Local Spin Polarization at Surfaces Probed by Hollow Atoms

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The relaxation of hollow atoms produced by slow multiply charged ions impinging on surfaces produces characteristic Auger electron spectra. These spectra, which serve as fingerprints of the interaction, can be used to probe local spin ordering at surfaces by relating changes in the intensities of different spin states to local spin polarization at the surface. The area from which the electrons are captured is of the order of a few $Å^2$, only. The potential of the method is illustrated by He^{2+} and N^{6+} ions interacting with a ferromagnetic Ni(110) crystal. From the Auger spectra we determine a spin polarization of $\approx -90\%$ at room temperature.

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Over the past few years, highly spin-polarized ferromagnetic materials have been the focus of numerous studies. This type of materials, like, e.g., magnetite (Fe_3O_4), are of great interest for spin electronics and magnetic storage devices [1,2]. Knowledge of the degree and the sign of the surface spin polarization (SSP), as well as the length scale of the magnetic correlations, is indispensable for understanding the magnetic properties of these materials. Surfaces and thin films often exhibit magnetic properties which are drastically different from those of the corresponding bulk material or the underlying substrate. An example is Ru which is nonmagnetic as a bulk material but is predicted to become magnetic as a thin film [3]. As a further illustration, antiferromagnetic NiO thin films grown on a ferromagnetic Fe(001) surface show a perpendicular, in-plane magnetic coupling to the substrate [4]. Moreover, the magnetic properties often depend sensitively on the geometrical structure and thickness of the films and the temperature. For example, the spin reorientation transition in Ni/Cu(001) shifts upon oxygen-assisted growth to lower Ni coverage [5]. Such effects are ascribed to the different electronic structure and the reduced dimensionality of the surface or thin film. The effect is most pronounced for the single top-most surface layer.

Here, we introduce a new method to probe local spin ordering at the top-most surface layer, namely, multiple electron capture spectroscopy (MECS) [6]. As diagnostics MECS uses the Auger electron emission from hollow atoms, i.e., atoms with populated outer shells and empty or sparsely populated inner shells. The hollow atoms originate when slow multicharged ions neutralize in front of a surface (see, e.g., Refs. [7–11]). The neutralization of a multiply charged ion approaching a (metallic) surface can be described by the classical over-the-barrier model [7] in which the electron transfer between the solid and the ion occurs at a distance where the potential barrier between the surface and the projectile is lowered to the Fermi level. The multiply charged ions become neutralized almost instantaneously. Because of the resonant nature of the charge transfer processes highly excited electronic levels in the ion are populated thereby creating the hollow atoms. The temporal state population is determined by an intricate interplay of electron capture and reionization [7]. In the neutralization processes the spin polarization of the captured electrons is conserved [12,13]. Therefore, the probability of ions capturing electrons into specific spin states depends on the respective densities of majority and minority electrons near the Fermi level. For a low spin polarization in the surface, on average lower spin states will be populated than for a high spin polarization. After the neutralization stage, the inner shell vacancies in low-Z ions are populated by Auger electron transitions. The relative intensities of the peaks in the Auger electron spectra corresponding to for example singlet and triplet states will change if the SSP changes (e.g., by varying the temperature of a ferromagnetic crystal). As multiply charged ions extract electrons from an area of a few up to several tens of $Å^2$ (depending on incidence angle), electron spectra may be used as a tool for sampling the short-range spin ordering at the top-most atomic layer of the surface.

