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Surface magnetization and hydrogen chemisorption on Gd: A spin-polarized photoemission study

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The spin polarization of photoelectrons emitted from polycrystalline Gd decreases linearly with temperature between 20 and 300 K. Submonolayer coverages of hydrogen, chemisorbed at 20 K, drastically reduce the observed spin polarization. This indicates a very short probing depth of spin-polarized photoemission, which arises from strong spin-exchange scattering. Hydrogen chemisorption is found to induce a canted or disordered spin structure at the Gd surface with a much lower ordering temperature than that of the clean Gd surface.

The magnetization near the surface of a semi-infinite ferromagnet is the subject of a large number of theoretical studies,[1] but until recently it hardly was investigated experimentally. New experiments utilizing electron-spin polarization in connection with photoemission,[2] elastic electron scattering,[3] or secondary electron emission,[4] now provide good tools for the study of surface magnetism.

In this Communication we present the temperature dependence of the spin polarization P of photoelectrons emitted from clean and hydrogen-covered gadolinium. We find that the observed spin polarization strongly reflects magnetic properties of the surface, as a consequence of strong spin-exchange scattering of the outgoing electrons. We have exploited this circumstance to study the magnetic behavior of the Gd surface and to follow the changes occurring upon hydrogen chemisorption.

In the case of $3d$-transition metals, on the other hand, spin-polarized photoemission reflects bulk features. In particular, the temperature dependence of the polarization of photoelectrons from Ni closely follows the bulk magnetization.[5] We will discuss below the striking difference of spin-polarized photoemission between Gd and Ni.

Apparatus and measurement of spin-polarized photoemission were described earlier.[6] Gd was deposited *in situ* on an iron substrate at room temperature with a series of short cycles of evaporation in pressures below 1×10^{-9} Torr (base pressure 2×10^{-10} Torr). Photoyield and polarization were measured at different stages of the evaporation. Reproducible and stable values of these parameters at the end of the film deposition indicated that the films were thick enough to be regarded as semi-infinite Gd polycrystals. The cleanliness of the surface was checked with Auger analysis: oxygen and carbon contaminations were below 0.1 at.%. Hydrogen is out of control with Auger analysis but strongly affects the spin polarization, as will be shown below. The polarization itself turned out to be the most sensitive monitor of hydrogen contamination. Good quality samples were achieved after long oven heatings, followed by many short cycles of evaporation, during which the 99.9% pure Gd droplet had reduced its hydrogen outgas rate, as was monitored with a quadrupole mass spectrometer and an ion gauge. We found that the highest polarization corresponds to the best quality sample, and a saturating polarization value was used as a criterion for a hydrogen-free film.

The films were magnetized along their surface normal. Curves of P at constant photon energy versus applied magnetic field showed that magnetic saturation occurred in a field of 26.5 (±2) kOe at low temperatures. We left this field unchanged during all the measurements at varying temperatures. The internal field therefore was not constant, since it is given by the applied field corrected with a temperature-dependent demagnetizing field. The internal field is large, however, only in the vicinity of T_C, where it can give rise to an induced magnetization.

Figure 1 shows the spin polarization P at constant photon energy $h\nu=3.4$ eV close to the photothreshold of 3.2 ± 0.1 eV versus temperature. The spectrum of spin polarization, i.e., P vs $h\nu$, at 220 K, is described in a previous publication.[7] Now we measured the spectrum at 30 K and established that the entire structure, in particular, the pronounced minimum at ~6 eV, persists but is slightly reduced in relative strength. This qualitatively is understood with the scattering model presented below. The polarization at 3.4 eV linearly decreases from 20 to 300 K and does not vanish below 400 K.

The persistence of the polarization above the bulk Curie temperature of 293 K may simply be attributed to the magnetic field. We note that at T_C the internal field as well as the susceptibility are large. We therefore, from the present data, cannot answer the question as to whether surface ferromagnetic order exists above T_C of the bulk, as was observed with

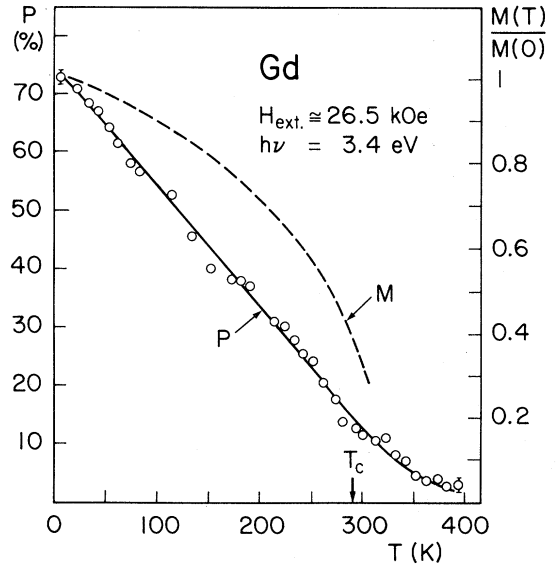

FIG. 1. Spin polarization P of the total photocurrent at $h\nu = 3.4$ eV and bulk magnetization M vs temperature of polycrystalline gadolinium. T_C denotes the bulk Curie temperature.

