Magnetic Reconstruction of the Gd(0001) Surface

H. Tang,[1,*] D. Weller,[2] T. G. Walker,[1] J. C. Scott,[2] C. Chappert,[2] H. Hopster,[1] A. W. Pang,[1] D. S. Dessau,[3] and D. P. Pappas[4]

[1]*Department of Physics and Institute for Surface and Interface Science, University of California, Irvine, California 92717*
[2]*IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*
[3]*Stanford Electronics Laboratory, Stanford University, Stanford, California 94309*
[4]*Naval Research Laboratory, Washington, D.C. 20375-5343*
(Received 18 January 1993)

The surface magnetism of Gd(0001) films is studied using spin resolved electron spectroscopies. Both a canted surface magnetization vector out of the plane of the film and an enhanced surface magnetic ordering temperature 60 ± 2 K higher than the bulk Curie temperature are observed. Our results show that the surface magnetic layer behaves as a separate entity from the bulk. The in-plane component of surface magnetization aligns ferromagnetically to the bulk. Spin resolved photoemission from the Gd $4f$ core levels shows $\approx 65\%$ spin polarization at 150 K, which extrapolates to $\approx 91\%$ at 0 K.

PACS numbers: 75.25.+z, 75.30.Gw, 75.30.Pd, 81.40.Rs

Magnetism at surfaces and in ultrathin films offers a great variety of phenomena different from the corresponding bulk behavior [1]. Surface magnetic reconstructions (SMR) (i.e., a different orientation of the spins at the surface than in the bulk) and enhanced surface ordering temperatures are among the most intriguing phenomena which have been predicted in surface magnetism [2]. Extensive studies have failed to demonstrate the existence of these phenomena in $3d$ transition metals. $4f$ rare earth materials, on the other hand, are more promising candidates for SMR due to the highly localized moments, which in turn give rise to a broad spectrum of magnetic ordering phenomena in the bulk and at surfaces. For example, evidence for an enhanced surface ordering temperature T_{CS} over the bulk Curie temperature T_{CB} was found by Rau and Eichner [3] on polycrystalline Gd surfaces with spin polarized electron capture spectroscopy. Weller *et al.* [4] subsequently showed that T_{CS} may exceed T_{CB} by as much as 22 K on single crystalline Gd(0001) surfaces, and attributed it to an enhanced and possibly antiferromagnetic surface-bulk coupling. Indeed, all-electron first principle electronic structure calculations of the Gd(0001) surface support a modified surface-bulk coupling [5], and experimental studies of the surface electronic structure by (nonspin resolved) photoemission spectroscopy [6] were found to be consistent with these calculations. Two recent spin resolved photoemission studies of thick Gd(0001)/W(110) films reported controversial results, one reporting no SMR [7] and the other reporting a reduced surface polarization [8]. In both of these studies, however, only the in-plane component of magnetization was determined. Moreover, in both cases the photoelectron polarization was considerably smaller than that expected from the fully polarized Gd $4f$ core levels. Ferromagnetic resonance studies [9] have shown that there is an intrinsic out-of-plane anisotropy in thin (1 monolayer) Gd films. In the films studied by SMR, however, the anisotropy was not strong enough to overcome the dipolar energy, and the magnetization remained in the plane of the films. In order to determine the orientation of the Gd(0001) surface magnetization of thick films, we have endeavored to measure all components (perpendicular and in the plane of the film) of the remanent magnetization as a function of temperature using spin resolved electron spectroscopy with a three-component electron spin analyzer.

