This thesis is devoted to the study of the use of slow ions as a tool for investigating surface and 2D magnetism. Exploiting the Auger emission from such slow, multiply charge ions impinging on magnetic surfaces, we have successfully developed a novel technique for probing nanoscale magnetism, namely Multiple Electron Capture Spectroscopy. The development of spin-polarized spectroscopic techniques has been the driving force in deepening the understanding of magnetic phenomena at surfaces on a microscopic level. The discovery of novel phenomena in magnetic systems has attracted a great deal of attention, both from a fundamental point of view as well as from the point of view of the continuing miniaturization of features in magnetic recording devices.

Bulk magnetism has been studied for a long time. More recently, due to advances in the growth and characterization of ultra-thin films, the problem of surface and interface magnetism has been in the focus of worldwide research. Interesting questions appear when investigating the surface of a bulk magnetic material, an ultra-thin film as a prototype of a 2D magnetic system, or transitions from 2D to 3D behaviour when increasing the thickness of a film. Due to their extreme surface sensitivity and, in the case of hyperthermal ions, nanoscale sensitivity, techniques based on the use of ion beams could provide some of the answers in the field of low-dimensionality magnetism.

In order to develop a method based on the use of slow ion beams and apply it on a routine basis, the features of the spin-polarized charge transfer between the ion and the solid surface have to be understood. The neutralization
mechanism of multiply charged ions is a nearly-resonant electron transfer from the surface into excited atomic levels which can be described by the classical over-the-barrier model [16]. The atomic species formed upon neutralization is a so-called 'hollow atom', with electrons in highly-excited states and sparsely populated inner shells. The decay of these exotic atoms takes place by photon and electron emission, as well as electron loss back to the solid [15–20,34]. If the surface is spin-polarized, it is expected that the capture probability in excited states of different spin character will change as function of the spin polarization of the surface. Therefore, the population of these states will be modified compared to the case of electron capture from an unpolarized target. More specifically, if the surface is spin-polarized, high spin states have an increased probability of being populated, while the probability of populating low spin states decreases as compared to electron capture from an unpolarized surface. One of the de-excitation mechanisms of the projectile is auto-ionization, in which one electron from a high-lying shell fills a core hole, while a second electron is emitted to the vacuum. The peak intensities in the auto-ionization spectra, corresponding to transitions from different excited states in the projectile, depend on the initial population of these states. Therefore, the spectral peak intensities can be related to the spin polarization of the surface. The associated method is Multiple Electron Capture Spectroscopy (MECS) (chapters 5-7). Next to MECS, the method of Electron Capture Spectroscopy (ECS) in which electron capture into singly-charged ions is used, gives access to macroscopic magnetization of the target.

In chapter 4 we described how Fe(110) and Ni(110) surfaces were investigated using ECS with keV He⁺ and He²⁺ ions. The method of ECS relies on the changes in the degree of circular polarization of the fluorescence light as function of the surface magnetization [1,25–28]. The spin of the captured electron couples with the total orbital angular momentum, shifting the population distribution over the magnetic sub-states. Depending on whether the shift in the distribution over $M_J$ is towards or away from $M_J = 0$, the degree of circular polarization of light $S/I$ will increase or decrease. Measuring the sign of the change in $S/I$ as function of the magnetization of the surface, parallel and antiparallel to the scattering-induced orientation of total orbital angular momentum $\vec{L}$, information can be obtained on whether mostly majority or minority electrons are captured from the surface. For Fe(110), the spin polarization of captured electrons is positive, while for Ni(110) the polarization of captured electrons is negative. The magnitude of the change in $S/I$ for Fe(110) and Ni(110) surfaces is similar, indicating that a spin-filtering mechanism is in place. However, a quantitative determination of the spin polarization of the surface with ECS is still not possible due to the complex kinematic effects involved [1, 27]. Detailed theoretical information on energy- and momentum-resolved SDOS is required in order to be able to describe more quantitatively the transfer of spin polarization in grazing
ion-surface scattering.

In chapter 5 we show that KLL Auger electron emission from neutralized slow, multiply charged ions can be used as a probe of surface spin polarization [9], an effect at the basis of Multiple Electron Capture Spectroscopy (MECS). Hyperthermal He$^{2+}$ and N$^{6+}$ ions impinging on a Ni(110) surface were used. In order to observe the evolution of the peak intensities in the KLL Auger spectra as function of the spin polarization of the surface, temperature-dependent spectral series were recorded. For a ferromagnet, the magnetic ordering is reduced with increasing temperature and destroyed above the Curie temperature of the material. For He$^{2+}$ ions, resonant electron capture from the Fermi level in the L shell takes place, allowing for a direct access of the spin polarization of electrons at the Fermi edge. The intensity peak ratio corresponding to triplet and singlet states changes dramatically with temperature, consistent with the high spin polarization of Ni(110) at the Fermi level. For N$^{6+}$ a similar effect was observed, but of smaller magnitude. The reduction of the observed effect is due to the fact that for N$^{6+}$, the L shell is populated by auto-ionization cascades from higher shells; also, for closer ion-surface distances, capture of electrons sitting deeper in the conduction band becomes possible, reducing the high polarization of the Fermi electrons. For both He$^{2+}$ and N$^{6+}$, no changes were observed in the spectral peak intensities for temperatures above the bulk Curie temperature of Ni, $T_C = 627$ K. From this we conclude that the surface Curie temperature coincides with the bulk one.