The He^{2+} and N^{6+} ions that we have used, have been produced in an electron cyclotron resonance ion source and after charge-over-mass separation guided into our setup, which is described in more detail elsewhere [14]. In order to decelerate the ions down to energies of a few tens of eV, the setup is floated on high voltage, the final ion energy being determined by the difference between the source and the setup voltages, plus a small contribution due to the plasma potential. The experiments are performed in a UHV chamber with μ-metal shielding, in order to prevent for stray magnetic fields, and a base pressure of some 10^{-10} mbar. Because of their low energies, the ions are reflected from the top-most surface layer. A Ni(110) crystal was chosen as target for its high imbalance between majority and minority electrons at the Fermi energy [15]. The target surface was cleaned by cycles of 20 keV Ar^+ sputtering and annealing. The sample could be demagnetized by applying an ac magnetic field and by heating to 700 K. The Auger electrons emitted from the neutralized projec-

tiles were detected by a rotatable, 180° spherical electrostatic analyzer, with an energy resolution of $\Delta E/E = 0.5\%$ and acceptance $11.2 \times 10^{-8} E$ (sr eV) (E being the electron's energy in eV). To probe surface magnetism on a macroscopic scale electron capture spectroscopy (ECS) can be used. In ECS the light emitted by the neutralized projectiles is detected and polarization analyzed (this method for probing surface magnetism is described elsewhere; see, e.g., Refs. [13,16–18]).

In Fig. 1 a series of *KLL* Auger spectra from 20 eV He^{2+} ions impinging at 20° on a demagnetized Ni(110) surface is shown for different target temperatures. The spectra were background subtracted using an algorithm according to Shirley [19] and normalized to the peak at ~36 eV. For clarity, a constant offset has been added to the spectra. Each of the two peaks has contributions from two different Auger transitions. The peak at ~34.5 eV results from decays of the $2s^2\,{}^1S$ and $2s2p\,{}^3P$ states while the peak around 36 eV originates from $2p^2\,{}^1D$ and $2s2p\,{}^1P$ states. From here on the first peak which contains contributions from the ^3P state will be labeled *triplet* while the second one which is purely due to singlet states will be labeled *singlet*.

As the temperature of the target is increased, the intensity of the triplet peak decreases strongly until the bulk Curie temperature of Ni is reached ($T_C = 627$ K). Above the Curie temperature, no more changes are observed in the intensity of the Auger peaks. This is illustrated by the spectra taken at 640 and 660 K which fall on top of the one taken at T_C (spectra were recorded for temperatures up to 50 K above T_C). As no changes in the Auger spectra are observed above T_C, we conclude that within the experimental uncertainties the surface's Curie temperature coincides with the bulk one. This result is in contrast to previous claims of a remarkable ferromagnetic order at the surface up to at least twice the bulk Curie temperature [20]. Auger electron spectra taken at other He^{2+} energies (50, 100, 170 eV) and incidence angles exhibit a similar temperature evolution [21]. The surface of the target being demagnetized, the changes in the Auger spectra must be due to local spontaneous magnetization. The ferromagnetic domains have sizes in the micrometer range. To check that the surface does not show magnetic ordering on a macroscopic scale we did electron capture spectroscopy using 14 keV He^{2+} ions and detecting the $He(1s3d\,{}^3D) \rightarrow He(1s2p\,{}^3P)$ triplet line at 587.5 nm [14]. Target temperatures up to 375 K could be used in order not to have the radiation of the heating filament interfere with the detection of the light emitted by the neutralized ions. In the inset of Fig. 1 the degree of circular polarization of the emitted light (Stokes parameter S/I) is shown as a function of the target temperature, and indeed, no changes are observed implying that there is no long-range magnetic order.

