Impact of interfacial magnetism on magnetocaloric properties of thin film heterostructures

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Polarized neutron reflectometry was used to determine the depth profile of the magnetic moment per Gd atom, m_{Gd}, in a Gd(30 nm)/W(5 nm) multilayer. Despite sharp interfaces observed by transmission electron microscopy, m_{Gd} is systematically suppressed near the Gd-W interfaces. Because the peak magnetic entropy change is proportional to $m_{Gd}^{2/3}$, this results in a reduction of the maximum achievable magnetocaloric effect in Gd-W heterostructures. By extension, our results suggest that creating materials with Gd-ferromagnet interfaces may increase the m_{Gd} relative to the bulk, leading to enhanced magnetocaloric properties. © *2011 American Institute of Physics*. [doi:10.1063/1.3555101]

I. INTRODUCTION

The magnetocaloric effect (MCE) is a thermodynamic phenomenon that enables the entropy (and ultimately temperature, T) of a material to be altered by applied magnetic fields. Renewed interest in fundamental MCE studies was sparked by the discovery of the giant MCE near room temperature in bulk $Gd_5(Si_xGe_{1-x})_4$.[1,2] While a wide range of materials have been studied thus far,[3–7] magnetocaloric materials have been largely unexplored on the nanoscale level. Because nanostructuring is a well known approach used to perturb and tune structure-property relationships,[8] associated techniques are being applied to study the MCE in nanoparticles and thin films.[9–11] Gd/W heterostructures were reported with magnetocaloric properties that differ from bulk Gd:[12] the amplitude and width of the magnetic entropy change ($\Delta S_M(T)$) were reduced and extended, respectively, though the relative cooling power (RCP, nominally the integral width of the $\Delta S_M(T)$ peak) remains on the same order as bulk Gd because the two former measures compete to determine the RCP. Here we have employed transmission electron microscopy (TEM) and polarized neutron reflectometry (PNR) as structural and magnetic probes to determine the origin of altered magnetocaloric properties in Gd/W multilayers. We find that although the interfaces between the Gd and W layers are sharp, there is a systematic depth dependence to the magnetic moment per Gd near the Gd-W interface that leads to a significant and intrinsic reduction in ΔS_M.

II. EXPERIMENT

Room temperature magnetron sputtering was used to deposit a W(5 nm)/$[Gd(30\ nm)/W(5\ nm)]_8$ heterostructure on a 1 cm^2 MgO [100] substrate in a system with a base pressure of approximately 30 μPa. The stated thicknesses were measured by PNR and confirmed by TEM. This sample was simultaneously deposited with the sample discussed in Ref.12 so we can safely assume that the samples have very similar magnetic properties.[13] Figure 1 shows cross-sectional TEM images of the sample taken with the MgO substrate tilted to the [100] zone axis. There is a distinct contrast between the immiscible Gd (light) and W (dark) layers, and the interfaces appear to be abrupt over a local lateral length scale on the order of approximately 10 nm. However, over larger lateral distances a "waviness" of the layer structure is observed. This point is qualitatively illustrated in Fig. 1(b) by parallel dashed lines placed over the W layers in 35 nm increments. At some positions the lines are well centered within the W layers, while at other positions the lines do not intersect W at all. Thus, we conclude that the Gd/W interfaces are locally sharp, but globally the interfaces are rough on a length scale comparable to the W layer thickness.

PNR measurements were conducted using the NG1 Reflectometer at NIST. A magnetic field $\mu_0 H = 200$ mT was applied in the plane of the sample and an incident 0.475 nm wavelength "cold" neutron beam was polarized to be alternately spin-up or spin-down relative to H. The specular reflectivity was measured between 100 and 315 K as a function of wavevector transfer along the surface normal Q_z. The non spin-flip reflectivities (the same incident and scattered neutron polarizations) depend on the depth (z) profiles of both the nuclear composition and the component of the in-plane magnetization (M) parallel to H, while the spin-flip reflectivities depend only on the in-plane M component perpendicular to H.[14,15] Spin-up scattering was not detected, thus we refer only to the non spin-flip spin-down and spin-up reflectivities. Figure 2 shows the fitted scattering data at selected T, multiplied for clarity by Q_z^4 (the approximate intensity falloff for a smooth surface). For both spin channels, the reflection critical edge is manifested as a peak just below $Q_z = 0.2\ nm^{-1}$, and is followed by multiple Bragg peaks corresponding to the multilayer periodicity. The intense Bragg peaks indicate significant contrast in the scattering potential between the Gd and W layers and are clearly spin and T

