Mössbauer Effect Study of Magnetism and Structure of fcc-like Fe(001) Films on Cu(001)

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Magnetic and electric hyperfine interactions observed *in situ* by conversion-electron Mössbauer spectroscopy in 3 and 7 monolayers thick Fe films grown epitaxially in UHV on Cu(001) at 300 K provide microscopic evidence for a thickness-dependent transition from a high-moment ferromagnetic state with an anisotropically expanded fcc (fct-like) structure ($c/a > 1$) to a low-moment antiferromagnetic isotropic fcc state. In similar films grown at ~90 K and annealed to 300 K, however, this high-moment fct-like phase was found to exist at both thicknesses. We conclude that the high-moment ferromagnetic state can exist in fct-like Fe only, but not in fcc Fe.

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The magnetic and structural properties of the metastable fcc (or fcc-like) phase of iron (γ-Fe) stabilized by epitaxial thin-film growth on a Cu(001) substrate remain a controversial topical subject [1–19]. This system is of considerable interest since calculations [20] have predicted various magnetic ground states [including a high-moment ferromagnetic (FM) or a low-moment antiferromagnetic (AFM) state] which depend sensitively on the lattice parameter and symmetry. Experimentally, films were generally found to be either high-moment FM [1–9,11] or low-moment AFM [10,11]. Recent experimental work [1,2] yielded a complex magnetic and structural phase diagram, with properties depending on Fe film thickness t and on film-growth temperature $T_{\rm prep}$. Three characteristic Fe thickness regions are distinguished there [1,2]: region I [$t < 5$ monolayers (ML) Fe], region II (~6 ML $\leq t \leq$~10 ML), and region III ($t >$~11 ML). In spite of tremendous experimental efforts, the correlation between details of the structure and magnetism in Fe/Cu(001) is still a matter of debate, mainly because precise crystallographic data are scarce and partially contradictory, and generally have not been obtained together with magnetic properties from the same samples. For instance, no published quantitative study of the precise structure of low-T grown films in regions I and II exists, and there is no experimental proof, so far, for the fct structure assumed for such films in Ref. [2]. Even for films grown near room temperature (RT), the precise structure in the film interior is not clear from published LEED or EXAFS reports: For region I, such films are described either as fct [15] with an expanded perpendicular interlayer distance ($c/a > 1$) or as anisotropically distorted fcc, but "... not due to a homogeneous tetragonal deformation of the fcc structure by compression or expansion ..." [13]. Even worse, the interior of 300-K-grown films in region II is reported to be either isotropic fcc [12,13] or expanded [15] or compressed [16] fct. Concerning the magnetism of films grown near RT in region II, the recent claim [2] of possible high-moment antiferromagnetism (with $\mu_{\rm Fe}$ considerably larger that $0.7\mu_B$) requires further investigations, since AFM fcc Fe is usually of the low-moment type ($\mu_{\rm Fe} < 0.7\mu_B$) [10,11,21].

In this Letter we report results obtained by *in situ* conversion-electron Mössbauer spectroscopy (CEMS) in zero external field on Fe/Cu(001). The Mössbauer effect is especially useful because it provides local information on both magnetism (via the magnetic hyperfine field) and structure (via the electric quadrupole interaction). Our new results provide experimental (model-independent) proof for the following properties in the film interior: (i) High-moment FM films in thickness region I exhibit an expanded fct-like local structure ($c/a > 1$), independent of $T_{\rm prep}$ and of the spontaneous spin orientation; (ii) the *same* fct-like structure exists for low-T grown high-moment FM films in region II up to (at least) 7 ML Fe; (iii) films in region II grown at 300 K are isotropic fcc and exhibit paramagnetism at 300 K and *low-moment* antiferromagnetism (with $\mu_{\rm Fe} < 0.7\mu_B$) at low T (45 K) in the film interior. This demonstrates that high-moment FM fcc Fe is structurally unstable; this magnetic state exists in the fct-like structure only.

The epitaxial layers were grown under molecular beam epitaxy (MBE) conditions (deposition rate ~0.2 Å/min, pressure during evaporation <5 × 10^{-10} mbar) by evaporation of 95.5% enriched ^{57}Fe metal onto a clean Cu(001) single crystal surface which was prepared using standard techniques [11]. Four types of specimens have been studied: 3 ± 0.5 ML Fe either grown at ~90 K and warmed up to RT before the measurements (sample A) or grown at ~300 K (sample B), and 7 ± 0.5 ML Fe either grown at ~90 K and warmed up to RT before the measurements (sample C) or grown at ~300 K (sample D). At 300 K, our films showed $p(1 \times 1)$ LEED patterns near 70 eV similar to those of the pure fcc-Cu(001) substrate [17] with rather sharp spots for samples B and D, and broad (diffuse) spots for samples A and C. (2 × 1) superstructure spots [1,12,14] could be observed upon cooling sample D. Directly after film deposition, contamination levels were below the detection limit of AES for the 7 ML thick films, while our 3 ML films exhibited traces of oxygen. RHEED intensity oscillations [17] demonstrate

