Evidence for ferromagnetic order at gadolinium surfaces above the bulk Curie temperature

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The electron-spin polarization P at the topmost layer of atomically clean, magnetized gadolinium (Gd) surfaces is measured by using electron capture spectroscopy. P varies almost *linearly* with temperature between 160 K ($P = -42\%$) and 315 K ($P = 0$). It is found that the surface Curie temperature T_{Cs} is far above—lying near 310 K—the bulk Curie temperature $T_{Cb} = 292.5$ K, indicating uniaxial anisotropic magnetic exchange interactions at the topmost surface layer of Gd.

There is presently considerable interest in ordering phenomena in two dimensions. Such ordering can occur in magnets, in fluids, and in solids.[1-3]

For magnetic systems, the influence of a two-dimensional surface on phase transitions has been investigated theoretically by numerous authors using various models.[1-3] However, there is a severe lack of experimental information, in particular concerning the temperature dependence of surface magnetic order. This is primarily due to the enormous difficulties in preparing atomically clean surfaces which remain uncontaminated and well defined during the multiple heating and cooling cycles that are prerequisites for reliable data.

In this paper we report electron-spin polarization (ESP) measurements performed at the topmost layer of atomically clean surfaces of the rare-earth metal Gd which is the prototype of an isotropic Heisenberg ferromagnet. The important question we address is this: Does isotropic magnetic behavior change in going from bulk to surface?

We demonstrate in this work that, for Gd, the *topmost* surface layer is magnetically *ordered* while the *bulk* is *disordered*. We use electron capture spectroscopy[4,5] (ECS) and show that at Gd surfaces long-range ferromagnetic order exists far above the bulk Curie temperature T_{Cb}.

The basic process in ECS is the capture of spin-polarized electrons during grazing-angle reflection of fast (150-keV) deuterons. The minimum distance of the ions towards the reflecting surface amounts to about 0.2 nm (incidence angle of 0.2°), showing that in real-space the ions probe only the exponential tail of the electronic wave functions at the surface. This reveals the extreme surface sensitivity of ECS. Further details on this technique are given in Ref. 5.

For the detection of long-range surface magnetic order, we make use of one-electron capture processes: Surface electrons are captured by fast deuterons at well-defined surfaces of ferromagnetics magnetized parallel to the surface plane. Defining the electron-spin polarization P parallel to the direction of the internal magnetizing field yields

$$P = (n^+ - n^-)/(n^+ + n^-) \, ,$$

where n^+ and n^- denote the electron numbers with magnetic moment parallel and antiparallel, respectively, to the magnetizing field, which is also used as quantization axis.

The ESP measurements are performed at atomically clean surfaces of 5000-Å-thick Gd films evaporated *in situ* on various substrates (nonmagnetic Cu and magnetic Gd). The C and O contamination of the films is less than 0.01 monolayer, as monitored with Auger electron spectroscopy after the film preparation and also between the measuring cycles. T_{Cb} is measured *in situ* by an inductive method. We find $T_{Cb} = 292.5$ K. At each selected value of the temperature T, the temperature of a specimen is kept constant within 0.01 K by an automatic regulation device which is absolutely calibrated within 0.1 K. Kerr effect measurements show a single Weiss domain at the surface of the specimen for all applied internal magnetic fields (≥ 24 kA/m $= 300$ Oe).

The magnetization of a sample is achieved by an internal magnetic field H_i^{Gd} using a closed magnetic circuit consisting of an iron toroid and of the specimen. For the evaluation of H_i^{Gd}, we calculate the total magnetic flux ϕ in the circuit which is generated by a magnetizing coil placed coaxially around the iron toroid. ϕ is given by $\phi = \mu_0 NI / \sum_x R_x^m$, with N the number of coil windings, I the current in the coil, and $R_x^m = l_x/(\mu_x A_x)$ the magnetic resistivity of an element x (iron toroid, $x =$ Fe; specimen, $x =$ Gd) in the circuit (l_x and A_x are the length and area of x parallel and normal, respectively, to the flux density lines; μ_x is the permeability of x). ϕ is also equal to

$$\phi = \mu_0 \mu_{Gd} H_i^{Gd} A_{Gd} = \mu_0 \mu_{Fe} H_i^{Fe} A_{Fe} \, ,$$

where μ_{Gd} and μ_{Fe} depend both on T and on H_i^{Gd}, respectively, H_i^{Fe} being the internal magnetic field in the iron toroid. Using numerical values for $\mu_{Gd}(T, H_i^{gd})$ evaluated from magnetization measurements,[6,7] and taking tabulated data for $\mu_{Fe}(T, H_i^{Fe})$ from Ref. 8, enables us to determine $H_i^{Gd}(I)$. In the following, the symbol H is used for H_i^{Gd}.