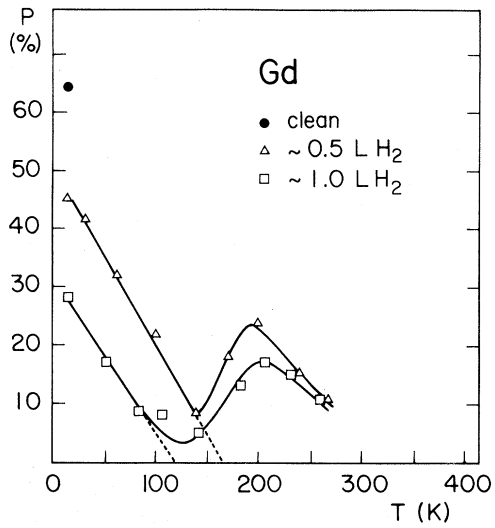

FIG. 2. Spin polarization of polycrystalline Gd with chemisorbed hydrogen. The hydrogen was admitted at 20 K and the data were taken with increasing temperature.

electron-capture experiments.[8] The exciting observation of surface ferromagnetism well above the bulk Curie temperature of Gd might best be confirmed using the technique of electron scattering from a single-magnetic-domain sample without applied field, in the way it was successfully applied to Ni.[9]

Also shown in Fig. 1 is the bulk magnetization (broken line) measured on a Gd sphere in the same external field of 26.5 kOe with a moving-sample magnetometer. The internal field in a sphere differs from the one in a film because of different demagnetizations. The difference, however, is considerable only at low temperatures where its influence on the magnetization is weak. Thus the two curves on Fig. 1 can be directly compared. We find that for Gd the spin polarization of photoelectrons strongly deviates from the bulk magnetization. In the case of Ni, spin-polarized photoemission essentially reflects bulk properties, but we will demonstrate that for Gd photoemission is predominantly determined by the surface magnetization. A direct experimental way to show this is to perturb the surface magnetization and observe how strong is the response of the spin polarization. Adsorption of hydrogen gives such a possibility, since hydrogen influences the magnetism of Gd and can be deposited on the surface. The surface of Gd was exposed at 20 K to 0.5 and 1 L (1 L $= 10^{-6}$ Torr sec) of hydrogen. Submonolayer coverage of hydrogen was found to strongly reduce the observed spin polarization at 20 K from $\simeq 70\%$ for the clean surface to 45% and 30%, respectively, as depicted in Fig. 2. This drastic reduction upon a small hydrogen exposure is clearly only possible because spin-polarized photoemission from Gd is strongly surface sensitive. Why is spin-polarized photoemission strongly surface sensitive in Gd and not so in Ni? Our conclusion is that spin-exchange scattering of the outgoing photoelectrons is strong enough in Gd so that the observed polarization reflects the surface magnetization.

As a first step in the discussion we must compare the thickness ξ of a magnetic surface sheet with the escape depth λ of the photoelectrons. The correlation length ξ below T_C is, in mean-field theory, given by $\xi(T) = \xi_0(1 - T/T_C)^{-1/2}$. ξ_0 is of the order of one lattice spacing, e.g., 2 Å for iron.[10] Calculation of the surface magnetization in the mean-field approximation for a Heisenberg ferromagnet yields a correlation length smaller than one layer spacing up to $\sim 0.8\,T_C$.[11] We estimate the escape depth λ, on the other hand, with the universal curve of the inelastic mean free path of hot electrons.[12] It is strongly energy dependent, $\lambda \cong 40$ layer spacings for $h\nu = 3.4$ eV and 6–8 layer spacings for 10 eV, respectively. Assuming conservation of the polarization during the emission process, the relative signal of the surface is approximately given by ξ/λ. This quantity, however, at $h\nu = 3.4$ eV and $T < 0.8\,T_C$ is much too small to account for the observed polarization. We note that in the case of Fe_3O_4, ξ/λ correctly describes the surface sensitivity of spin-polarized photoemission. ξ/λ approaches unity, and the energy dependence of λ was observed to give rise to different $P(T)$ for different $h\nu$[2]. We have to conclude that in Gd the polarization is not conserved during the emission process, i.e., the mean free path for elastic spin-

exchange processes is short compared to the escape depth λ.