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that we have produced atomically flat 3 and 7 ML films at $T_{prep} = 300$ K (samples B and D), in agreement with Refs. [18,19]. However, for $T_{prep} \sim 100$ K, RHEED oscillations do not exist [17], and typical 3D RHEED patterns up to 300 K indicated rough surfaces for samples A and C [22]. The γ radiation from a 100 mCi ^{57}Co(Rh) source was in normal incidence to the sample plane. As the measuring time per spectrum was of the order of 24 h, the sample surface was certainly covered by adsorbed residual gas atoms (mostly CO according to mass spectrometry). As we did not observe differences in spectra measured in sequential time intervals of ~ 2 h we may conclude that residual gas adsorption had no effect on the properties of the film interior which are of interest here.

In Fig. 1 we compare typical spectra of samples A and B (region I) and in Fig. 2 of sample C (region II). The spectra show broadened outer lines indicating a distribution of hyperfine (hf) fields $P(B_{hf})$. For these samples at low T, a dominant high-field peak (located at $B_{peak} \sim 31$ T in Fig. 1(a) and Fig. 1(c), and ~ 29 T in Fig. 2(b) [subspectrum (1)]) is observed in the $P(B_{hf})$ curves. Obviously the overwhelming fraction of ^{57}Fe nuclei [e.g., $\sim 84\%$, according to $P(B_{hf})$ in Figs. 1(a) 1(c)] experiences large B_{hf} values ($B_{hf} > 15$ T) at low T. Assuming roughly proportionality between B_{hf} and μ_{Fe}, and a conversion factor [23] of about 15 T/μ_B, we conclude that in the average the *large majority of Fe atoms in these films is in a high-spin FM ground state* (μ_{Fe} being $\sim 2\mu_B$), in good agreement with recent results on MBE-grown fcc-Fe/Cu(001) superlattices by

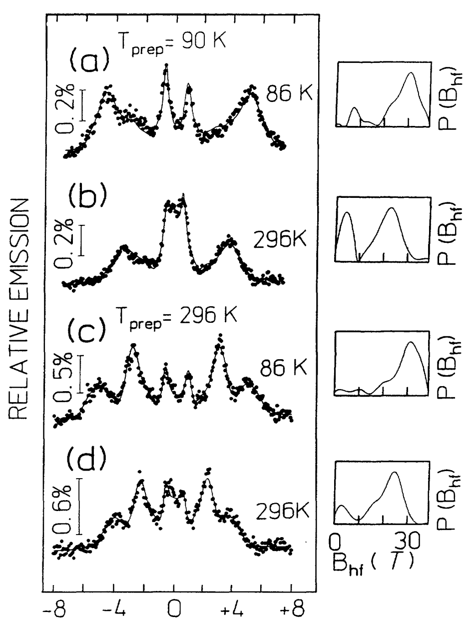

FIG. 1. CEM spectra of 3 ML Fe/Cu(001): sample A measured at 86 K (a) and 300 K (b); sample B measured at 86 K (c) and 300 K (d). The full-drawn lines are least-squares fits for a distribution of hyperfine fields $P(B_{hf})$ (right-hand side).

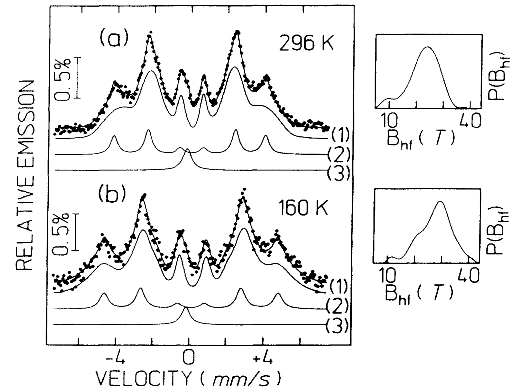

FIG. 2. CEM spectra of 7 ML Fe/Cu(001), sample C, at 295 K (a), and 160 K (b), with corresponding distributions $P(B_{hf})$ (right-hand side) of the fct phase [subspectrum (1)]. Subspectrum (2) and (3) are explained in Ref. [29].

