Observation of Surface-Enhanced Magnetic Order and Magnetic Surface Reconstruction on Gd(0001)

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Epitaxial Gd(0001) has been investigated with spin-polarized low-energy-electron diffraction and the magneto-optic Kerr effect. The ferromagnetic critical temperature of the surface layer is found to lie up to 22 K above the bulk Curie point, demonstrating the existence of surface-enhanced magnetic order. Furthermore, spin-resolved photoemission spectroscopy reveals that the $4f$ spins of the surface are not ferromagnetically coupled to the bulk moments.

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The concept of universality in the field of phase transitions has stimulated renewed interest for this mature field of solid state physics, because a variety of apparently very different phenomena can be described by the same theoretical principles. In this sense, for example, *prewetting criticality* and *pure surface-enhanced transitions* are essentially the same phenomenon.[1] On the other hand, advances in experimental techniques today allow the crosschecking of such far-reaching predictions. *Magnetic* systems as *model* systems have always been appealing to experimentalists and theorists. Recently systems with free surfaces have been investigated extensively both analytically[2-4] and by Monte Carlo simulations.[5] For systems exhibiting a *continuous* bulk phase transition the critical behavior is found to be related to the ratio of J_1/J_b of the parallel coupling J_1 between surface spins in the top layer and that J_b between bulk spins. For values of J_1 below a certain critical value J_{1c} the surface and the bulk will have the same critical temperature, while for $J_1 > J_{1c}$ a pure "surface transition" has been predicted to occur. In such a case the surface spins undergo a critical ordering transition in the presence of disordered bulk spins.[5]

One purpose of this Letter is to report the first direct observation of such a critical surface transition on epitaxial Gd(0001) by means of the surface-sensitive technique of spin-polarized low-energy-electron diffraction (SPLEED). For an *in situ* comparison with the corresponding bulk transition the magneto-optical Kerr effect was used. An interaction which is not included in the above model is that case when the *perpendicular* coupling between the topmost surface layer and the layer(s) below is different from J_b. It is a further goal of this paper to investigate this question by means of spin-polarized photoemission. In fact, we find for the first time that the $4f$ spins of the surface atoms of Gd(0001) undergo a so-called "magnetic surface reconstruction."[6] This observation has become possible by our making use of the surface-induced binding-energy shift of the $4f$ levels.[7-9]

The SPLEED technique as well as the spin-, energy-, and angle-resolved photoemission technique used for the present investigations were described previously.[10,11] The Gd films were grown epitaxially on a single-crystal W(110) substrate. During evaporation the pressure remained below 2×10^{-9} Torr. The magnetic properties of the Gd films strongly depend on the details of preparation, e.g., substrate temperature and film cleanliness.[12] Here growth rates and substrate temperatures in the range 0.1–1 Å/s and $450 \leq T_s \leq 500$ °C were used. Cleanliness and growth habit of the films were checked by Auger electron spectroscopy. No contaminants could be detected within the spectrometer sensitivity (≤ 0.05 monolayer). The films grow in the Stranski-Krastanov mode, i.e., the formation of at least one epitaxial monolayer followed by island growth on top, with the onset of coalescence at thicknesses of 50 to 100 Å. *In situ* LEED measurements performed on Gd layers of different thicknesses exhibit a sharp diffraction pattern of hexagonal symmetry. The Curie temperature of the bulk region was obtained by a magneto-optic Kerr effect technique ($T_{cb} = 293 \pm 1$ K). The SPLEED and photoemission measurements were performed "in remanence," i.e., without the presence of an applied external magnetic field. The observation of very low saturation ($\lesssim 20$ G) and coercive fields ($\lesssim 5$ G) suggests that the Gd samples were essentially single-magnetic-domain films. Hence *intrinsic* surface magnetic properties are measured.

In this sense the present study differs markedly from earlier experiments on the surface magnetism of Gd,[13,14] where polycrystalline thin films in the presence of external magnetic fields were investigated. Especially the electron-capture-spectroscopy measurements of Rau and Eichner[13] have to be mentioned. The main conclusion of surface-enhanced magnetic order (SEMO) up to $T \approx 310$ K drawn from those experiments, however, is based on an incorrect linear extrapolation of the measured polarization to zero field. Furthermore fields of at least 250 G were used, making an estimation of the Curie temperature very unreliable. With the present data, however, the ex-

istence of SEMO can be shown unequivocably.

SPLEED probes the magnetization of the surface region to a depth of a few atomic layers. This magnetization is related to the (magnetic) exchange-scattering asymmetry

$$A_{ex}=(1/|\mathbf{P}_0|)(I_{\uparrow\uparrow}-I_{\uparrow\downarrow})/(I_{\uparrow\uparrow}+I_{\uparrow\downarrow}),$$

where $I_{\uparrow\uparrow}$ ($I_{\uparrow\downarrow}$) is the scattered intensity for parallel (antiparallel) orientation of the spin of the incident electron and of the magnetization of the Gd sample.[15] $|\mathbf{P}_0|$ is the polarization of the incident electrons of energy E. For the range of thicknesses $140 \leq d \leq 500$, Å. the system can be considered as semi-infinite as long as boundary effects can be neglected. This is the case when $|T-T_{cb}|>1$ K because then d is much larger than the magnetic coherence length perpendicular to the surface: $\xi_\perp=\xi_{0\perp}|1-T/T_{cb}|^{-\nu}$, where $\nu=0.7$ and $\xi_{0\perp}$ is of the order of one interatomic spacing.

