Direct Evidence for Perpendicular Spin Orientations and Enhanced Hyperfine Fields in Ultrathin Fe(100) Films on Ag(100)

N. C. Koon, B. T. Jonker, F. A. Volkening,[a] J. J. Krebs, and G. A. Prinz
Naval Research Laboratory, Washington, D.C. 20375
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Conversion-electron Mössbauer measurements have been used to study hyperfine fields in Fe/Ag(100) single-crystal multilayer films at temperatures down to 15 K. The Fe layer thicknesses corresponded to 1.0, 2.4, and 5.5 monolayers (ML). From the relative intensity of the Mössbauer lines we show conclusively that the orientation of the magnetic moment of the 1.0- and 2.4-ML films in zero applied field is perpendicular to the film plane while the orientation of the 5.5-ML sample is in plane at room temperature and partially out of plane at low temperatures. The low-temperature hyperfine fields are enhanced compared to bulk Fe.

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Recent advances in sample preparation and characterization techniques have made possible the synthesis of very-high-quality layered structures with features as thin as one monolayer (ML). This has led to renewed interest in the magnetic and electronic properties of thin films, surfaces, and interfaces. One of the most interesting of the systems investigated is epitaxial α-Fe(100) on Ag(100).[1-7] It can be grown in high-quality single-crystal form with well defined, flat interfaces. Furthermore, Fe and Ag have very little overlap of the valence electron bands,[1,2] leading to only a small degree of band hybridization and thus permitting the approximate realization of quasi two-dimensional Fe films. Among the properties of such systems which are of intense interest are the size of the magnetic moments, theoretically predicted to be enhanced relative to bulk Fe,[1,2] the magnetic anisotropy (e.g., the preferred direction of magnetization),[3,4,6] the magnetic hyperfine fields,[7] and the magnetic ordering process, which should exhibit two-dimensional behavior for the thinner films.[8,9]

The importance of magnetic anisotropy was recently emphasized by the work of Junker *et al.*,[3] who carried out spin-polarized photoemission studies of epitaxial Fe(100) on Ag(100). It was shown that at room temperature there was no in-plane moment for films less than 3 ML. It was suggested that this resulted from a perpendicular anisotropy strong enough to compete with the demagnetization field ($4\pi M = 21.5$ kG in bulk α-Fe) which forced the magnetic moments to lie along the surface normal. Theoretical efforts by Gay and Richter[4,6] to calculate the anisotropy of a monolayer of Fe from band-structure theory suggested that the out-of-plane configuration is the most energetically favorable for a free-standing monolayer,[4] but were inconclusive for a monolayer of Fe on Ag(100).[6] They point out, however, that while the demagnetization energy increases with the volume of the film, the perpendicular anisotropy is proportional to the surface area,[10] which remains constant. This implies that for thicker films the demagnetization energy eventually overwhelms the anisotropy energy and pulls the moment back into the plane, consistent with the data of Jonker *et al.*[3]

Band-structure calculations have made striking predictions about Fe atoms near the surfaces and interfaces of both free-standing Fe and Fe/Ag films, including enhancement of the Fe moment to the order of $3\mu_B$ or more[1,2] from the bulk value of $2.2\mu_B$, and wide variations in the magnetic hyperfine field $H_{\rm hf}$ away from the bulk value of 340 kG at low temperatures.[7] Mössbauer spectroscopy of ^{57}Fe hyperfine interactions is a powerful tool for testing these predictions as well as determining spin orientations because it is sensitive enough to measure only a few (sometimes even one) layers of ^{57}Fe.[11-14] The relative intensities of the various absorption and emission lines are strongly dependent on the angle between the direction of the magnetic hyperfine field $H_{\rm hf}$ and the incident γ-ray direction, while the line separations are closely related to the magnitudes of the hyperfine interactions.

It was the aim of the present experiment to determine the orientation of the magnetic moments and the size of the magnetic hyperfine fields in high-quality ultrathin Fe(100)/Ag(100) single-crystal films as a function of temperature by means of normal-incidence Mössbauer spectroscopy, which gives the most information about perpendicular spin alignment. Previous pioneering studies of ^{57}Fe/Ag films and interfaces have generally involved Fe(110) on Ag(111)[11] or Ag-covered Fe(110),[12] or have been done on polycrystalline films.[13]

The Fe/Ag(100) system is particularly favorable for epitaxial growth because there is only a 0.8% mismatch between the α-Fe(100) and Ag(100) surface nets, with the Fe slightly expanded for pseudomorphic growth. This is due to the fact that the lattice constants of bcc α-Fe and fcc Ag differ by a factor very near $\sqrt{2}$, producing almost perfect registry of the two (100) surface nets after a rotation of 45° about the surface normal.[15] Previous work has shown that the growth of α-Fe on