In this Letter, we show for the first time that there is a perpendicular component of magnetization localized at the surface of the Gd(0001) films. In addition, we have observed enhancements of T_{CS} which are nearly a factor of 3 larger than those previously observed [4]. Finally, we demonstrate that the in-plane Gd $4f$ polarization saturates to $\approx 91\%$ at 0 K. The studies were carried out using both spin polarized secondary electron emission spectroscopy (SPSEES) and spin polarized $4f$ photoemission spectroscopy (SPPES) in a UHV chamber (base pressure 2×10^{-10} Torr) [10]. The Gd was evaporated from a W crucible onto a single crystal W(110) substrate at a rate of 0.7 Å/sec to a final thickness of 400 Å. The pressure always remained below 1×10^{-9} Torr during film deposition. The substrate temperature was held at 300 K to promote layer-by-layer growth [11]. While this resulted in initially poorly ordered films, as inferred by diffuse LEED patterns, subsequent annealing to 825 K for 3–5 min resulted in sharp (1×1) sixfold LEED patterns which were in registry with the substrate [12]. Auger electron spectroscopy (AES) measurements showed that Gd(0001) films prepared by this method are very clean, with only trace amounts of oxygen contamination detectable [$I_O(503\text{ eV})/I_{Gd}(138\text{ eV}) \approx 0.03$, or 0.04 equivalent monolayer of oxygen] with a single pass cylindrical mirror analyzer at 3 keV primary electron energy. After preparation, each film was cooled to 150 K and simultaneously magnetized with a single pole UHV compatible magnet and a nominally in-plane magnetic field of about 100 Oe whose direction was 15° off one of the three symmetry axes in the hcp (0001) basal plane. *In situ* magneto-optical Kerr effect measurements demonstrated

0031-9007/93/71(3)/444(4)$06.00
© 1993 The American Physical Society

that the bulk magnetization of these annealed Gd films shows complete remanence, with the magnetization collinear to the field axis up to the bulk Curie temperature [13]. They are different from films grown at 673 K [11] in which higher coercivities and reduced remanence near T_{CB} were found [13].

For the SPSEES studies, low-energy secondary electrons were generated with a 1 keV primary electron beam (< 1 mm diameter) impinging at 50° off normal and collected at normal emission angle with the sample biased at −30 V. The photoemission measurements were performed with photons from an undulator beam line at Stanford Synchrotron Radiation Laboratory (spot size ≈5 mm×3 mm). The radiation was incident on the surface at 45° off normal and the photoemitted electrons were collected in an angle resolved mode along the normal direction with an acceptance angle cone of ±3°. The electrons were energy selected in a 90° electrostatic spherical analyzer and transported to a spin analysis chamber. All three components of the spin polarization vector were measured with a medium-energy retarding field Mott analyzer which is calibrated to within 5%, and all polarization measurements were performed on samples in their remanent state.

Because of the high chemical reactivity of Gd, we found it advantageous to conduct the photoemission studies at $h\nu = 149$ eV. At this energy, photoemission of the Gd $4f$ electrons occurs through a $4d$-$4f$ resonant excitation channel [14] as well as the direct photoionization process. We find that the Gd $4f$ polarization is the same on resonance as off, in agreement with the results of Kachel *et al.* [15]. The resonant photoemission also provides a factor of 10 increase in intensity. With the increased intensity, we were able to acquire one complete temperature cycle in about 1 h, well before the films had adsorbed enough contamination to significantly alter the magnetic properties at the surface.

In Fig. 1 we show the first evidence of a SMR in the form of a perpendicular component in the Gd(0001) surface magnetization. The data were taken using SPSEES from a film which was gradually warmed from 150 to 375 K. The secondary electrons are highly polarized due to significant contributions from the $4f$ core electrons [16], and clearly show both perpendicular and in-plane polarization. The in-plane data show a resemblance to the earlier SPLEED data [4], with an enhanced T_{CS} in this film which is 40 K higher than T_{CB} (compared to a 22 K enhancement from Ref. [4]). We also observe a perpendicular component that persists up to T_{CS}. It is important to stress here that in the present experiment the sample was left in its remanent state as the temperature was ramped, whereas in the previous SPLEED experiment the sample was remagnetized at each temperature step. Therefore, the present data contain in its sign the added information on the relative directions of the in-plane polarizations above and below T_{CB}. The lack of a sign reversal of the polarization on going through T_{CB} shows that the *in-plane* component of the surface and bulk moments are ferromagnetically aligned. The sign of the perpendicular component depends solely on the sign of the vertical field component during cooling or magnetizing. It could be switched from positive to negative.

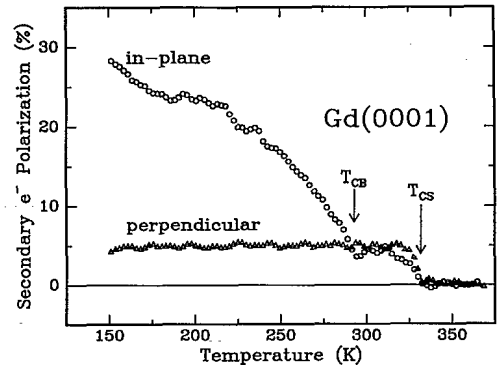

FIG. 1. Temperature dependence of the spin polarization of 2 eV secondary electrons from a 400 Å film of Gd(0001)/W(110) grown at 300 K and annealed to 825 K for 3.5 min. T_{CS} and T_{CB} indicate the surface and bulk magnetic ordering temperatures, respectively.