Figure 1 shows the temperature dependence of A_{ex}. Data collected at different scattering conditions are shown in Fig. 2. The sizable scattering asymmetry detected at temperatures well above the bulk Curie point is direct evidence for the existence of SEMO on the Gd(0001) surface. For the epitaxial layer of Fig. 1 the surface Curie temperature is $T_{cs}=315\pm1$ K, which is 22 K higher than the bulk Curie temperature.

The enhancement of the surface ordering temperature T_{cs} relative to T_{cb} is not always the same for different films with the same thickness. This indicates the sensitivity of this magnetic surface to the details of sample preparation, primarily surface purity. Indeed SEMO is not detected on samples with surfaces contaminated either by extended exposure to residual gases present in the UHV chamber, or by purposely adsorbing oxygen or hydrogen [1-L (langmuir) doses]. In both cases, however, a nonzero exchange-scattering asymmetry is still measured at temperatures below the bulk Curie point (see Fig. 1). Therefore, adsorbates tend to reduce the strength of the surface coupling constant J_{1c}, thus giving rise—in accordance with theoretical predictions[5]—to a surface critical temperature equal to the bulk one. The critical exponent β_1 for the surface magnetization of contaminated samples is found to be in the range 0.5–0.8, indicating that the surface transition is then "ordinary,"[2-5] as found on clean Ni surfaces.[15] The sensitivity to surface contamination furthermore demonstrates that the enhancement of the magnetic coupling is basically confined to the top Gd layer.

Near the critical region Gd behaves like a Heisenberg system ($n=3$). SEMO is, however, possible only for an Ising system, i.e., $n=1$.[16] Consequently, a reduction of the symmetry in the case of Gd(0001) surfaces occurs which could be a result of the surface anisotropy being of the Ising type. A similar reduction of the dimension of the order parameter at the surface of a semi-infinite Ni system has been suggested previously.[15] More generally, effects of surface exchange anisotropies on the local symmetry have been recently discussed in the frame of renormalization-group theory.[17]

The remanent surface magnetization of Gd(0001) shows an additional important feature, a sharp mini-

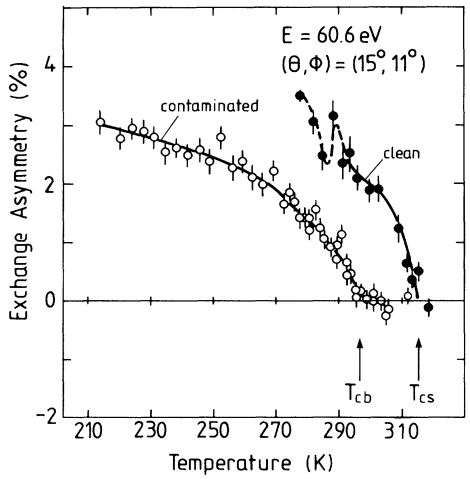

FIG. 1. Temperature dependence of A_{ex} at $E=60.6$ eV for a film of 140-Å thickness. The surface magnetization exhibits a critical transition at $T_{cs}=315$ K, 22 K higher than the Curie point $T_{cb}=293$ K of bulk Gd.

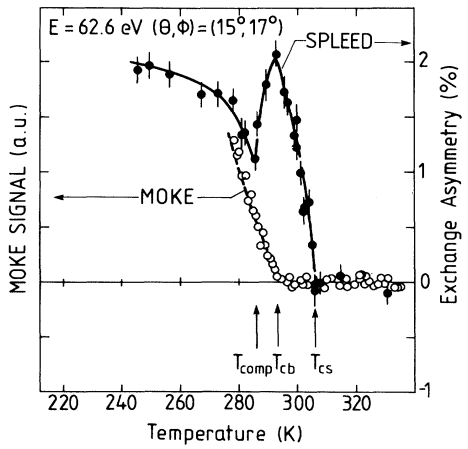

FIG. 2. Same as Fig. 1 for a Gd(0001) film of 500-Å thickness and $E=62.6$ eV. The dashed line (open circles) shows a bulk magnetization measurement performed *in situ* by a magneto-optic Kerr effect (MOKE) technique giving $T_{cb}=293$ K in contrast to $T_{cs}=307$ K obtained by SPLEED.

mum at a characteristic temperature $T_{comp}=289$ K (see, e.g., Fig. 2). This feature is always observed when SEMO is present, for various films and scattering conditions (E,θ,ϕ). We thus exclude multiple-scattering effects as its origin. A plausible explanation of the SPLEED data is readily at hand, if one assumes that the Gd surface spins do not couple ferromagnetically to the underlying bulk spins. T_{comp} could then be interpreted as the temperature beyond which the magnetization of the second atomic layer decreases below that of the first surface layer. The increase of A_{ex} in the temperature range $T_{comp} < T < T_{cb}$ can be interpreted as being due to the rotation of the surface magnetization axis from a more or less antiparallel direction into a parallel direction relative to the external magnetic field. It would be interesting to perform electron-capture-spectroscopy measurements on magnetized single crystalline Gd(0001) films to confirm this picture. Thus we would expect a change of sign in the measured electron spin polarization on going from $T < T_{cb}$ to $T > T_{cb}$ provided that the sample is remagnetized at each temperature point as done in our case.

