SPECTROSCOPIC INVESTIGATIONS OF FERROMAGNETIC SURFACES AND FERROMAGNETANTIFERROMAGNET INTERFACES

Doctoral Dissertation of:
Giulia Berti

Supervisor:
Prof. Alberto Brambilla

Tutor:
Prof. Franco Ciccacci

The Chair of the Doctoral Program:
Prof. Paola Taroni

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An expert is a person who has made all the mistakes that can be made in a very narrow field.

Niels Bohr
TRANSITION METALS and their oxides have been widely studied over the last decades because of the great interest in their basic physical properties and in the large range of applications they can be employed into. When dealing with thin films, moreover, the behavior of surfaces and interfaces is not yet fully understood in terms of structural, electronic, and magnetic properties.

After an overview on the main peculiar properties of these materials, and an explanation of the spectroscopic techniques used for the characterization, the present dissertation treats two of the most important systems in this field, namely Ni/W and Cr/Fe, of particular importance in spintronics applications.

For what concerns the former, the martensitic transition of Ni was analyzed. In this system the bcc-to-fcc transition proceeds through three distinct structural phases as a function of Ni coverage. A pseudomorphic bcc structure observed below 1 Ni monolayer is followed by an intermediate phase showing a $(7 \times 1)$ surface reconstruction, which eventually evolves into a bulk-like fcc structure. The pseudomorphic Ni bcc phase in the submonolayer regime has particularly attracted the attention since either a paramagnetic or a ferromagnetic ground state is expected depending on the lattice constant. Particular attention is given to the film electronic structure by analyzing the evolution of both occupied and empty electron states by means of angle resolved photoemission and inverse photoemission spectroscopy.

The Cr/Fe system has been thoroughly investigated both from the electronic and the magnetic point of view. The peculiarity of thin Cr films to protect the underlying Fe substrate is highlighted, being Fe highly reactive towards oxygen exposure. On the contrary, in the case of Ni, this protection does not
take place and, as a consequence of oxygen exposure, Ni atoms tend to be buried, promoting Fe ions segregation towards the surface, and forming a Fe oxide overlayer on top of metallic Ni. The surface magnetic properties of Cr/Fe are analyzed by different techniques, revealing that, if an oxygen monolayer is present on the surface of the Fe substrate, this enables the formation of a sharp interface with the Cr layer grown at high temperature. The effect of this lies in the observation of an antiferromagnetic stacking of Cr magnetic moments starting right from the Cr/Fe interface.
Results presented throughout this dissertation were acquired during the last three years within the Doctoral Program in Physics of Politecnico di Milano.

In addition to the topic of the main project, I have been involved in some other projects, whose results were not included in the final dissertation. Part of these results comes from the collaboration with IIT, Istituto Italiano di Tecnologia, for what concerns the photoemission analysis of organic materials employed in the development of hybrid solar cells and flexible microelectronics. I had, then, the opportunity to work within a collaboration with Università Statale di Milano, Università di Pavia and the Spanish groups of Universidad de Castilla-La Mancha and Universidad de Cordoba, with whom I shared some beamtimes at the ESRF, European Synchrotron Radiation Facility, in Grenoble, for the study via extended X-ray absorption spectroscopy of the structural transitions in frustrated pyrochlores. Finally, I spent six months of the last year of Ph.D. at the Zernike Institute for Advanced Materials of the University of Groningen by the group of Prof. Petra Rudolf, where I focused on the deposition of hybrid perovskite layers with the Langmuir-Blodgett method, and on the growth and characterization of the Ni/graphene/Ni trilayer as a spin filter.

This dissertation is divided into seven chapters, relative to different experiments performed during the three years of Ph.D. that I spent by the Surfaces Group of the Physics Department of Politecnico. Photoemission and inverse photoemission measurements were done at the VESI (Versatile Electron Spectroscopy Instrumentation) lab at Politecnico, while absorption measurements were done at beamline BACH (Beamline for Advanced diCHroism) of the ital-
ian synchrotron Elettra, in Trieste.

Each of the chapters reporting experimental results is preceded by a short introduction in which the relative experiments are briefly summarized.

- **Chapter 1** gives an introduction about the materials used for the experiments, namely transition metals and their oxides. General properties are reported together with examples taken from the literature.

- **Chapter 2** explains the details about photoemission (with spin polarization) and absorption spectroscopy techniques, which are used for the characterization and analysis in the following chapters. This same chapter also includes a thorough description of the experimental apparatus of VESI lab, which enables spin polarized photoemission and inverse photoemission acquisitions *in situ*, and the photoemission characterization of the Fe(100)-$p(1\times1)$O surface used as a substrate in most of the measurements object of this thesis.

- **Chapter 3** reports on the photoemission analysis for both empty and full electron states of the Ni/W(110) system, following the changes in spectroscopic features and diffraction patterns across the martensitic transition from a bcc to the fcc crystal structure of Ni.

- **Chapter 4** is dedicated to the analysis of the post-oxidation of thin Cr films deposited on the oxygen passivated Fe(100) surface, highlighting how the Cr overlayer completely covers and protects the metallic substrate, which is not affected by oxygen exposure, up to very high temperature exposures.

- **Chapter 5** is devoted to the magnetic characterization of submonolayer-range Cr films deposited on the same Fe(100)-$p(1\times1)$O substrate; after a recall of some previous results obtained by scanning tunneling microscopy, showing two peculiar surface reconstructions of Cr atoms, the magnetic circular dichroism findings are presented, giving evidence for the antiferromagnetic alignment of Cr spins on the Fe substrate.

- **Chapter 6** develops the topic of the previous one, describing the spin polarized photoemission acquisitions taken on Cr/Fe(100)-$p(1\times1)$O samples for Cr coverages as high as about 6 atomic layers. The most important results in this case are the absence of chemical mixing at the interface, made possible by the presence of oxygen on the substrate surface which acts as a surfactant for the layer-by-layer growth of Cr, and the observation of its layered antiferromagnetic stacking, by measuring the oscillations in polarization values retrieved from spin polarized photoemission spectra.
Chapter 7, finally, traces the conclusions, with a summary of the previous chapters and some future perspectives.
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CHAPTER 1

Introduction

IN THIS FIRST Chapter, an introduction will be given regarding the materials used for the experiments shown in this dissertation. After a brief summary, some informations are presented about the growth mode and the electronic and magnetic properties. The whole discussion is mostly based on Freund, Kuhlenbeck and Staemmler, "Oxide surfaces" [1].

1.1 Transition metals and their oxides

Transition metals are those elements of the periodic table belonging to the $d$-block (groups 3 to 12), as highlighted in Fig. 1.1. The term "transition" refers to the changing of character, from metallic ($s$-block) to non-metallic ($p$-block). The electronic configuration of the outer shells is written in the form \((n-1)d^{1\div10}ns^{1\div2}\).

Most important about technological applications and fundamental physics are their oxides (TMOs, transition metal oxides). They are commonly employed in contexts in which either their catalytic activity or their semiconductive or magnetic properties are exploited, but they span over almost all aspects of material science and physics [2]. The crystal structure consists of close-
packed interpenetrating arrays of oxygen anions and metal cations [3]. Bulk properties of such compounds are well understood and are of interest in non-linear optics or high-$T_C$ superconductors, for example [4]. Conversely, knowledge about surfaces and 2D materials is rather little and they are still matter of research studies (see, e.g., Refs. [5] and [6]).

In order to understand the surface structure of an oxide, one can not simply make the assumption that they are ideal crystals, in which the external surfaces reproduce the atomic structure of the bulk. Surfaces can be generated by cleaving a bulk crystal structure along its planes [3]. Nevertheless, after the cleavage, the arrangement of atoms on the surface may be different from that of the corresponding bulk. As-cleaved surfaces, indeed, tend to achieve the most stable configuration by minimizing the surface Gibbs energy through reconstruction [7]. The overall stability of the surface is then established in terms of surface polarity, degree of saturation and defect sites.

TMOs possess a wide variety of surface structures resulting in different surface chemical properties. Also the catalytic properties are much affected by the surface reconstruction, through the relative acidity and basicity of the metal cations and oxygen anions on the surface. For this reason, structural defects in TMOs play a relevant role in this field. Moreover, another property of these compounds, which has been the object of intense research studies, is their optical response, as this would make them appealing for photocatalysis.
applications [8–10].

