Second- and First-Order Phase Transitions in the Magnetic Reorientation of Ultrathin Fe on Gd

C. S. Arnold and D. P. Pappas
National Institute of Standards and Technology, Boulder, Colorado

A. P. Popov
Moscow State Engineering Physics Institute, Moscow, Russia
(Received 24 March 1999)

Ultrathin Fe films grown on the Gd(0001) surface exhibit a magnetic in-plane to out-of-plane spin-reorientation transition with increasing temperature. We provide evidence that this reorientation transition is accomplished in two steps. The first step, at low temperature, is a continuous reorientation of the surface moment from in-plane to canted out-of-plane with a corresponding peak in the susceptibility. The second step is a thermally irreversible rotation from this canted direction to perpendicular to the film plane. These two steps therefore have the characteristic signatures of second- and first-order phase transitions, respectively.

PACS numbers: 75.70.Ak, 75.30.Kz

Reorientation transitions (RT's) in magnetic films are remarkable phenomena of fundamental physical interest because, in the ultrathin film limit, magnetic anisotropies present at surfaces and interfaces compete with the demagnetizing energy of the films. In many cases, the RT of the magnetization from in-plane to out-of-plane (or vice versa) is driven by changing the film thickness or temperature [1–3]. Recent theoretical and experimental studies of ultrathin films have focused on thermodynamic classification of RT's [4–6]. Most importantly, the connection of RT's to the general theory of phase transitions remains uncertain in experimental work to date. For example, it is unclear that discontinuous RT's, in which the magnetization direction abruptly changes, are truly first-order phase transitions [5]. Similarly, it is unclear that continuous RT's, in which the magnetization direction changes smoothly from one orientation to another, are second-order (or higher) phase transitions [6]. In this Letter, we apply two principles of phase transitions to classify the RT in ultrathin Fe films grown on Gd(0001). We find evidence that this RT is composed of two distinct phase transitions, one of second order and one of first order.

In an ultrathin film, the magnetization is uniform and makes an angle θ with the film plane that is determined by a balance of the second- and fourth-order magnetic anisotropies K_2 and K_4 [4,7]. In current literature, the temperature-driven trajectories $\{K_2(T), K_4(T)\}$ are used to predict the behavior of RT's [4,8]. Two types of transitions have been identified: discontinuous and continuous. The free-energy formalism employed to describe these RT's is a Landau expansion with the order parameter $\cos(\theta)$ [or $\sin(\theta)$, depending on the convention used] [4,7,9]. Using the Landau theory for classification criteria [9], the discontinuous transition is a first-order phase transition, whereas the continuous reorientation is actually comprised of two second-order phase transitions, separating three distinct phases: in-plane, canted, and perpendicular.

However, before identifying phase transitions within an RT, it is necessary to identify salient characteristics of first- and second-order behavior. For example, Ehrenfest [10] provided three criteria to identify a first-order phase transition: (i) hysteresis, (ii) latent heat, and (iii) an abrupt change in the order parameter. Additionally, phase coexistence is a common feature [5,11,12]. In second-order phase transitions, a divergence in the susceptibility is expected [9]. In particular, in a continuous RT where two second-order phase transitions occur, two divergences in the magnetic susceptibility will occur if the field is applied perpendicular to the local magnetization (i.e., along a hard axis) [13]. In this case, the susceptibility peaks are due to rotation of the moment. In the present study, we observe behavior of both first- and second-order phase transitions in the RT of ultrathin Fe/Gd using thermal hysteresis and magnetic susceptibility measurements, respectively.

In contrast to ultrathin film systems where RT's have been observed [1–3,8], the Fe/Gd(0001) system is an ultrathin ferromagnet on a thin-film ferromagnet. Previous magnetic studies determined that the Fe film couples antiferromagnetically to the underlying Gd, with an ordering temperature higher than that of the Gd [14,15]. An important property of this system is that the underlying Gd and the ultrathin Fe film have *different* ordering temperatures: one at the bulk Gd Curie temperature of T_C^{Gd}, 293 K, and a second transition for the Fe film (above 350 K for 1.5 atomic layers of Fe) [13]. Monte Carlo simulations [16] show that the surface of a magnetic thin-film system remains ordered above the ordering temperature of the bulk if the exchange coupling at the surface is sufficiently stronger than in the bulk. From the known Fe-Gd, Fe-Fe, Gd-Gd exchange couplings, this criterion is tenably satisfied [13,17]. At low temperatures, where the magnetization of the system is dominated by the Gd, the shape anisotropy orients the Gd magnetization direction in the plane. Because the Fe overlayer is exchange coupled to the Gd, it is also held in-plane. The Fe/Gd

