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The influence of the surface on the spontaneous magnetization of Gd thin films

R Skomski, C Waldfried and P A Dowben†

Department of Physics and Astronomy and the Center for Materials Research and Analysis, Behlen Laboratory of Physics, University of Nebraska, Lincoln, NE, USA 68588-0111

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Abstract. Spin-polarized photoemission data on strained Gd(0001) films grown on Mo(112) are presented and explained in terms of an adequate mean-field approach. Experiment shows that the films exhibit a magnetic surface transition which occurs at about 10% above the bulk Curie temperature. The calculation yields an exponentially decaying surface magnetization mode whose penetration depth depends on the relative strengths of the interlayer exchange couplings $J(\boldsymbol{r}-\boldsymbol{r}')$. Second-order perturbation-theory refinements with respect to the long-range RKKY interactions yield a renormalization of the exchange between adjacent layers and small long-range magnetization contributions.

Gadolinium, terbium and fcc iron exhibit magnetic surface transitions whose Curie temperature T_C^S is higher than the bulk Curie temperature T_C^B. For unstrained gadolinium (0001) one obtains $T_C^B = 293$ K and a T_C^S ranging between 310 K [1, 2] and 350 K [3, 4], whereas strained gadolinium (0001) films grown on Mo(112) [5] exhibit an enhanced surface Curie temperature of 370 ± 25 K and bulk Curie temperatures of 340 ± 20 K [6]. The Curie-temperature enhancement at the surface reflects the strength of the effective interatomic exchange coupling. When the surface exchange interaction is weaker than the bulk exchange, then there is only one bulk phase transition at T_C^B. Just below T_C^B, there would be no magnetic order in a free-standing surface, but the surface–bulk exchange coupling gives rise to some spontaneous magnetization. On the other hand, when $T_C^S > T_C^B$ then the surface orders between T_C^B and T_C^S, but this ordering is unable to yield a finite spontaneous magnetization in the bulk because the amplitude of the magnetization mode decays exponentially as a function of the distance from the surface [7, 8]. It is important to emphasize that surface transitions are predicted by both mean-field theories and renormalization-group approaches [7, 8], so that mean-field theory is justified so long as one is not interested in the film's behaviour in the immediate vicinity of the critical point.

In contrast to other well known surface transition magnets, such as fcc Fe(001), rare-earth films are characterized by a nearly ideal localization of the atomic moments, which has sparked interest in rare-earth surface magnetism [9–13]. Although the magnitude $m \approx 7\ \mu_B$ of the localized Gd^{3+} moments is nearly temperature independent, thermal excitations

† Corresponding author: Peter Dowben, Department of Physics and Astronomy, Behlen Laboratory of Physics, University of Nebraska, Lincoln, NE, USA 68588-0111. Fax: 402-472-2879. Phone 402-472-9838. E-mail address: pdowben@unlinfo.unl.edu

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give rise to the local-moment fluctuations $\boldsymbol{m}_{4f} = m\boldsymbol{e}(\boldsymbol{R}_i, t)$. The understanding of these fluctuations at the surface and in the bulk is the aim of this paper.

Atomically, the gadolinium 4f shells spin polarize the itinerant valence and conduction electrons by 5d/4f exchange interaction [14], which gives rise to a band-structure-dependent RKKY-type interaction. The effective interaction $J(\boldsymbol{r}_i, \boldsymbol{r}_j)$ between two gadolinium atoms located at $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ is an integral over all occupied and exchange-split 5d/6s band-structure levels. For example, approximating the valence and conduction electrons by a free electron gas yields an effective exchange scaling as $(\sin x - x\cos x)/x^4$, where $x = 2k_F|\boldsymbol{r}_i - \boldsymbol{r}_j|$. In the following, we will consider the exchange integrals as parameters and neglect the small 5d/6s contribution to the magnetic moment.

The 4f/5d interaction yields a small 5d/6s exchange splitting which can be investigated by photoemission spectroscopy. Gadolinium has a relatively simple 5d/6s band structure, which makes it easy to distinguish surface states near the Fermi level from the bulk bands at 1–2 eV binding energy [5, 9]. From spin polarized photoemission spectra, an exchange splitting can be determined separately for the surface and the bulk, providing some insight into the distinct nature of the ferromagnetic ordering at the surface as opposed to the bulk [5, 6, 9]. The surface state exchange splitting is large at the Brillouin zone centre ($\Delta_{ex} \approx 0.45$ eV) and at the Brillouin zone edge ($\Delta_{ex} \approx 0.57$ eV), but develops a minimum of the exchange splitting at the Brillouin zone interior ($\Delta_{ex} \approx 0.10$ eV) [6].

