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ION–SURFACE INTERACTION TO STUDY ION-INDUCED CAPTURE AND EMISSION OF POLARIZED ELECTRONS: NOVEL MEANS TO INVESTIGATE SURFACE MAGNETISM *

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The electron spin polarization (ESP) at surfaces of bulk and thin film ferromagnetic materials has been investigated using electron capture spectroscopy (ECS), which probes the ESP of the *topmost* surface layer. At surfaces of PtMnSb, Tb and $Fe_{80}B_{20}$, we find *nonzero ESP* due to long-ranged or short-ranged ferromagnetic order. The *sign* of the ESP at surfaces of the Heusler alloy PtMnSb is in agreement with recent band structure calculations. At surfaces of the rare-earth Tb, we find that, contrary to bulk behavior, long-ranged ferromagnetic order exists *far above* the bulk Curie temperature ($T_{Cb} = 220$ K) up to a surface Curie temperature $T_{Cs} = 248$ K. At surfaces of the spin glass $Fe_{80}B_{20}$, we find, in agreement with ECS data, that the ESP of ion-induced emitted polarized *secondary* electrons is *extremely* sensitive to the cleanness of the topmost surface layer.

1. Introduction

At present, there is considerable interest in studies of the physical properties of magnetically ordered surfaces of bulk and thin film materials, both from a theoretical and experimental point of view. Magnetic materials serve as ideal systems to explore basic concepts in theoretically physics such as phase transitions and critical behavior of thermodynamic quantities in two or three dimensions [1,2]. Furthermore, the magnetic properties of surfaces are of pivotal importance in modern magnetic storage devices.

The use of ion–surface interaction at small angles of incidence provides a powerful means by which to study the magnetic and electronic properties of the *topmost* atomic layer of a surface. At *grazing* angles of incidence, ions cannot penetrate into a surface, they are specularly reflected. This simple fact reveals the extreme surface sensitivity of experimental methods where ion–surface interaction is used to retrieve information on the physical properties of surfaces.

In this paper, we report on fundamental information on surface magnetic properties obtained by using capture of spin-polarized electrons and emission of spin-polarized secondary electrons during grazing-angle reflection of fast ions at magnetic surfaces.

Using electron capture spectroscopy (ECS) [3], we have studied the surface magnetic order of the half-metallic ferromagnetic Heusler alloy PtMnSb which is a promising candidate for future magnetic high density storage media. We find that the surface orders ferromagnetically at room temperature. There is no evidence for so-called magnetically dead layers at the clean surface. The sign of the electron spin polarization (ESP) at the surface is in agreement with predictions from recent spin-polarized bulk band structure calculations [4].

We have further used ECS to investigate the ESP at the topmost surface layer of the 4f rare-earth metal Tb which is known to possess a giant magnetic anisotropy. We find that the long-range and the short-range surface magnetic order, characterized by the long-range and the short-range ESP, depends strongly on temperature. Long-range surface magnetic order at the atomically clean surface of Tb exists up to a surface Curie temperature $T_{Cs} = 248$ K which is far above the bulk Curie temperature $T_{Cb} = 220$ K. Short-range ferromagnetic order exists even above T_{Cs} and vanishes only at around 300 K. From our ECS measurements, we further find that the ESP is strongly dependent on surface contamination.

We demonstrate that ferromagnetic order exists on surfaces of the amorphous spin glass $Fe_{80}B_{20}$. It is well known that thin films of materials such as $Fe_{80}B_{20}$ are expected to possess unlimited potential for use in many technologically important applications [5]. We use ECS to investigate the short-range ferromagnetic order *and* to induce the emission of spin-polarized secondary electrons at surfaces of thin films of $Fe_{80}B_{20}$. Details about the measuring techniques are discussed in section 2. At room temperature, we find that the short-range ESP amounts to about 55%. The spin polarization of simultaneously emitted secondary electrons amounts to around 15%–20%.

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2. Experimental

We use electron capture spectroscopy (ECS) to study the long-range and short-range ferromagnetic order at surfaces of magnetic materials [3]. The fundamental physical process in ECS is the capture of spin-polarized electrons during small-angle surface reflection of fast deuterons D^+. For an angle of incidence of 0.2°, the distance of closest approach of the deuterons to the surface is about 0.8 to 1.5 Å. Therefore, only the deuterons probe the spin-polarized local electron densities of state of the topmost surface layer of the sample [3].

We briefly discuss the experimental technique: a well-collimated beam of 150 keV D^+ ions is reflected at grazing-angle on the target surface, which is magnetized parallel to the surface plane and perpendicular to the direction of the incoming beam. Next, specularly reflected particles pass a transverse electric field, which separates the remaining D^+ from the neutral D^0 and ionic D^- produced in one- and two-electron capture processes, respectively. Then, the D^0 atoms hit a tritium(^{3}H)-target inducing the nuclear reaction ^{3}H(d, n)^{4}He. The emitted ^{4}He particles are detected using two perpendicular surface barrier solid-state detectors.