## 1.2 Growth modes of oxide surfaces

Since the main interest in these oxides lies in their surface properties, the need of clean and stable surfaces has upmost importance. In particular, characterization experiments must be performed under ultra-high vacuum (UHV) conditions, in order for the sample surface itself not to experience any degradation or modification. For the same reason, samples have to be prepared in situ, so that any possible contamination is kept at a minimum level.

One of the desirable and straightforward preparation methods is cleavage, which consists in the transfer of mechanical pressure to a razor blade inside the UHV chamber so that, after the sample is cleaved, a very clean and stoichiometric surface is obtained. However, this method allows only to cut along certain crystallographic directions, so, when preparing TMO surfaces by cleavage, not any of them might be achievable. For a non-polar surface, the surface potential has a finite value, and cleavage along this direction would be successful. On the other hand, the surface potential for a polar surface is given by [11, 12]

\[
V = \frac{2\pi}{S} [Nb(2\sigma - 1) + (1 - \sigma)b]
\]

(1.1)

in which \(S\) is the area of the surface unit cell, \(N\) the number of layers, \(b\) the distance between each of them, and \(\sigma\) is the surface charge in units of the charge on the corresponding bulk layer. In a polar-terminated crystal, the number of layers \(N\) is extremely large, meaning that the potential \(V\) diverges as well, and the cleavage of a crystal structure along this direction is not possible. Thus, for the preparation of different surface orientations, cleavage is not the most appropriate technique. A number of surfaces that have successfully been prepared by cleaving methods and are well characterized are listed in Table 1.1 [13–36].

When dealing with polar surfaces, the increase in surface charge makes the surface itself unstable. A closer inspection of Eq. 1.1 reveals anyway that \(V\) for a polar surface can be non-divergent provided that \(N\) is small, i.e. in thin films. Another possibility might be that the surface charge \(\sigma\) decreases after its formation. In particular, for \(\sigma = 1/2\) the first term in Eq. 1.1 vanishes. Such a reduction of the \(\sigma\) parameter can be achieved indifferent ways, e.g., by a decreasing of either the number of ions or of the charge carried by each of them in the topmost layer; by surface reconstruction; by adsorption of charged
species, such as OH\(^-\). By consequence, it is possible to prepare stable polar surfaces if some different approach is employed in the preparation process. One possibility is to clean the crystal in UHV environment with sputtering (ion bombardment) and annealing (heating) cycles: the latter can be performed in an oxygen atmosphere to avoid oxygen vacancies induced by the ion bombardment treatment. Even in this case, however, the preparation of polar surfaces could be non-trivial, because of their tendency to facet along some preferential direction during the process.

Another approach for obtaining particular oxide surfaces is to grow thin films on metallic substrates [37]. In this case, the structure of the oxide film depends on the geometry of the metallic substrate, and it is possible to obtain non-polar as well as polar surfaces. The main drawback related to this type of preparation is that the quality of the deposited film greatly depends on the lattice mismatch between the film itself and the substrate. This also means that it may be possible to control the defect density in the film by tuning the mismatch, or, in other words, by changing the structure of the substrate. The approach of growing thin films on top of metallic substrates can be divided into three main categories [38], as follows:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Orientation</th>
<th>Quality</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>(100)</td>
<td>+</td>
<td>[13–18]</td>
</tr>
<tr>
<td>CaO</td>
<td>(100)</td>
<td>+</td>
<td>[15, 19]</td>
</tr>
<tr>
<td>NiO</td>
<td>(100)</td>
<td>+</td>
<td>[15, 20–22]</td>
</tr>
<tr>
<td>CoO</td>
<td>(100)</td>
<td>+</td>
<td>[15, 23]</td>
</tr>
<tr>
<td>MnO</td>
<td>(100)</td>
<td>+</td>
<td>[15, 24]</td>
</tr>
<tr>
<td>EuO</td>
<td>(100)</td>
<td>+</td>
<td>[15, 25, 26]</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>(100)</td>
<td>−</td>
<td>[27]</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>(001)</td>
<td>−</td>
<td>[27]</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>(110)</td>
<td>±</td>
<td>[27–29]</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>(110)</td>
<td>±</td>
<td>[30]</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>(100)</td>
<td>±</td>
<td>[30]</td>
</tr>
<tr>
<td>Ti(_2)O(_3)</td>
<td>(10\bar{1}2)</td>
<td>+</td>
<td>[31, 32]</td>
</tr>
<tr>
<td>V(_2)O(_3)</td>
<td>(10\bar{1}2)</td>
<td>+</td>
<td>[33]</td>
</tr>
<tr>
<td>V(_2)O(_5)</td>
<td>(001)</td>
<td>+</td>
<td>[34, 35]</td>
</tr>
<tr>
<td>ZnO</td>
<td>(0001)</td>
<td>+</td>
<td>[36]</td>
</tr>
<tr>
<td>ZnO</td>
<td>(000\bar{1})</td>
<td>+</td>
<td>[36]</td>
</tr>
</tbody>
</table>
i. The top surface of a single crystal can, in most cases, be oxidized by exposure to a controlled quantity of oxygen. The final structure of the film will clearly be affected by the lattice mismatch between the metal and its oxide, possibly resulting in a high number of defects and dislocations. An example is represented by the NiO(100)/Ni(100) system (mismatch value close to 20%), in which the top oxide layer is not well ordered, and its poor crystallinity is reflected in the broadened spots in low electron energy diffraction patterns [1].

ii. Since usually it is difficult to find a good epitaxial relation between a metal and its oxide, a possible way to grow higher quality films is to start from an inert metal substrate. The deposited overlayer can be oxidized during deposition, by evaporation in a controlled oxygen atmosphere (reactive deposition), or after being deposited (post-oxidation). By a careful choice of substrate and overlayer geometries, it is possible to achieve long-range ordered structures, with very low defect density. A slight variation in this method consists in growing a buffer layer in between the substrate and the top film in order to gradually relax the lattice mismatch.

iii. The third option, the oxidation of alloy surfaces, is similar to the first one, except for the fact that here the structure and properties of the starting alloy may facilitate the growth of an ordered, defect-free oxide film. For example, when post-annealing an Al$_2$O$_3$ film on top of metallic Al, the substrate starts melting well before the reordering of the overlayer; on the other hand, if the system is grown on top of a NiAl alloy, the oxide top film can be annealed above 1000°C without affecting the substrate [39].

1.3 Electronic structure of oxide surfaces

In this section the electronic structure of TMOs will be discussed. A technique that is largely employed for this kind of studies is photoemission spectroscopy, PES.

As will be explained more in detail in Ch. 2, during a PES experiment a photon excites an electron bounded to the material. Once in vacuum, an electron analyzer will detect it based on its kinetic energy, and from this it is possible to retrieve information about the initial binding energy it had inside the sample.

A complete theoretical treatment of the process is beyond the aim of this thesis; however, it must be noticed that, when dealing with non-conducting materials, the creation of an electronic hole due to the incoming photon beam might affect neighbouring atoms which will try to screen it (final state effects).
This leads to a mixture of oxide (insulating) and metal character in the bands, making it substantially impossible to rely on the simple band structure model for the description of the system [40]. By consequence, a complete band structure study of an oxide should comprise proper theoretical calculations taking into account many-body effects. In a PES experiment, indeed, also spectral structures due to the aforementioned effects may considerably change the spectral function $A(\omega, k)$, including redistribution of intensities over several states with comparable weight, in a way that the initial band structure can be strongly modified.

Another effect to consider in PES experiments is the peculiar electronic structure of the surface: in some cases, in fact, surface atoms are subjected to a different potential with respect to the bulk because of their reduced coordination number. This gives rise to a change in the energy levels in the proximity of the surface, inducing the appearance of surface states within the gap of the bulk band structure. Such states can be detected via PES [41]. They have no dispersion in the $k$-space projection perpendicular to the surface and their presence and energy position may strongly depend on the presence of adsorbates on the surface.

A recent literature example of this subject is given by the study of Plucinski and coworkers [42], who were able to detect a surface state in a Fe(001) sample and assign its spin character thanks to the addition of spin polarization in their PES measurements. Their results were also supported by density functional theory calculations. In this work, the effect of oxygen adsorption is first analyzed, showing that electron states in the $\Gamma$ point of the Brillouin zone (normal emission conditions) near the Fermi edge are mainly of minority spin character (see Fig. 1.2), but the intensity of the same feature close to the Fermi energy (Fig. 1.2) is not affected by the amount of oxygen adsorbed on the surface, meaning that its electronic origin must be of bulk nature, rather than surface.