Expansive strain [15, 16] and the decrease in the c/a ratio [16] are expected to enhance the magnetization due to an increased localization of the in-plane bands, and the band structure is indeed quite different from that of unstrained gadolinium [5, 6]. The generally increased band localization and smaller band dispersion of states near the Fermi level, in turn, should result in increased d–f hybridization [6]. This increased d–f hybridization results in increased polarization of the itinerant d and s electrons which seems (judging by the increased Curie temperatures) to more than overcome the loss in coupling due to the missing surface neighbours and the reduced overlap of the 5d orbitals. Gd(0001) films with an expansive strain of about 4% were obtained by growing 10 monolayers or more of gadolinium on Mo(112) as described elsewhere [5]. Thinner films of 3 to 10 monolayers on Mo(112) adopt a structure akin to a 4% strained Gd(10$\underline{1}$2) surface [5]. Note that the band structure of strained Gd(10$\underline{1}$2) differs from that of strained Gd(0001), which is manifested in the negligible dispersion of the bulk bands (1–2 eV below E_F) [5, 6]. In particular, the exchange splitting of the bulk bands is small throughout the surface Brillouin zone and exceeds the experimental resolution of 0.05 eV only near the zone edge ($\Delta_{ex} \approx 0.07$ eV).

Gadolinium is one of very few systems with a direct experimental confirmation of an enhanced Curie temperature at the surface as compared to the bulk [1–5, 9]. Figure 1 shows the temperature dependence of the 5d/6s exchange splitting and polarization for strained Gd(0001). The existence of a separate surface transition is evident from the collapse of the net bulk exchange splitting and spin polarization in the temperature region $T_C^B < T < T_C^S$. Above the bulk Curie temperature 340 ± 20 K but below T_C^S we continue to observe some background polarization caused by the surface. A mean-field description of the thickness-dependent magnetization of rare-earth thin films on ferromagnetic substrates is based on the Landau–Ginzburg formalism [10–12]. The question arises as to what extent continuum approaches such as the Landau–Ginzburg theory and photoemission [9] and susceptibility [13] measurements are able to provide a layer-resolved description of surface and bulk properties of Gd films on a nonmagnetic substrate. In the simplest case, layer-resolved mean-field theory yields Ising-type equations $m_i = \tanh(\beta\Sigma_j J_{ij} m_j)$, where $\beta = 1/k_B T$ and the summation is restricted to intraplane contributions J_{ii} and interactions between nearest-neighbour layers. For simple cubic lattices and nearest-neighbour interactions it is very easy

to analyse the behaviour between T_C^S and T_C^B: the spontaneous magnetization m_i of the ith layer decays exponentially with i, and the penetration depth scales as the bulk correlation length ξ [7].

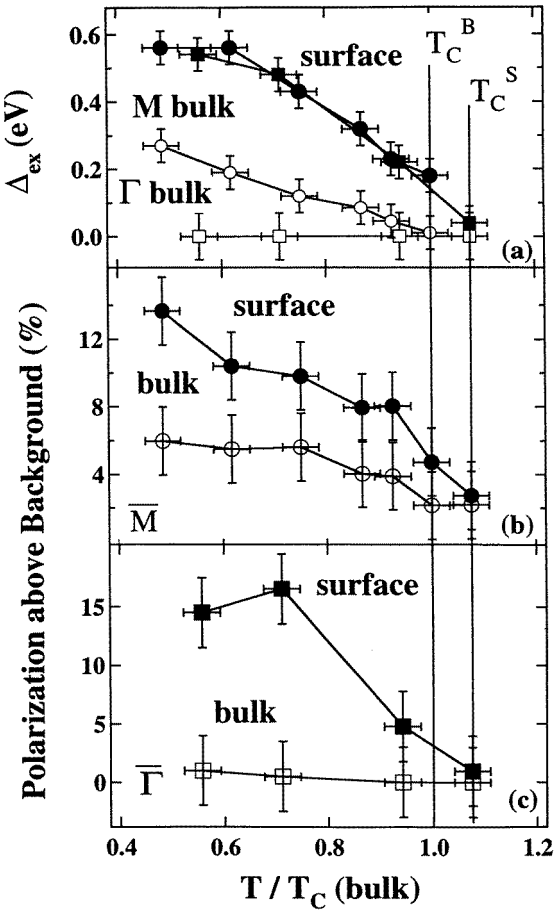

Figure 1. Temperature dependent exchange splitting and spin asymmetries for strained Gd(0001): (a) exchange splitting at $\bar{\Gamma}$ (boxes) and $\bar{M}$ (circles), and (b) and (c) spin asymmetries above background at $\bar{M}$ and $\bar{\Gamma}$, respectively. Filled and open symbols indicate surface and bulk polarizations, respectively.