After evaluating the behavior of more than 100 Gd films we note here that, while there are wide variations in the enhancement of T_{CS}, the general trend is that the least contaminated films have the highest T_{CS}. The effect of deliberate contamination of the films was that the polarizations above T_{CB}, both in-plane and perpendicular, vanish after a film has been exposed to ≈1 monolayer equivalent of oxygen. Prolonged exposure to residual gases also tends to reduce T_{CS}. The growth at low temperature and subsequent anneal is also critical for a high T_{CS}. Since Auger electron studies [11] show that Gd grows on W(110) in a layer-by-layer (Frank–van der Merwe) growth mode at 300 K as opposed to a three-dimensional (Stranski-Krastanov) growth at 673 K, we argue that the increase in T_{CS} for films grown at 300 K is most likely due to reduced surface roughness. This conclusion suggests that future scanning tunneling microscopy studies should be able to correlate the Gd surface roughness to the magnetic ordering temperature. We further note that, as best revealed in the perpendicular component of Fig. 1, the surface magnetic transition is extremely abrupt, reminiscent of a two-dimensional system or possibly even a first order phase transition [17]. The dip evident in the Fig. 1 in-plane data at 187 K is seen consistently. Because of the facts that the characteristics of the dip are sensitive to contamination [18] and that we see no evidence of a corresponding dip in the magneto-optical Kerr effect signal, we conclude that the cause of the dip is localized in the topmost layers of the Gd film. While there is no magnetic transition at 187 K in Gd at zero field, the dip is similar to changes in the magnetoelasticity near the bulk spin reorientation transi-

tion temperature at $T_{SR}=225$ K [19]. This similarity may be coincidental, however. Further investigations into the nature of the dip are necessary to understand the origin of this effect.

The most striking aspect of Fig. 1 is that the perpendicular component is completely insensitive to the bulk magnetic transition, and remains constant within statistical variations until it vanishes abruptly at T_{CS}. As a result of the intrinsic averaging over the emission region of spin resolved electron spectroscopy, a signal with both perpendicular and in-plane polarizations may indicate either a canted magnetization configuration at the surface or the coexistence of purely perpendicular and in-plane surface domains which are smaller than the emission region. These two cases are shown in Figs. 2(a) and 2(b), respectively. The domain state as shown in Fig. 2(b) is unlikely, primarily because the domain state is expected to be only stable for a very narrow temperature range (< 20 K wide) where the perpendicular anisotropy and (dipole energies)/(unit volume) are nearly equal [20–22]. Above and below this temperature, the films are typically magnetized in macroscopic single domains over a wide range of temperature. Furthermore, the SMR effects become more pronounced when the films are deposited in a layer-by-layer mode with low levels of contamination. As the surface integrity increases, there are fewer pinning sites (e.g., impurities or steps) which could stabilize a domain configuration. We therefore conclude that the surface magnetization is most likely in a canted state, as shown in Fig. 2(a).

In order to illustrate the effects of growth temperature on the magnetic behavior of the Gd films, we show the temperature-dependent Gd $4f$ photoemission polarizations in Figs. 3(a) and 3(b) for films grown at 300 K vs 673 K, respectively. Figure 3(a) shows a finite polarization which persists to 60 ± 2 K above T_{CB} which was taken from a film grown at room temperature and postannealed to 825 K, as described above. The magnitude of the in-plane polarization in the temperature region above T_{CB} and below T_{CS} is relatively small compared to the secondary electron polarizations from Fig. 1 because the 149 eV photoemitted electrons are relatively insensitive to the surface magnetization [23]. An increased surface sensitivity of SPSEES agrees well with a number of studies which show that the polarization of low-energy electrons is sensitive to very thin layers (5–10 Å) of Gd on various surfaces [23–26]. Evidence of perpendicular and in-plane SMRs were therefore not consistently evident in the photoemission data due to the low surface sensitivity combined with the relatively large emission region (5×3 mm^2), which averaged over most of the face of the crystal. This problem is circumvented in the secondary electron polarization study because we used a relatively well-focused electron beam for excitation.