One-electron capture processes ($D^+ + e^- = D^0$) at ferromagnetic surfaces yield D^0 atoms with polarized electron shells. A nuclear polarization of the D^0 atoms is induced by hyperfine interaction and is measured by the asymmetry in the angular distribution of the ^{4}He particles emitted in the nuclear reaction described above. Nuclear polarization is a direct measure of the electron spin polarization of the captured electrons.

A target magnetizing field is applied to align otherwise randomly oriented Weiss domains, thereby producing a macroscopic magnetization along which the sign and magnitude of the ESP is measured. With P the ESP along the target magnetizing field, we have $P = n^- - n^-)/(n^+ + n^-)$, where n^+ and n^- are the fractional numbers of electrons with spin moment antiparallel (majority spin electrons) and parallel (minority spin electrons), respectively, to the target magnetizing field. A weak magnetic field, parallel to the target magnetizing field, provides a well-defined quantization axis for the ESP. Spin-polarized electrons, captured by different deuterons, originate at widely separated points on the target surface. Therefore, in one-electron capture measurements, long-range ESP is detected.

For the measurement of short-range ferromagnetic order, we study two-electron capture processes ($D^+ + 2e^- = D^-$) [6]. Here, the measurement technique is significantly different compared to the technique described above. The only stable bound state of D^- is the $1s^2\ ^1S$ state. Therefore, D^- can only be formed by capture of electrons with opposite spins. At present, we use either 20 keV hydrogen ions or 150 keV deuterons for the ESP measurements. For this energy range, the characteristic length, within which 2 electrons are captured by a single ion, amounts to about 5–20 Å. Thus, two electron capture processes are sensitive to short-range ferromagnetic order existing on an atomic scale within a few atomic neighbors. It is obvious that two-electron capture will be strongly suppressed by the presence of short-range ferromagnetic order where, on an atomic scale, predominantly electrons with parallel oriented spins are available for capture by a single ion. The reduction in the D^-/D^+ or H^-/H^+ ratio in the reflected beam, relative to that for a nonmagnetic target such as Cu, therefore, provides a direct measure of the short-range ESP at a magnetic surface [6].

For the measurement of ion-induced secondary electrons, using an einzellens, we focus electrons emitted along the surface normal (emission cone angle: 11°) of a remanently magnetized target, on an electrostatic energy analyzer for energy anlysis.

For spin analysis, the electrons were then accelerated to 150 eV and hit a small and compact "low-energy, diffuse scattering spin analyzer". This spin analyzer was recently pioneered by Pierce, Celotta and Unguris and allows for a fast and efficient determination of the ESP [7]. It is based on low-energy (150 eV) diffuse scattering of electrons from a high Z target (preferably Au). For zero-ESP calibration, the Au target is replaced by an Al target. The spin–orbit interaction provides the physical basis of this spin analyzer. Using two channeltrons, positioned at equal angles to the right and the left of the direction of the incoming electron beam, we detect electrons elastically backscattered from the Au target at angles of 120°. In our version of this detector, we focused the incoming electron beam on a Au target of 2 mm in diameter. This certifies that the measured count ratios of backscattered electrons in the channeltrons depend only on the counting statistics. The count ratio of the electrons, detected in the two channeltrons, provides a direct measure of the ESP of the electrons emitted from the magnetic surface. For further details on this simple and efficient ESP detector, we refer to ref. [7].

Numerous experimental difficulties must be overcome in order to maintain clean surfaces during the ESP measurements. At all temperatures, before and after each measurement, the residual surface contaminations C, S and O were shown, using a cylindrical mirror analyzer for Auger electron spectroscopy, to be less than 0.01 monolayer. All ESP measurements, besides the low-energy ion reflection experiments, are performed at working pressures of about 5×10^{-11} mbar. At present, in our low-energy experiments, the working pressure is at about $1–2 \times 10^{-9}$ mbar. Therefore, the experimental ESP data, resulting from these measurements, are considered to represent lowests limits of the

original ESP at the surfaces investigated so far. Further details on our experimental procedures can be found in ref. [3].

3. Results and discussion

Contrary to a wealth of theoretical literature on surface magnetism, there is a lack of reliable experimental results on magnetism at the surfaces of bulk and thin film materials [8]. One of the reasons for the lack of experimental data is, that there are not many experimental techniques of experimental probing depth of the order of, or less than, a lattice constant normal to the surface.