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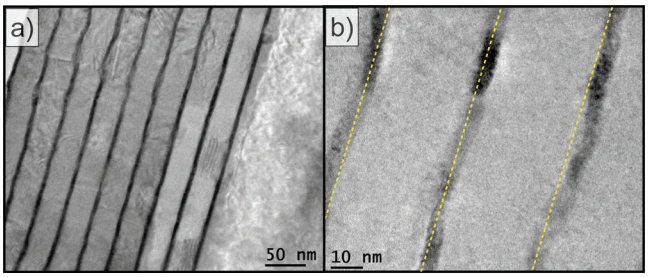

FIG. 1. (Color online) (a) Low and (b) high magnification cross-sectional TEM images of the Gd/W multilayer. Parallel dashed lines are placed at 35 nm increments in (b) as guides to the eye.

dependent, demonstrating sensitivity to the evolution of the magnetic profile with T.

Using fully dynamical calculations,[15] the data at all T are fitted well by a simple depth profile model with identical like layers, Gaussian interlayer transitions, and a T-dependent magnetic component. The nuclear profile used to fit all of the data is shown in Fig. 3, with the individual layers delineated by variations in the complex neutron scattering length density, ρ. A cross-sectional TEM image of the sample with the z-axis on the same scale as that of the displayed profile is shown in the background of Fig. 3 and indicates good agreement between TEM and PNR. In units of 10^{-4} nm^{-2}, the expected ρ for the compounds in this sample are $\rho_W = 3.06$, $\rho_{MgO} = 6.01$ (from experimentally determined scattering lengths),[16] and $\rho_{Gd} = 3.06–3.33i$ for 0.475 nm neutrons (ρ_{Gd} is strongly wavelength-dependent for cold neutrons, thus this value is determined from theory).[17] This model uses the expected ρ for the Gd layers and the MgO substrate; a reduction of ρ_W was required for best fits to the data, even for isolated fits taken above the Curie temperature T_C where the scattering is purely nuclear in origin (e.g., at 315 K). Since Gd and W should be immiscible, and TEM images show distinct layering, the low ρ_W should not be interpreted as evidence of alloying. This is most likely a consequence of probing the *average* depth profile (i.e., the 1-dimensional projection of the sample cross-section) of the globally wavy but locally sharp Gd/W interfaces. Thus, the entirety of the nominally W layers in the profile is most

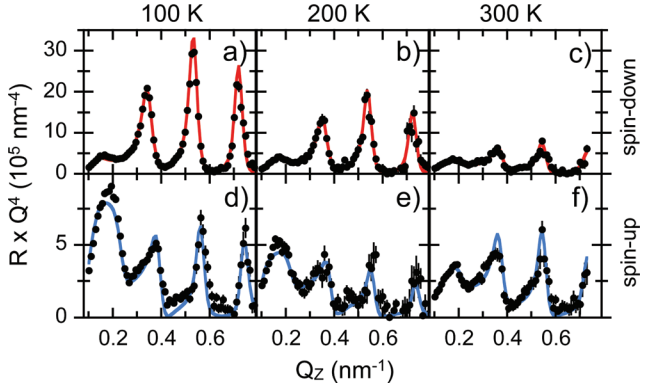

FIG. 2. (Color online) Fitted PNR data at selected T. Note that large M results in significantly higher spin-down intensity at lower T. Error bars correspond to $\pm 1\sigma$.

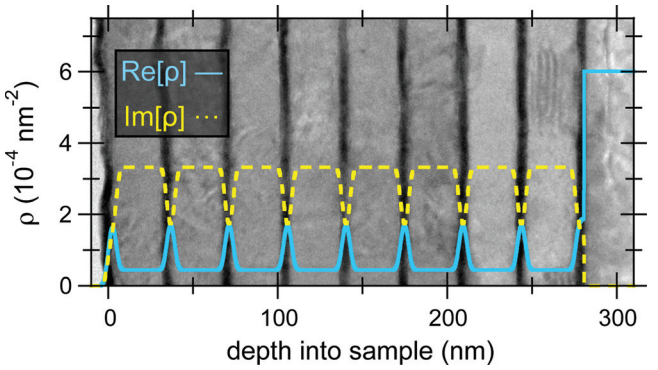

FIG. 3. (Color online) Nuclear composition used to fit the PNR data at all T. Gd is evident by decreased Re$\{\rho\}$ and increased Im$\{\rho\}$. The background is a scaled cross-sectional TEM image.

appropriately interpreted as a distribution of Gd/W interfaces at varying depths along the z direction.