surface, however, possesses a strong perpendicular magnetic anisotropy [18]. At temperatures above T_C^{Gd}, the surface is free to orient along its own easy axis. Previous work determined that ultrathin Fe films less than six atoms thick reorient from in-plane to perpendicular as a function of temperature [14]. For the present study, we focus on 1.5 atomic layers of Fe on Gd(0001) films because earlier experiments suggested a discontinuous RT at this Fe thickness [15].

Film growth, structural and chemical characterization, and magnetic measurements were made in an ultrahigh vacuum system with a base pressure of 4×10^{-9} Pa (3×10^{-11} torr). A Y(0001) single crystal substrate was cleaned by neon-ion sputtering, and 15 nm of Gd was deposited at 473 K by electron-beam evaporation [19]. A final anneal of 700 K for one minute yielded a film that was highly ordered according to low energy electron diffraction (LEED), uncontaminated according to Auger electron spectroscopy (AES), and magnetically soft with a coercive field less than 800 A/m (10 Oe) from 150 K to T_C^{Gd}. Fe was then deposited at room temperature, also by electron beam evaporation. From the LEED pattern, quenched at only 1 atomic layer of Fe, and the AES uptake curves, which show intermixing, we conclude that the ultrathin Fe film is more accurately described as an Fe-rich, amorphous Fe/Gd surface alloy. Surface magnetic measurements were made with spin-polarized secondary electron emission spectroscopy (SPSEES). A 1 keV electron beam was used to generate secondary electrons from the surface region. The low energy electrons were collected, and the spin polarization was measured in a 30 keV retarding potential Mott detector. Because of the short mean-free path of low energy electrons in a material, the resultant polarization was proportional to the magnetization in the first few atomic layers of the surface [20]. The magneto-optic Kerr effect (MOKE) was used in the polar (out-of-plane) and longitudinal (in-plane) geometries. As shown below, the MOKE measurements probed both bulk and surface magnetism.

Figure 1 provides an overview of the RT of 1.5 atomic layers of Fe on Gd(0001). Magnetic remanence measurements using MOKE [Fig. 1(a)] and SPSEES [Fig. 1(b)] were made in differential mode, with the magnetization reversed at each temperature by applying field pulses of approximately 1 kA/m for 10 μs. These differential measurements were thermally reversible. The temperature dependence of longitudinal MOKE measurements is nearly identical to that of clean Gd. However, the polar MOKE shows the RT of the surface. The polar and longitudinal measurements give comparable magnitudes for the MOKE rotations even though the RT is localized to the surface because of the following effects. First, the polar Kerr effect is usually more than 10 times greater than the longitudinal [21]. Second, Fe has a greater magneto-optic rotation than Gd. Figure 1(b) shows the in-plane (x) and out-of-plane (z) components of the secondary electron polarization. The x component is approximately 30% of the corresponding value for the clean Gd(0001) [13] or for the clean Fe(001) surface [2]. This reduction is a compensation effect due to the ferrimagnetic order at the Fe-Gd surface [14,15]. Comparing the longitudinal MOKE data in Fig. 1(a) to the secondary electron x-polarization in Fig. 1(b), the in-plane magnetization at the surface has a different temperature dependence than the bulk. Surface and bulk in-plane components disappear near the T_C^{Gd}. Both the polar MOKE and the secondary electron z-polarization show that the surface magnetization has a z component that persists below 200 K.

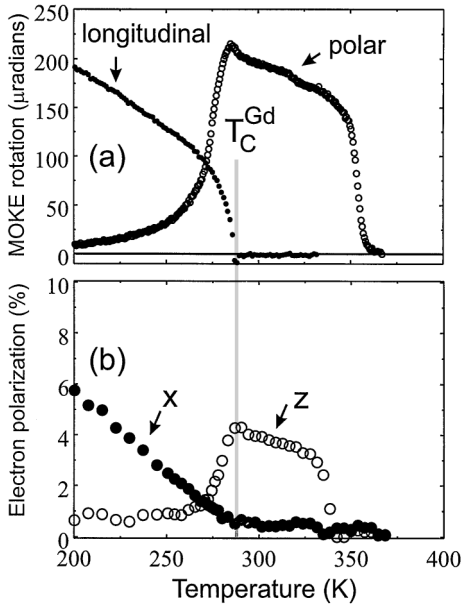

FIG. 1. The reorientation transition in 1.5 atomic layers of Fe on 15 nm of Gd observed in remanent magnetization measurements using (a) MOKE and (b) secondary electron polarization.