Figure 1(b) shows the electron-spin polarization $P(T,H)$ measured with $H = 48$ kA/m (600 Oe), using atomically clean surfaces of Gd films evaporated on Gd
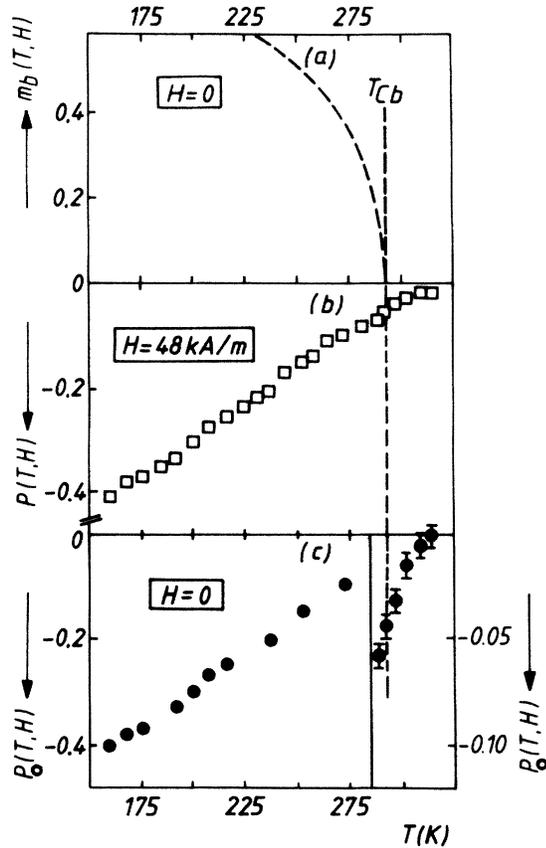
FIG. 1. (a) Temperature dependence of the bulk spontaneous magnetization $m_b(T,H=0)$ for Gd, taken from Fig. 6 of Ref. 6; (b) temperature dependence of the electron-spin polarization $P(T,H)$ for $H=48$ kA/m; (c) temperature dependence of the spontaneous electron-spin polarization $P(T)$ using $T_{Cs}=315$ K for the extrapolation.

substrates. A preliminary account of some results has appeared in Ref. 9(a). Note that an oxidized Gd surface exhibits zero polarization.

These data are obtained from numerous heating and cooling cycles. At each temperature, the polarization data are reproducible within the experimental errors ($\pm 0.45\%$), which are only due to counting statistics. In order to make sure whether there is any flux focusing effect in the Gd films, we used also nonmagnetic Cu as a substrate. In that case, the polarization values exhibit no significant differences compared to those obtained at the surface of Gd films evaporated on Gd. This clearly indicates that magnetic flux focusing effects in the films play

no role in the experiment, contrary to what the high P values above T_{Cb} may suggest.

At this point, we note two important features of these measurements:

(1) The existence of a nonzero polarization below T_{Cb} is in agreement with Ruderman-Kittel-Kasuya-Yosida (RKKY) (Ref. 10) theory, in which a spin polarization of the $(5d,6s)$ conduction electrons is predicted. The negative sign of the ESP measured at a polycrystalline surface is a very interesting fact, implying directly that the polarization at single-crystalline Gd surfaces should give a negative ESP at least for one low-index surface plane.[9(b)]

(2) The temperature dependence of P at the topmost surface layer [see Fig. 1(b)] is drastically different from the bulk magnetization [see Fig. 1(a)]. Between 160 and approximately 300 K, P changes almost linearly with temperature T. We note that neutron-diffraction experiments[11] show that below and above T_{Cb}, the magnetization of the $4f$ electrons in the bulk is proportional to the total conduction electron polarization, which is again proportional to the polarization of the Fermi electrons. This should also hold for the surface region.[12] Therefore the measured P values should reveal the temperature behavior of the magnetization of the $4f$ spins in the topmost surface layer. The proportionality between the $4f$ magnetization and the polarization of the Fermi electrons implies that the exchange splitting between the spin-up and spin-down electron bands is temperature independent, as predicted by "local" band theory[13] and recently found in electron-capture spectroscopy and photoelectron emission experiments.[4,14]

For the analysis of the experimental data, we first assume that the Gd surface orders with the bulk ($T_{Cs}=T_{Cb}$). In this case, the measured nonzero polarization values for $H\neq 0$ above T_{Cb} should be correlated to the tail of the magnetization $m_b(T,H)$ of the sample, which always exists above T_{Cb} for $H\neq 0$. For the calculation of the normalized ESP $p(T,H)=P(T,H)/P^{sat}$,[15] we use $P^{sat}=-87\%$, which is derived from a linear extrapolation of the P values towards $T\rightarrow 0$. Note that if P^{sat} is smaller than -87%, then the calculated $p(T,H)$ data, where $P^{sat}=-87\%$ is used, should be interpreted as the lowest values for $p(T,H)$. In Table I we have listed, for the interesting temperature region between 292.5 and 315 K, values of $p(T,H)$ for $H=24$ kA/m ($=300$ Oe), together with data for the normalized bulk magnetization $m_b(T,H)=M_b(T,H)/M_b^{sat}$,[15] where $M_b(T,H)$ is the bulk magnetization.