If we assume that ρ in the nominally W layers of the profile is representative of a combination of W and Gd, the nuclear profile can be plotted in terms of the volume Gd concentration, $x_{Gd} = (\rho - \rho W)/(\rho Gd - \rho W)$, shown as the dashed line in Fig. 4(a). The average $x_{Gd} > 0.5$ throughout the multilayer stack with an uncertainty of approximately ± 0.1. This simply suggests that the global variations over the 1 cm^2 area are comparable to the nominal W layer thickness. The solid line in Fig. 4(a) shows the magnetic component of the profile (expressed in units of magnetization) at 100 K. M drops more sharply with proximity to the nominal W layer than does the Gd concentration. Assuming a standard Gd density $N_{Gd} = 30$ nm^{-3}, the relationship between structure and M can be more easily understood by recasting the x_{Gd} and M profiles in units of magnetic moment per Gd atom (magneton number), $m_{Gd} = M/(C x_{Gd} N_{Gd})$ where $C = 9.274$ μ_B μA^{-1} nm^{-2} is a conversion constant. The m_{Gd} profiles shown for selected T in Fig. 4(b) are not constant with depth, instead dropping sharply with proximity to the center of the nominal W layer for all T. The discrepancy between the

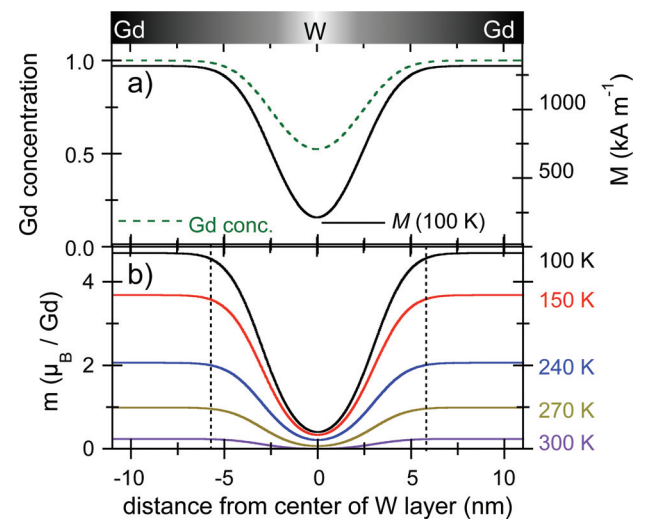

FIG. 4. (Color online) (a) Profile of the Gd concentration (dashed line) and the 100 K magnetization (solid line) near the Gd/W interface. (b) Magnetic moment per Gd atom at selected T. Vertical dashed lines in (b) delineate the interfacial region.

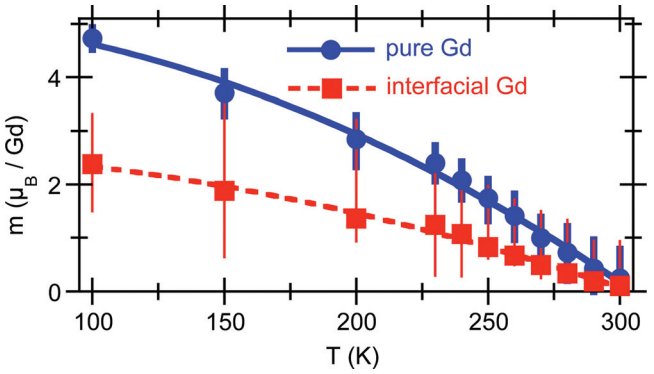

FIG. 5. (Color online) T-dependent moment per Gd for the pure and interfacial Gd regions defined in Fig. 4. Lines are power-law fits intended as a guide to the eye. Error bars correspond to $\pm 1\sigma$.

