CHAPTER

ONE

Introduction

The interaction of ions and atomic particles with solids provides valuable information on the properties of the solid materials. In particular, slow ions, with energies ranging from meV to tens of eV, are a suitable tool for probing the surface properties of solids, as the interaction processes take place at the vacuum-solid interface. Ions with keV kinetic energy in grazing incidence scattering are sensitive to the top-most layer of the surface as well [1, 2]. Not only information on the geometrical structure and composition can be obtained, but also electronic characteristics are accessible. Specifically, the magnetic properties of surfaces have aroused a high interest due to the fact that often the reduced dimensionality gives rise to peculiar behaviour, distinctly different from the one of the bulk material. For example, ferromagnetic Fe films exhibit anti-ferromagnetic coupling if separated by Ge spacers of a specific thickness [3], while antiferromagnetic NiO(111) surface spins remain ordered at higher temperatures than in the bulk [4]. Furthermore, highly spin-polarized materials, such as half-metals, are of great interest to the field of spintronics, where they are used as spin-filter interfaces [5, 6].

Therefore, many surface science techniques have been and still are being developed to obtain information on the magnetic order of surfaces. A combination of techniques based on the use of ion or electron beams offers the possibility to probe layer-dependent magnetization at surfaces [7, 8]. Moreover, techniques using hyperthermal ions have the potential of accessing nanoscale properties, as the surface area that an ion probes is in the order of a few (tens) of Å^2 [9, 10].

As, for example, the features in magnetic and electronic devices are constantly decreasing in size, gaining insight into local electronic properties is of high relevance.

The interaction of ions with solid surfaces is a dynamic problem, and understanding the details of charge exchange processes between the surface and the ion is a prerequisite to a more general use of ion beam-based techniques as surface magnetism probes. The gross features of the electron dynamics occurring in the ion-surface interaction can be understood if the solid is considered as a nearly free-electron gas weakly interacting with the ion cores of the lattice, with the charge density having a sharp boundary at the surface (the so-called jellium model - see e.g. ref. [1] and references therein). The foundations underlying the description of ion-surface interaction have been laid in the pioneering work of Hagstrum [11–14] on ion neutralization spectroscopy. He studied the collision of low-energy singly- and doubly-charged rare gas ions with metallic surfaces, and found that the main part of the electrons emitted into vacuum originate from various Auger processes. Auger processes are two-electron processes in which one electron fills a core hole, while the other one is emitted into vacuum, taking away the excess energy as kinetic energy. Auger electron emission is the main de-excitation mechanism for low-Z ions, while higher-Z ions deexcite radiatively [15].

The part of the spectrum that contains the emitted Auger electrons that leave the metal corresponds to a self-convolution of the surface density of states (SDOS), which makes the analysis rather complex. Part of the electron spectra originates from auto-ionization processes following resonant capture of electrons from the Fermi level of the metal into excited states. This gives rise to sharp atomic lines, as in this case the Auger electrons are emitted from atomic levels.

Later, extensive studies have been done on the interaction of slow, multiply charged ions with surfaces, where the creation of the 'hollow atom' has been observed, i.e., a highly excited atom with sparsely populated inner shells [15–20]. The neutralization of highly charged ions (HCI's) in front of surfaces can be described in the framework of the classical over-the-barrier (COB) model [16], which was first developed for HCI-atom interactions [21–23]. From the analysis of the Auger spectra it was concluded that resonant electron capture leads to the creation of the hollow atoms, followed by de-excitation by auto-ionization, at least for large ion-surface distances. For closer distances, capture of electrons with energies farther from the Fermi level also occurs.

