Gd(0001): A Semi-Infinite Three-Dimensional Heisenberg Ferromagnet with *Ordinary* Surface Transition

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By comparing the surface and bulk magnetization of smooth, well-ordered Gd samples, we show that the surface has an *ordinary* transition, i.e., a common Curie temperature for surface and bulk. A quantitative statistical analysis of the temperature dependent magnetization is presented. Critical exponents for both surface, $\beta_S = 0.83 \pm 0.04$, and bulk, $\beta_B = 0.376 \pm 0.015$, are consistent with the semi-infinite three-dimensional Heisenberg model with homogeneous exchange.

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Surface sensitive experiments on ferromagnetic samples near the Curie temperature (T_C) offer a unique opportunity to study the thermodynamics of a semi-infinite system at the critical point. Several factors may influence the magnetization at the surface relative to the bulk [1–12]. First, the reduced coordination at a surface can result in an enhanced magnetic moment due to narrowing of the conduction band [13]. A competing effect, also due to the reduced coordination, is a reduced average magnetization due to the larger amplitude of thermal fluctuations [1–12,14]. This produces critical exponents for the surface that are distinct from those for the bulk [3,4,11–13,15]. Some authors speculated that the modification of electronic structure by the surface can change the local exchange coupling [6,16,17]. As shown by Binder and Landau [4], this will modify the phase transition at T_C, leading to a change in the critical exponents at the surface. A significant increase in the surface exchange coupling also produces an *extraordinary* transition, marked by a separate, higher T_C for the surface relative to the bulk [4,18,19]. The possibility that such a transition could occur at the surface of gadolinium has motivated numerous studies and has led to considerable controversy. Some authors have reported that the Gd surface may exhibit an *extraordinary* transition, with large disparities in the reported enhancement of T_C [20–29], ranging from 15 °C to 85 °C. Other studies indicate that the surface transition is *ordinary,* with the same T_C for surface and bulk [30–37].

In contrast to measurements on surfaces, extensive and reproducible experimental work has been conducted on bulk samples [38–42]. Even so, only recently has a successful theoretical model been applied to the temperature dependence of the bulk Gd magnetization near its T_C [42]. The Gd moment is highly localized to the $4f$ shell and is in an approximately $6s$ state, which favors isotropic exchange coupling. It is therefore a good physical realization of a Heisenberg ferromagnet, which assumes local moments coupled by an isotropic nearest-neighbor exchange interaction. Because of its simplicity, Gd is an attractive material for studies of surface magnetism. With controversy surrounding a quantity as rudimentary as the surface T_C, however, the important problem of the thermodynamic classification of the surface transition has been ignored.

In this Letter, we classify the Gd surface experimentally as that of an *ordinary* three-dimensional (3D) Heisenberg ferromagnet, and show conclusively that the surface and bulk have the same T_C. This conclusion is based on the high magnetic resolution of our surface and bulk measurements, a robust thermometry system, and an exhaustive study of dozens of samples prepared under all known recipes. Smooth, well-ordered films have reproducible magnetic properties and, for the first time, the data are good enough to support critical exponent analysis of surface and bulk with consistent results. This offers a number of important new physical insights. First, the semi-infinite, 3D-Heisenberg critical exponents are observed in the expected temperature range, in agreement with theories for both the semi-infinite critical behavior and the predominantly 3D-Heisenberg behavior observed in the bulk. Second, the surface and bulk are observed to have the same T_C within our experimental uncertainty of 0.3 °C. Finally, the observed critical exponents show that the exchange interaction is not significantly modified at the surface, consistent with the equality of T_C for surface and bulk.

Challenges in experimental studies of surface magnetism surface stem from the difficulty of preparing and characterizing clean, structurally and magnetically ordered Gd surfaces. These experiments must therefore be conducted in an ultrahigh vacuum environment. Evaporative film deposition on a lattice-matched substrate is an effective way to produce chemically pure, structurally ordered films and surfaces. In general, films thicker than 10 nm show bulk thermodynamic behavior. However, the magnetic properties depend strongly on the atomic structure and morphology of the sample. This is particularly important in the present study, which focuses on the fundamental aspects of an idealized semi-infinite ferromagnet.