Doyama *et al.* [24] who obtained a value $\mu_{Fe} = (2.0 \pm 0.2)\mu_B$ from magnetization data [25]. The large width of the high-field $P(B_{hf})$ peak is a manifestation of the atomic disorder in the distorted fcc structure observed by EXAFS [13]. In Fig. 1, one can also notice a low-field part in $P(B_{hf})$ for $B_{hf} < 15$ T at 86 K and $B_{hf} < 10$ T at 296 K, with relative contributions of 16% for both samples A and B at 86 K. At low T (86 K), this contribution might be assigned to a fraction of Fe atoms either in a low-spin or nonmagnetic state, e.g., at the Fe/Cu interface. Increasing T to 296 K raises the low-field contribution only for samples A (to 33%), very likely due to superparamagneticlike fluctuations for some Fe magnetic moments in samples A (film with large roughness). In fitting the spectra with $P(B_{hf})$ in Figs. 1 and 2 [subspectra (1)] a weak linear correlation between B_{hf} and isomer shift δ had to be taken into account. The isomer shift (referred to bcc Fe at 300 K) of the high-field peak in $P(B_{hf})$ was found to be +0.153(13), +0.105(18), and +0.13(2) mm/s for samples A, B, and C, respectively, all at 300 K. $\delta > 0$ indicates a smaller s-electron density at the ^{57}Fe nucleus [26] (and qualitatively *a larger atomic volume*) for FM fct-like Fe, as compared to low-spin AFM fcc Fe ($\delta = -0.088$ mm/s) [10,11].

Direct information about the average spin orientation in zero external field [given by the angle θ between the incident γ-ray direction (or film normal direction) and the direction of B_{hf}, i.e., the spin direction] is obtained from the line-intensity ratios $3{:}x{:}1{:}1{:}x{:}3$, where x is related to θ by $\langle \cos^2\theta \rangle = (4-x)/(4+x)$. The measured T dependence of $\langle \theta \rangle = \arccos(\langle \cos^2\theta \rangle)^{1/2}$ for samples A and B is shown in Fig. 3(a). Sample A shows almost complete perpendicular magnetic anisotropy independent of $T(\langle\theta\rangle \sim 18°-33°)$, in agreement with reports [2,4–6] for similar samples. Samples B and C (not shown) exhibit $\langle\theta\rangle \sim 80°$, indicating T-independent preferential in-plane spin alignment; this proves indirectly that these films are FM, since the dominant shape anisotropy forces the

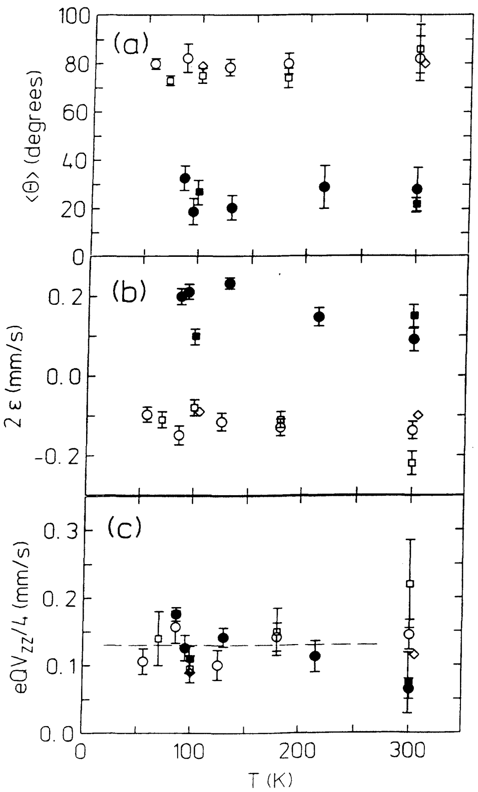

FIG. 3. Temperature dependence of (a) average angle $\langle\theta\rangle$, (b) quadrupole line shift 2ϵ, (c) quadrupole-coupling constant $eQV_{zz}/4$, for samples A (full symbols), and samples B (open symbols).

magnetization into the film plane. Our observation of an in-plane easy axis for sample C agrees with Ref. [2]; for sample B (grown at RT), however, it apparently contradicts reports of perpendicular magnetic anisotropy in similar films [1,2,5,7]. Traces of oxygen contamination on our freshly prepared 3 ML films might cause this difference [4b], as CO adsorption has no effect on the perpendicular easy axis [1]; however, the out-of-plane easy axis is not affected in sample A.