To obtain a mean-field description of strained and unstrained Gd films we exploit the fact that the magnetization $m(\boldsymbol{r}_i) = \langle M_z(\boldsymbol{r}_i)\rangle / M_s$ close to T_C^S is small and write

$$m(\boldsymbol{r}_i) = \beta \Sigma_j J(\boldsymbol{r}_i, \boldsymbol{r}_j) m(\boldsymbol{r}_j). \tag{1}$$

In the high-temperature limit, where $\beta = 0$, (1) reproduces the paramagnetic limit $m(\boldsymbol{r}_i) = 0$. Nonzero magnetization modes evolve when $k_B T$ reaches the largest eigenvalue of the secular matrix $J(\boldsymbol{r}_i, \boldsymbol{r}_j)$.

Since the films are periodic in the x and y directions parallel to the surface, we can average J and m with respect to the lateral dimensions. This yields coupling constants $J(z_i, z_j)$ and layer magnetizations $m_i = m(z_i)$, where the indices i and j refer to the ith and jth layers, respectively. Furthermore, we assume that the surface and bulk ith layers are

located at $z = 0$ and $z = (i-1)a$, respectively. There are three types of coupling parameter: the surface intralayer coupling $J(0, 0) = J_s$, the bulk intralayer coupling $J(z_i, z_i) = J_L$ and the interlayer couplings $J(z_i, z_j) = J_{|i-j|}$. In terms of these parameters, the equations for the surface (m_1) and the bulk (m_i) are

$$m_1 = \beta J_s m_1 + \beta J_1 m_2 + \beta J_2 m_3 + \beta J_3 m_4 + \cdots \tag{2a}$$

$$m_i = \cdots + \beta J_2 m_{i-2} + \beta J_1 m_{i-1} + \beta J_L m_i + \beta J_1 m_{i+1} + \beta J_2 m_{i+2} + \cdots. \tag{2b}$$

In the present context, J_s, J_L and J_1 are large and positive, whereas the J_i ($i \geqslant 2$) are positive or negative parameters of comparatively small magnitudes. Strongly negative coupling constants J_i give rise to nonferromagnetic types of ordering neither observed nor considered here. Note that (2) is not restricted to the Ising model, because the mean-field exchange constants J_s, J_L and J_i contain $S(S+1)/3$-type Brillouin factors accounting for the discrete level splitting of the Gd^{3+} ions.

A simple approximation is to neglect all interlayer coupling constants except the 'short-range' coupling J_1. In terms of exchange parameters J_s, J and J_L describing surface–intralayer, bulk–interlayer and bulk–intralayer couplings, respectively, (2) is then solved by the *ansatz* $m_i = m_0 \exp(-z_i/L)$. Here the *penetration depth* $L = a/\ln((J_s - J_L)/J)$ must not be confused with the surface's effect on the band structure of bulk layers: L may diverge even if the electronic interaction $J(\boldsymbol{r} - \boldsymbol{r}')$ remains short-range. By definition, L is positive, so that surface ordering is restricted to couplings $J_s > J_L + J$. In this case, there is a surface Curie temperature

$$T_C^S = \frac{1}{k_B}\left(J_s + \frac{J^2}{J_s - J_L}\right) \tag{3}$$

larger than the bulk Curie temperature $k_B T_C^B = J_L + 2J$. Figure 2 shows the Curie-temperature mode m_i for two realistic parameter combinations. In most cases the dependence of L on $J_s - J_L$ is very weak, so that it is safe to say that the mode decays after a few interatomic spacings in the bulk. A notable exception is the immediate vicinity of T_C^B, where mean-field critical fluctuations yield an Ornstein–Zernike $1/\sqrt{T - T_C^B}$ contribution to the correlation length.

A detailed analysis of T_C^S requires the consideration of the atomic structure. Let us assume that the bulk interatomic coupling between two nearest neighbours is J_0, whereas the nearest-neighbour coupling at the surface is $J^* > J_0$. Then for fcc (111) and fcc (001) surfaces we have the respective sets of parameters $J_s = 6J^*$, $J = 3J_0$, $J_L = 6J_0$ and $J_s = 4J^*$, $J = J_L = 4J_0$. In both cases $k_B T_C^B = 12J_0$, but the critical values for surface ordering differ: $J* \geqslant 1.5J_0$ and $J^* \geqslant 2J_0$ for (111) and (001) surfaces. For simple cubic (001) surfaces, which are of minor practical importance, the mean-field condition is $J^* \geqslant 1.25J$ [7]. To distinguish hcp (0001) and fcc (111) films it is convenient to introduce a small parameter ΔJ so that $J_L = 6(J_0 + \Delta J)$ and $J = 3(J_0 - \Delta J)$. This conserves $k_B T_C^B = 12J_0$ and yields a surface transition for $J^* > 1.5J_0 + 0.5\Delta J$.