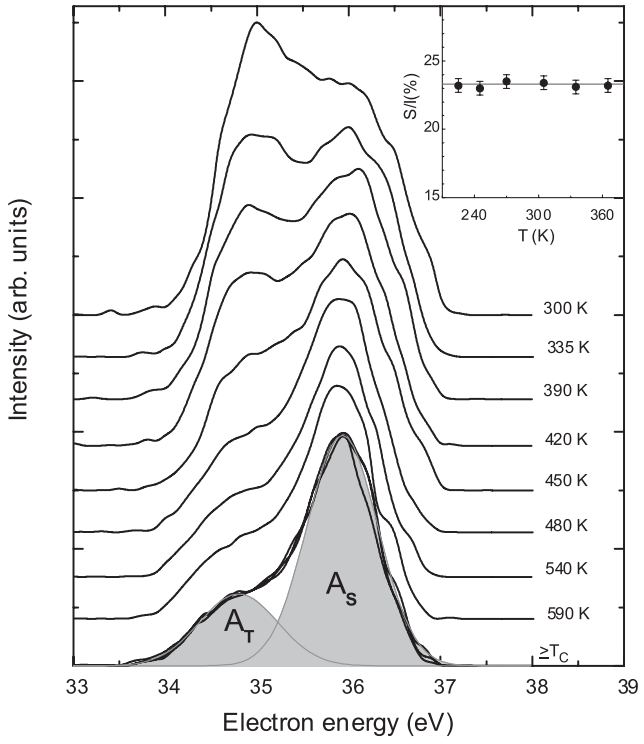

FIG. 1. *KLL* Auger electron spectra for 20 eV He^{2+} ions impinging on Ni(110) under 20° incidence for different temperatures of the target. At T_C a two-Gaussian fit to the spectra is shown in gray. Inset: Stokes parameter S/I of light emitted from 5° incident, 14 keV He^{2+} ions scattered from the same Ni(110) surface.

In order to relate the SSP to the changes in the Auger peak intensities, we propose a simple model to link the relative peak intensities to the probability of capturing two parallel or antiparallel spins into either triplet or singlet atomic states. Because of the difficulties in modelling the full system along the full trajectory, only electrons emitted by autoionization on the incoming trajectory are treated. The Auger deexcitation, which is the major deexcitation process, is not included here, as it gives a broad distribution at lower energies. We detect only the high-energy tail of these electrons, treating them as background to the autoionization signal. We assume that the ions get neutralized practically instantaneously at a distance in front of the surface at which resonant over-the-barrier transitions become possible. For creation of He^{**} this occurs at about 8 a.u., the neutralization distance for He^{+*}, according to the classical over-the-barrier model [7]. The states are assumed to be populated statistically according to $(2L + 1)P_{\text{spin}}$, with P_{spin} the probability for populating a specific spin system. The probability P_{spin} is linked to the SSP which is defined by $P = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, where $n_\uparrow$ and $n_\downarrow$ are the fractions of spin-up and spin-down electrons, respectively, $(n_\uparrow + n_\downarrow = 1)$. The statistical probabilities of capturing into a triplet or singlet are given by $P_t = n_\uparrow n_\uparrow + n_\downarrow n_\downarrow + n_\uparrow n_\downarrow$ and $P_s = n_\uparrow n_\downarrow$, respectively. These probabilities can be expressed in terms of the SSP as follows $P_t = (3 + P^2)/4$ and $P_s = (1 - P^2)/4$. For zero polarization one finds the statistical 3/1 ratio between triplet and singlet

states. For the decay of the hollow helium atoms only the time window between neutralization and quenching of the atomic states at the surface is available [7,22,23] (for our experiments, this time is in the order of tens of fs). Using autoionization rates from Lindroth [24] and an estimated rate of 5×10^{14} s^{-1} for resonant electron loss into the solid we calculated the Auger peak intensities. The peak intensity ratios turn out not to be very sensitive to the exact values of the ionization rate as long as the rates are high ($\geq 10^{14}$ s^{-1}) [21]. The influence of spin-flip processes is negligible for the elastically scattered electrons, while inelastically scattered electrons will show up as a broad spectral feature largely outside the atomic lines [25,26].

