V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986); V. L. Moruzzi, Phys. Rev. Lett. **57**, 2211 (1986).

[8] J. B. Newkirk, Trans. Am. Inst. Min. Metall. Pet. Eng. **209**, 1214 (1957).

[9] W. A. Jesser and J. W. Matthews, Philos. Mag. **15**, 1097 (1967), and **17**, 595 (1968).

[10] A. Knappworst and G. E. Bockstiegel, Z. Elektrochem. **57**, 700 (1953); S. C. Abrahams, L. Guttman, and J. S. Kasper, Phys. Rev. **127**, 2052 (1962); G. J. Johanson, M. B. McGirr, and D. A. Wheeler, Phys. Rev. B **1**, 3208 (1970).

[11] U. Gonser, C. J. Meechan, A. H. Muir, Jr., and H. Wiedersich, J. Appl. Phys. **34**, 2373 (1963); D. L. Williamson, W. Keune, and U. Gonser, in *Proceedings of the International Conference on Magnetism, Moscow, 1973* (Nauka, Moscow, 1974), Vol. 1, p. 246.

[12] W. Kümmerle and U. Gradmann, Solid State Commun. **27**, 33 (1977), and Phys. Status Solidi (a) **45**, 171 (1978); U. Gradmann and H. O. Isbert, J. Magn. Magn. Mater. **15–18**, 1109 (1980).

[13] U. Gradmann and P. Tillmanns, Phys. Status Solidi (a) **44**, 539 (1977).

[14] W. Keune, R. Halbauer, U. Gonser, J. Lauer, and D. L. Williamson, J. Appl. Phys. **48**, 2976 (1977), and J. Magn. Magn. Mater. **6**, 192 (1977); W. Becker, H.-D. Pfannes, and W. Keune, J. Magn. Magn. Mater. **35**, 53 (1985).

[15] R. Halbauer and U. Gonser, J. Magn. Magn. Mater. **35**, 55 (1983).

[16] W. Wiartalla, W. Becker, W. Keune, and H.-D. Pfannes, J. Phys. (Paris), Colloq. **45**, C5-461 (1984).

[17] J. A. C. Bland, D. Pescia, and R. F. Willis, Phys. Rev. Lett. **58**, 1244 (1987).

[18] A. Amiri Hezaveh, G. Jennings, D. Pescia, R. F. Willis, K. Prince, M. Surman, and A. Bradshaw, Solid State Commun. **57**, 329 (1986).

[19] P. A. Montano, G. W. Fernando, B. R. Cooper, E. R. Moog, H. M. Naik, S. A. Bader, Y. C. Lee, Y. N. Darici, H. Min, and J. Marcano, Phys. Rev. Lett. **59**, 1041 (1987).

[20] M. F. Onellion, C. L. Fu, M. A. Thompson, J. L. Erskine, and A. J. Freeman, Phys. Rev. B **33**, 7322 (1986).

[21] D. Pescia, M. Stampanoni, G. L. Bona, A. Vaterlaus, R. F. Willis, and F. Meier, Phys. Rev. Lett. **58**, 2126 (1987).

[22] C. Rau, C. Schneider, G. Xing, and K. Jamison, Phys. Rev. Lett. **57**, 3221 (1986).

[23] D. Liljequist, in *Scanning Electron Microscopy III,* edited by O. Johari and R. A. Sharma (SEM, Inc., AMF O'Hare, Chicago, 1983), p. 997.

[24] D. Liljequist, M. Ismail, K. Saneyoshi, K. Debusmann, W. Keune, R. A. Brand, and W. Keune, Phys. Rev. B **31**, 4137 (1985); W. Keune, Hyperfine Interact. **27**, 111 (1986).

[25] D. Liljequist and M. Ismail, Phys. Rev. B **31**, 4131 (1985).

[26] A. Clarke, P. J. Rous, M. Arnott, G. Jennings, and R. F. Willis, Surf. Sci. **192**, L843 (1987).

[27] P. Ehrhard, B. Schönfeld, H. H. Ettwig, and W. Pepperhoff, J. Magn. Magn. Mater. **22**, 79 (1980).

[28] Y. C. Lee, H. Min, and P. A. Montano, Surf. Sic. **166**, 391 (1986).

[29] M. Onellion, M. A. Thompson, J. L. Erskine, C. B. Duke, and A. Paton, Surf. Sci. **179**, 219 (1987).

[30] W. Kiauka, K. Debusmann, W. Keune, R. A. Brand, N. Hosoito, and D. Liljequist, Solid State Commun. **58**, 641 (1986).

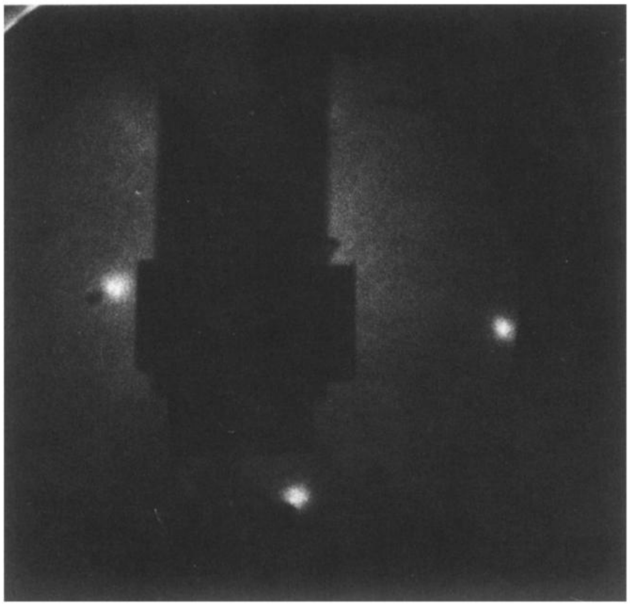

FIG. 1. $p(1\times1)$ LEED pattern of 11-ML fcc Fe(100) on Cu(100) at 78-eV electron energy. [A (11) spot of the quadratic diffraction pattern is hidden by the sample holder.]