Nevertheless, in the same paper the density functional theory calculations (not reported here) predict that a surface state just below the Fermi edge should be visible. By consequence, it must be in another point of the Brillouin zone, and in order to see it by PES, the authors span the band structure along $\Gamma H$ in off-normal emission conditions. Fig. 1.3 shows the results of oxygen adsorption (similarly to the previous case) for this off-normal emission mapping. In this second case, the minority peak closer to the Fermi level near the $X$ point of the Brillouin zone (see Fig. 1.3) is much affected by oxygen adsorption, nicely indicating it can be related with a surface state.

As mentioned above, surface states have a two-dimensional origin and their binding energy does not depend on the perpendicular component $k_\perp$ of the $k$ vector. This can be used as a fingerprint to confirm the surface origin of the
Figure 1.2: Effect of oxygen adsorption on the Fe(001) electronic band structure near the $\Gamma$ point of the Brillouin zone. Spectra taken at $h\nu = 64$ eV are shown both in the spin integrated (left and center panels) and spin polarized mode (right panel, ▲ for majority electrons and ▽ for minority ones). Reprinted with permission from Plucinski et al., "Surface electronic structure of ferromagnetic Fe(001)", Physical Review B 80 184430 [42]. © 2009 by The American Physical Society.

state by PES, if it is possible to perform the experiment with different photon energies (i.e., by using synchrotron radiation). Fig. 1.4 shows a series of spectra from the experiment of Plucinski et al., in which the combination of photon energies and emission angles were set so as to keep $k_\parallel$ constant while $k_\perp$ is different: the surface origin of the feature near the Fermi edge is confirmed by its appearance at the same binding energy in all spectra (see vertical dashed line in the figure).

1.4 Magnetic properties of metallic multilayers

Systems involving transition metals have also, especially during the last years, been studied for their magnetic properties. It is possible, in fact, to obtain magnetic layered structures with the growth of transition metals on top of metallic substrates. For example, the alternation of Ni and Fe thin films in its fcc crystal structure can lead to a system with easy axis of magnetization direction switching at each layer [43, 44]. The Ni/W(110) was chosen as a starting template for the growth of such a system, and preliminary results obtained on the
study of its electronic properties are presented in Ch. 3. Another system of the same kind that is treated in this dissertation is Cr/Fe (see Chapters 4, 5, and 6). The main reason for its importance lies in its magnetic properties, since it represents a model ferromagnetic/antiferromagnetic (F/AF) heterostructure. Magnetic properties were predicted theoretically for single atomic layers in the proximity of surfaces and interfaces (see, e.g., Refs. [45–47]). Experimental studies on such systems had been carried out since late 80’s, not just aimed at the confirmation of theoretical predictions, but also to the synthesis of materials with specific properties tailored for applications, for example in magnetic recording devices or sensors relying on the giant magnetoresistance effect [48–50]. The AF structure of bcc Cr can be described as a sequence of magnetically ordered Cr sheets each with a direction of polarization which is opposite with respect to the underlying layer (layered antiferromagnetism). This makes the Cr/Fe system an ideal model for the study of magnetism in thin films, as, in principle, it is possible to achieve the desired direction of magnetization on the top Cr layer, by controlling the thickness of the deposited Cr film.
on top of the Fe substrate.

One of the most important and pioneering works is represented by the paper by Unguris et al. [51], in which the spin polarization of secondary electrons was analyzed for the trilayer Fe/Cr/Fe, revealing the existence of two different oscillation periods (2 and 12 Cr ML, respectively) of the magnetization direction of the Fe upper layer with respect to the Fe substrate. The sample was in fact designed in such a way as to have a Cr wedge interlayer between the two Fe slabs: it was then possible to analyze several Cr thicknesses at a time during one measurement (see Fig. 1.5).

The main finding presented in the paper regards the observation of two different periods of oscillation of the Fe overlayer magnetization direction. As shown in Fig. 1.6, when Cr is grown at room temperature the magnetization direction of the Fe overlayer starts to oscillate (with respect to the substrate reference, see lower panel in Fig. 1.6) with a period which is approximately

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**Figure 1.4:** Set of spectra acquired with different photon energies and emission angles in a way as to keep $k_\parallel$ constant. Reprinted with permission from Plucinski et al., "Surface electronic structure of ferromagnetic Fe(001)", Physical Review B 80 184430 [42]. © 2009 by The American Physical Society.
equal to 10-12 Cr monolayers (ML). This kind of "long-period" oscillation was already known in the past, although not fully understood within the RKKY theory [52–54].

**Figure 1.5:** Schematic view of the sample structure with the Fe substrate, the Cr wedge and the Fe overlayer. The arrows indicate the direction of magnetization of each domain. Reprinted with permission from Unguris et al., "Observation of two different oscillation periods in the exchange coupling of Fe/Cr/Fe(100)", Physical Review B 67 140 [51]. © 1991 by The American Physical Society.

**Figure 1.6:** Image taken at the scanning electron microscope with polarization analysis showing the domains of the Fe substrate (lower panel), and of the Fe overlayer (top panel), in which the change in magnetization direction is well clear. The horizontal scale represents the thickness of the Cr wedge interlayer. Reprinted with permission from Unguris et al., "Observation of two different oscillation periods in the exchange coupling of Fe/Cr/Fe(100)", Physical Review B 67 140 [51]. © 1991 by The American Physical Society.
However, if Cr growth is performed at high (200°-300°C) temperature, the film quality increases, and a new period of oscillation of the AF stacking is retrieved, the so-called "short period". This time the magnetization direction of the top Fe layer switches every 2 Cr ML. The two different periods of oscillation are compared in Fig. 1.7.

Figure 1.7: Comparison between the two different period of oscillations for room temperature (lower panel) and high temperature (upper panel) grown samples. In the latter a shorter period is retrieved. Reprinted with permission from Unguris et al., "Observation of two different oscillation periods in the exchange coupling of Fe/Cr/Fe(100)", Physical Review B 67 140 [51]. © 1991 by The American Physical Society.

This result is the starting reference for the measurements presented in Ch. 6, where the spin polarization (and so the magnetization direction) is analyzed in photoemitted electrons. The advantage here is that PES is a chemical sensitive technique, so it has been possible to distinguish, even with some limitations due to the proximity of Cr and Fe 3d states in the valence band, contributions either from Fe or Cr in valence band spectra, attributing a magnetic behavior to a specific chemical species.

The same authors, indeed, also performed some measurements of the bare Cr wedge, before the top layer of Fe was deposited [55]. These are shown in Figs. 1.8a–1.8d.

An accurate determination of the Cr layer thickness was done by analyzing reflection of high energy electron diffraction (RHEED) intensity oscillations:
at each maximum of intensity of the graph shown in Fig. 1.8a corresponds the completion of a Cr monolayer. When high coverages are reached, the amplitude of the oscillations decreases, suggesting the formation of non-well ordered layers. The spin polarization of the Cr overlayer is reported in Fig. 1.8b. The starting value of the polarization is 29% and is relative to the Fe substrate; it decreases rapidly with increasing Cr coverage until the curve is dominated by the oscillations in the Cr polarization. If an exponential decrease is subtracted to the graph of Fig. 1.8b, it is possible to obtain the polarization of the Cr wedge alone, $P(\text{Cr})$. This is represented in Fig. 1.8c with the scale magnified by 4. In order to make a comparison between Cr and Fe behaviors, Fig. 1.8d shows the spin polarization $P(\text{Fe})$ of electrons coming from the Fe overlayer. Comparing graphs in Figs. 1.8c and 1.8d, it is possible to notice that the values of $P(\text{Fe})$ are opposite to those of $P(\text{Cr})$. This is in agreement with spin-polarized photoemission measurements [56], which found that the Cr interface layer is aligned antiparallel with respect to Fe, assuming that the Cr polarization direction does not change after the deposition of the Fe overlayer.
When the Cr deposition is performed at relatively high temperatures, however, the interface between the two chemical species experiences a strong intermixing. This can also be understood after careful analysis of Fig. 1.8c, in which the first oscillations are not well defined. In order to overcome such an issue, experiments on the Cr/Fe system presented hereafter were done with the addition of an oxygen monolayer initially chemisorbed on the Fe substrate. This layer acts as a surfactant for Cr growth, so that a sharp interface can be achieved even at high temperature growing conditions.