For comparison with the data the ratio of the intensities of the triplet and singlet Auger peaks A_T/A_S (cf. Figure 1) is used. The intensity ratio is related to the SSP as

$$\frac{A_T}{A_S} = \frac{A(^1S) + A(^3P)}{A(^1P) + A(^1D)} = c_S + c_T \frac{3 + P^2}{1 - P^2} \qquad (1)$$

where the constants $c_S = A(^1S)[A(^1P) + A(^1D)]^{-1}$ and $c_T = A(^3P)\{3[A(^1P) + A(^1D)]\}^{-1}$ are the calculated intensity ratios at $P = 0$. For the specific energy and incidence angle of the helium ions used in Fig. 1 the values of c_S and c_T are calculated to be 0.21 and 0.05, respectively.

The peaks in the Auger electron spectra were fitted with two Gaussians, see Fig. 1, in order to extract the intensity of each peak. The area ratios of the two fitted Gaussians (A_T/A_S) are shown in Fig. 2 as a function of the target temperature. The curve is the A_T/A_S ratio calculated from Eq. (1) assuming that in the temperature range of our experiments, the polarization varies linearly with the temperature [17,27,28].

Given the assumptions of our model, the data and the calculations agree very well. As the ratio varies quadratically with the spin polarization [Eq. (1)], the sign of the SSP can not be obtained directly. In order to determine the sign of the polarization, a complementary ECS measurement was performed while the sample was kept in a state of single-domain remanent magnetization. The sign of the SSP turns out to be negative [14]. Using the sign information, we obtain from the MECS measurements a value for the SSP of $-90 \pm 7\%$ at room temperature. This high value is in agreement with calculations [15], from which values of above -90% are expected for Ni(110). Values of around -95% were observed in magnetized Ni(110) by, e.g., spin-polarized photoemission spectroscopy [29] and by one-electron capture spectroscopy [20]. A further detailed investigation of polarization in magnetized surfaces versus local spin polarization in nonmagnetized systems is of high interest.

For the He^{2+} ions, direct capture of metal conduction electrons from the Fermi edge into the L shell takes place, facilitating a direct access to the SSP in the *KLL* Auger electron spectra. For higher charged ions such as N^{6+} at low impact energy the direct filling of the inner L shell plays a minor role; rather the autoionization cascade from

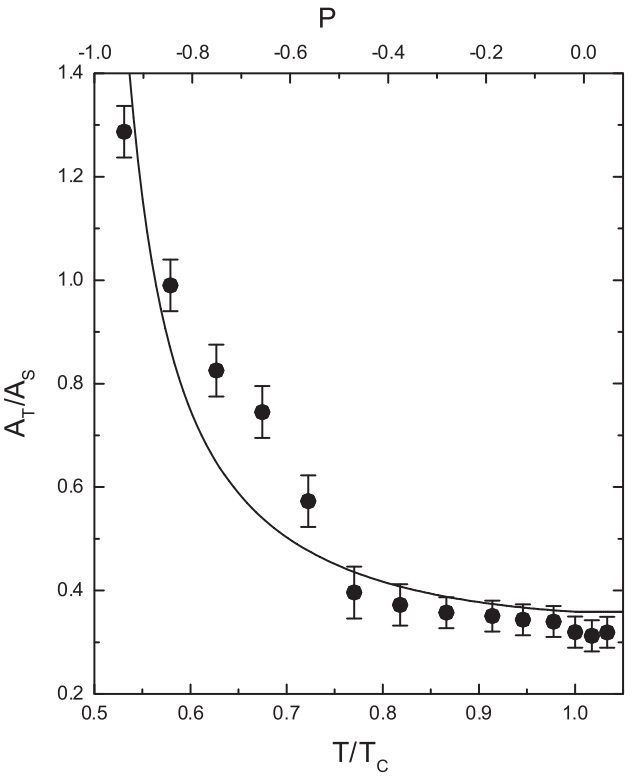

FIG. 2. Temperature dependence of the intensity ratio of the peaks indicated in Fig. 1. The solid curve is the ratio calculated from Eq. (1) as a function of spin polarization (P, top axis).

higher shells populates the L shell [30]. In this respect, it is very interesting to compare effects of the SSP in the *KLL* Auger electron spectra originating from He^{2+} and N^{6+}, as for N^{6+} the polarization of the captured conduction electrons might be affected by the several stages that they have to undergo before contributing to the *KLL* Auger electron emission.

