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NOVEL STUDIES OF SPIN-POLARIZED ELECTRONS EMITTED DURING GRAZING INCIDENCE ION REFLECTION AT MAGNETIC SURFACES *

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Using a new technique, spin-polarized electron emission spectroscopy (SPEES) and electron capture spectroscopy (ECS), the electron spin polarization (ESP) at the *topmost* surface layer of ferromagnetic materials is investigated. All surfaces are well characterized using AES, LEED, RHEED and STM. Nonzero ESP is found at remanently magnetized surfaces of atomically clean, amorphous $Fe_{s_0}B_{20}$ and (110)-surface-oriented Ni picture-frame single crystals. The angle-resolved energy distribution of the *ton-induced* emitted electrons is *strongly* different from that of electron-induced *secondary* electrons and contains most valuable information on the surface magnetic structure of Ni(110) and on the spin dependence of various electronic transition processes occurring at surfaces. The ESP of electrons (energies between 9 and 12 eV) emitted during grazing-angle ion reflection amounts to +5.5% which is close to the total net Ni-magnetization of +5.6%.

1. Introduction

In this paper, we show that the use of ion-surface interaction at *small* angles of incidence provides a powerful means to study the magnetic and electronic properties of the *topmost atomic layer* of magnetic materials. 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 data on the physical properties of surfaces with unprecedented sensitivity [1].

Another important aspect of studies on particlesurface interactions is that they open the way to carefully study both electronic transition processes occurring near surfaces and the electronic structure of surfaces. In cases where an angle- and energy-resolved spin analysis of the emitted electrons is performed, it is possible to obtain detailed information on the surface magnetic structure of magnetic materials and on the spin dependence of various electronic transition and charge exchange processes taking place near surfaces.

In this paper, we present information on a new technique, spin-polarized electron emission spectroscopy (SPEES), which uses the ion-induced emission of spin-polarized electrons from magnetic surfaces to obtain data on surface electronic and magnetic structures.

At present, there are only a few other techniques possessing such an extreme surface specificity: Spin-

0168-583X/89/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) polarized metastable atom de-excitation spectroscopy (SPMDS) [2], spin-polarized low-energy positron spectroscopy (SPLEPS) [3] and electron capture spectroscopy (ECS) [1]. SPMDS and SPLEPS enable us to investigate long-ranged ferromagnetic order at surfaces and ECS allows us to study long-ranged and shortranged ferromagnetic order at surfaces. Most valuable experimental data on surface magnetic structures, phase transitions at surfaces, surface critical exponents and thin film magnetism have already been achieved with these spectroscopies. Furthermore, these spectroscopies have already allowed us to partially unravel the fundamentals of the physical processes involved in particle– surface interactions.

For our experiments, we use well-defined surfaces of Ni(110) picture-frame single crystals and surfaces of amorphous $Fe_{80}B_{20}$. It is well known that materials such as $Fe_{80}B_{20}$ are expected to possess unlimited potential for use in many technologically important applications [4].

Using electron capture spectroscopy (ECS) [1], we have studied the magnetic order, characterized by the short-ranged electron spin polarization (ESP), at surfaces of the amorphous ferromagnet $Fe_{80}B_{20}$. We find that the surfaces order ferromagnetically at room temperature. There is no evidence found for so-called magnetically dead layers at atomically clean surfaces. At room temperature, the short-ranged ESP amounts to about 55%.

Further, we used spin-polarized electron emission spectroscopy (SPEES) to study the emission of spinpolarized electrons at surfaces of thin films of amorphous $Fe_{80}B_{20}$. The spin polarization of the emitted electrons amounts to around 15–20% which clearly

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establishes the existence of long-ranged ferromagnetic order at these surfaces and proves that SPEES is a useful tool for surface magnetometry.

Using SPEES at surfaces of Ni(110) picture-frame single crystals, we have studied the *energy- and angle-re-solved* ESP of the electrons emitted during ion-surface interaction. The energy distribution of the electrons is *strongly* different from that of electron-induced secondary electron spectra [5] and shows pronounced energy-dependent features.

The found energy and spin distributions of the electrons, originating from the *topmost* surface layer, contain valuable information about electronic and magnetic properties at Ni(110) surfaces and about various atomic processes taking place at surfaces. Our experimental data do not support theoretical models that are based on a pure statistical electron emission [6].

