RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

Surface magnetism of Gd(0001) films: Evidence for an unexpected phase transition

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(Received 28 May 1993)

By spin- and angle-resolved photoelectron spectroscopy we have investigated the surface magnetism of ultrathin Gd(0001) films on W(110). The binding energy shift of the Gd $4f$ surface emission allows us to study separately the surface and the subsurface in-plane magnetization. These two components show an unexpected and distinctly different behavior over an extended temperature range. The results indicate that the in-plane ordering temperature of the surface is by 80 K higher than that of the inner layers. In correspondence to the onset of the in-plane magnetic ordering inside the film the surface magnetization shows changes which could be related to an extraordinary phase transition.

It is well known that the magnetic order can be modified at the surface of a ferromagnetic material. The loss of the translational symmetry perpendicular to the surface plane and the reduced atomic coordination can result in magnetic interactions which differ from those in the bulk. For example, the surface magnetization, as well as other surface quantities, is described by critical exponents which generally do not correspond to those of the bulk.[1]

A particularly interesting case occurs when ferromagnetic order at the surface is established at higher temperature than in the bulk. In a nearest-neighbor Ising model with bulk coupling constant J, there exists a critical value of the surface coupling constant J_S, above which the surface orders at a temperature (T_S) higher than the bulk Curie temperature (T_B).[1] In this case the surface critical behavior at T_S is known as a "surface transition." For $T_B < T < T_S$ the surface behaves as a two-dimensional system, with the magnetic order decaying almost exponentially within the bulk. At T_B, when the bulk magnetic order sets in, the surface undergoes a so-called "extraordinary transition."

Although in most systems one expects the magnetic ordering to be weakened at the surface by the reduced atomic coordination, there exist a few experimental cases for which $T_S > T_B$ has been reported. For thick epitaxial Gd films on W(110) (Ref. 2) and for polycrystalline Gd,[3] it has been found by spin-polarized low-energy electron diffraction and by spin-polarized electron capture that the surface Curie temperature is enhanced by 15–30 K with respect to the bulk Curie temperature of 293 K. A similar observation has been reported for epitaxial Tb films,[4] with a surface enhancement of the Curie temperature by 30 K. A linear dependence of the surface magnetization over a range of temperature encompassing T_B has been reported for polycrystalline Gd films.[5] It is worthwhile to point out that, despite these findings, the mechanism responsible for the enhancement of the surface Curie temperature in these systems is still not at all understood in terms of fundamental atomic properties.

We have performed a spin-resolved photoemission experiment on ultrathin (eight atomic layers) and epitaxial Gd films grown on W(110). We exploit the well-known binding energy shift of the Gd $4f$ surface levels in order to separate the surface and the bulk magnetization. We will show that these two components present an unexpectedly different behavior over an extended temperature range. The results indicate that a surface transition occurs 80 K above the in-plane ordering temperature of the bulk of the film and possibly show a manifestation of an extraordinary transition.

The experiment has been performed with a spin- and angle-resolved photoemission apparatus at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) TGM-5 wiggler-undulator beamline.[6] A more complete description of the experimental system is given in Ref. 7. Gd epitaxial overlayers (eight atomic layers thick) have been prepared *in situ* on W(110) by *e*-beam evaporation. Gd films of this thickness turn out to be convenient because their Curie temperature is strongly reduced by a finite-size effect.[8] We have followed the preparation procedure described by Farle *et al.*[8] to obtain smooth Gd layers with a good low-energy electron-diffraction pattern. The Gd layers have been deposited at room temperature and subsequently annealed at 600 K for 1 min. No W emission from the substrate could be detected in the photoemission spectra. An extended discussion of the dependence of their magnetic and structural properties on the growth conditions is given in Ref. 8. The base pressure ($< 10^{-10}$ mbar) increased to 2×10^{-10} mbar during Gd evaporation. The Gd cleanliness was checked by Auger and by photoemission spectroscopy. The latter is very sensitive to small amounts of contaminants as shown in a previous work.[9] Further evidence for the cleanliness of the layers is given by the polarization measurements as it will be discussed in the following. The photoemission spectra have been measured in magnetic remanence with a 90° spherical

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analyzer coupled to a 100 kV Mott detector. The spectra have been measured with light polarization along the ⟨1000⟩ direction for normal electron emission. The films have been magnetized with a pulse along the in-plane ⟨1200⟩ direction. The spin-resolved measurements have been performed by alternating the sample magnetization direction, in order to check the magnetic origin of the polarization. The polarization component along the in-plane ⟨1200⟩ direction has been determined. The photoelectron polarization is defined as usual as $N_\uparrow - N_\downarrow / N_\uparrow + N_\downarrow$, where $N_\uparrow$ and $N_\downarrow$ are the number of electrons with spin momentum parallel and antiparallel to the sample magnetization direction, respectively.