To study long-range surface magnetism, Electron Capture Spectroscopy (ECS) can be used. ECS was first developed by Rau and Sizmann [24]. By means of a nuclear reaction, they determined the spin-polarization of electrons captured by fast deuterium ions, scattered grazingly on the surface. It was hoped that the extreme surface sensitivity of the grazing incidence ions would help in ad-

dressing peculiar problems of surface magnetism, like the existence of magnetic order at the surface even above the Curie temperature of the bulk. But this measurement method is rather indirect, and the data analysis is not straightforward, some of the reported results (like magnetic ordering of a Ni(110) surface at up to two times the bulk Curie temperature) could not be confirmed by other measurements. A later, more successful version of ECS uses electron capture into excited atomic levels, which decay by emission of (partially) circularly polarized light [1, 25–28]. This kind of ECS was successfully applied to investigate magnetic properties of Fe surfaces and magnetic coupling between layers of different magnetic thin films. It has proved difficult to quantitatively relate the changes in the degree of circular polarization of the emitted light to the spin polarization of the surface. Nonetheless, the sensitivity of ECS to the magnetization orientation in the top-most surface layer makes it a useful tool for probing magnetic correlations between, e.g., ultrathin magnetic films.

In order to address local properties of spin-polarized surfaces, it is proposed to use the Auger electron emission from hollow atoms formed in front of such surfaces, as the area from which the electrons are captured is in the order of a few tens of $Å^2$. This novel method, called Multiple Electron Capture Spectroscopy (MECS) [9, 10], is introduced in this thesis and is shown to be a very promising surface-sensitive method for investigating surface magnetism. It makes use of the changes in the peak intensities in the Auger spectra corresponding to emission from different spin states. Specifically, if the surface has a high degree of spin polarization, there is a higher capture probability into high spin states (e.g., triplet states), while for an unpolarized surface, lower spin states (e.g. singlet states) are more likely to be populated in the excited projectile.

This thesis presents results on the potential of using slow, multiply charged ion beams as probes for surface magnetism, namely the method of Multiple Electron Capture Spectroscopy:

- In chapter 2, an overview is given of the fundamental concepts in ion-surface interactions relevant to the scope of this thesis. The COB model is presented, detailing concepts like charge-image charge interaction and resonant neutralization of ions in front of surfaces. Also, the main charge exchange and de-excitation processes which are relevant in the eV-keV energy range of the ions are described. Finally, electronic structure effects are discussed, namely the energy shift of the atomic levels in front of the surface and the kinematic effects in the electron capture process.

- In chapter 3, the experimental set-up is described, together with the main features of the experimental techniques used throughout this thesis or relevant for the results presented. First, a description is given of the Electron Cyclotron Resonance Ion Source (ECRIS), the ion beam collimation and

deceleration system and the actual experimental set-up. Thereafter, a short overview of the main techniques in surface magnetism is presented. The last part of the chapter deals with Low Energy Ion Spectroscopy (LEIS), which is used in this work to check the chemical composition of the target surfaces, as well as the stoichiometry of the iron oxides studied in chapter 7.

- Chapter 4 contains the ECS results on Fe(110) and Ni(110) surfaces obtained by analysis of the degree of circular polarization emitted upon neutralization of He^+ ions scattering from these surfaces. The data, interesting by itself, are mainly used as complementary information to the MECS data in chapter5, 6 and 7.

- In chapter 5 the novel method of Multiple Electron Capture Spectroscopy is introduced, and the basic features of the method are presented. The link between the changes in the temperature-dependent spin polarization of Ni(110) and the changes observed in the KLL Auger spectra from hyperthermal He^{2+} and N^{6+} ions impinging on this surface is discussed.

- An atomic model used to quantitatively extract the spin polarization from the peak intensity ratio in the KLL Auger spectra originating from the neutralization of He^{2+} in front of Ni(110), is detailed in chapter 6. By making use of this 'free-atom model', the temperature dependence of the spin polarization of the Ni(110) surface is obtained, and its behaviour is discussed in the frame of established models of surface magnetism. Also, the locality of the information accessible with MECS is presented.

- In chapter 7 MECS is applied to study the spin polarization of Fe(110) and half-metallic magnetite, Fe_3O_4, using He^{2+} ions. For the case of magnetite, a structural phase transition to anti-ferromagnetic FeO is investigated.