Before showing experimental results on the Ni/W(110) and Cr/Fe(100) systems, the following chapter will first show the main experimental techniques employed for the measurements shown hereafter, namelyphotoemission and absorption spectroscopy.
CHAPTER 2

Photoemission and absorption spectroscopies

IN THIS CHAPTER, the main experimental techniques that were used for the measurements of this dissertation will be described. The apparatus is described in detail as well, together with some remarks on the detection of spin polarization in photoemission experiments.

2.1 Photoemission spectroscopy

Photoemission spectroscopy (PES) is one of the main and most diffuse techniques which allows to investigate material surface composition and to gain information on the atomic orbitals and on the nature of the bondings that are formed (see Fig. 2.1). It is based on the photoelectric effect: a monochromatized photon beam impinges on the surface of the sample; the beam, after penetrating the material, transfers all or part of its energy to the electrons there. If the energetic transfer is high enough, some electrons will be able to escape.

the material with a kinetic energy that is characteristic of the element and of the specific atomic energy level. Not all the excited electrons can be emitted, since they can undergo inelastic collisions along their path, which make them lose energy: for this reason, PES provide us with a surface sensitive analysis, up to few nanometer thickness.

![Figure 2.1: XPS survey scan of a Ni sample. Peaks corresponding to different core level orbitals are highlighted, together with peaks due to Auger transitions.](image)

Once emitted, electrons have to be analyzed on the basis of the kinetic energy they possess in order to track down the binding energy they had inside the material. This is made possible by knowing the photon energy and the value of the analyzer work function following the scheme depicted in Fig. 2.2.

Sample and analyzer are put in electrical contact, so the Fermi level (E_F) is the same for both systems. The work functions (φ_S for the sample and φ_A for the analyzer) are the parameters which characterize the two materials. They represent the barriers to be overcome by the electron so that it can be effectively emitted and analyzed. E_{KS} and E_{KA} represent the kinetic energies possessed by the electron inside the sample and in the analyzer, respectively. Finally, E_B is the electron binding energy in the material, while ℏω is the impinging photon energy. Following the scheme in Fig. 2.2, it is simple to derive the relationship between photon energy and electron binding energy with respect to the Fermi level E_F = 0:

$$E_B = -(\hbar \omega - E_{KA} - \phi_A)$$  \hspace{1cm} (2.1)

It is then made possible to know the binding energy of the electron from the measurement of its kinetic energy and from the knowledge of photon energy.
and analyzer work function.

### 2.1.1 The photoemission process

The most accurate way for the description of the photoemission process lies in the so-called *one-step model*, in which the whole process of the electron from inside the solid to the analyzer is treated with a rigorous approach following the laws of quantum mechanics [58–60]. A simpler way to handle the description of the process is found in the *three-step model* [61]: the photoemission is treated in three independent steps which makes the understanding easier, but is not as accurate as the previous one. Within this model, the process is splitted in three parts:

**i.** The excitation of the electron from a bound state to a final one inside the material.

**ii.** Its propagation towards the surface.

**iii.** The crossing of the material/vacuum interface.

Within this model, the total probability of having an emitted electron is given by the product of the probabilities of each step cited above.
i. Excitation of the electron  The probability for exciting the electron is given by the Fermi golden rule and estimates the single-event current inside the material following this behavior (taking into account just direct transitions in which the wave vector \( k \) does not change is a good approximation since it is usually affected by minor changes in the process):

\[
I_{\text{int}}(E, \hbar \omega, k) \propto \sum_{f_i} m_{fi} f(E_i) \delta(E_f(k) - E_i(k) - \hbar \omega) \delta(E - E_f(k))
\]  

(2.2)

in which \( m_{fi} \) is the matrix element between initial and final state and \( E_{i,f} \) refers respectively to the energy of the initial and final states. The function \( f(E_i) \) gives the Fermi distribution. Note that the final state must have an energy \( E_f > E_{\text{vac}} \) greater than the vacuum energy of the material.

ii. Propagation towards the surface  The second probability to take into account is about the path travelled by the electron through the solid. Along its way, it is possible for it to undergo some inelastic events and lose information about its initial energy. This would contribute to the secondary background, that is always present in photoemission spectra. The probability for the particle to get to the surface without collisions is dependent on the inelastic mean free path (IMFP) \( \lambda \). Since \( \lambda \) depends, in turn, on the energy, this second step is described by the transport probability \( D(E, k) \) as

\[
D(E, k) \propto \lambda(E, k)
\]  

(2.3)

\( \lambda \) values are typically within the 0.5 nm to 20 nm range, and it is the reason for the high surface sensitivity of the technique.

iii. Crossing of the interface  Third and last step of the model regards the transmission from the solid towards vacuum. This transmission can be treated by imposing the electron wave function continuity in the material (Bloch wave) and inside the vacuum (free electron wave function). The parallel component of the wave vector must be conserved, so the two internal and external \( k_\parallel \) must either be equal, or differ by a generic reciprocal lattice vector \( G_\parallel \):

\[
k_\parallel^{\text{ext}} = k_\parallel^{\text{int}} + G_\parallel
\]  

(2.4)

According to Eq. 2.4, this third step contributes to the total photoemission current with the transmission rate

\[
T(E, k) \delta(k_\parallel^{\text{int}} + G_\parallel - k_\parallel^{\text{ext}})
\]  

(2.5)
2.2. Inverse photoemission spectroscopy

This section is dedicated to the description of basic principles of inverse photoemission spectroscopy (IPES) and it follows the same approach as used in Ref. [62].

The complete IPES process is schematically shown in Fig. 2.3. An electron beam with energy E is impinging on a solid surface. After this, the electron occupies an empty energy state in the conduction band of the sample and decays to a state at lower energy in a very short time. If the decay is radiative, an emitted photon can be detected, making it possible to analyze unoccupied states of the material.

\[
I^{\text{ext}}(E, \hbar \omega, \mathbf{k}^{\text{ext}}) \propto \sum_{\mathbf{k}} m_{\mathbf{k}} f(E_{\mathbf{k}}) \delta(E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar \omega) \delta(E - E_f(\mathbf{k}))
\times \delta(k^{\text{int}} + G_{||} - k^{\text{ext}}) D(E, \mathbf{k}) T(E, \mathbf{k}_{||})
\]  

(2.6)

2.2 Inverse photoemission spectroscopy

In the apparatus that will be described in Sec. 2.3, the detection of the emitted photons is performed in the isochromat mode, i.e. the energy of the detected
A photon $\hbar \omega$ is held constant, while the incoming electron energy is swept. By doing this, the obtained spectrum is a representation of the unoccupied density of states. Since IPES is, roughly speaking, the temporal inverse of PES (which leads to a projection of occupied states), the two kind of spectroscopy are somehow complementary and they offer a more comprehensive description of the electronic structure of solids.

In the following, a brief theoretical description of the process will be provided. The interaction Hamiltonian associated with the electromagnetic field employed in the description of the theoretical basis is given by:

$$H' = \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})$$  \hspace{1cm} (2.7)$$

where $\mathbf{A}$ is the vector potential and $\mathbf{p}$ the momentum. No inconsistency arises if $\mathbf{A}$ is treated in a classical way for the description of the standard photoemission process. However, for what IPES is concerned, one should have to deal with an excited electron system but no electromagnetic field before the radiative decay. In this case, we would have $H' = 0$, and vanishing transition probability. Here, the quantization of the field is necessary, so that spontaneous emission can be stimulated by its zero point motion. To treat the system in this way, the classical vector $\mathbf{A}$ is replaced by the operator $\hat{\mathbf{A}}(\mathbf{x}, t)$ defined by:

$$\hat{\mathbf{A}}(\mathbf{x}, t) = \frac{1}{\sqrt{V_p}} \sum_{\mathbf{q}} \sum_{\alpha} \frac{2\pi \hbar c}{\omega} (\hat{a}_{\mathbf{q},\alpha}(t) \hat{\epsilon}^\alpha e^{i \mathbf{q} \cdot \mathbf{x}} + \hat{a}^\dagger_{\mathbf{q},\alpha}(t) \hat{\epsilon}^\alpha e^{-i \mathbf{q} \cdot \mathbf{x}})$$  \hspace{1cm} (2.8)$$

where the symbol $\hat{\epsilon}^\alpha$ denotes the polarization vector, $\mathbf{q}$ is the photon propagation vector and $\hat{a}_{\mathbf{q},\alpha}$ and $\hat{a}^\dagger_{\mathbf{q},\alpha}$ are the operators for the annihilation and creation of a photon in the state $(\mathbf{q}, \alpha)$, respectively. The sum is done over all the possible polarization directions, indicated by the index $\alpha$. $V_p$ represents the normalization volume.