Figure 1 shows a photoemission spectrum of the valence-band region of an 8 ML thick Gd layer. The emission from the localized $4f$ levels at 8 eV binding energy is well separated from the $5d6s$-valence states near the Fermi level.[9] In Fig. 2 a Gd $4f$ spectrum is shown on an expanded binding energy scale. The Gd $4f$ emission, as it is well known, is composed of two sets[10] of closely spaced multiplets.[11] These two contributions are shifted with respect to each other by 0.45 eV by the so-called "surface shift."[10,12] Figure 2 contains a fit of the $4f$ spectrum, decomposed into "surface" and "bulk" (or "subsurface") components. This decomposition makes use of the parameters from Ref. 10. It is also in full agreement with the data analysis by Weller *et al.*[2] and by Mulhollan, Garrison, and Erskine.[13] As a further check we have measured the $4f$ spectra at various photon energies, obtaining results that are also in agreement with Ref. 10. No difference could be detected between these thin-film $4f$ spectra and those of bulk samples. This could be expected because the surface shift is a short-range effect due to the modification of the local atomic environment. In fact the $4f$ surface shift in rare-earth metals is limited to the very outermost layer.[12] In our experimental conditions the "bulk" $4f$ component actually carries information only from the first two to three atomic layers below the surface because of the short electron probing depth. Hereafter for better clarity, we will refer to this component as due to "subsurface" emission.

Spin-resolved spectra of the $4f$ levels measured at two different temperatures are presented in Fig. 3. The $4f$ emission at 80 K [Fig. 3(a)] is highly spin polarized, as shown by its most intense signal in the spin-up channel. The $4f$ polarization is proportional to the in-plane component of the spin moment of the half-filled $4f$ subshell, which carries most of the total magnetic moment in Gd. After subtraction of the weak and little polarized (+20%) inelastic background, we determine the $4f$ spin polarization to be $+72\pm2\%$ at 80 K. At this temperature the polarization under the whole $4f$ energy spectrum is found to be of constant sign and magnitude, within an experimental accuracy of 5%. This result rules out an antiferromagnetic coupling between surface and subsur-

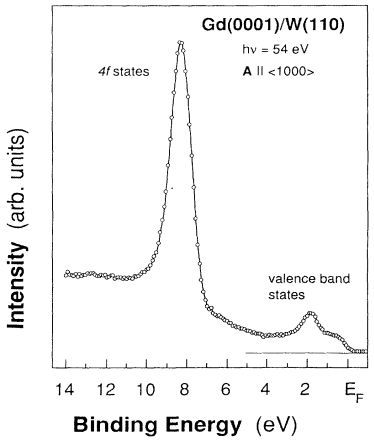

FIG. 1. Photoemission energy distribution curve of the valence-band region measured for normal electron emission with 54 eV photon energy.

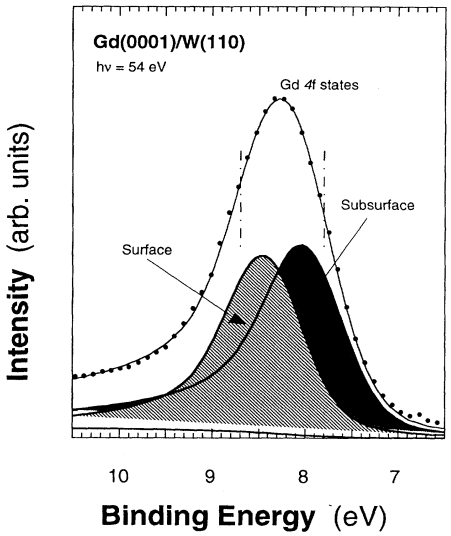

FIG. 2. Photoemission spectrum (dots) of the Gd $4f$ emission. The continuous line through the data points is the results of the curve fitting based on the decomposition in surface (light shadowed) and subsurface (dark shadowed) contributions. The tick marks on the two sides of the peak indicate the binding energies at which the temperature dependence of the polarization, reported in Fig. 4 (see text), has been measured.

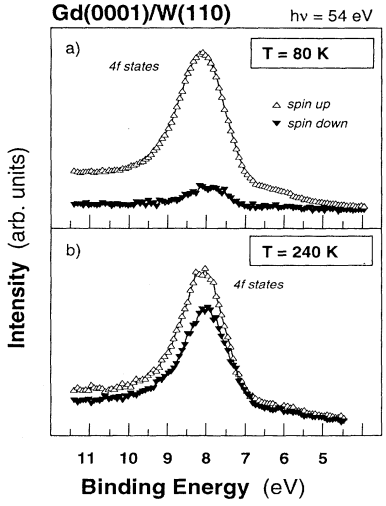

FIG. 3. Spin-resolved spectra of the Gd $4f$ levels at two different temperatures [(a) $T=80$ K and (b) $T=240$ K]. Spin-up and spin-down energy distribution curves are represented by open triangles and solid triangles, respectively.