Two effective procedures have been developed by earlier investigators [30,36,43–46] for preparing magnetic Gd samples of acceptable quality. The first is deposition on W(110) at room temperature with a subsequent anneal to intermediate temperature (500–700 K) [30,43–45].

Although this method produces smooth samples, there is considerable strain in the first few atomic layers. Deviations from this recipe lead to significant differences in both the bulk and surface magnetic properties. For example, underannealing produces a poorly ordered film, while overannealing results in island formation. The second method is deposition of Gd on an Y(0001) single crystal surface at elevated temperature with subsequent anneal [36,46]. Because of the good match between lattices and surface tensions of Gd and Y, the resulting sample is unstrained and smooth. In our experiments, films prepared using both procedures were studied. The resulting magnetic properties, i.e., remanent magnetization, coercive field, and Curie temperature, were reproducible and consistent for the two procedures.

Surface magnetization measurements were made with spin-polarized secondary-electron emission spectroscopy (SPSEES). Secondary electrons were generated by exciting the Gd surface with a 1 keV electron beam. Low energy (0 to 5 eV) secondary electrons were then collected and spin analyzed in a Mott detector. At each temperature, *in situ* coreless coils produced field pulses of greater than 100 kA/m along the positive and negative inplane directions to reverse the magnetization [47]. The secondary electron spin polarization can be calculated from the difference between the positive and negative signals, and has been shown to be proportional to the magnetization of the first few atomic layers due to the short escape depth of low energy electrons in a solid [14,48].

Bulk magnetization measurements were made with the magneto-optic Kerr effect (MOKE). Linearly polarized light was produced by a HeNe (633 nm) laser and focused onto the substrate with an angle of incidence of 60° relative to the surface normal. Polarization measurements were made with a pair of polarizing crystals in a nominally crossed configuration. This technique measures primarily the bulk magnetization because the light's penetration depth is greater than the sample thickness.

Both the surface and bulk temperature-dependent magnetization are shown in Fig. 1. The bulk data have been scaled to coincide with the surface data at low temperature to allow a better comparison. Below approximately $0.9T_C$, ($T_C = 293$ K), the shape of the curves is the same, as predicted by low temperature spin-wave theory [1,2]. Above $0.9T_C$ the surface's magnetization decreases faster than that of the bulk. Both the surface and bulk magnetization vanish at the same temperature within our experimental uncertainty (0.3 °C). Qualitatively, these curves are consistent with magnetization measurements because they are continuous, have a steep slope at the ordering temperature, and are zero for all higher temperatures. These curves are reproducible for subsequent temperature scans of the same film, of different films, and between films grown on the W(110) and Y(0001) substrates. We have found that the only exception to this behavior is a loss of magnetization due to overannealing ($T > 700$ K) or to surface contamination.

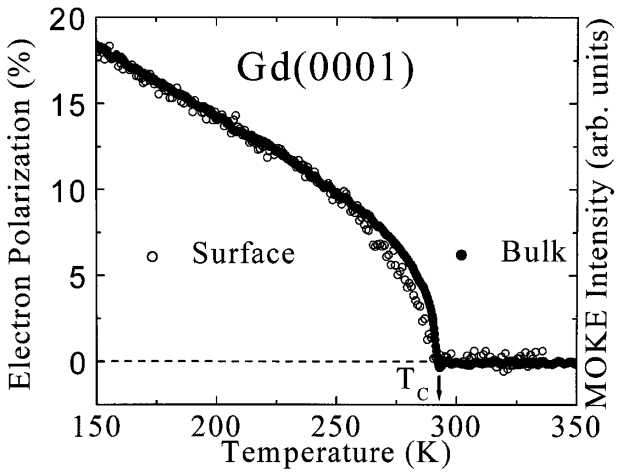

FIG. 1. The temperature dependence of surface and bulk magnetization as measured by spin-polarized secondary electron emission spectroscopy (SPSEES) and the magneto-optic Kerr effect (MOKE), respectively. Surface and bulk magnetization go to zero at the same T_C.