An important question is the influence of long-range RKKY interactions on T_C^S. Since distant couplings may be negative the magnetization mode ceases to obey a simple exponential law and adopts some oscillatory character. Due to the complicated structure of the $J(\boldsymbol{r} - \boldsymbol{r}')$ there is no closed solution to the problem, but well above T_C^B it is possible to treat the problem perturbatively. From (2) we see that second-order perturbation theory yields

$$k_B T_C^S = J_s + (\Sigma_i J_i^2)/(J_s - J_L). \tag{4}$$

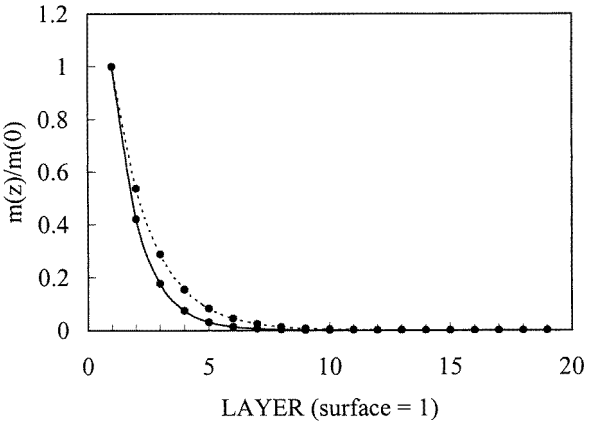

Figure 2. The polarization of the paramagnetic bulk by the ferromagnetic surface layer. The surface-induced magnetization of the bulk is shown as a function of layer depth. The data have been obtained by a mean-field approach, assuming an enhanced surface Curie temperature of $T_C^S = 1.1T_C^B$ (dashed line) and $T_C^S = 1.2T_C^B$ (solid line).

Comparing (3) and (4) we obtain an effective interlayer coupling parameter $J_{eff} = (\Sigma_i J_i^2)^{1/2}$, where the asymptotic behaviour of the RKKY interaction ensures that the renormalized coupling constant J_{eff} is finite. An interesting property of (4) is that both ferromagnetic ($J_i > 0$) and antiferromagnetic ($J_i < 0$) interactions *enhance* T_C^S. This phenomenon is common in many-sublattice magnets (see e.g. [17]) and occurs, for example, in rare-earth transition-metal intermetallics, where both ferromagnetic (light rare-earth) and antiferromagnetic (heavy rare-earth) interactions enhance T_C.

For two reasons, (2) goes beyond the Landau–Ginzburg (LG) mean-field formalism. First, each layer keeps its individual character, whereas the Landau–Ginzburg theory is a continuum approach. Secondly, the involvement of the operator $\nabla = \partial/\partial \boldsymbol{r}$ amounts to the consideration of short-range interactions in terms of a gradient expansion, as opposed to the relevant long-range RKKY-type interactions. In agreement with the Landau–Ginzburg theory, we obtain an exponential decrease of the spontaneous magnetization for short-range interactions. However, it goes beyond the LG approach by expressing the penetration depth in terms of ratios of interatomic couplings.

The effect of the long-range RKKY-type interactions is a more delicate question, because the Curie-temperature estimate (4) has been obtained without explicit consideration of $m(z)$. In fact, long-range interactions $J(\boldsymbol{r} - \boldsymbol{r}')$ give rise to long-range fluctuations in the bulk and bring into question the simple phase-transition picture based on an exponential magnetization decay. It is well known that mean-field theory gives rise to spatial correlations proportional to the integral $\int \exp(\mathrm{i}kz)/(k_B T - J_k)\,\mathrm{d}k$, where J_k is the Fourier transform of $J(z)$. For ∇^2-type short-range interactions—and close to T_C^B, where ξ is much larger than any finite-range interaction—one obtains the relation $J_k = k_B T_C^B + c_2 k^2$ yielding an exponential decay of correlations. To describe the interactions in the intermediate regime $T_C^B < T < T_C^S$ we can make the crude assumption that J_k is constant between $\pm k_0$, where $k_0 \propto k_F$ is an atomic cut-off wave-vector. In this case, the integral yields the *long-range* bulk magnetization mode $m(z) = m(0)\sin(k_0 z)/k_0 z$. However, the denominator of the integral causes the magnitude of these oscillations to be rather small.

In conclusion, magnetization modes in Gd thin films deposited on nonmagnetic substrates have been analysed in terms of a mean-field approach. The spontaneous

magnetization of the surface polarizes the bulk and yields an exponential penetration depth for short-range interactions. The penetration depth exhibits a weak dependence on parameters such as the c/a ratio in the case of hexagonal Gd(0001) surfaces. Long-range interactions caused by the sharpness of the Fermi surface give rise to small but long-range bulk oscillations whose observation and quantification poses a challenge to experiment. There is every reason to expect a similar surface influence on the thin film magnetism of all films of terbium and gadolinium that exhibit an enhanced surface Curie temperature.

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