In order to quantitatively link the changes in the peak intensity ratio to the surface spin polarization, an atomic model was developed for the case of KLL Auger emission from doubly excited He atoms [10]. Using concepts from the COB model [16] and including a spin polarization-dependent capture probability into triplet or singlet states in He$^{**}$, auto-ionization spectra could be simulated. Including also effects due to the dynamic response of the metal [38], very good agreement was found between the calculated and the measured spectra. Using this so-called ‘free-atom model’, the temperature dependence of the Ni(110) surface spin polarization was extracted from the changes in the KLL Auger peak ratios. The spin polarization of Ni(110) was found to follow an decrease with temperature specific for ferromagnetic surfaces [96–98].

By varying the incidence angle of the He$^{2+}$ ions, a dependence was found between the observed polarization and the distance along the surface that the projectile travels between the first and the second electron capture. Strikingly, the observed spin polarization drops to zero for grazing incidence, indicating that MECS can provide information on local magnetic properties like the spin correlation length. A comparison of the total intensity changes in the measured Auger spectra with the model calculations indicates directions to be followed for extending the free-atom model: for example, inclusion of ion-surface dis-
Concluding remarks

In chapter 7 we illustrated how MECS was applied to study the Fe(110) and half-metallic Fe$_3$O$_4$(111) surfaces. For Fe(110), a spin polarization value of almost 40% was found, in line with previous measurements [7,75,76]; therefore, we find no support for a predicted small negative polarization in the above-surface region [74]. The temperature dependence of the spin polarization of the Fe(110) surface follows, like for Ni(110), the expected behaviour for ferromagnetic surfaces.

Half-metallic magnetite, Fe$_3$O$_4$, is interesting to study due to its high predicted spin polarization, of $-100\%$ [107]. This high value makes magnetite a very good candidate for use in spintronics applications as spin valve. The predicted high spin polarization has only been recently confirmed. Values up to $-85\%$ have been measured [5,6,108–110]. The main difficulty in finding a high spin polarization proved to be the quality of the films [111,112]. For the results presented in chapter 7, Fe$_3$O$_4$(111) films were grown by oxidizing a Fe(110) single crystal. The good quality of the films was confirmed by STM measurements. Using MECS, a high value of almost $-90\%$ was found at room temperature. The sign of the polarization was determined using ECS. The decrease of the spin polarization of the Fe$_3$O$_4$(111) surface with increasing temperature is slower than expected for a ferromagnetic surface. Whether this behaviour is due to the peculiar electronic structure of magnetite, the small thickness of the film or other reasons is still an open question.

The challenge of obtaining stoichiometric magnetite films has also been addressed. Smentkowski et al. [117] observed that magnetite films grown on Fe single crystals undergo a structural phase transition to FeO at elevated temperatures, due to Fe diffusion from the substrate. We could monitor this phase transition with MECS, as it is accompanied by a magnetic phase transition from ferrimagnetic Fe$_3$O$_4$ to paramagnetic FeO. We found that the starting temperature for this phase transition is $\sim 650$ K and observed a small non-vanishing spin polarization for the FeO film, a result which confirms very recent observations by Busch et al. [125].

The results presented in this thesis show that slow, multiply charged ion beams can be used as a probe of local magnetic properties of surfaces. The ‘free-atom model’ used to extract the spin polarization from the KLL Auger spectra proved to be quite robust, in spite of its simplicity. Nevertheless, an extension of the model including more detailed information on the dynamics of the charge exchange processes, like e.g. distance-dependent decay rates and anisotropy in the electron density, would allow for a deeper understanding of effects like sensitivity of MECS to local electronic correlations.

Due to the fact that the interaction of these ions with the surface takes place...
over an area comparable with atomic length scales, the technique of Multiple Electron Capture Spectroscopy could prove a valuable complementary tool to, e.g., spin polarized STM, which provides site-specific information as well. After benchmarking MECS on well-studied surfaces of Ni(110) and Fe(110), the next step would be to fully exploit its extreme surface and nanoscale sensitivity for investigating magnetic phenomena of reduced dimensionality on sub-nanometer length scales in magnetic nanostructures and ultra-thin magnetic films.