If we now consider a process with initial state $|n\rangle$ with $n$ electrons and no photons, and a final state $|n+1\rangle$ with $n+1$ electrons and one photon with wave vector $\mathbf{q}$, a cross section can be calculated

$$\frac{d\sigma}{d\Omega} = \alpha \frac{\omega}{2\pi mc^2 \hbar k} \frac{1}{|\langle n+1 | \hat{\epsilon} \cdot \mathbf{p} | n \rangle|^2}$$  \hspace{1cm} (2.9)$$

with $\alpha$ the fine structure constant.

If one makes the same assumptions and approximates the matrix element to be equal in PES and IPES, the calculated ratio between the two cross sections is then retrieved to be

$$r \equiv \left( \frac{d\sigma}{d\Omega} \right)_{\text{IPES}} \left( \frac{d\sigma}{d\Omega} \right)_{\text{PES}}^{-1} = \frac{\omega^2}{\alpha^2 \hbar k^2} = \left( \frac{\lambda_e}{\lambda_p} \right)^2$$  \hspace{1cm} (2.10)$$
with $\lambda_e$ the electron wavelength and $\lambda_p$ the photon one. This last result is the reason why IPES typical count rate is inherently low. For example, at an energy of 10 eV in the UV region, the ratio $r$ comes out to be about $10^{-5}$.

### 2.3 Experimental setup

In this section, the apparatus used for photoemission and inverse photoemission experiments is described in detail. It is made up of three ultra-high vacuum (UHV) chambers, interconnected with each other. One of them is dedicated to the preparation of the samples; the second one to the activation of the photocathodes used as spin-polarized electron sources in IPES experiments. The third one is the measurement chamber in which the PES and IPES experiments are performed. The whole apparatus is sketched in Fig. 2.4.

The preparation chamber is equipped with several facilities for the growth of samples in-situ and cleaning of surfaces. Growth is performed by molecular beam epitaxy (MBE), while deposition rate is checked with a quartz microbalance, so that film thickness can be precisely controlled. An Ar$^+$ ion gun is present and it is mainly used to remove contaminants from the sample surface. A low energy electron diffractometer (LEED) is used to check surface crystal structure on crystalline samples. The preparation chamber is also equipped with a gas inlet for oxygen exposure and a manipulator able to reach temperatures as high as about 800 K. When higher temperature annealings are required, the sample is put on a dedicated heating stage on which over 2000 K can be reached.

The second chamber is designed for the preparation of the spin-polarized electron sources. In fact, if the impinging electron beam in an IPES experiment has a defined spin polarization, the analysis of electronic levels above the Fermi edge can be provided with the additional information on the spin. Spin polarized electrons are emitted from GaAs crystals which underwent an activation process and are made in negative electron affinity. The activation will not be treated in detail here, but it is basically a procedure to cover the GaAs surface with a thin cesium oxide layer, which makes negative electron affinity possible. After the photocathodes are being activated, the switching between the two spin polarization is achieved by switching the direction of polarization of incident light, which has to be circularly polarized (see blue arrow in SP-IPES inset in Fig. 2.4). The idea is to exploit the splitting of the photocathode valence band near the $\Gamma$ point of the Brillouin zone (see Fig. 2.5).

The energy difference between the heavy-hole band (fourfold degeneracy), and light-hole one (twofold degeneracy) is of 0.34 eV. If a circularly polarized photon beam impinges on the GaAs crystal, the selection rules for optical
Figure 2.4: Schematics of the experimental setup. The facilities for SP-PES and SP-IPES are highlighted. In the SP-IPES inset (right-hand side), the GaAs photocathode is excited with circularly polarized light, denoted with a blue arrow. The insets and the main picture are rotated with respect to each other as can be seen from \((x, y)\) axes directions. Note that, when going from the IPES position to the PES one, the sample is rotated by 90° around the \(x\) direction: being in our scheme the \(y\) axis rigidly coupled to the sample, it undergoes a 90° rotation passing from IPES to PES. After Berti et al., "Direct observation of spin-resolved full and empty electron states in ferromagnetic surfaces", Review of Scientific Instruments 85 073901 [57]. © 2014 by AIP Publishing LLC.

transitions require \(\Delta m_j = +1\) for positive helicity \((\sigma^+)\) and \(\Delta m_j = -1\) for negative helicity \((\sigma^-)\). The excitation of electrons from the heavy-hole band alone results in a non-vanishing polarization, given the transition probabilities in Fig. 2.6. In particular, \(P = \pm 50\%\) with \(\sigma^\pm\) for \(P = (n^\uparrow - n^\downarrow)/(n^\uparrow + n^\downarrow)\) with \(n^\uparrow\) and \(n^\downarrow\) the number of carriers for the respective spin channel.

The third chamber is devoted to PES and IPES measurements, both with the addition of spin polarization (SP-PES and SP-IPES). Since a magnetic field is usually needed in such experiments, samples are magnetized by a current pulse sent to a coil surrounding it. The acquisition is done with zero applied field (magnetic remanence) to allow electrons to reach the analyzer, in PES, or the sample, in IPES [63]. This system is able to provide magnetic fields up to some 0.2 T, but for what concerns the work presented herein, much smaller
Figure 2.5: GaAs band structure near the Γ point of the Brillouin zone.

Figure 2.6: Transition probabilities from the valence to the conduction band for different $m_j$ values and light polarizations.

values are generally required, since ultra-thin films are often characterized by relatively low coercive fields. The external magnetic field can be applied along two perpendicular directions, namely, along the manipulator axis ($x$ axis in Fig. 2.4) and perpendicular to it ($y$ axis in Fig. 2.4).

The system for SP-IPES works in the isochromat mode as described in Sec. 2.2. The impinging electrons are controlled through an electron optics system
as fully described in Refs. [64, 65]. Control over the angle of incidence is
achieved by rotating the sample with respect to the electron source, so that an
angle-resolved analysis is made possible. The UV emitted photons are detected
by a bandpass detector discussed in Ref. [66]: briefly, the filtering is obtained
by the combination of a KBr coated photocathode (high-pass), and the use of a
CaF$_2$ window for the low-pass side.

Once raw data are retrieved (denoted with $N_{\uparrow}$ and $N_{\downarrow}$ for spin up and spin
down channels, respectively) they have to be normalized with respect to the
polarization of the incident electron beam $P_0$ [62]

$$n_{\uparrow,\downarrow} = \frac{1}{2} \left( 1 \pm \frac{A}{P_0} \right) \left( N_{\uparrow} + N_{\downarrow} \right) \quad (2.11)$$

in which $A$ is the asymmetry of counts

$$A = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} \quad (2.12)$$

As a remark, it must be noticed that the SP-IPES system described above is
sensitive to the spin polarization along the direction of polarization of the in-
coming electron beam. Since after the spin rotator (see inset of Fig. 2.4 and
Ref. [64]) the electron beam is polarized along the $x$ direction, this part of the
apparatus is only sensitive to this component of the sample magnetization.

In the same chamber also the SP-PES measurements take place. The above
cited electron analyzer is a 150 mm mean radius hemispherical electron an-
alyzer (HEA) [67]. Photoelectrons are excited in the core level region by X-ray
radiation coming from an X-ray tube with both Mg and Al anode sources (Mg $K_\alpha = 1253.6$ eV and Al $K_\alpha = 1486.6$ eV). Due to the range of radiation energy,
this kind of photoemission is called X-ray photoemission spectroscopy (XPS).
When valence band electrons are analyzed, a He discharge lamp is used, with
primary emission line in the UV range (He I = 21.2 eV) and, by consequence,
referred to as ultraviolet photoemission spectroscopy (UPS).

SP XPS and UPS spectra acquisition is made possible with a micro-Mott
polarimeter [68] based on the "Rice University" design [69], mounted after the
exit slits of the HEA. Part of the electrons at the exit side of the analyzer are
detected with six non-spin resolving channeltrons (three per side), while some
of them are fed through a 7 mm diameter aperture into a transfer acceleration
lens, and focused onto a Th target biased at 25 kV. This latter target is responsi-
ble for the spin information in SP-PES experiments: electrons scatter from this
target with a scattering direction that depends on their spin and, after deceler-
ating to nearly ground potential, they are detected by four channeltrons in the
Mott detector. These are positioned in such a way so that each pair determines one spin direction (see Fig. 2.4).

