Spin-polarized electron emission spectroscopy (SPEES) at Ni(110) and PtMnSb surfaces *

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We have shown that using grazing-angle scattering of H^+ and He^+ ions at atomically flat surfaces of well characterized Ni(110) picture-frame single crystals and polycrystalline PtMnSb samples exhibit spin- and energy-dependent electron spectra which show a dramatic difference compared to that of traditional secondary electron spectra. We studied the energy- and spin-resolved intensity distribution of electrons, emitted along the surface normal. The distinct peak structure of the energy spectrum, which lacks a strong secondary electron background, allows us to compare our data with available theoretical data on the electronic structure of Ni(110) and PtMnSb. We further obtain important information on particle-surface interaction mechanisms.

1. Introduction

Small-angle ion-surface reflection has been shown to be a very powerful tool to investigate physical properties of surfaces, in particular, the electronic, magnetic and chemical properties of surfaces. In these experiments, the energy component of the beam normal to the surface is quite small. This small energy component of the ions normal to the surface prevents the penetration into the surface. Therefore, they are specularly reflected. Thus spectroscopies taking advantage of this characteristic are extremely surface sensitive, as has been shown in electron capture spectroscopy [1–3], which probes long- and short-ranged surface magnetic order in ferromagnetic samples.

In addition, grazing-angle particle-surface interaction experiments allow us to study electronic transition processes occurring near surfaces. Many of these processes should depend on the local surface electronic and magnetic structure and on the ion species used in the experiments.

Several spin-sensitive spectroscopies have been developed to study surface magnetism [4,5] with various sensitivities, being very surface and spin sensitive but not element-specific. SPEES, spin-polarized electron emission spectroscopy [6,7], however, is sensitive to all three attributes. We show that grazing-angle ion surface reflection can be used to induce the emission of spin-polarized electrons from the topmost layer of magnetic surfaces. The analysis of the obtained electron spectra

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allows us to detect element-specific, spin-polarized Auger electrons, and this makes SPEES a very unique spectroscopy. Using glancing angles of incidence helps to suppress secondary electron cascades, which are created during large-angle electron or ion bombardment. Careful comparison of polarization spectra with known spin data enables us to deconvolute the intensity spectra into its inherent spin-resolved components. The information obtained so far will also help us towards a better understanding of electronic processes occurring during particle–surface interactions, which is an area of great interest [8–10].

For initial experiments, we use (110)-surfaces of Ni picture-frame single crystals where the spin-polarized, surface electronic band structure is well known [11,1,2,4,5]. Furthermore, we use polycrystalline surfaces of the Mn-based, ternary Heusler alloy PtMnSb [12,13], which is a very promising material for normal magnetic recording. At present, it is not known whether the magneto-optical parameters of this material are only related to the magnetism of Mn or whether the nonmagnetic Pt and Sb components in this ternary alloy play an important role in causing the observed giant magnetooptic effects.

We find that the energy distributions of grazing-angle, ion-induced (H^+ or He⁺ ions) electrons emitted along the surface normal of magnetized Ni(110) picture-frame single crystals or polycrystalline PtMnSb are completely different from that of electron-induced [14] or ion-induced [15] secondary electron spectra and show pronounced energy dependent features. For PtMnSb, we observe nonzero electron spin polarization not only for Mn (d-like) Auger electrons, but also for Pt (d-like) and Sb (p-like) Auger electrons.

2. Experimental

In SPEES, we employ grazing-angle (1°) surface reflection of 15-30 keV hydrogen and helium (predominantly singly ionized) ion beams to study the emission of spin-polarized electrons as a measure of surface ferromagnetic order.

Fig. 1 shows the experimental setup used for SPEES experiments. Using an einzellens system ([2] in fig. 1) to focus the electron beam into the energy analyzer, we detect electrons emitted along the surface normal (emission cone angle: 11° [3] in fig. 1) of a remnantly magnetized target (not shown in fig. 1). The sample is magnetized along the direction of the incident ion beam. The energy of the electrons is analyzed using an electrostatic cylindrical energy analyzer ([4] in fig. 1) and the intensity is maximized for optimal transmission at each electron energy measured. For spin analysis, the monoenergetic beam of electrons is accelerated to 150 eV and enters a precisely calibrated low-energy diffuse scattering electron spin detector ([8] in fig. 1) which allows for a fast and efficient determination of the long-ranged electron spin polarization (ESP) [16]. The entire electron