The magnetic susceptibility measurements of Fig. 2 were obtained using polar MOKE and a field amplitude of 200 A/m (2.5 Oe) out-of-plane. These data are for a different 1.5 atomic layer Fe/Gd(0001) film than that of Fig. 1. For comparison, the *polar* MOKE signal from clean 15 nm Gd/Y(0001) films (not shown) was less than 0.1 μrad/(80 A/m), for all $T > 100$ K. The real (in-phase with the applied field) and imaginary (out-of-phase) parts of the polar susceptibility, Re$\{\chi\}$ and Im$\{\chi\}$ respectively, both measured in cooling, are shown in Fig. 2(a). The Re$\{\chi\}$ rises from zero above 200 K, forming a broad peak near 240 K, labeled $T_{\mathrm{s.o.}}$, while perpendicular remanence, as measured by Im$\{\chi\}$ [22], rises from zero above this temperature. A second peak forms in both parts near T_C^{Gd} (293 K). A third peak (not shown) appears above 350 K, where the Fe overlayer disorders. By changing the annealing temperature of the Gd, the peaks near T_C^{Gd} were unaffected; however, the position of the peak at $T_{\mathrm{s.o.}}$ could be varied. For example,

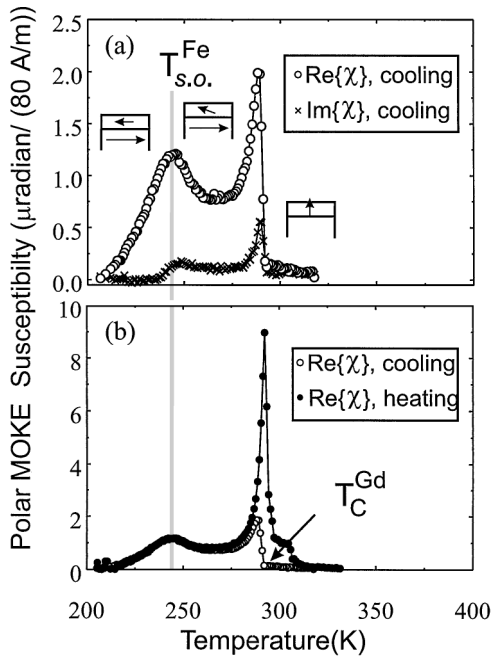

FIG. 2. The magnetic susceptibility with the applied field perpendicular to the film measured with polar MOKE. (a) Real and imaginary parts, measured simultaneously in cooling, show that the moment falls in-plane continuously at 240 K and remains in-plane at lower temperatures. The peak in Re$\{\chi\}$ at $T_{\text{s.o.}} = 240$ K is a signature of a second-order phase transition. (b) Thermal hysteresis in Re$\{\chi\}$ is observed near $T_C^{\text{Gd}} = 293$ K.

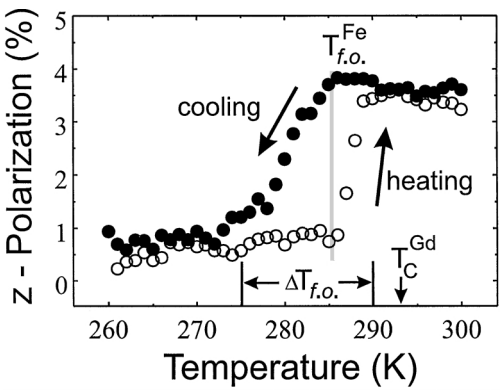

FIG. 3. The z component of the secondary electron polarization measured in zero field, both in cooling and in heating after magnetizing the film in the z direction at 310 K. Thermal hysteresis is strong evidence that this part of the reorientation transition is first order.

the $T_{\text{s.o.}}$ peak in Re$\{\chi\}$ for the data of Fig. 1 was at 150 K. Our studies indicate that this behavior correlates with the reduction of the magnetocrystalline anisotropy in the Gd film, as determined by the coercive field. Figure 2(b) shows Re$\{\chi\}$ measured in both cooling and heating, and is characteristic of all the films measured. The peak at $T_{\text{s.o.}}$ is thermally reversible, independent of annealing conditions. Thermal hysteresis was observed in the peak at higher temperature, and diminished with higher applied field amplitudes.