Let the bulk photoelectrons scatter through a magnetic surface sheet of thickness ξ and average magnetization M_s. P_0 is the polarization before scattering. We define σ^+ as the inverse mean free path for a process where a spin-down converts into a spin-up (say a magnon creation), and σ^- correspondingly. If the number of photoelectrons is conserved one finds

$$P=(1-\alpha)P_0+\alpha(\sigma^+-\sigma^-)/(\sigma^++\sigma^-)$$

with $\alpha=1-\exp[-(\sigma^++\sigma^-)]$. The lack of quantitative calculations of $\sigma^{\pm}$ might justify the following crude approximation: $\sigma^+\sim N_\uparrow$ and $\sigma^-\sim N_\downarrow$, where $N_{\uparrow(\downarrow)}$ are the average numbers of up (down) spins per atom in the surface sheet. Then $P(T)=(1-\alpha)P_0(T)+\alpha m_s(T)$, where $m_s=M_s(T)/M_s(0)$ is the reduced surface magnetization. This relation illustrates how for large spin-flip scattering the surface magnetization is observed in spin-polarized photoemission. Without quantitative calculations the exact relation between $P(T)$ and the surface magnetization cannot be given, although the linear behavior of $P(T)$ invites postulating a simple proportionality. We recall that a linear surface magnetization is predicted in some theories[1] and supported by spin-polarized low-energy-electron diffraction experiments on Ni.[3]

The $4f$ moments are responsible for the high spin-flip probability. In a recent experiment depolarization of initially spin-polarized photoelectrons was observed in a paramagnetic Gd sheet deposited on Ge.[13] A very short mean free path $(\sigma^++\sigma^-)^{-1}\simeq 4$ Å was found for paramagnetic Gd. This finding concurs with the present interpretation. We emphasize, however, that $(\sigma^++\sigma^-)^{-1}$ is expected to be smaller than 4 Å and remains very small even in the ferromagnetic regime far below T_C. The calculation of $\sigma^{\pm}$ implies the solution of a scattering problem involving the exchange Hamiltonian $H_{\rm ex}\sim\Sigma J(\vec{r}-\vec{R}_n)\cdot\vec{s}\cdot\vec{S}_n$. $\vec{s}$ and $\vec{S}_n$ are the spins of the electron at $\vec{r}$ and the ion at the lattice site $\vec{R}_n$, respectively. The resulting cross sections are proportional to the square of the Fourier transform of J and proportional to the spin S of the ion at the scattering site.[14] The large differences in S and J between Gd and Ni explain the absence of strong spin-flip scattering in Ni.

Regardless of this scattering mechanism being operative, the interpretation of the spectrum of spin polarization[7] remains valid. We note that the spectral features are attenuated by the spin-exchange scattering. The one-electron $4f$-$5d$ decay therefore must be considerably stronger than was estimated in Ref. 7. More significant consequences are expected for angle-resolved photoemission since the angular information might be destroyed by the scattering.

Of particular interest is the temperature dependence of the polarization for hydrogen-covered surfaces, shown in Fig. 2. Measured with increasing temperature the polarization first decreases linearly, shows a minimum at 130 K, rises again, and runs at $\sim$200 K into the curve of clean Gd. Gd and most of the rare earth are known to rapidly absorb hydrogen above $\sim$195 K.[15] The hydrogen, absorbed at low temperatures, disappears from the surface when approaching 200 K; it is utterly diluted in the bulk, and the spin polarization of clean Gd is restored at temperatures above $\sim$200 K. Indeed, subsequent cooling of the sample showed the polarization to closely follow the curve of the clean[16] surface. Extrapolating the low-temperature linear part of the curves we find that chemisorbed hydrogen strongly reduces the ordering temperature at the surface. We report, as a rough estimate, $T_C^H=160$ and 120 K for a polycrystalline Gd surface exposed to 0.5 and 1 L, respectively, of hydrogen. Owing to the strong spin-exchange scattering the polarization is predominantly determined by the degree of alignment of the $4f$ spins. From the reduced polarizations at the lowest temperatures we conclude that at $T=0$ the $4f$ moments are not fully aligned, i.e., hydrogen chemisorption induces a canted or disordered spin structure at the Gd surface.

The interplay of hydrogen chemisorption and surface magnetism is an exciting issue in catalysis and, consequently, hydrogen storage in a solid. Hydrogen generally is difficult to detect with standard surface physics techniques. The above example illustrates how spin-polarized electron spectroscopy enables one to study the kinetics of hydrogen absorption, since surface magnetism most sensitively responds to the chemical state of the surface.

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