Fig. 1. Experimental set up used in SPEES experiments: [1] electron beam extraction lens; [2] and [7] einzellenses; [3] electron beam collimating aperture; [4] electrostatic energy analyzer; [5] reference voltage for [4]; [6] electron beam steerers;
[8] electron spin detector with Au-Al target, Au evaporation source and channeltrons A and B.

detector system is completely shielded against stray magnetic fields to prevent any disturbing magnetic field effects. In the ESP detector, the electron beam is precisely focussed on a Au target of 2 mm in diameter. The relative electron intensities, backscattered in two channeltrons, positioned at 135° to the incoming beam direction, are a direct measure of the ESP. For zero ESP calibration, the Au target is replaced by an Al target. Further zero ESP calibration is performed by using a nonmagnetic Cu sample or by heating the ferromagnetic target above the Curie temperature where only nonpolarized electrons are available for emission.

A magnetizing field is provided by a magnetizing coil, wrapped around one part of the picture-frame crystal. In the case of PtMnSb samples, we use a C-shaped magnetizing device with pole-shoes attached to the PtMnSb target. The field is applied along the surface plane of the targets to magnetically saturate the samples and to produce a macroscopic magnetization along which the sign and magnitude of the ESP are measured. Magnetic saturation is checked by using the magneto-optical Kerr effect. The ESP, P, along the magnetizing field is then measured using the previously described spin detector. P is given by

$$P = \frac{1}{S(\theta)} \frac{N_{\rm A} - N_{\rm B}}{N_{\rm A} + N_{\rm B}},$$

where $S(\theta)$ is the Sherman function and N_A and N_B represent the count rates in the channeltrons A and B, respectively (see fig. 1).

The Ni(110) and PtMnSb samples are prepared and characterized in a target preparation chamber at 1×10^{-10} mbar as described in ref. [2] and then transferred to the SPEES measurement chamber operating at a working pressure of 9×10^{-10} mbar, where 90% of the residual gas consists of hydrogen, for Ni(110) studies, and at 3×10^{-10} mbar for PtMnSb experiments.

3. Results and discussion

In our SPEES experiments, we use an angle of incidence of 1° towards the reflecting surfaces. The distance d_{\min} of closest approach of the ions with the surface is characterized by the energy component E_{\perp} of the ions normal to the surface, $E_{\perp} = E_0 \sin^2 \alpha \approx E_0 \alpha^2$. With $E_0 = 25$ keV, E_{\perp} amounts to 7.6 eV for a reflection angle of 1°. Using appropriate planar surface potentials (see fig. 9 in ref. [2]), d_{\min} amounts to approximately 0.1 nm for $\alpha = 1^\circ$, which shows that, under these conditions, the ions do not penetrate the Ni(110) surfaces, d_{\min} for the PtMnSb surfaces amounts to approximately 0.15 nm.

The spin P(E) and the intensity I(E) distribution of electrons emitted during grazing-angle (1°) surface reflection of 25 keV H⁺ ions at magnetized Ni(110) surfaces are given in figs. 2a and 2b [7]. Using 25 keV He⁺ ions instead of 25 keV H⁺ ions for surface reflection at Ni(110), results in the I(E) and P(E) data given in figs. 2c and 2d [7]. We observed four low-intensity peaks (located at 14, 20, 36 and 56 eV; labels 2,3,4 and 5 in fig. 2d) and one high-intensity peak (label 1 in fig. 2d) located with a maximum at around 4.5 eV.

As seen from figs. 2b and 2d, the I(E) spectra are completely different from that of electron-induced secondary electron spectra (see dashed lines [14] in figs. 2b and 2d). The suppression of the well-known strong background of secondary electrons is most evident in these spectra. We note that the use of larger angles of incidence (6°), $E_{\perp} \approx 270$ eV, where the ions can deeply penetrate the surface, prevents the occurrence of such distinct peaks (see dashed-dotted line in figs. 2b and 2d).

These remarkable findings show that by using grazing-angle ion-surface reflections, cascading effects, caused by energetic secondary ions or energetic secondary electrons, are nearly totally suppressed. It also reveals that these energetically well-defined peaks in I(E), originating from electrons emitted (along the surface normal) from the topmost surface layer, can be used to unravel the nature of the underlying physical processes, which is a long standing goal in the area of particle-surface interaction physics [8-10].