nuclear and magnetic profiles is caused by a reduction of the magnetic moment of the interfacial Gd atoms and cannot be attributed simply to the effects of averaging over the entire sample area. For comparison to Gd in the "pure" Gd region, we choose to define the Gd/W "interfacial" region as depths with $x_{Gd} < 0.99$, denoted by dashed lines in Fig. 4(b). Figure 5 shows the T-dependence of the average Gd moment in this interfacial region compared to that in the pure Gd region; a reduced m_{Gd} within the interfacial region is clear for all T.[18] These results are in accord with previous multilayer studies on Gd/W via magnetometry[19] and Gd/Y via polarized neutron scattering.[20] The profiles are consistent with some reduction in T_C near the W interface however, uncertainty associated with the model parameters prohibits any definitive claim about the distribution of T_C. Alternate models featuring separate interfacial sub-layers of T-dependent thickness and M can also be used to fit the data, but present no obvious advantage in fitting quality; ours is the simplest model that describes the system.

III. DISCUSSION

These results are important for the MCE, as the maximum ΔS_M at T_C is proportional to $m^{2/3}$.[21] Thus, from the m-profiles near T_C we can determine a maximum expected ΔS_M relative to a bulklike film (i.e., the interfaces and film center have identical m). Since the interfacial moment is clearly suppressed, it is not surprising that we find a suppressed maximum expected ΔS_M. Extrapolating between m-profiles measured at 280 and 290 K, our T_C measurement of 282–284 K indicates a maximum relative ΔS_M of 0.59–0.64. Our peak ΔS_M should thus be bounded above by 59–64% of the bulk Gd value, as denoted by the dashed lines in Fig. 6. Our measured peak ΔS_M of 2.8 J kg^{-1}K^{-1} for $\Delta H = 3$ T is about 47% of the peak value we measured for bulk Gd (5.9 J kg^{-1}K^{-1}); the remaining discrepancy is most likely related to a combination of purity, defects, and polycrystallinity, which adversely affect the entropy peak value.[22] As an extension of these findings, interlayering Gd with higher T_C ferromagnets may enhance the observable ΔS_M in Gd. Indeed, previous x-ray resonant magnetic scattering and magnetic circular dichroism measurements of Gd/Fe superlattices observed interfacial Gd with magneton numbers exceeding that of bulk Gd,[23] lending credence to this hypothesis.

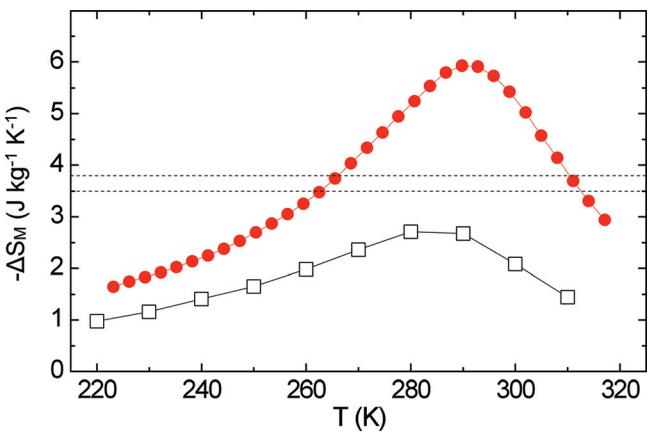

FIG. 6. (Color online) Entropy changes with $\Delta H = 3$ T for bulk Gd (red, solid circles) and W(5 nm)/[Gd(30 nm)/W(5 nm)]$_8$ (black, open squares). The horizontal dashed lines indicate our estimated upper bounds for the peak entropy change in films as a result of the suppressed interfacial moment.

IV. CONCLUSIONS

In summary, TEM and PNR have been used to directly probe the interfacial magnetic properties of a Gd/W multilayer that exhibits magnetic entropy changes that differ from bulk Gd. TEM reveals the Gd/W interfaces to be locally sharp, but with global variations. This leads to an effective smearing of the interface as observed by PNR, which is sensitive to averages over the full area of the sample. PNR measurements indicate that the average sample magnetization falls off at a faster rate than the Gd concentration, clearly demonstrating a reduction in the Gd moment near the W interface. Therefore, the collective properties of the multilayer emerge from an aggregate of Gd atoms with varying magnetic moments and are not representative of magnetically identical Gd atoms. This distribution of magnetic species suppresses the entropy change of the Gd/W multilayers relative to bulk Gd. These insights suggest that layering MCE materials with ferromagnetic layers, which can increase the interfacial moment of the MCE material, may be a route to enhancing the magnetocaloric response beyond that of the bulk material.

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