The value of

$$m_b(T,H=24\text{ kA/m})=M_b(T,H=24\text{kA/m})/M_b^{sat}$$

TABLE I. Comparison of $m_b(T,H)$ and $p(T,H)$ data for an applied internal magnetizing filed $H=24$ kA/m.

T (K)	292.5[a]	298	303	310	315
$m_b(T,H)^b$	0.090	0.020	0.010	0.006	
$m_b(T,H)^c$	0.031	0.005	0.001	0	0
$p(T,H)$	0.055	0.041	0.024	0.010	0.007

[a]$T_{Cb}=292.5$ K.
[b]Evaluated from Ref. 7.
[c]Evaluated from Ref. 6.
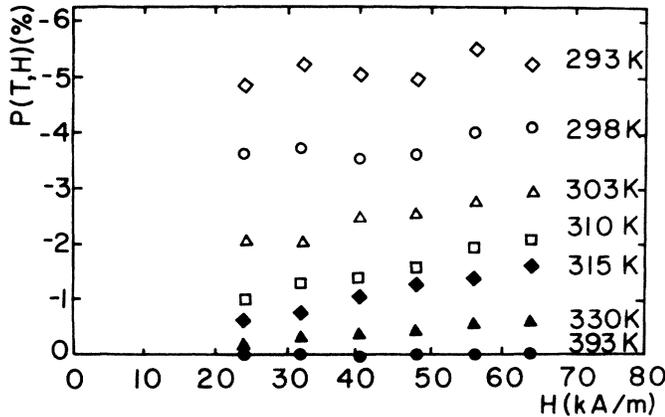
FIG. 2. Electron-spin polarization isotherms $P(T,H)$ as a function of the internal magnetizing field H.

is taken from experimental values of the bulk magnetization $M_b(T,H)$ at $H = 24$ kA/m.[6,7] From Table I we see that for $T = 303$ K, e.g., p is at least 2.4 times larger than m_b, which clearly shows that the measured ESP values above T_{Cb} cannot be linked to the tail of m_b for $H \neq 0$. Consequently, the measured P values above T_{Cb} must be attributed to the existence of ferromagnetic order above T_{Cb} ($T_{Cs} > T_{Cb}$).

Further evidence for this conclusion can be obtained by evaluating data for the spontaneous polarization $P_0(T) = P(T,H = 0)$. To further test the above interpretation of these data, we have performed more detailed $P(T,H)$ measurements in the critical temperature region (see Fig. 2).

In terms of the reduced temperature $t = |T_{cr} - T|/T_{cr}$ and the internal normalized magnetic field $h = \mu_0\mu_a H/kT_{cr}$ (μ_a is the atomic magnetic moment, $k = 1.38 \times 10^{-23}$ J/K), $M(t,h)$ is, from scaling theory,[16] a linear function of h in the region $t \gg h$.[17] This linear re-

lation is used to determine $M_0(T)$ by extrapolation towards $h \to 0$ of the $M(T,H)$ data for a single Weiss-domain specimen.

Assuming that $T_{Cs} = T_{Cb}$, the condition $t \gg h$ [$H \ll (k/\mu_0\mu_a)|T_{cr} - T|$] is satisfied for $T \geq 298$ K. From the $P(H)$ values at 298, 303, and 310 K (see Fig. 2), it is clear that the $P(H)$ values do not extrapolate to zero, establishing unambiguously $T_{Cs} \neq T_{Cb}$.

Likewise, assuming $T_{Cs} = 298$ K would lead to a vanishing polarization $P(T)$ as $H \to 0$ for $T = 303$ K, which is clearly disproved by the data. From these considerations and the data of Fig. 2, we conclude that T_{Cs} lies between 303 and 315 K.

The spontaneous polarization $P_0(T)$ is shown in Fig. 1(c) for $T_{Cs} = 315$ K. For comparison, we show in Fig. 1(a) the temperature dependence of the reduced bulk spontaneous magnetization $m_{b0}(T) = m_b(T,H = 0)$, taken from Fig. 6 of Ref. 7 [$m_{b0}(T = 0) = 1$].

It may be mentioned that, in a recent theoretical work, Selzer and Majlis[18] studied the effect of anisotropy in the surface exchange interaction of a Heisenberg ferromagnet with energy $J(S_i^x S_j^x + S_i^y S_j^y + \eta S_i^z S_j^z)$, where J is the surface exchange-coupling constant and η measures the anisotropy of the exchange interaction in the topmost surface layer. These authors find that for η larger than a critical value of 1.41, T_{Cs} is above T_{Cb}.

Our results for Gd are consistent with η ranging between 1.51 and 1.58. The shape of the $P(T,H)$ and $P_0(T)$ curves [see Figs. 1(b) and 1(c)] for temperatures near T_{Cb} reflects the onset of bulk magnetization as evaluated by Selzer and Majlis. A related experiment has been performed[19] in which, using spin-polarized low-energy electron diffraction at Gd surfaces, surface Curie temperatures between 305 and 315 K have been observed.

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