For H^+ ions incident at Ni(110), we observe three low intensity (located at 2.5–3, 20 and 56 eV; labels 1, 3

and 4 in fig. 2b) and one high-intensity peak (label 2 in fig. 2b) located with a maximum at around 4.5 eV. The corresponding spin distributions P(E) of the emitted electrons (figs. 2a and 2c) show several pronounced, characteristic peaks (labels 1-4 in fig. 2a and labels 2-5 in fig. 2c). We use sign and magnitude of the ESP as additional 'labels' to identify the underlying charge exchange processes.

In the following, we discuss the electron spectra in terms of XVV Auger transitions (see fig. 3) [17]. We remark that a very promising and refined theory on Auger-type electron transition processes, which would allow for a more quantitative discussion of our data, has been published most recently [18]. We denote by X an electronic level either of the incoming ion or of atoms located at the surface with valence band levels denoted by V. We assume that XVV Auger peaks where X is an energy level of the incoming ion, should undergo a shift in energy when the H⁺ ions are replaced by He⁺ ions. XVV Auger transitions, where X is an empty electronic level of a surface atom, should not undergo such a shift.

For Ni(110) surfaces, it is known that V band electrons, originating from energy levels near (i.e. within 0.5 eV) the Fermi energy, possess a predominant minority spin orientation (negative ESP), whereas V electrons from energy levels below this energy range overwhelmingly possess a majority spin orientation (positive ESP) [11,1,2,4,5].

This information can be profitably used to identify



Fig. 2. Intensity distribution I(E) (energy resolution: $\Delta E = 0.3$ eV) and electron spin polarization P(E) (experimental error: $P = \pm 2\%$) of spin-polarized electrons emitted during grazing-angle surface reflection of 25 keV protons (fig. 2a and 2b; peaks 3 and 4 in fig. 2b are enhanced by a factor 100) and of 25 keV He⁺ ions (fig. 2c and 2d; peak 2 in fig. 2d is enhanced by a factor 4 and peaks 3, 4 and 5 are enhanced by a factor 100) at magnetized Ni(110) as function of electron energy E. The data were recorded 0.2 eV apart of each other. In order to give a clear plot not all data are plotted.



Fig. 3. Auger-type, two-electron charge transfer processes for a H^+ or He^+ ion near a solid surface. (a) XVV Auger transition with X being an energy level of the ion. (b) XVV Auger transition with X being an ion-induced hole of a surface atom. V denotes valence band levels, ϕ the work function and E_F the Fermi energy of the metal.

and unravel the nature of the various physical processes involved in electron emission in SPEES. For instance, V electrons originating in k space from energy levels located 0.5 eV or less below 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 side, V 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.

Fig. 3 illustrates two possible two-electron charge exchange processes in terms of XVV Auger neutralization. Process (a): neutralization of an incoming hydrogen or helium ion at a metal surface and emission of an Auger electron. Process (b): XVV Auger electron emission where the X, produced by the incoming ion, is a hole either in the valence (V) bands or lower levels of the surface atoms.

We discuss several XVV Auger transitions which could occur near Ni(110) surfaces and contribute to the emission of spin-polarized electrons in SPEES.

(a) XVV Auger transition in which X is a level of the incoming ion which undergoes Auger neutralization. For Ni(110) and incident H⁺ ions, we would obtain a maximum kinetic energy of the ejected Auger electrons of $E_x - 2\phi \approx 3.5$ eV [21]. The dynamic screening of the 1s hole of the incoming proton by 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 electron to slightly lower values. Using this information and the band structure of Ni(110), one would expect that P(E)first exhibits a negative value at around 3 eV followed by an immediate change to positive P values with decreasing electron energy, which is consistent with the experimental data. We further remark that these findings are also in agreement with available ECS data [2] where also negative ESP values are found for E_{\perp} values smaller than 11 eV.

As another test of Auger neutralization occurring at the surface, we use He⁺ ions instead of H⁺ ions. We observe an energetic shift of this peak (peak 1 in fig. 2b) by 11 eV which is the difference between the He⁺(1s) ($E_x = -24.6$ eV) [17] and H⁺(1s) ground state energies. This is observed in the data (peak 2 in fig. 2d) and further corroborated by the occurrence of a change of P from negative to positive values (peak 2 in fig. 2c) as discussed before for the H⁺ data.