By means of spin-resolved photoemission spectroscopy with synchrotron radiation we have investigated the nature of the spin coupling on the Gd(0001) surface by making use of the so-called surface-induced core-level binding-energy shift. Such energy shifts of core levels have already been reported[7,9] and are found to be generally in good agreement with theoretical model calculations.[8] For magnetic surfaces with localized moments these energy shifts are expected to lead to a different coupling of the localized spins, and possibly, to a so-called "magnetic surface reconstruction." Figure 3 shows results of energy and angle-resolved intensity as well as spin-polarization measurements for a film of thickness $\bar{d}=50$ Å. The intensity distribution has been deconvoluted into surface and bulk contributions by the same procedure as described previously.[9] Seven Doniach-Sunjic photoemission lines accounting for the 0.8-eV-wide ^7F_j final-state multiplet of Gd are superimposed for both bulk- and surface-atom contributions and are convoluted with the experimental resolution function of our experiment.[18] To account for the enhanced $4f$-binding energy of surface atoms, the $4f$ surface multiplet is shifted by $\Delta E_s=0.5$ eV towards higher binding energies.

Considering now the spin-polarization measurement of the clean sample in Fig. 3(b) we find a rather small polarization of $P\approx 13\%$ in the region of the $4f$ emission at a temperature $T=225$ K. Moreover, the sign of P changes at about 8-eV binding energy. At first glance these observations seem to be puzzling, because the $4f$ states of bulk Gd are known to be in a $^8S_{7/2}$ ground-state configuration at $T=0$ K implying 100% spin polarization. However, there are two surface-related phenomena which explain the discrepancy. Essentially the first and second surface atomic layers are being probed in the photoemission experiment. This together with the more or less linear temperature dependence of the spin polarization of the surface region[14] reduces the polarization to $P\approx 28\%$ at $T=225$ K. But this is still a factor of 2 larger than experimentally observed and it does not explain the change in sign of P. A quantitative agreement with the experiment can be obtained by the assumption of an antiferromagnetic coupling between surface and bulk spins as indicated in Fig. 3. By calculating the polarization from the deconvoluted intensities with an up-spin polarization for the bulk and down spin for the surface contribution we obtain the solid line in Fig. 3(b), which describes the polarization spectrum reasonably well within the experimental error. Further spin-polarized measurements on different samples gave consistent results with respect to intensity and polarization spectra.[18]

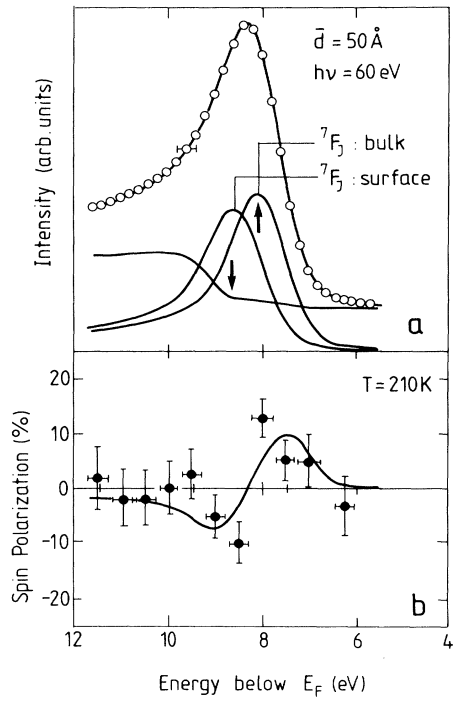

FIG. 3. (a) Experimental $4f$ photoemission intensity spectrum (circles) fitted with bulk and surface contributions and a smooth background for a film of average thickness $\bar{d}=50$ Å. (b) Experimental and calculated (solid line) energy-resolved spin polarization as obtained from the fitted data of (a) with the assumption that bulk and surface spins are antiparallel.

We have presented SPLEED and magneto-optical Kerr effect studies performed *in situ* that demonstrate the existence of surface-enhanced magnetic order. Clean Gd surfaces are found to order magnetically at

temperatures up to 22 K above the bulk critical temperature. These observations can be viewed as a confirmation of the results of Monte Carlo calculations by Binder and Landau[5] predicting SEMO for a magnetic coupling J_1 between spins at the surface larger than a certain critical value J_{1c} relative to the bulk one J_b. Furthermore, our spin-resolved photoemission experiments show that the surface magnetic moments are not ferromagnetically coupled to the underlying bulk layers. These results suggest new Monte Carlo calculations for systems with antiferromagnetic *perpendicular* surface layer coupling $J_{1\perp}$.

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