A quantitative determination of the critical temperatures and critical exponents of surface and bulk is shown in Fig. 2. In the range $280 < T < 291$ K, or reduced temperature $t = (1 - T/T_C)$ of $0.04 > t > 0.003$, surface and bulk data were fitted to the functional form $M(T) = M_0(1 - T/T_C)^{\beta}$, where β is the critical exponent of the magnetization and M_0 is a constant. Although the fitted values were not significantly altered by extending the lower limit of the fit to 270 K, the value of 280 K was chosen to exclude the noncritical region with certainty. For the upper limit of the fit, the last 1 °C was not included to exclude effects such as a variation of T_C across the sample [30] or a crossover to dipolar-dominated interactions [38–42]. It is imperative that both β and T_C be treated as fitting parameters (unless T_C is determined in a separate experiment, as in [45]) because the fitted value of β depends strongly on

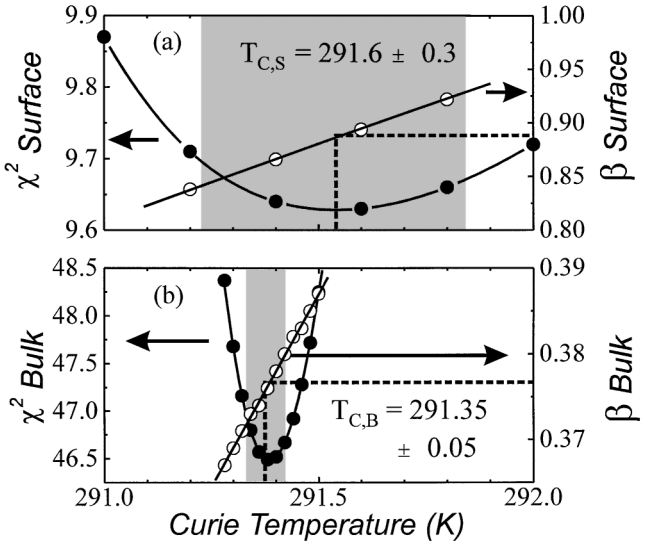

FIG. 2. The statistical χ^2 and critical exponent β for surface and bulk as a function of the fitted T_C.

the assumed T_C. To illustrate, the statistical χ^2 residual and fitted β are plotted as a function of T_C. The best estimate of T_C is near the minima in χ^2 for the surface and bulk. Within 68% confidence intervals (grey areas) of 0.7 and 0.1 °C respectively, the surface and bulk have the same T_C. Not included in the figure is an additional systematic error of 0.1 to 0.2 °C that arises from moving the sample between SPSEES and MOKE positions due to strain in the thermocouple attached to the sample. We have found this to be a significant effect, requiring extraordinary care in attaching the thermocouple to the sample. In Fig. 2, lines joining the open circles show the dependence of the fitted β on the trial T_C. For the best estimated T_C, we find the surface and bulk critical exponents of $\beta_S = 0.88 \pm 0.15$ and $\beta_B = 0.376 \pm 0.015$, respectively. These values are stable with respect to small changes in the range of fit. In the case of the MOKE measurements, however, a small deviation from the fit could be resolved very close to T_C ($t < 0.003$). If a nonuniform distribution of T_C values caused this deviation, simulations of the bulk data near T_C limit the width ΔT_C of the distribution to less than $\Delta T_C \leq 0.5$ °C. This has a negligible effect on the fits of the critical exponent and T_C.