ECS is sensitive to the magnetic order existing at the *topmost* layer of a surface thus enabling us to determine *intrinsic* surface magnetic properties. For the measurement of the long-range surface magnetic order, a sample is magnetized to saturation in the surface plane, and the long-range electron spin polarization at the surface is determined using ECS.

At the surface of poly- and single-crystalline material of the ternary transition metal intermetallic compound PtMnSb, we obtain a long-range spin polarization of +15% and +12%, respectively. Nonzero ESP proves the existence of long-ranged *ferromagnetic* order and the absence of so-called magnetically *dead* layers at these surfaces. The plus sign of the ESP (majority-ESP) can be attributed to a predominance of electrons with spin moment parallel to the applied magnetizing field. From the analysis of our Auger data, we find at both surface strong deviations from the bulk composition ratio 1 : 1 : 1.

Recently, the bulk band structure of this Mn-based Heusler alloy has been calculated [4]. According to these calculations which are performed for the composition ratio 1 : 1 : 1, the semiconducting minority-spin bands of NiMnSb and PtMnSb exhibit a gap around the Fermi level, whereas the metallic majority-spin bands cross the Fermi level giving rise to a 100% ESP around the Fermi level. Although the *sign* of the ESP is in agreement with the predictions, the magnitude of the ESP is in disagreement. The discrepancy between the experimental and the theoretical data can arise from strong deviations of the surface composition from the ratio 1 : 1 : 1.

At surfaces of Tb, we have investigated the temperature dependence of the *long-range ESP* between 140 K and 300 K. In a recent study, we have already reported on the temperature dependence of the short-range ESP at Tb surfaces [9]. Surprisingly, we found that short-range ferromagnetic order exists up to 300 K.

As regards the long-range ferromagnetic order, we find that long-range ESP exists up to a surface Curie temperature $T_{Cs} = 248$ K which is far above the bulk Curie temperature $T_{Cb} = 220$ K. Similar behavior had already been found in our earlier studies of Gd. But, whereas for Gd [3] the ESP always decreases monotonically up to the surface Curie temperature at which it vanishes, the ESP of the topmost layer of Tb exhibits a very pronounced minimum close to the bulk Néel temperature $T_{Nb} = 228$ K, beyond which it steeply increases within the next 10 degrees, to ultimately suddenly drop to zero at a surface Curie temperature $T_{Cs} = 248$ K.

In a preliminary interpretation of these most striking data, we are tempted to account for such remarkable behavior of the ESP of the *topmost layer* by invoking the change of the magnetic coupling of the latter to the bulk, and assuming that the first layer is antiferromagnetically (or at least helically) coupled to the second and deeper surface layers. This interpretation is consistent with the observation that the ferromagnetic order, which sets in as the temperature is lowered below T_{Cs}, decreases in the neighborhood of T_{Nb}, where antiferromagnetic (or helical order) appears in the bulk. A similar argument applies to the subsequent increase of the ESP below T_{Nb}, as helical order gradually gives way to ferromagnetic order [10]. We note that there is strong evidence from our recent work on single crystalline Tb films on W substrates that the behavior observed here is not due to the polycrystalline nature of the present Tb samples.

Recently, in a series of pioneering experients, it has been shown that polarized secondary electrons emitted from magnetic surfaces provide a novel way to study magnetism at surfaces [11]. It was shown that the spin polarization of true secondary electrons provides an efficient surface magnetometer with a tunable probing depth up to 10–20 Å [11].

In all experiments with spin analysis, the emission of secondary electrons was induced by incident primary electrons. On the other hand, there already exists most promising experimental literature on ion-induced secondary electron emission [12,13]. Spin analysis of the electrons emitted from ferromagnetic surfaces, however, was not performed.

In our first ECS experiments, we use grazing-angle reflection of 20 keV protons at surfaces of the amorphous spin glass $Fe_{80}B_{20}$. At room temperature, we find a short-ranged ESP of 55%. This value is very close to the spin polarization of photoelectrons emitted *near* photo-threshold in photo-emission experiments [14] at surfaces of $Fe_{83}B_{17}$.

For the spin polarization of ion-induced secondary electrons, we find polarization values between 15% and 20%. These values clearly show that these surfaces are indeed ferromagnetic. Typically, for an electron energy resolution of 15%, we obtain an incoming electron beam of several nA on the Au target which provides a very good performance of the detector. We further find that the ESP depends strongly on the cleanliness of the surfaces.

We believe that ion-induced emission of polarized secondary electrons can develop into a very sensitive technique by which to study surface magnetism. More experiment and theoretical work is needed to establish a correlation between angle-, energy- and spin-resolved experimental data from this unique and simple technique and theoretical values derived from spin-polarized surface band structure calculations.

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