face layers, in contrast to earlier data from thicker films[2] indicating antiparallel coupling. Evidence for ferromagnetic coupling between the surface and the underlying layers has also been recently reported for a Gd single crystal[13] and for thick films.[14,15] At 100 K we find the $4f$ polarization from the thin layers to be considerably larger ($68\pm2\%$) than from a bulk Gd single crystal (52%).[13] The high $4f$ polarization gives evidence for a high in-plane magnetic remanence, which is expected to be favored by the shape anisotropy of thin layers, and for surface cleanliness. Indeed we find the $4f$ polarization to be extremely sensitive to surface contamination. Exposures to molecular oxygen at 80 K reduces it to 50% with 0.2 L (langmuir, 1 L $=1\times10^{-6}$ Torr s), to 32% with 0.5 L, to 18% with 1 L.

The Gd $4f$ polarization is strongly reduced at 240 K [Fig. 3(b)]. A detailed examination of these spin-resolved curves shows that the $4f$ peak is more strongly polarized on the high binding energy side. Further evidence of this is given by the temperature dependence of the $4f$ spin polarization, measured at the binding energies indicated in Fig. 2. These two binding energies have been chosen in order to enhance in the two cases the contribution from the surface and from the subsurface, respectively. The results are presented in Fig. 4(a). The two curves have been measured simultaneously in order to be strictly comparable. The results were found to be reversible upon temperature cycling and could be obtained either by cooling down or warming up the sample. No detectable change of the $4f$ line shape and binding energy takes place in this temperature range.

The data in Fig. 4(a) show a complex and unexpected temperature dependence of the magnetization. In particular the results demonstrate that at high temperature the polarization at the surface differs from that of the underlying layers. Below 190 K the two curves have similar shape and magnitude. First, near 200 K they both show a first pronounced decrease, followed by a second decrease at about 280 K. Above 200 K the polarization on the two sides of the $4f$ peak is remarkably different. The polarization at the lower binding energy, which is mostly sensitive to the subsurface magnetization, decreases more markedly near 200 K. Conversely the polarization at the higher binding energy, mostly due to the surface, remains higher between 200 K and 270 K.

From the data in Fig. 4(a) the polarization of the surface and of the subsurface emission can be calculated using the spectral weights shown in Fig. 2. Cross checks have been done on the polarization measured over the whole $4f$ energy distribution spectra [e.g., see Figs. 3(a) and 3(b)]. The resulting curves representing the polarization of the surface and the subsurface emission are shown in Fig. 4(b).[16] These curves emphasize the differences between the surface and subsurface magnetization already pointed out above. Below 180 K the in-plane magnetization of the surface and subsurface are found to be similar within the experimental accuracy. The subsurface in-plane magnetization decreases abruptly near 210 K. At 210 K the surface magnetization also presents an unusual change of slope which appears to be related to the changes of the magnetic ordering in the inner layers. Be-

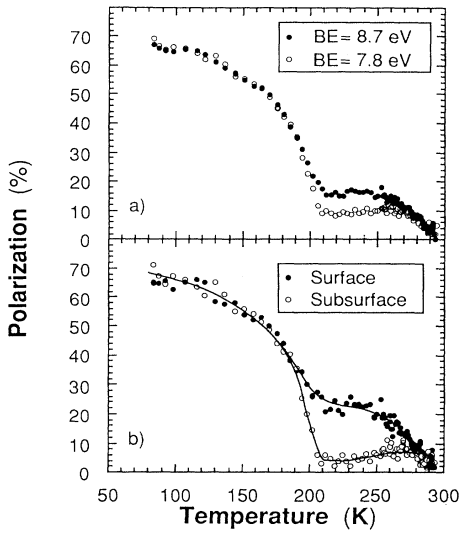

FIG. 4. Top panel: spin polarization of the $4f$ emission at the binding energies indicated by the tic marks in Fig. 2. Bottom panel: spin polarization of the surface (black dots) and subsurface (open dots) $4f$ emission.

tween 210 K and 290 K the in-plane ferromagnetic order decays rapidly below the surface, as it is shown by the low polarization of the subsurface component. The loss of in-plane ferromagnetic order of the surface layer occurs at 290 K.