Ag(100) proceeds layer by layer for the first three layers and then exhibits island growth for thicker films.[3,16]

The samples were grown in a PHI Model 400 molecular-beam-epitaxy system, and characterized *in situ* with Auger-electron spectroscopy and reflection high-energy electron diffraction (RHEED). The Fe/Ag superlattices were grown at room temperature on a Ag(100) film $\simeq$500 Å thick grown on a 0.2-μm ZnSe epilayer, which had been grown on a GaAs (100) substrate. This procedure optimizes surface morphology as indicated by sharp, well defined streaks in the RHEED pattern. The ^{57}Fe and Ag were deposited from shuttered Knudsen-cell-type sources at rates of 1-2 ML/min and 5-7 ML/min, respectively. Samples were grown with 7 to 45 superlattice periods in which the ^{57}Fe layer was varied from 1 to 5.5 ML (1 ML = 1.43 Å), and the Ag layer ranged from 4 to 7 ML (1 ML = 2.045 Å). Each growth was terminated with an extra period of Ag, and the sample was finally coated with 75 Å of Al before removal from the molecular-beam-epitaxy system to prevent oxidation or tarnish on exposure to atmosphere.

The single-crystal nature of each layer was verified during growth by RHEED; Fig. 1 shows RHEED patterns obtained at various stages during the growth of a sample consisting of 45 periods of 1 ML of ^{57}Fe and 4 ML of Ag. Figures 1(a) and 1(b) are obtained from the initial Ag(100) film surface just before the growth of the superlattice, with the electron beam incident along the ⟨110⟩ and ⟨100⟩ azimuths, respectively. The patterns exhibit well defined streaks and low background intensity characteristic of a well ordered, single-crystal surface, and reflect the symmetry of the Ag(100) surface net (on the assumption of a simple termination of the bulk Ag lattice). RHEED shows that the Fe layers exhibit a surface net identical to that of the Ag, as expected. Figures 1(c) and 1(d) show the patterns obtained upon completion of the Fe and Ag layers in the fifth period, respectively, with the electron beam incident along the ⟨110⟩ direction. The layers exhibit very well ordered, single-crystal surfaces throughout the growth of the superlattice, as evidenced by the RHEED patterns produced by the 45th and final period, shown in Figs. 1(e)-1(h). Figures 1(e) and 1(f) show the pattern produced along the ⟨110⟩ direction, and 1(g) and 1(h) show the pattern obtained along the ⟨100⟩ direction for the 45th ^{57}Fe and Ag layers, respectively.

The conversion-electron Mössbauer spectrometer used is of the cylindrical-mirror-analyzer type, with an acceptance angle of 30°-60° and an energy resolution of approximately 4%. The samples were mounted on a Cu block connected via a Cu braid to a closed-cycle refrigerator, the first stage of which was used to cool a radiation shelf that also served as a cryopumping surface. The transducer and source were inside the vacuum chamber, eliminating the need for a lengthy drive-rod assembly and window. The γ rays were incident perpendicular to the plane of the sample.