Figure 3 shows a temperature series of *KLL* Auger spectra arising from 60 eV N^{6+} ions impinging at 20° on a demagnetized Ni(110) surface. The *KLL* Auger peaks in hollow N atoms originate from $1s2s^x2p^y nl^{(6-x-y)}$ electronic configurations (with $n \geq 3$ and $2 \leq x + y \leq 6$). The peaks at 347 and 358 eV arise from configurations with only two electrons in the L shell [23]. The 347 eV peak results from configurations in which the two L electrons form a singlet state ($2s^{21}$S), while in case of the peak at 358 eV they form a triplet state ($2s2p^3$P) [8]. The broad structure between 360 and 380 eV is due to contributions from many states with 3 or more electrons in the L shell and of all possible spin character. Qualitatively, the *KLL* Auger spectra from Fig. 3 follow a temperature evolution similar to the one for He^{2+} ions, i.e., a decrease of the higher spin states with increasing temperature and no changes above T_C. This implies that the electrons originally stem from the conduction band in line with the results of spin analysis of high-energy (*KLL* region) electrons emitted from fast, grazing incidence N^{6+} ions on a magnetized Fe(001) surface [12]. A quantitative analysis of the

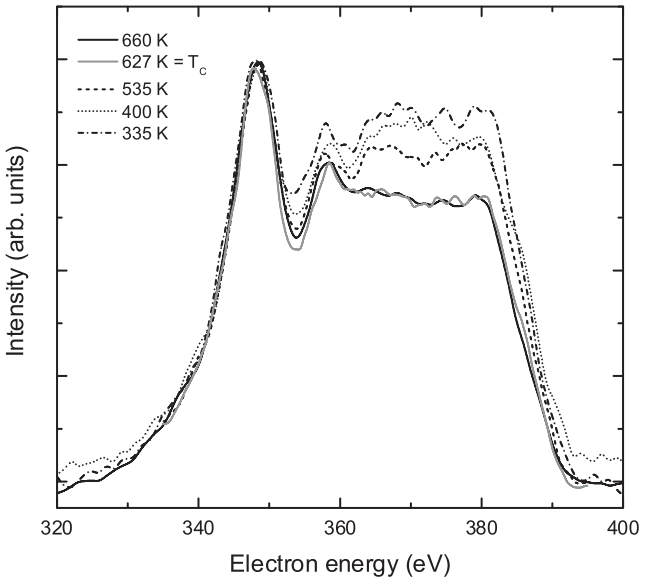

FIG. 3. *KLL* Auger electron spectra from 60 eV N^{6+} ions impact on Ni(110) under 20° incidence, for different temperatures of the target crystal.

evolution and its relation to surface spin ordering is even more challenging than for He^{2+}, because complete state-specific autoionization cascades need to be tracked. Also, at close ion-surface distances electrons sitting deeper in the band are captured as well, smearing out the high polarization of electrons coming from the Fermi edge. However, first theoretical efforts based on the over-the-barrier model [31] look very promising.

In conclusion, we found that changes in Auger electron spectra emitted by slow, multicharged ions scattering off a ferromagnetic surface contain information on the spin polarization of the surface. From the evolution of the He^{2+} *KLL* Auger spectra and making use of a simple model, the temperature dependence of the surface spin polarization for the Ni(110) was extracted, finding a high value of $\approx -90\%$ at room temperature and no indication of ferromagnetic ordering of the surface above the bulk Curie temperature. Realizing that the multicharged ions extract electrons from a small area of the top-most surface layer, this new technique, multiple electron capture spectroscopy, could be used as a probing tool for the spin polarization of magnetic nanostructures and overlayers, as well as for investigating the antiferromagnetism of surfaces.

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