It can happen that some sort of asymmetry arises that is not of physical origin, but because each spin channel has a different sensitivity to incoming electrons. This results in the presence of the so-called instrumental asymmetries. This kind of artifact was avoided in the experiments presented in this work by acquiring spectra with two opposite directions of magnetization each time. Channeltrons 1 and 2 measure the polarization perpendicular to the axis of the manipulator, i.e., the $y$ axis of Fig. 2.4, while channeltrons 3 and 4 measure the parallel one ($x$ direction in Fig. 2.4). During each scan, four spectra (one for each channeltron) are acquired in parallel.

The two in-plane components of the polarization can be found by applying the formula [70]

$$P_{x,y} = \frac{1}{S_{\text{eff}} X_{x,y} + 1}$$

in which $S_{\text{eff}}$ is the value of the Shermann function of the detector, which is directly correlated to its figure of merit (FOM) as $\text{FOM} = \left(\frac{I}{I_0}\right)^2 S_{\text{eff}}^2$ with $I_0$ representing the incoming current and $I$ the scattered one. $X_{x,y}$ are found as

$$X_{x,y} = \frac{N_{3,1}^\uparrow N_{4,2}^\downarrow}{N_{3,1}^\downarrow N_{4,2}^\uparrow}$$

being $N$ the number of counts for the respective spin channel, and the arrows indicating the magnetization direction.

From the information on the polarization value it is possible to extrapolate the spin-polarized spectra normalized to the detector efficiency as [70]

$$I^\pm = \frac{I_M}{2} (1 \pm P)$$

where $I_M$ is the mean intensity of all the spectra (four respectively taken for each magnetization direction).

The SP-IPES system has been used by the group for several years and no further calibration was needed at this time. On the contrary, the SP-PES system was installed in the acquisition chamber only recently and a calibration procedure was needed. This had been done by analyzing a reference Fe/W(110) sample and by comparing with literature results [71].

The reference sample substrate is a tungsten single crystal W(110) which had been previously cleaned by cycles of 1500 K annealing in oxygen atmosphere and 2300 K very fast annealing (flash) in UHV. Iron was grown on top
of it by MBE, carefully keeping its thickness in the range 20 Å to 60 Å, so that the easy axis of magnetization would lie along the [110] direction. Sample was mounted on the sample holder in order to have this crystallographic direction along the axis of the manipulator. As Refs. [71, 72] report, in this case the photoemitted electron spin polarization should reach a plateau of about 80% at binding energies higher than 1 eV (see inset in Fig. 2.7). By adjusting the value of the polarization in this energy range, we can get the value of the Shermann function (S) characterizing our Mott detector.

The results indicate a value for S of 0.14, which is well within the range of the specifications for this kind of devices [69]. Normalized spin resolved spectra are then retrieved according to Eq. 2.15 [70, 73].

### 2.4 Substrate preparation and characterization

The experimental results discussed in the following chapters are mainly dealing with the characterization of ferromagnetic (F)/antiferromagnetic (AF) interfaces. As will be shown later, Cr and Cr oxide were chosen as the AF over-
layers, while the F substrate is typically an Fe crystal. The Cr/Fe interface is the most common system studied in this framework, in particular because of its original importance in the discovery of the giant magneto resistance effect [50,74] and, more in general, for its applications in spintronic devices [75].

While the coupling between the two materials will be analyzed in the following, here the characterization of the Fe substrate is shown.

Even if one might think that the best choice for the substrate would be an iron bulk crystal, the latter is typically very difficult to clean from contaminants when compared to films, because of the material high reactivity. An alternative route has been found on relatively thick Fe films grown by MBE on MgO(001) single crystals. When the thickness exceeds 300-400 nm, indeed, such a film presents the same electronic properties of the corresponding bulk. The advantage is found in the relative easiness in cleaning it; moreover, the coercive field is lower and the magnetic field required to remanently magnetize it decreases by consequence, with respect to that needed for bulk samples. Another characteristics of films is the modified shape anisotropy, which, in the case of Fe(001), makes the in-plane magnetization easier than that out-of-plane.

As just said, Fe is highly chemically reactive and a clean surface would "survive" only few hours, even if put in UHV. Since, generally, acquisition times for spin resolved photoemission experiments is quite large, this deterioration of the surface has to be avoided. In order to do this, a passivation procedure was carried out each time the substrate was prepared. This consists in the controlled chemisorption of an overlayer that protects the underlying material from oxidation and, more in general, contamination. In our case, moreover, the adsorbate may strongly influence the magnetism of the system, by enhancing the local magnetic moments and by inducing some magnetic moment in the overlayer itself [76, 77]. To our purpose, oxygen was employed: when deposited on the Fe(001) surface, it is known to show the chemical and magnetic advantages described above, while keeping the same surface symmetry. Namely, oxygen atoms occupy the fourfold hollow sites on top of the iron surface [78], forming the so-called Fe(001)-p(1×1)O surface. The Fe-p(1×1)O surface is obtained when the clean Fe(001) surface is exposed to 30 L (1 L = 10^{-6} Torr·s) of molecular oxygen being kept at 450 K; the procedure is then completed by a flash-annealing at 900 K [79–81].

The same research group studied in the past empty electron bands with the addition of spin polarization in IPES experiments [79, 82]. Anyway, for what concerns full energy levels, while several groups employed synchrotron radiation sources for SP-PES [42, 83], very little work has been done with UV discharge lamps, as in the case of this apparatus. Moreover, these latter studies were only performed on oxygen-free Fe(001) samples [84].
Fig. 2.8 shows the SP-PES and SP-IPES graphs for this passivated Fe surface. On the left-hand and right-hand side of the figure, spectra taken in the valence and conduction band regions are shown, respectively. In both cases, the sample has been previously magnetized along the $x$ or $y$ direction, with respect to the axis of the manipulator (see Fig. 2.4). In the former case (magnetic field applied along $x$) spin channels 3 and 4 show an asymmetry in the counts. When, instead, the applied field is parallel to the $y$ direction, asymmetry is visible from channels 1 and 2. Either the magnetic field is along $x$ or $y$, the sample is magnetized along its easy axis, since it lies along one of the equivalent in-plane ⟨100⟩ directions. After normalizing by the S function of the Mott detector, SP spectra show no qualitative differences (see left panel of Fig. 2.8).

Figure 2.8: Spin-polarized spectra taken close to the Fermi level on the Fe(001)-$p$(1×1)O sample. Up triangles represent majority spins, down triangles minority ones. For SP-IPES spectra a beam polarization of 27% was taken into account. SP-PES acquisitions were performed at a pass energy of 7 eV. The energy resolutions are 150 and 350 meV (HWHM, half width at half maximum) for the SP-PES and SP-IPES measurements, respectively. After Berti et al., “Direct observation of spin-resolved full and empty electron states in ferromagnetic surfaces”, Review of Scientific Instruments 85 073901 [57]. © 2014 by AIP Publishing LLC.

SP-IPES data are shown in the right panel of Fig. 2.8 again for the two magnetizations along $x$ and $y$. In the first case, a non-zero asymmetry is retrieved, as seen from the difference between spectra acquired for majority and minority electrons, in agreement with already published results [79]. When,
instead, the magnetic field is applied in the \( y \) direction and empty energy levels are observed, spectra still show the double peak structure related to exchange splitting between the majority and minority empty states in Fe [79], but in this case no polarization dependence can be seen: this is in agreement with what previously asserted about the polarization sensitivity of the SP-IPES system, which is just along one direction because of the only direction of polarization of the incoming electron beam [85] (see also SP-IPES inset in Fig. 2.4).

This concludes the photoemission characterization of the Fe(001)-\( p(1 \times 1) \)O surface, used as substrate in the experiments shown in the following chapters of this dissertation. Before showing the magnetic characterization of the AF/F system, a spin integrated XPS and UPS analysis will be presented in Chapter 4, to show growth and oxidation models.

The following section will, instead, report some basic principle about X-ray absorption spectroscopy and magnetic dichroism on which the results presented in Chapter 5 are based.

### 2.5 X-ray absorption spectroscopy and dichroism

Some basics about X-ray absorption techniques will be given in this Section, following de Groot and Kotani [86]. These notes will be useful when discussing results about the magnetic coupling of ultra-thin Cr oxide films on Fe-\( p(1 \times 1) \)O in Chapter 5.