To better investigate the thermal hysteresis near the T_C^{Gd}, remanent magnetization measurements were made in cooling and in heating without applied fields during or between data points. For these measurements, the film was initially magnetized out-of-plane with a *single* field pulse at 300–310 K, cooled in zero field to a temperature below that for which hysteresis was observed, typically to 250–260 K, and then reheated in zero field to the starting temperature. The measurements were then repeated after a second field pulse in the opposite out-of-plane direction [23]. Magnetization measurements were acquired continuously during the thermal cycle. Figure 3 shows a thermal hysteresis loop in the z component of the secondary electron polarization. In cooling, the z-polarization remained near 3.6% down to $T_{\text{f.o.}} = 285$ K. With further cooling, it reduced to below 1%. Then, in heating, the polarization remained at this level up to $T_{\text{f.o.}}$. With further heating, it returned to 3.6%. The width of the hysteresis loop, $\Delta T_{\text{f.o.}}$, was approximately 15 K.

The polar susceptibility data in Fig. 2(a) shows that the onset of the RT from in-plane to out-of-plane is continuous and bears the signature of a second-order phase transition. The appearance of out-of-plane remanence, as measured by Im$\{\chi\}$ [22], coincides with the peak in Re$\{\chi\}$ at $T_{\text{s.o.}}$. Remanent magnetization measurements show a substantial out-of-plane moment only at higher temperatures. Thus, the peak in Re$\{\chi\}$ appears at the onset of canting out-of-plane and is evidence that the onset of the RT at low temperature is a second-order phase transition [13]. Other observations that support the assertion that the moment is canted out-of-plane above $T_{\text{s.o.}}$ are that, in thermal hysteresis experiments (as in Fig. 3), the film would not remain in a single domain state if it was cooled below $T_{\text{s.o.}}$. This type of demagnetization is expected for a transition from in-plane to canted when the film is warmed because the nucleation of canted-up and canted-down domains is equally likely. Additionally, if the film was *not* cooled below $T_{\text{s.o.}}$, then it remained single domain upon warming. This second-order behavior in the RT at low temperature is markedly different from that near T_C^{Gd}.

The thermal hysteresis observed near T_C^{Gd} in Fig. 2(b) and Fig. 3 is strong evidence that the completion of the RT is a first-order phase transition [10–12]. For a first-order phase transition, the thermal width, $w \equiv \Delta T/T_{\text{f.o.}}$ is a measure of the first-order strength [24]. From Fig. 3, $w \simeq 0.05$ is very large, comparable to that of pure water near its freezing point [25], and is an order of magnitude larger than that observed in the melting of the Abrikosov flux lattice in high-T_C superconductors or nematic-isotropic liquid crystal transitions [24,26]. This excludes nonequilibrium effects, such as critical slowing down, and supports a first-order phase transition as the origin of the hysteresis.

This study shows that ultrathin Fe layers on thin Gd(0001) films have a two-step RT. At low temperatures, the Fe remains in-plane, antiferromagnetically coupled to the Gd. At the intermediate temperature $T_{\mathrm{s.o.}}$, the Fe/Gd surface undergoes a continuous rotation to a canted direction. A similar effect, i.e., a small-angle RT with a corresponding susceptibility peak, has been seen in thick Gd films and bulk Gd [27]. The addition of Fe produces a perpendicular magnetic anisotropy at the surface that may allow the transition to occur at $T_{\mathrm{s.o.}}$ for thin Gd films as well. Because the exchange coupling in Gd is small, domain walls are narrow, and we expect an inhomogeneous magnetization depth profile in the Gd thin films in this intermediate temperature range. Pinning of this domain wall near the surface, due to either defects or magnetostriction, provides a mechanism for the thermal hysteresis observed as the system is cycled through T_C^{Gd}. Available models in ultrathin films assume a homogeneous magnetization and exclude the coexistence of continuous and discontinuous behavior within one 90° reorientation. The inclusion of a magnetization depth profile is probably necessary to reveal the underlying physics in this system.

This work was supported by NATO, NSF, Research Corporation, Jeffress Trust, and NIST. Useful discussions with J. Kirschner, Y. Millev, and D. Venus are acknowledged.