We interpret the temperatures of 290 and 210 K as the surface (T_S) and the subsurface in-plane ordering temperature (T_{Subs}), respectively.[17] These unexpected large differences in the surface and subsurface magnetic behavior can be attributed either to changes in magnitude or in orientation of the correspective magnetization vectors. In the first case, the results can be explained by a surface enhancement of the Curie temperature by 80 K with respect to the ordering temperature of the whole film.[8] Indeed T_{Subs} corresponds to the Curie temperature of a 7–8 ML thick Gd film determined in Ref. 8, which is reduced with respect to the bulk ordering temperature by finite-size effects. The enhancement of the Curie temperature is limited to the topmost layer and is almost by a factor 3 larger than for thicker Gd films.[2,3] This unusual property could be due to the coexistence of finite-size effects and surface-enhanced magnetic ordering in films of a few atomic layers, a combination which has not been deeply investigated until now. These systems can present unusual magnetic behaviors due to the inequivalent boundary conditions at the interfaces with the substrate and with the vacuum. It is interesting that, in contrast to the large reduction of the critical temperature inside the thin film, the Curie temperature at the surface would be almost as high as in the "semi-infinite" case.[2,3] This suggests that in Gd the surface ordering transition is little influenced by the thickness of underlying paramagnetic material. the magnetization curves in Fig. 4(b) give further support to this view, since the low subsurface magnetization between T_S and T_{Subs} indicates a weak coupling with the topmost layer.

The in-plane surface magnetization shows an unusual structure near T_{Subs} which could be related to an extraor-

dinary transition. The surface magnetization across an extraordinary transition has been investigated for a semi-infinite system with various theoretical methods. There is some controversy on its expected behavior. According to theoretical analysis based on mean-field theory[18] the surface magnetization should present a discontinuity across an extraordinary transition only in the second derivative. A discontinuity in the first derivative of the surface magnetization is found instead in correspondence to the extraordinary transition by a self-consistent random-phase approximation of a Heisenberg semi-infinite ferromagnet with surface exchange anisotropy.[19] Similar conclusions have been reached within a renormalization-group framework for an Ising system.[20] The overall shape of the calculated surface magnetization from Refs. 19 and 20 resembles that of our data in Fig. 4(b). Also Ohno and Okabe[21] inferred from a renormalization-group study that the coefficient of the linear term in the temperature dependence changes value in correspondence to T_B. This result has been refuted by a recent work of Diehl and Smock.[22] A continuous slope of the first layer magnetization is found in the vicinity of the bulk transition in a Monte Carlo simulation for an Ising film.[23] On the basis of these more recent results the changes in the surface magnetization at the extraordinary transition should be weaker than those we detect.

It is important, however, to take into account that the present experiment determines only an in-plane component of the magnetization rather than its total value. An alternative explanation for the behavior of the in-plane (surface and subsurface) magnetization observed near T_{Subs} can be given by a reorientation of the magnetization direction. A reorentation of the easy magnetization axis in the direction perpendicular to the hcp basal plane is known to take place in bulk Gd near 200 K. Also, the uniaxial anisotropy of thin Gd(0001) films is enhanced and perpendicular to the plane of the film.[24] At low temperature the orientation of both the surface and subsurface magnetization is in the surface plane or very close to it, as shown by the high in-plane $4f$ polarization. The (in-plane) shape anisotropy of the thin film competes with the perpendicular anisotropy and prevails below T_{Subs}. The sharp decrease of the subsurface in-plane magnetization near T_{Subs} shows that either the layers inside the film become magnetically disordered, as discussed in the previous paragraphs and suggested by the results of Ref. 8, or their magnetization is reoriented perpendicularly to the (0001) surface plane, as in bulk Gd. In both cases the surface magnetization above T_{Subs} might be forced out of the surface plane by a perpendicular anisotropy, consistently with the measured reduction of its in-plane component [Fig. 4(b)]. The presence of an uniaxial magnetic anisotropy is a necessary condition for the ferromagnetic ordering of a two-dimensional Heisenberg system at finite temperature and it is thus a relevant aspect in the scenario of a surface-enhanced ordering temperature. It is also interesting to observe that the existence of strong surface anisotropies has already been suggested in connection with the surface-enhanced magnetic order of epitaxial Tb(0001) films.[4]

In summary, the surface magnetism of ultrathin Gd(0001) films has been studied by spin- and angle-resolved photoemission. Surface and subsurface in-plane magnetization have been separated by measuring the spin polarization of the Gd $4f$ photoelectrons. These two components show an unexpected distinctly different behavior over an extended temperature range. The results show that the in-plane ferromagnetic order of the surface occurs 80 K higher than that of the layers underneath. The magnetization of the surface layer presents features which could be a manifestation of an extraordinary transition.

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[16]These data are not corrected for the contribution due to the weak inelastic background. The corrections would amount to less than 5% (*relative* change) of the (absolute) polarization values and have no effect on the curve shape.

[17]An alternative explanation would be to assume a Stranski-Krastanov mode of growth and attribute the higher binding energy emission to three-dimensional islands and the lower binding energy one to areas in between little covered by Gd. This possibility is in contradiction with the absence of a W signal in photoemission, with the well-known binding energy of bulk Gd (Ref. 11) and with the shift to higher binding energy of Gd monolayer on W (Ref. 15).

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