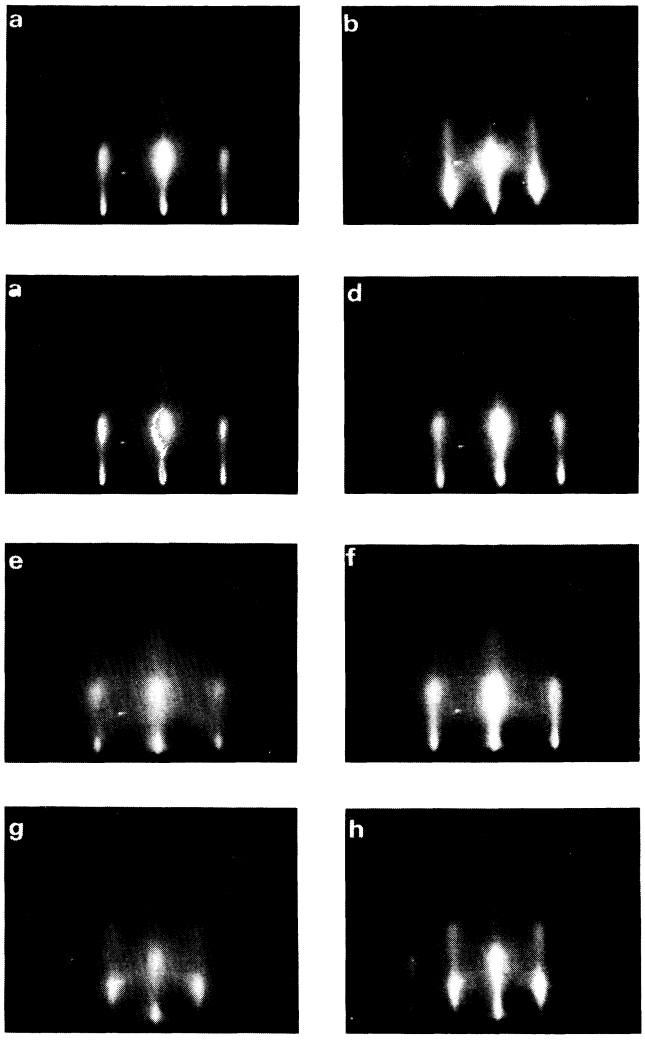

FIG. 1. RHEED patterns (10 keV) obtained at various stages of growth of an ^{57}Fe/Ag superlattice consisting of 45 periods of 1 ML of ^{57}Fe and 4 ML of Ag each. (a),(b) The initial surface of the 500-Å Ag(100) film, with the electron beam incident along the ⟨110⟩ and ⟨100⟩ directions, respectively. (c),(d) The patterns obtained from Fe and Ag layers in the fifth period, respectively, for ⟨110⟩ incidence. The patterns exhibited by the 45th period, as follows: (e) Fe, for ⟨110⟩ incidence; (f) Ag, ⟨110⟩; (g) Fe, ⟨100⟩; and (h) Ag, ⟨100⟩.

Clear evidence for almost complete perpendicular alignment of spins in the 2.4-ML sample is given in Fig. 2, where we compare its Mössbauer spectrum at 15 K with that of a thick film ($\simeq$500 Å), which is known to have its moment in plane. Information about the orientation of the spins is contained in the ratios of line intensities, which for pure magnetic hyperfine splitting is given by $3{:}x{:}1{:}1{:}x{:}3$, where $x=4\sin^2\theta/(1+\cos^2\theta)$ and θ is the angle between the incident γ-ray direction and the

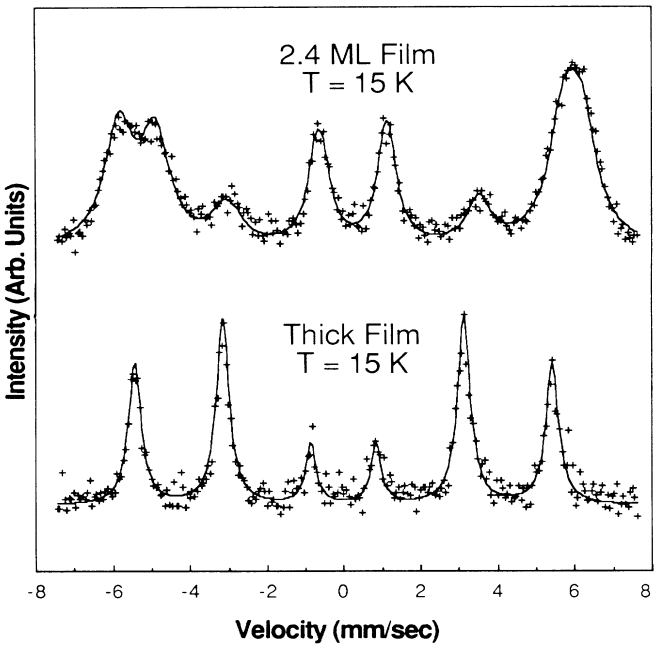

FIG. 2. Conversion-electron Mössbauer spectra taken at 15 K for a thick film ($\simeq$500 Å) of ^{57}Fe compared to that of a 2.4-ML multilayer film of ^{57}Fe(100) on Ag(100).