All spectra in Figs. 1 and 2 exhibit a slight left-right asymmetry in the apparent peak positions suggestive of a weak electric quadrupole interaction locally correlated with the (stronger) magnetic hf interaction. This leads to an asymmetric nuclear level shift ϵ [26]. Figure 3(b) displays measured average 2ϵ values for samples A and B. From $P(B_{\rm hf})$ of sample C, we obtained 2ϵ values of $-0.16(2)$ mm/s at 160 K and $-0.06(1)$ mm/s at 300 K. The observed nonzero 2ϵ values provide direct (model independent) proof of a distorted fcc structure in 3 ML and (low-T grown) 7 ML films. Because of symmetry arguments we may assume that the main component of the electric field gradient (EFG) V_{zz} is oriented approximately perpendicular to the (001) film plane, and that the asymmetry parameter η is about equal to zero (local axial symmetry). Then, the angle Φ between the direction of V_{zz} and the local spin direction is equal to θ. 2ϵ is given by $eQV_{zz}(3\cos^2\Phi - 1)/4$ ($Q = 0.21b$ is the nuclear quadrupole moment). By taking measured 2ϵ values [Fig. 3(b)] and measured $\langle\cos^2\theta\rangle$ values [from Fig. 3(a)] we may obtain values for $eQV_{zz}/4$ in samples A and B [see Fig. 3(c)]. Similarly we obtained $eQV_{zz}/4$ values of $+0.18(3)$ mm/s at 160 K and $+0.07(2)$ mm/s at 300 K for sample C. Obviously within error bars both types of 3 ML Fe films and the low-T grown 7 ML Fe films are characterized by the *same* mean quadrupole-coupling constant of $+0.13(5)$ mm/s, or, equivalently, by the same V_{zz} value of $(+1.2 \pm 0.5) \times 10^{17}$ V/cm^2, below 300 K. (At 300 K the scattering of the data points [Fig. 3(c)] does not allow a definite conclusion except that $V_{zz} > 0$). The unique sign of V_{zz} strongly suggests an average *homogeneous static lattice distortion along the film normal direction,* as, for instance, in an fct structure, being the same and independent of T in samples A, B, and C within experimental accuracy. Since $V_{zz} > 0$, the fct-like structure is *expanded* perpendicular to the film plane ($c/a > 1$). This conclusion follows from the experimental and theoretical observation [27] that $3d$ or $4d$ metals with five or more d electrons (like Fe) and an axially symmetric structure exhibit $V_{zz} > 0$ ($V_{zz} < 0$) for axial expansion (compression). From extrapolation of the nearly linear correlation of relevant V_{zz} data [27] with c/a values, we may estimate $c/a \sim 1.035 \pm 0.010$ for fct-like Fe. Thus, our result provides microscopic evidence for an expanded fct-like structure throughout the whole film in region I (in qualitative agreement with recent LEED results [28]), and for the same fct-like structure extending into region II for low-T grown films, as was assumed in Ref. [2]. We emphasize that no sextet typical for bcc Fe can be detected [29] in Fig. 2.

The spectra (Fig. 4) of RT-grown 7 ML Fe/Cu(001), sample D, are strikingly different from those of samples A, B, and C. A least-squares fit of the spectrum measured at 295 K [Fig. 4(a)] results in a dominant narrow (Lorentzian) single line [spectral area ~80%, subspectrum (1)] and a less intense (asymmetric) pair of quadrupole-split lines [spectral area ~20%, subspectrum (2)]. The single line has a width (FWHM) of 0.29 mm/s, which is only insignificantly broader than the observed linewidth of a standard α-Fe calibration foil (0.26 mm/s), indicating a paramagnetic cubic local environment. Its measured isomer shift δ of -0.08 mm/s is typical for that of paramagnetic fcc-Fe films on Cu(001) at 295 K [10]. Subspectrum (2) has been attributed to Fe atoms with Cu neighboring atoms located at and near the Fe/Cu interface [10]. Our finding of the fcc structure for this film agrees with EXAFS [13] and LEED [12] results, but contradicts reports on an expanded [15] or compressed [16] fcc structure in the "bulk" of comparable films obtained from LEED. Evidence for magnetic ordering is provided by a broadening of the fcc-Fe single line at low T [Fig. 4(b)]. The average hf field estimated from the line broadening is rather small (~0.7 T) at 45 K, and is

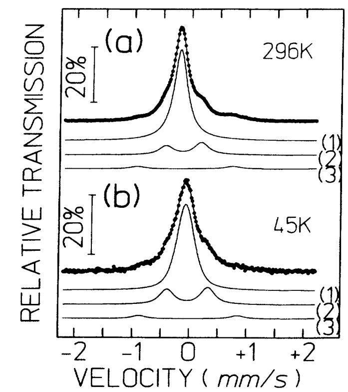

FIG. 4. CEM spectra of 7 ML Fe/Cu(001), sample D, at 295 K (a) and 45 K (b). Subspectra (1) and (2) are described in the text [subspectrum (3) corresponds to the inner two lines of the α-Fe sextet and is an artifact of the α-Fe coated sample-holder frame in this case].

similar to that of AFM γ-Fe precipitates in a Cu matrix [30] which have $\mu_{\mathrm{Fe}} \sim 0.7\mu_B$ [21]. Hence, our result is at variance with conclusions by Li *et al.* [2] who claim that μ_{Fe} is considerably larger than $0.7\mu_B$ in the AFM state. Summarizing, our results prove the occurrence of a transition from a high-moment FM fct-like state (at 3 ML) to a *low-moment* AFM fcc-ground state (at 7 ML) in the *interior* of RT-grown Fe films [31].

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