[1] U. Gradmann and J. Muller, Phys. Status Solidi **27**, 313 (1968).
[2] D. P. Pappas, K.-P. Kamper, and H. Hopster, Phys. Rev. Lett. **64**, 3179 (1990).
[3] Z. Q. Qiu, J. Pearson, and S. D. Bader, Phys. Rev. Lett. **70**, 1006 (1993).
[4] Y. Millev and J. Kirschner, Phys. Rev. B **54**, 4137 (1996). See also A. Moschel and K. D. Usadel, Phys. Rev. B **51**, 16 111 (1995), and references therein.
[5] H. P. Oepen, M. Speckmann, Y. Millev, and J. Kirschner, Phys. Rev. B **55**, 2752 (1997).
[6] M. Farle, B. Mirwald-Schultz, A. N. Anisimov, W. Platow, and K. Baberschke, Phys. Rev. B **55**, 3708 (1997).
[7] H. Fritzsche, J. Kohlhepp, H. J. Elmers, and U. Gradmann, Phys. Rev. B **49**, 15 665 (1994).
[8] M. Farle, Rep. Prog. Phys. **61**, 755 (1998).
[9] Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985), 2nd ed.
[10] Robert M. White and Theodore H. Geballe, *Long Range Order in Solids* (Academic, New York, 1979).
[11] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1973), Vol. 8.
[12] Martin Brokate and Jürgen Sprekels, *Hysteresis and Phase Transitions* (Springer-Verlag, New York, 1996).
[13] D. Venus, C. S. Arnold, and M. J. Dunlavy, Phys. Rev. B (to be published).
[14] T. S. Sherwood, S. R. Mishra, A. P. Popov, and D. P. Pappas, J. Vac. Sci. Technol. A **16**, 1364 (1998).
[15] D. P. Pappas, C. S. Arnold, and A. P. Popov, in *Magnetism and Electronic Correlations in Local-Moment Systems: Rare-Earth Elements and Compounds*, edited by M. Donath, P. A. Dowben, and W. Nolting (World Scientific, Singapore, 1999).
[16] K Binder, in *Phase Transitions and Critical Phenomena* (Ref. [11]). See also R. W. Wang and D. L. Mills, Phys. Rev. B **46**, 11 681 (1992); U. Bovensiepen, F. Wilhelm, P. Srivastava, P. Poulopoulos, M. Farle, A. Ney, and K. Baberschke, Phys. Rev. Lett. **81**, 2368 (1998).
[17] S. L. Gnatchenko, A. B. Chizhik, D. N. Merenkov, V. V. Eremenko, H. Szymczak, R. Szymczak, K. Fronc, and R. Zuberek, J. Magn. Magn. Mater. **186**, 139 (1998).
[18] S. Lee, A. Miller, and H. Blackstead, J. Appl. Phys. **60**, 3982 (1986); V. Harris, K. Aylesworth, B. Das, W. Elam, and N. Koon, Phys. Rev. Lett. **69**, 1939 (1992).
[19] M. Gajdzik, T. Trappmann, C. Sürgers, and H. Löhneysen, Phys. Rev. B **57**, 3525 (1998).
[20] D. L. Abraham and H. Hopster, Phys. Rev. Lett. **58**, 1352 (1987); D. P. Pappas *et al.*, Phys. Rev. Lett. **64**, 3179 (1990).
[21] S. D. Bader and J. L. Erskine, in *Ultrathin Magnetic Structures II*, edited by B. Heinrich and J. A. C. Bland (Springer-Verlag, Berlin, 1991).
[22] A. Aspelmeier, M. Tischer, M. Farle, M. Russo, K. Baberschke, and D. Arvanitis, J. Magn. Magn. Mater. **146**, 256 (1995).
[23] This second cycle with the film magnetized oppositely from the first cycle is required to remove instrumental asymmetries. See Joachim Kessler, *Polarized Electrons* (Springer-Verlag, Berlin, 1985), 2nd ed.
[24] T. Riste and L. Dobrzynski, Phys. Rev. Lett. **74**, 2737 (1995).
[25] Charles A. Knight, *The Freezing of Supercooled Liquids* (Van Nostrand, Princeton, 1967); A. R. Ubbelohde, *The Molten State of Matter* (Wiley, New York, 1978).
[26] H. Safar, P. L. Gammel, D. A. Huse, D. L. Bishop, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett. **69**, 824 (1992).
[27] A. Berger, A. W. Pang, and H. Hopster, Phys. Rev. B **52**, 1078 (1995), and references therein.