Details about these new measuring techniques are discussed in the next section.

2. Experimental

We use ECS to study the long-ranged or short-ranged ferromagnetic order at surfaces of magnetic materials [1]. The fundamental physical process in ECS is the capture of one or two spin-polarized electrons during small-angle surface reflection of fast deuterons (D^+) or protons (H^+) . For an angle of incidence of 0.2°, the distance of closest approach of the ions to the reflecting surface is about 0.8–1.5 Å. Therefore, the ions solely probe the spin-polarized local electron densities of state of the topmost surface layer of the sample [1].

Further, we report on a recent methodological advancement of ECS, angle- and energy-resolved spinpolarized electron emission spectroscopy (SPEES).

We briefly discuss the ECS technique as regards the investigation of short-ranged ferromagnetic order. Details about the detection of long-ranged ferromagnetic order are discussed in ref. [1].

For the measurement of short-ranged ferromagnetic order, we use protons and study two-electron capture processes $(H^+ + 2^- = H^-)$. The only stable bound state of H^- is the $1s^{21}S$ state [7]. Therefore, stable H^- ions can only be formed by capture of electrons with opposite spins. In the experiments reported here, we use 20 keV hydrogen ions for the ESP measurements. For this energy range, the characteristic length within which two electrons are captured by a single ion, amounts to about 5-10 Å. Thus, two electron capture processes are sensitive to short-ranged ferromagnetic order existing within a range of a few atomic neighbors. It is obvious that two electron capture will be strongly suppressed by the presence of short-ranged ferromagnetic order where predominantly electrons with parallel oriented spins are available for capture by a single ion. The reduction in

the 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-ranged ESP at a magnetic surface [8].

In angle- and energy-resolved, spin-polarized electron emission spectroscopy (SPEES), we use again grazing-angle surface reflection of 10 to 30 keV H⁺ and study the emission of ion-induced, spin-polarized electrons as a measure of long-ranged surface ferromagnetic order. Using an einzel lens, we record electrons emitted along the surface normal (emission cone angle: 11°) of a remanently magnetized target. For energy analysis of the electrons, we use an electrostatic energy analyzer.

For spin analysis, the electrons are accelerated to 150 eV and enter a precisely calibrated low-energy spin detector which allows for a fast and efficient determination of the long-ranged ESP [9]. In the detector, the electron beam hits a Au target of 2 mm in diameter. This certifies that the measured count ratios of back-scattered electrons in two channeltrons, positioned at 135° to the incoming beam direction, depend only on the counting statistics. The count ratios of electrons, detected in the two channeltrons, provides a direct measure of the ESP. For further details, we refer to ref. [9].

A target magnetizing field (along the [111] direction in the (110) surface plane of a Ni picture-frame single crystal) is applied to magnetically saturate the sample and to produce a macroscopic magnetization along which sign and magnitude of the ESP are 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 emitted electrons with spin moment antiparallel (majority spin electrons) and parallel (minority spin electrons), respectively, to the target magnetizing field. Emitted spin-polarized electrons originate at widely ($\equiv 2$ mm) separated points at the target surface. Therefore, in SPEES measurements, long-ranged ESP is detected.

The samples are prepared in a target preparation chamber at 1×10^{-10} mbar, and the residual surface contaminations C, S and O were shown, using Auger electron spectroscopy, to be less than 0.01 monolayer. Further details are given in refs. [8,10,11]. Then the samples are transferred to a measurement chamber and the cleaning procedures are repeated in this chamber. At present, in our low-energy experiments, the working pressure is only at about 8×10^{-10} mbar where 90% of the residual gas consists of hydrogen.

Therefore, the experimental ESP data obtained so far are considered to represent lowests limits of the original ESP existing at atomically clean surfaces. For the same reason we note that, at present, a precise and absolute energy calibration of our energy analyzer is difficult. The presence of a residual surface contamination and the presence of steps at the Ni surface directly influence the work function which has to be precisely known in order to be able to perform a precise absolute energy calibration. For this reason, the experimental data on the spin and energy distribution of the emitted electrons are only given as a function of the analyzer voltage. Further details are discussed in the next section.

3. Results and discussion

As mentioned in section 1, at present, there are only a few spin-sensitive, experimental methods of experimental probing depth of the order of, or less than, a lattice constant normal to the surface [1-3]. At present, in the literature, there are only few experimental data available on the magnetic order existing at the topmost surface layer of magnetic materials [12,1].