The main advantage of Gd $4f$ photoemission is that a quantitative understanding of the polarization is possible: Since the $4f$ shell is half filled, Hund's rule requires the polarization to be 100% at 0 K, and at finite temperatures the polarization should scale with the magnetization. This is, in fact, what we observe from the films grown at low temperature. When extrapolating the polarization to 0 K, it should be considered that the magnetization of Gd follows a T^2 law from 1.4 to 50 K, and a $T^{3/2}$ law from 50 to 200 K [27]. However, the roll-off below 50 K away from a $T^{3/2}$ fit is much less than the statistical error of the fit. Therefore, extrapolating the polarization in Fig. 3(a) using a $T^{3/2}$ fit, we obtain a value of (91 ± 5)% at 0 K.

On the other hand, for a film grown at 673 K [4,7], shown in Fig. 3(b), both the $4f$ polarization and the enhancement of T_{CS} are reduced. Extrapolation to low

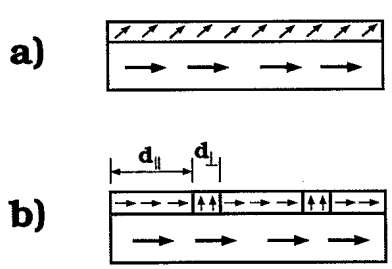

FIG. 2. Schematic of the possible domain configurations which give both in-plane and perpendicular signals when averaged over the emission spot size. Panel (a) shows a magnetic state with canted spins on the surface, and panel (b) shows a combination of perpendicular and in-plane domains.

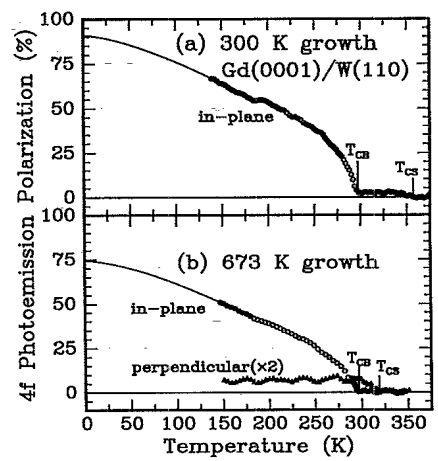

FIG. 3. Spin resolved photoemission polarization from the Gd $4f$ core levels vs temperature taken with $h\nu=149$ eV. The data in panel (a) were taken from a 400 Å film of Gd grown on W(110) at 300 K and annealed to 825 K for 3.5 min, while the panel (b) data are from a film grown at 673 K. T_{CS} and T_{CB} indicate the surface and bulk magnetic ordering temperatures, respectively. An extrapolation to zero temperature is shown using a $T^{3/2}$ fit with prefactors of 1.6×10^{-4} and 1.8×10^{-4} deg$^{-3/2}$ for (a) and (b), respectively. For comparison, the bulk Gd prefactor is 0.98×10^{-4} deg$^{-3/2}$.

temperature yields only $(75 \pm 5)\%$, and the perpendicular surface magnetization persisted only up to 20 K above T_{CB}. The reduced polarization and ordering temperature enhancement are presumably due to increased surface roughness.

We have shown in this study that a perpendicular component exists in the surface magnetization of Gd(0001). Enhancements of the surface magnetic ordering temperature are reported which are nearly a factor of 3 higher than any previously measured. Furthermore, we have shown that the polarization of the Gd $4f$ photoemission is saturated, being reduced primarily by finite temperature effects. We hope that this work will stimulate future research into correlating the actual surface morphology of Gd films grown under these conditions with the magnetic properties reported herein.

We thank the staff of the Stanford Synchrotron Radiation Laboratory (SSRL) for their technical support. SSRL is operated by the Department of Energy, Division of Chemical Sciences. H.T. and H.H. also gratefully acknowledge support from the IBM Almaden Research Center. D.P.P. acknowledges support from the Office of Naval Technology and IBM Almaden Research Center, and would like to thank J. J. Krebs and G. A. Prinz for helpful discussions. This work is supported in part by the NSF through Grants No. DMR 8821293 and No. DMR 9119815.

*Present address: Mail Stop 66, Stanford Linear Accelerator Center, Stanford, CA 94309.