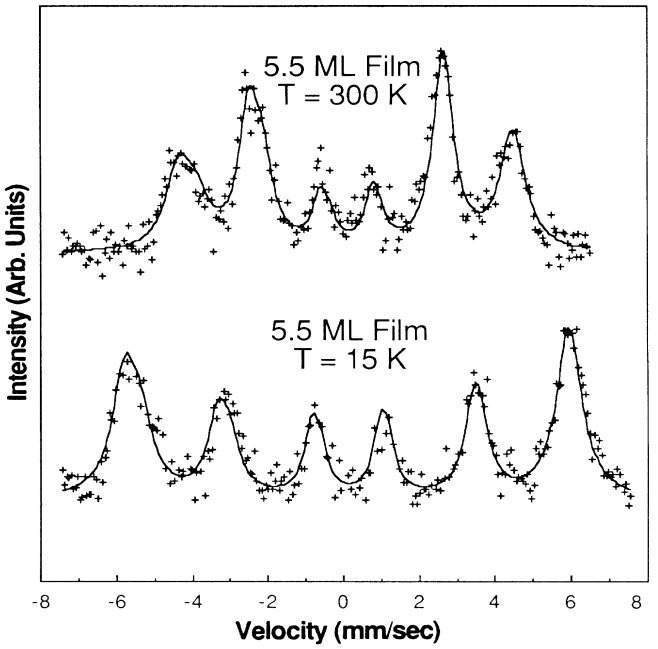

FIG. 3. Conversion-electron Mössbauer spectra taken at 15 and 300 K on a 5.5-ML multilayer film of ^{57}Fe(100) on Ag(100).

direction of the magnetic hyperfine field. For the thick film the ratios are 3:4:1; exactly what should be observed if the Fe moments lie in the plane (θ=90°). It is clear in the 2.4-ML spectrum, however, that the second and fifth major lines are very weak compared to those of the thick film, indicating close alignment of the spins to the perpendicular direction (θ=0).

The structure in the spectrum of the 2.4-ML film indicates the presence of more than one crystallographically inequivalent site (as expected for 2.4 ML). To estimate quantitatively the hyperfine fields and the integrated intensities we fitted the spectra assuming only two types of Fe sites. This yielded average integrated intensity ratios of 3:0.5:1 and hyperfine fields of 358 and 344 kG (compared to 340 kG for bulk Fe). The corresponding values of the quadrupole splitting (QS; indicative of deviation from cubic symmetry), isomer shifts (IS; a measure of the conduction electron-spin density at the nuclei), and the weighting factors are given in Table I. From the integrated intensity ratios we calculate a uniform spin deviation from perpendicular of 28° or, equivalently, that approximately 22% of the spins lie in the plane and 78% are perpendicular to it. Because of domain formation and imperfections in the films the correct physical picture probably lies in between these two extremes.

TABLE I. Hyperfine-field parameters for bulk Fe and for the 2.4- and 5.5-ML films. The parameters were determined with a two-site fit as described in the text.

	Weighting factor	H_{hf} (kG) 15 K (300 K)	QS (mm/s)	IS (mm/s)
Bulk Fe	1.0	340 (330)	0.0	0.0
2.4 ML	0.52	358	−0.11	0.06
	0.48	344	0.16	0.49
5.5 ML	0.65	363 (274)	0.0	0.06
	0.35	352 (258)	0.0	0.28

For temperatures above 50 K the spectra for the 2.4-ML film exhibit broadening suggestive of a relaxation process. At all temperatures where the lines are split by the hyperfine magnetic field, however, the pronounced perpendicular anisotropy of the film (deduced from the line intensities) still persists, indicating that the relaxation is not due to 3D superparamagnetic clusters. Although a quantitative theory does not yet exist, it seems probable that the relaxation is intimately connected with the 2D nature of the film. This will be discussed in greater detail in a later paper.

Similar results showing a perpendicular spin orientation were also obtained for a 1-ML Fe/Ag multilayer film, with the main difference being that at the lowest temperature reached (15 K) there were still relaxation effects in the spectra.

Spectra for the 5.5-ML sample at room temperature and 15 K are shown in Fig. 3. The line intensity ratios at room temperature are 3:4:1, indicating that the magnetization is in the plane of the film. At 15 K the intensity ratios are 3:1.6:1, which corresponds to a uniform angle from perpendicular of 49° or to 57% of the spins oriented in the plane and 43% perpendicular.

This suggests that at low temperatures the perpendicular anisotropy of the 5.5-ML film is comparable to the demagnetization field, whereas at room temperature the demagnetization field dominates. The perpendicular anisotropy energy therefore increases faster than the demagnetization energy as the temperature is lowered.

The 5.5-ML spectra were also fitted by the two-site model with the parameters given in Table I. The best fits to the 15-K data were generally obtained with zero quadrupole splitting and slightly larger hyperfine fields than for the 2.5-ML film. The fit at room temperature was calculated by our allowing only the hyperfine magnetic fields to vary from the 15-K values. The decrease in H_{hf} from 15 to 300 K is much greater than for bulk Fe, suggesting a lower Curie temperature for the film. It is also interesting to note that the 0.65 to 0.35 weighting factors are in almost exactly the ratio of interior to interface atoms that one would expect for a 5.5-ML film, which suggests that the higher-field component (363 kG) of the spectrum is due to interior atoms, while the lower-field one (352 kG) is due to interface atoms. This is also consistent with the respective values of the isomer shift, which should be small for interior atoms.