ECS and SPEES are sensitive to the magnetic order existing at the *topmost* layer of a surface thus enabling us directly to determine *intrinsic* surface magnetic properties.

For the measurement of long-ranged ESP, a sample is magnetized to saturation in the surface plane, and the long-ranged ESP of the captured or emitted electrons is measured using SPEES or ECS. For the measurement of short-ranged ESP, using ECS, the samples need not be macroscopically magnetized because, even in demagnetized samples, the size of existing microscopic domains, which are always spontaneously magnetized, is larger than the overall distance within which two individual electrons are captured [8].

In our low-energy ECS experiments, we use smallangle reflection of 20 keV protons at surfaces of the amorphous ferromagnet $Fe_{80}B_{20}$. At room temperature, we find a short-ranged ESP of 55%. This value is very close to the spin polarization of electrons emitted near photo-threshold in photo-emission experiments [13] at surfaces of $Fe_{83}B_{17}$.

Using SPEES at surfaces of $Fe_{80}B_{20}$, we find polarization values between +15% and +20%. These values clearly show that these surfaces indeed are ferromagnetic. For these SPEES experiments, we used an angle of incidence of 3°. The obtained ESP data compare favorably with the value of the total average magnetization (+21%) [14] and with the ESP of electron-induced secondary electrons emitted from surfaces of amorphous $Fe_{83}B_{17}$ amounting to +10% [5]. We remark that for such large angles of incidence, the incident ions can penetrate into the solid and induce the emission of electrons also from layers located deeper than the topmost surface layer. We note that already from these experimental data it is evident that SPEES can be used as a new probe to study surface magnetism.

In order to obtain a deeper insight into the specific physical processes underlying SPEES, we performed

SPEES experiments at (110) surfaces of Ni picture-frame single crystals. From our ECS experiments [1] and from other spin-sensitive experiments at Ni(110) [15], it is known that electrons originating from energy levels near (< 0.5 eV) the Fermi energy possess a predominant minority spin orientation (negative ESP) of about -96%, whereas electrons from energy levels below this energy range overwhelmingly possess a majority spin orientation (positive ESP). This information can be profitably used to identify and unravel the nature of the various physical processes involved in the electron emission in SPEES. For instance, electrons originating in k-space from energy levels located 0.5 eV near the Fermi level, being emitted without any spin-flip process involved, would contribute to the negative part of the P(E) curve. On the other hand, electrons originating from levels located at least 0.5 eV below the Fermi level would contribute to the positive part of the P(E) curve.

Reducing, for 25 keV incident protons, the angle of incidence from 3° to 1°, thereby preventing nearly completely the penetration of the protons into the solid, results in a characteristic change in the energy distribution n(E) of the emitted electrons.

In fig. 1 results on the energy distribution n(E) and on the electron spin polarization P(E) as a function of the analyzer voltage are given for spin-polarized elec-



Fig. 1. (a) Energy distribution n(E) and (b) electron spin polarization (ESP) of spin-polarized electrons emitted during grazing-angle surface reflection of 25 keV protons at magnetized Ni(110) as a function of the analyzer voltage.

I. ATOMIC PHYSICS

trons emitted along the surface normal of Ni(110) at 300 K.

It is well-known from literature data that, for nongrazing angles of incidence, the shape of ion- or electron-induced electron spectra is characterized by a steep increase from zero to a maximum at low energies (< 2 eV) [16], being nearly independent of projectile type and energy, followed by a smooth decrease with increasing energy, reaching zero at around 40-70 eV. Conventionally, two general types of electron emission processes are distinguished in the literature: potential emission and kinetic emission. For kinetic or potential electron ejection, the source of energy is either the kinetic or the potential energy of the ions which penetrate into the solid and cause the ejection of electrons. For further information, we refer to an article by Benazeth [17]. In the interpretation of the experimental data, mostly statistical models are used which, in some cases, take into account the emission of Auger electrons from the target atoms inside the solid. Breakthroughs in the interpretation of experimental data, taking the electronic structure of the solid or the surface electron band structure into account, were achieved in the pioneering works by Hagstrum [18]. Unfortunately, in these experiments no spin analysis of the ejected electrons was performed. The aim of this paper is to show, for the first time, that the spin of the ejected electrons can be used as an additional "label" to identify the various processes occurring in ion-surface interactions at grazing incidence. We selected grazing angles of incidence to possibly avoid cascading effects caused by energetic secondary ions or energetic secondary electrons.