The observed changes in the ESP (15% for H^+ and 10% for He⁺) are moderate as compared to the changes observed in spin-polarized photo-emission experiments which amount to 70–120% [4]. At present it is unknown whether these moderate changes in the ESP, as observed using SPEES, are due to changes in the electronic structure in going from the bulk to the surface into the 'vacuum' region (tail of the local surface electronic density).

The electron peak located at around 36 eV (peak 4 in fig. 2c) was already observed by Hagstrum and Becker using ion neutralization spectroscopy (INS) [17] and quite recently by Niehaus and coworkers [20] and was interpreted by the latter group as a two-electron capture process from $He^{++}-Cu(110)$ collisions leading to $He^{**}(2p^2)$ decaying to $He^+(1s)$ followed by the emission of an electron of 36 eV kinetic energy. Note that, in the present experiments, 10-20% of the ionic He beam consists of He^{++} ions. We observe nonzero ESP values (peak 4 in fig. 2c) which is consistent with the findings of Hagstrum [17].

(b) XVV Auger transitions in which a hole is created by the incident ion in the valence or lower electronic levels of the surface atoms. By comparing figs. 2b and 2d, we see that three peaks located at around 4.5, 20 and 56 eV (peaks 2, 3 and 4 in fig. 2b and peaks 1, 3, 5 in fig. 2d) are independent of the ion species used in the experiments and are not shifted in energy.

The peak located at 56 eV (peak 4 in fig. 2b and peak 5 in fig. 2d) can be identified as a $M_{23}VV$ ($M_{23}M_{45}M_{45}$)Ni Auger decay. This peak has been observed before (see references in ref. [14]). More notably, recently, Allenspach, Mauri, Taborelli, and Landolt [22] using spin-polarized Auger electron spectroscopy, observed this peak at a Ni(110) sample and measured the spin polarization of this peak. We note that, after background subtraction, these authors find similar *P* values for this peak. The surface dynamical interaction of the ion with the sample can create a deeper core hole through collisions with surface defects, or through electron-hole excitation processes [18].

The peak located at around 20 eV (label 3 in figs. 2b and 2d) depends upon the surface cleanness of the sample and, therefore, can be used to calibrate against surface contamination.

The major peak in both SPEES spectra (peak 2 in fig. 2b and peak 1 in fig. 2d) at around 4.5 eV, induced by H⁺ and He⁺, respectively, would tend to imply that this feature is due to the substrate. A kinematic enhancement of a XVV Ni Auger process with X a level in the lower part of the valence band could be a possible source of these electrons, but since there are differences in the polarization (P = 18% versus P = 4% at 4.5 eV), there is not enough evidence for this type of transition to be present as is for the M₂₃M₄₅M₄₅ Ni peak.

From our SPEES experiments (angle of incidence of the H⁺-ions: $\alpha = 1^{\circ}$) using magnetized surfaces of PtMnSb, we observe three distinct peaks between 12 and 30 eV with maxima located at 13.5, 18.4 and 22.6 eV. Using the bulk band structure of PtMnSb [12], these peaks possibly could be attributed to the emission from predominant Pt d-like band electrons, predominant Mn d-like band electrons and predominant Sb p-like band electrons. In addition, electron holes could be created due to symmetric and/or asymmetric collisions between surface atoms. These holes could be filled via XVV type Auger processes mentioned previously.

Unfortunately, at present, for PtMnSb no spinpolarized surface electron band structure is available, which, in combination with data from single-crystalline surfaces, would allow a more precise classification in terms of spin-polarized surface electron band states. We note, however, that the existence of a nonzero electron spin polarization over the electron energy range 12–30 eV directly implies that, besides Mn-like electrons, also Pt- and Sb-like electrons are spin-polarized and, therefore, inherently involved in causing the observed giant magneto-optical rotation effects. The nonzero ESP of these electrons can be caused by hybridization and spin-orbit coupling effects.

We note that, at present, a quantitative theory of SPEES does not exist. Provided the availability of such a theory, one could directly link the measured electron intensity and spin distributions to the spin-polarized, local electronic structure of the topmost surface layer of ferromagnetic materials. The availability of such a theory would also a require detailed knowledge of all electronic transfer processes inherently involved in SPEES.

In conclusion, we remark that the presently available experimental information not only poses a challenge for future theoretical work in this area of research, it already shows that SPEES is a very promising experimental technique of great potential.

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