A similar identification can be made for the 2.4-ML film, although the weighting factors yielded by the fitting process for the two sites are nearly equal instead of being in favor of interface atoms. However, both the isomer shift and the quadrupole interactions are larger for the smaller hyperfine field than for the larger one, which is again consistent with the smaller hyperfine magnetic field being associated with interface atoms.[1,2]

The hyperfine-field calculations which appear to most closely match the conditions realized in this experiment are those of Ohnishi, Weinert, and Freeman,[7] who treated the problem of a Fe/Ag(100) seven-layer slab where the outer two layers were Ag. For the center Fe layer they calculated $H_{hf}=359$ kG, with a decrease to 339 kG for the next-to-interface layer and 335 kG for the interface Fe layer. With a simple two-site fit we obtain 363 (65%) and 352 kG (35%), which is in qualitative agreement if one identifies the larger hyperfine field with interior atoms as described above. For the 2.4-ML sample there is at present no model calculation whose assumptions permit reasonable comparison with our data.

In this Letter we have shown conclusively that for single-crystal Fe films on Ag(100) there is a contribution to the anisotropy which favors the direction perpendicular to the surface. This contribution is due mainly to Fe atoms at the Fe/Ag interface and is large enough at low temperatures to overcome the demagnetizing field and produce perpendicular spin orientations for Fe layer thicknesses less than about 5.5 ML. On the basis of the temperature-dependent spin orientation of the 5.5-ML sample we conclude that this anisotropy increases fairly rapidly as the temperature is lowered. We have also shown for 2.4- and 5.5-ML samples that the magnetic hyperfine fields at low temperatures are enhanced compared to that of bulk Fe, and it appears that interface atoms have lower hyperfine fields than the film interior, in qualitative agreement with theoretical calculations.

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[a]Permanent address: Sachs Freeman Associates, Landover, MD 20785.

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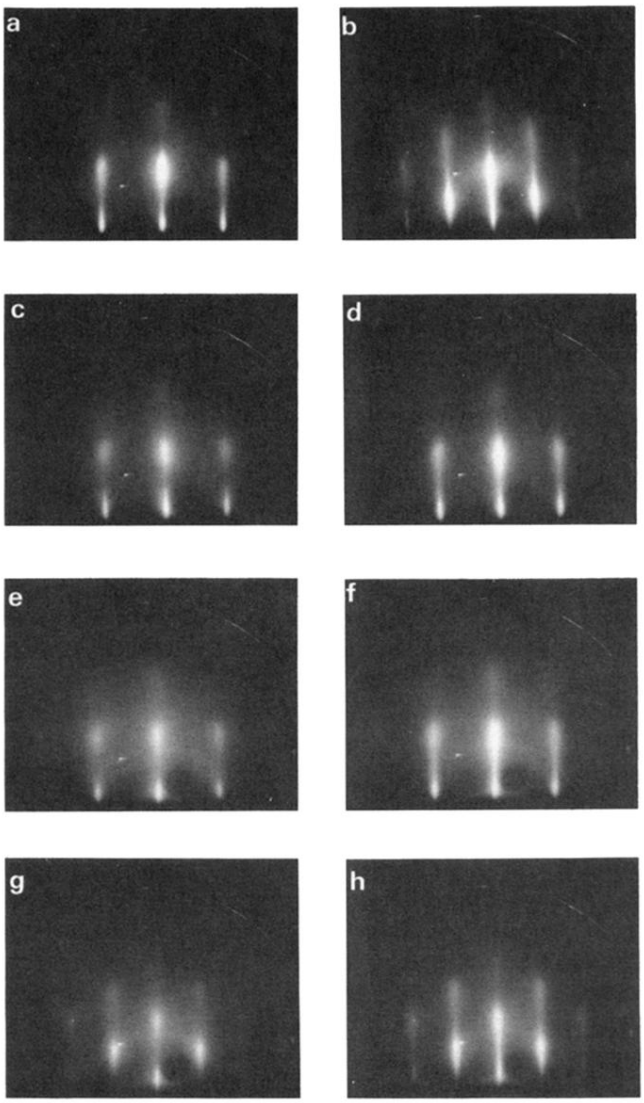

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