To investigate reproducibility and refine the estimate of the surface critical exponent, more than a dozen separate Gd films were grown on both W(110) and Y(0001). Several temperature scans were taken from each film. Only data sets that passed the statistical tests [49] were used to determine critical exponents. The scatter of the values for the fitted betas is consistent with the uncertainty estimates from the fits, giving a standard deviation of 0.12. An average over these data sets results in a refined $\beta_S = 0.83 \pm 0.04$.

We also investigated the effect of contamination of the Gd surface with oxygen. We find a strong dependence of the secondary electron polarization to low exposures of O_2, as expected for a clean Gd surface [50]. The MOKE signal changed only in the first 1 L (1.3×10^{-4} Pa s $\equiv$ 1 L) of exposure [51], and then remained fixed. These measurements show that the electron polarization is dominated by the surface magnetization, as shown previously [14,48], whereas the MOKE signal is dominated by the bulk magnetization. In addition, contamination did not reduce the surface or bulk T_C.

In our experiments on clean Gd surfaces, no evidence of enhanced surface Curie temperatures was found. To eliminate the possibility that other sample preparation techniques might produce this effect, we explored a wide range of other film preparation parameters. In particular, the high-temperature growth recipe of Weller *et al.* [21] produced rough films with depressed remanent magnetization temperatures, above which zero magnetization is measured due to a collapse into domains. Overannealing (too high a temperature, or too long a duration) films grown at room temperature produced the same effect, while underannealing reduced the Curie temperature. In addition, our recent study of ultrathin Fe on Gd(0001) was a good example of a semi-infinite magnet with a surface enhancement of its Curie temperature [52]. That study showed that both MOKE and SPSEES have the required sensitivity to see enhanced surface magnetism, where it exists, in agreement with the arguments of others [31,34,35]. We conclude that the surface and bulk of Gd have the same T_C. Our results cannot be reconciled with the reports of an enhanced T_C at the Gd surface. As described above, thermometry of these refractory materials is difficult, and may account for some of the early reports where the thermocouple was not bonded to the sample [21,23]. In later reports [25,26], where the sign of the surface exchange coupling was of interest, instrumental asymmetries were not removed in the standard manner [53]. Therefore, these studies were vulnerable to instrumental artifacts that would normally have been removed. Finally, in the most recent report of an enhanced surface T_C [29], the lateral magnetic length scale of the measurement was less than 2 nm. In addition, the nonmonotonic nature of their asymmetry curves as a function of temperature are inconsistent with $M(T)$ curves. A determination of T_C from these data is therefore unreliable.

The critical exponent analysis has several implications. Referring to Table I, the refinement of $\beta_S = 0.83 \pm 0.04$ excludes the possibility of a 3D Ising exponent and closely matches the 3D Heisenberg value. This close agreement also confirms that the SPSEES measurement is sensitive primarily to the Gd surface. Although any one of these temperature scans does not resolve the small differences between the various theoretical surface critical exponents, all of the theoretical surface exponents are widely separated from the bulk values. As a result, surface exponents are distinguishable from bulk values in our experiments. Because bulk and surface exponents match the 3D Heisenberg values that were derived with homogeneous exchange, we conclude that surface and bulk exchange couplings are approximately the same. For comparison, theoretical models that lead to enhanced Curie temperatures at the surface predict β_S exponents markedly smaller than bulk values. The close agreement with the 3D Heisenberg value is characteristic of a clean surface; this, in combination with our surface chemical analysis and oxygen exposure tests, eliminates the possibility that the surface T_C was affected by contamination.

In conclusion, we have performed a temperature-dependent magnetic study at the surface of the localized ferromagnet Gd(0001). Our experiments show that *the surface and bulk have the same Curie temperature* regardless of preparation conditions. Furthermore, Gd films are good realizations of semi-infinite, 3D Heisenberg ferromagnets with homogeneous exchange.

TABLE I. Some surface and bulk critical exponents.

Semi-infinite model	β_B	β_S
3D Ising [4]	5/16	0.78
3D Ising with enhanced surface T_C [4]	5/16	~0.1
3D Heisenberg [11]	0.367	0.84

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