#### 2.5.1 X-ray absorption spectroscopy (XAS)

In XAS, the absorption of X-rays by a sample is measured. Once a photon beam is directed towards a solid, it can be scattered or annihilated in the photoelectric effect. The latter case was described at the beginning of the Chapter with photoemission spectroscopy. All the remaining photons are transmitted through the sample and experience no changes in the direction of propagation. The intensity of the incoming beam (\( I_0 \)) and that of the transmitted one (\( I \)) are measured. The absorption edge is located at an energy equal to the binding energy of the corresponding core level. More precisely, the edge identifies transitions from the ground state to the lowest empty state.

While a PES spectrum is obtained by impinging with fixed photon energy and changing the detection energy of the outcoming electrons, XAS spectrum acquisition requires the tuning of the incoming photon energy. This is the reason why an absorption experiment can only be performed at synchrotron radiation sources, where high brilliance, tunable X-ray beams are available over a wide range of photon energies.
The probability for absorption of an X-ray is based on the selection rules, which determine that the dipole matrix element $M$ is different from zero if the orbital quantum number of the final state differs by 1 from the one of the initial state and the spin is conserved, or, in symbols, $\Delta L = \pm 1$ and $\Delta S = 0$. Within the dipole approximation, the XAS spectrum lineshape looks like the partial density of the $(\Delta L = \pm 1)$ empty states projected on the absorbing site, plus a convolution with a Lorentzian function. This Lorentzian broadening is a direct consequence of Heisenberg’s indetermination principle, which predicts an uncertainty in the energy ($\Delta E$) of the core hole due to its finite lifetime ($\Delta t$):

$$\Delta E \cdot \Delta t = \hbar$$

To understand the behavior of the transmitted intensity, let’s now consider an infinitely thin slice of the sample material, of thickness $d\ell$. The incident intensity $I_0$ is reduced by $dI$ on passing through $d\ell$. $dI$ is proportional to $d\ell$ and $dI$ is also proportional to the total intensity $I$, that is

$$dI = \mu I \cdot d\ell$$

where $\mu$ is a proportionality constant called the "linear absorption coefficient" and takes into account all the effects due to photoelectric and scattering events. Integrating Eq. 2.17 over the whole thickness gives the Lambert-Beer law ($\mu$ is expressed as a function of the X-ray energy, indicated with its frequency $\Omega$)

$$I_x(\Omega) = I_0(\Omega) \cdot \exp(-\mu(\Omega)x)$$

Transmission detection

As stated above, the intensity ($I_0$) of the incoming photon beam must be measured. This is usually done by letting it pass through a thin metallic grid just before impinging on the sample. The X-ray then interacts with the material and, when the acquisition is performed in transmission geometry, its intensity after the sample is evaluated by means of an ionization chamber or a photodiode. Transmission mode is the standard configuration for acquisition of absorption spectra in the hard X-ray range. This method is, however, unsuitable if the sample is not completely homogeneous, since any thickness variation can induce some effect on the spectrum lineshape, giving rise to the so-called nonlinear responses. This can be a severe drawback in extended X-ray absorption fine structure (EXAFS) analysis, where features are only slightly visible over the huge background signal. Another important limitation in the use of transmission mode might be the difficulty in growing samples on suitable substrates. In general, the combination of all these factors makes it possible to
employ transmission mode well above 1 keV photon energy. For soft X-rays, other detection modes, such as fluorescence or electron yield, must be used.

**Fluorescence yield**

The decay of the core hole gives rise to an avalanche of electrons, photons, and ions coming out of the sample surface. It is possible to measure the intensity of any of these, so as to bypass the problem of homogeneity coming from the bulk and measure samples of a wider range of thicknesses. One of the most used alternatives is the detection of the fluorescent decay of the core hole. It can be shown (Fig. 2.9) that the amount of X-ray yield increases with atomic number, Z, while the amount of Auger decay dominates for all elements below Z = 20.

![Auger/Fluorescence yield as a function of the Z number of the analyzed element.](https://commons.wikimedia.org/wiki/)
Electron yield

Another route for the measurement of absorption of X-rays by a sample is that of the total electron yield: all electrons at any energy coming from the sample surface are detected. Concerning the detection, there are several possibilities that may be employed, for example a pico-ampere meter catching the current flowing to the sample. Electrons’ interaction with matter is much stronger than that of photons, and, by consequence, the sample probing depth gets affected by this. Since electrons can travel in a solid for distances of the order of $3\times10^{-10}$ nm, particles that are to be detected must originate from a thickness very close to the surface, making this a surface sensitive technique (similarly to PES).

2.5.2 X-ray magnetic circular dichroism (XMCD)

![Figure 2.10: Sketch of an XMCD experiment, in which the spins align with respect to the applied magnetic field direction. The probability of absorption of a photon depends on light helicity and electron spin.](image)

Dichroism is a property some materials possess that makes them absorb X-rays with different yields depending on the polarization of impinging light. It is based on the different optical response of the sample on the relative orientation between the light polarization direction and the symmetry axes of the crystal. In particular, for what about the work presented in this dissertation, such a symmetry axis is given by the magnetization direction of the sample. With X-rays, in some cases, a difference can be observed between the absorption
of positive and negative helicity light (also called left- and right-circularly-polarized light) [X-ray magnetic circular dichroism (XMCD)] or for different orientations of the polarization vector of linearly-polarized light with respect to a given quantization axis [X-ray magnetic linear dichroism (XMLD)].

The definition of the sign of XMCD is the same as the one used by Baudelet et al. [87]. The quantization axis is the $+z$ direction, which is also the direction on which the wave vector of incident photons lies. The external magnetic field $B$ is applied in the $-z$ direction to align the magnetization of the material system (see Fig. 2.10). Positive helicity is intended with right circularly polarized X-rays; the XMCD spectrum $\Delta \sigma$ is then defined by

$$\Delta \sigma = \sigma^+(B) - \sigma^-(B)$$

(2.19)

where $\sigma^+$ ($\sigma^-$) is the XAS spectrum for the incident photon with $+$ ($-$) helicity.

An example of XMCD signal is shown in Fig. 2.11 for the $L_{2,3}$ edges of Fe.

![Figure 2.11: XAS spectra (red and black lines for clockwise and counterclockwise circularly polarized light, respectively) and retrieved XMCD signal (blue line) taken on the Fe(001)-p(1×1)O sample.](image)
CHAPTER 3

Growth of Ni thin films on W(110)

This chapter describes the characterization of the Ni/W(110) interface performed by means of PES, IPES and LEED. Thin nickel films grown on bcc metal single crystals, such as tungsten, represent paradigmatic systems to investigate the physico-chemical properties of magnetic films during the bcc-to-fcc phase transition. From a structural point of view, the latter can be characterized by precursor phases \cite{88}, intra-phases \cite{89}, dislocations \cite{90}, etc. during which the electronic and magnetic properties of the film change. Within specific thickness ranges of the bcc-to-fcc transition, Ni films display peculiar magnetic properties, such as perpendicular magnetic anisotropy \cite{91, 92}. As a paradigmatic case, here the Ni/W(110) system will be analyzed, which is characterized by almost no interdiffusion up to 400°C and an excellent lattice matching. In this system, the bcc-to-fcc transition proceeds through three distinct structural phases as a function of Ni coverage \cite{93}. A pseudomorphic bcc structure observed below 1 ML is followed by an intermediate phase showing a (7×1) surface reconstruction, which eventually evolves into a bulk-like fcc structure. The pseudomorphic Ni bcc phase in the submonolayer regime has particularly attracted the attention since either a paramagnetic or a ferromagnetic ground state is expected depending on the lattice constant \cite{94}. In
this Chapter, a systematic study of the evolution of the Ni/W(110) system as a function of the Ni layer thickness across the structural transition will be shown, from the pseudomorphic phase to the bulk-like film. In particular we focus on the film electronic structure by analyzing the evolution of both occupied and empty electron states by means of angle resolved PES and IPES (ARPES and ARIPES, respectively).

3.1 Experimental methods

All the experiments have been performed in the ultrahigh vacuum (UHV) system described in detail in Ch. 2. The W(110) single crystal (MaTecK GmbH) was cleaned according to standard procedures, which involve annealing in an O\textsubscript{2} atmosphere in order to desorb segregated carbon [95] and then heating at 2000 °C in UHV. LEED analysis showed sharp diffraction spots, suggesting a high crystal quality of the tungsten surface. The concentration of contaminant species was below the detection limits of the XPS apparatus.