[1] L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. Hopster, D. N. Lambeth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, J. Mater. Res. **5**, 1299 (1990).

[2] D. L. Mills, Phys. Rev. B **3**, 3887 (1971); K. Binder and P. Hohenberg, Phys. Rev. B **6**, 3461 (1972); D. L. Mills, Phys. Rev. B **8**, 4424 (1973); C. Demangeat, D. L. Mills, and S. Trullinger, Phys. Rev. B **16**, 522 (1977); J. C. S. Levy, Surf. Sci. Rep. **1**, 39 (1981), and references cited therein; G. Allan, Surf. Sci. Rep. **1**, 121 (1981); D. L. Mills, Phys. Rev. B **39**, 12306 (1989).

[3] C. Rau and S. Eichner, in *Nuclear Methods in Materials Research*, edited by K. Bethge, H. Baumann, H. Jex, and F. Rauch (Vieweg, Braunschweig, 1980), p. 354; Phys. Rev. B **34**, 6347 (1986).

[4] D. Weller, S. F. Alvarado, W. Gudat, K. Schröder, and M. Campagna, Phys. Rev. Lett. **54**, 1555 (1985).

[5] R. Wu, C. Li, A. J. Freeman, and C. L. Fu, Phys. Rev. B **44**, 9400 (1991).

[6] Dongqi Li, Jiandi Zhang, P. A. Dowben, and M. Onellion, Phys. Rev. B **45**, 7272 (1992).

[7] G. A. Mulhollan, K. Garrison, and J. L. Erskine, Phys. Rev. Lett. **69**, 3240 (1992).

[8] D. Li, J. Zhang, P. A. Dowben, and K. Garrison, J. Phys Condens. Matter **5**, L73 (1993).

[9] M. Farle, A. Berghaus, and K. Baberschke, Phys. Rev. B **39**, 4838 (1989).

[10] D. P. Pappas, K.-P. Kämper, and H. Hopster, Phys. Rev. Lett. **64**, 3179 (1990).

[11] D. Weller and S. F. Alvarado, J. Appl. Phys. **59**, 2908 (1986).

[12] U. Stetter, M. Farle, K. Baberschke, and W. G. Clark, Phys. Rev. B **45**, 503 (1992).

[13] C. Chappert, D. Weller, H. Tang, J. C. Scott, H. Hopster, and D. P. Pappas, in Proceedings of the MRS 1993 Springer Meeting (to be published).

[14] F. Gerken, J. Barth, and C. Kunz, Phys. Rev. Lett. **47**, 993 (1981).

[15] T. Kachel, R. Rochow, W. Gudat, R. Jungblut, O. Rader, and C. Carbone, Phys. Rev. B **45**, 7267 (1992).

[16] H. Tang, T. G. Walker, H. Hopster, D. P. Pappas, D. Weller, and J. C. Scott, Phys. Rev. B **47**, 5047 (1993).

[17] D. Weller and S. F. Alvarado, Phys. Rev. B **37**, 9911 (1988).

[18] H. Tang, D. Weller, T. Walker, J. C. Scott, C. Chappert, H. Hopster, D. P. Pappas, A. W. Pang, and D. Dessau, J. Appl. Phys. (to be published).

[19] D. C. Jiles and S. B. Palmer, J. Phys. F **10**, 2857 (1980).

[20] D. P. Pappas, C. R. Brundle, and H. Hopster, Phys. Rev. B **45**, 8169 (1992).

[21] R. Allenspach and A. Bischof, Phys. Rev. Lett. **69**, 3385 (1992).

[22] Y. Yafet and E. M. Gyorgy, Phys. Rev. B **38**, 9145 (1988).

[23] O. Paul, Ph.D. thesis, ETH, Zürich, 1990 (unpublished).

[24] F. Meier, D. Pescia, and M. Baumberger, Phys. Rev. Lett. **49**, 747 (1982).

[25] F. Meier, G. L. Bona, and S. Hüfner, Phys. Rev. Lett. **52**, 1152 (1984).

[26] M. Taborelli, R. Allenspach, G. Boffa, and M. Landolt, Phys. Rev. Lett. **56**, 2869 (1986).

[27] B. Coqblin, *The Electronic Structure of Rare-Earth Metals and Alloys: The Magnetic Heavy Rare-Earths* (Academic, London, 1977), pp. 203–205.