For the discussion of our experimental data in terms of the kinetic energy of the emitted electrons, taking the work function of the target and the analyzer into account, we refer to an energy scale of the electrons where the zero point of the kinetic energy of the emitted electrons is located at around 29 eV.

The energy distribution of the ejected electrons, which is nearly independent of the energy of the primary ions, is characterized by a low-intensity peak at around 2.5 eV, followed by a maximum at around 4 eV and a decrease of n(E) with increasing energy reaching zero at around 12 eV (see fig. 1a). The corresponding spin distribution P(E) of the emitted electrons shows several pronounced, characteristic peaks which will be used to identify various possible mechanisms involved in SPEES.

In the following, in a first qualitative attempt, we discuss several mechanisms which could occur near the Ni(110) surface and contribute to the emission of spin-polarized electrons in SPEES.

(1) Neutralization of the incoming ion and ejection of an Auger electron from the Ni(110) surface. For the work function of Ni(110), we use a value of 5.04 eV and for the 1s ground state of hydrogen a value of -13.58eV which gives a maximum kinetic energy of the ejected Auger electrons of 13.58 eV -2×5.04 eV = 3.5 eV. Note that screening of the 1s hole of the incoming proton by the electrons at the Ni(110) surface would decrease the binding energy of the hydrogen 1s bound state and consequently reduce the maximum kinetic energy of the ejected Auger electron to slightly lower values. Taking into account the surface band structure of Ni(110), P(E) should exhibit a negative value at around 3 eV followed by an immediate change to positive P values with *decreasing* electron energy. This is indeed observed in the experiment.

(2) Transfer of electrons to resonant ¹S, ³S, ¹P of ³P autoionizing states of H⁻ located near the n = 2 threshold with an electron affinity around -3.4 eV [19]. Taking screening effects into account, which drastically increase the electron affinity and broaden the energy levels, the energy range of the ejected electron is restricted to the energy range between 3.5 and 6.78 eV (13.58 eV -2×3.4 eV). Taking again the surface band structure of Ni(110) into account, P(E) should exhibit negative values at around 3.5 eV followed by a change to positive P values with *increasing* electron energy. This is indeed observed in the SPEES experiments.

(3) Transfer of electrons to the stable bound $1s^2$ [7] or the unstable bound $2p^2$ state of H⁻ and subsequent electron loss to continuum states. The electron affinity of the $1s^2$ state of H⁻ is at around 0.92 eV [20] and that of the unstable $2p^2$ state at around 0.009 eV [21]. Taking screening effects into account which strongly increase the electron affinity and broaden the energy levels, the energy range of the ejected electrons is restricted to the energy range 3.5 eV to (13.58 eV - 2 × 0.92 eV =) 11.74 eV or, respectively, to 13.58 eV - 2 × 0.009 eV = 13.56 eV for the $2p^2$ state. Again P(E) is expected to exhibit negative P values at around 3.5 eV, followed by a change to positive P values with *increasing* electron energy.

(4) Besides the above mentioned processes, which solely take into account the potential energy provided by the incoming ions, part of the kinetic energy of the incoming ions can be transferred by inelastic collisions during the interaction of the ions at steps and other structural inhomogeneities at the surface. It is tempting to correlate these processes to the overall average ESP of Ni of +5.5% observed for electron energies between 9 and 12 eV.

Work is in progress to study P(E) and n(E) at nonmagnetic Cu surfaces and at Ni(110) surfaces far above the Curie temperature where Ni exhibits a loss of long-ranged ferromagnetic order. Further studies involve SPEES to investigate the spin polarization of characteristic MVV or LMM Ni Auger electrons located at 61 eV or at 848 eV, respectively. We note that, for observation angles not normal to the beam direction, electrons originating from the moving electron emitting particles exhibit a Doppler shift. These shifts in the electron energy do not occur for electrons emitted from the solid, a fact which helps to identify a specific emission process.

We note that, at present, a quantitative theory of SPEES does not exist. If such a theory become available, one could directly link the measured electron energy and spin distribution to the spin-polarized electron densities of state at the topmost surface layer of ferromagnetic materials.

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