Electron-beam heating was used to sublimate Ni from a high purity rod. The Ni deposition rate was previously calibrated using an oscillating quartz microbalance. The cited rate resulted to be of about 2.0 ML/min, 1 ML being a single atomic Ni layer, referred to the fcc (111) surface, with a thickness of 2.033 Å.

Following the literature [96, 97], we applied a two-step procedure for the Ni growth: i) the W crystal was kept at 300°C during the growth of the first Ni monolayer, in order to favor the Ni atom mobility on the substrate and hence to obtain a high quality monolayer; ii) the substrate was then kept at room temperature (RT) for further Ni depositions. After the growth, each sample was analyzed by LEED and XPS (Mg K\textsubscript{α} radiation, h\textnu = 1253.6 eV) at RT. Samples were magnetized in-situ by applying a pulsed magnetic field of 600 Oe along the [001] direction of the W substrate, which represents the easy axis of magnetization of the thin pseudomorphic Ni films, and analyzed at magnetic remanence, at RT. In order to improve the quality of the photoemission spectra, the spectroscopic analysis was performed on samples cooled down to 30 K. Photoemission spectroscopy (PES) was performed by exciting electrons out of the sample by HeI radiation (h\textnu = 21.2 eV) and detecting them by means of a 150 mm hemispherical analyzer (see Ch. 2), with angular resolution of ± 1°. Typical energy resolution (full width at half maximum) values are ± 25 meV and ± 350 meV for PES and IPES, respectively.
3.2 Ni film evolution

Although the general trend of the growth of ultrathin Ni layers on W(110) is well established (at least regarding the sequence of the different crystal structures involved), the specific procedure followed during the film preparation might influence the final spectroscopic results. This is due to the crucial role played by the surface stress (a parameter closely related to the sample preparation mode), as pointed out by Stojić [98] and Sander [99]. For this reason, here we present a systematic overview of the structure and the electronic states evolution in films of different thicknesses prepared in strictly the same conditions.

A LEED analysis of the film structural evolution is presented in Fig. 3.1. Starting from the clean tungsten crystal (Fig. 3.1a) up to 0.4 ML of Ni (Fig. 3.1b) the diffraction peaks show only a reduction of their intensities, suggesting a progressive covering of the substrate. The resulting 0.4 ML film structure is of high quality, as indicated by the sharpness of the LEED pattern. No evidence of extra spots is observed, as expected for a genuine pseudomorphic bcc growth. Instead, we could reproduce the LEED pattern of the first Ni layer grown at RT [95, 100] (not reported here), which is affected by a higher background intensity and the diffraction spots are larger and milky, hinting at a worst quality of the pseudomorphic Ni phase. Nevertheless, we have checked that the electronic properties of such lower quality crystal samples (grown at RT) are substantially comparable with those obtained for better quality films (1 ML grown at 300 °C as discussed in Sec. 3.1).

The Ni pseudomorphic (1×1) phase is observed up to a coverage of about 0.5 ML. Above this thickness, new extra-spots appear in the LEED pattern, indicating surface reconstruction, as it is clearly visible for a coverage of 0.8 ML (Fig. 3.1c). At this stage, four extra spots aligned along the [001] direction of the substrate and symmetrically placed in proximity of each spot of the original (1×1) pattern are visible. With the help of the intensity profiles shown in Fig. 3.1, we observe that the original peaks are weakened in intensity and that the separation \( z \) (see panel c) between the (-1,1) diffraction spot and the first-neighboring extra spot is about 1/7 of the full separation between the (-1,1) and the (1,1) spots, indicating the presence of a (7×1) surface reconstruction, as already reported [93]. Conversely, we did not observe any trace of the (8×1) reconstruction, previously reported, to our knowledge, only in the work of Schmidthals et al. [93].

When the Ni film thickness is further increased, the intensity of the (7×1) diffraction spots is progressively reduced and disappears at coverages above 2 ML, and eventually a sharp Ni(111) fcc diffraction pattern becomes visible (Fig. 3.1f). The Ni coverage range where the (7×1) phase is detected (i.e. from...
Figure 3.1: LEED pattern evolution during the progressive growth of the Ni film on W(110). a) clean W(110) crystal; b) 0.4 ML; c) 0.8 ML; d) 1.5 ML; e) 2.0 ML; f) 8.0 ML. The crystallographic directions for both the W(110) and the Ni(111) overlayer are reported in panels a and f, respectively. At the bottom of each image, the intensity profile along the straight dashed lines drawn over the LEED diffraction peaks is reported and compared with the intensity profile from the W(110) substrate (dotted line). The angular separation $z$ (panels c and d), between the (-1,1) diffraction peak and the first neighbour extra spot is $1/7$ of the full angular separation between the (-1,1) and (1,1) spots.
0.5 to 2 ML) is in good agreement with previous results [93, 101].

The evolution of the electronic structure of the Ni/W(110) films is presented in Fig. 3.2, which shows a direct comparison between PES and IPES results (acquired at normal emission and normal incidence, respectively) on the same sample kept at 30 K. Each selected Ni coverage, characteristic of a peculiar phase, can be related with the corresponding LEED analysis of Fig. 3.1. In Fig. 3.2a, the peak labeled A is the characteristic tungsten $d$-band feature, which is well visible only in thinner Ni film. At very small coverages, a Ni-related structure appears at about 700 meV. At the transition from the bcc layer to the $(7 \times 1)$ phase, the peak clearly splits (structure labeled B). This feature is related to the formation of a close-packed Ni layer [95]. At 1.5 ML, when the Ni film approaches the transition to the fcc phase, a shoulder (C) appears close to the Fermi level ($E_F$). The Ni 3$d$-band spectrum (D feature) is clearly observed only when a thicker (8 ML) film is grown.

In the IPES spectra (see Fig. 3.2b), we observe a progressive reduction of
the tungsten peak, labeled E, placed at 3.5 eV above \( E_F \), during the deposition of the very first Ni layers. It is interesting to note that the tungsten peak disappears for a Ni film thickness above 8 ML, when the Ni bulk fcc structure is stabilized. At this stage, a spectral feature (labeled F) characteristic of bulk Ni appears very close to \( E_F \), which is usually interpreted as a result of transitions to the uppermost minority \( d \) band \([102]\). In the region corresponding to the \((7 \times 1)\) reconstruction, a shoulder appears close to \( E_F \), which recalls the previously discussed Ni bulk peak. Interestingly, we observe that the spectral features corresponding to both filled and empty Ni states shift closer to \( E_F \) as the Ni coverage is increased. This evolution of the electronic bands is tentatively ascribed to a change in the surface strain of the reconstructed Ni film: as pointed out by Schmidthals and co-workers \([93]\), there is indeed a progressive but significant reduction of the surface tensile strain from the pseudomorphic bcc, to the \((7 \times 1)\) phase, and eventually to the final fcc structure.

### 3.3 Ultrathin films: martensitic transition to the fcc phase

In Fig. 3.3a, the 0.8 ML related sample has been studied at various electron emission/incidence polar angles: the rotation of the sample around the W[001] direction (refer to Fig. 3.1) allows to span the \( \Gamma - M \) direction of the Ni(111) surface Brillouin zone \([95]\), from \( k_\parallel = 0 \ \text{Å}^{-1} \) (normal emission) to about \( k_\parallel = 1.8 \ \text{Å}^{-1} \) (\( \Theta = 50^\circ \)). The main spectroscopic structure (labeled \( B_1 \) in Fig. 3.3a), placed at 0.77 eV, disappears for emission angles exceeding 10°. The Ni 3\( d\)-derived feature (\( B_2 \)) at 0.54 eV shows a dispersion towards higher BE with increasing angle of emission. At 10°, the \( B_2 \)-feature is characterized by a shoulder, placed at 450 meV below \( E_F \) marked by an arrow in Fig. 3.3, which evolves in the G structure clearly visible at higher angles, and which had already been observed in Refs. \([95, 96]\). The evolution of the empty states (Fig. 3.3, panel b) is characterized by a weak dispersion of both the W peak (labeled as E) and the characteristic Ni structure (F) towards higher energies and a progressive broadening of the line shape.

### 3.4 Bulk-like films

The 8 ML PES signal (Fig. 3.4) is compatible with previous photoemission data for thick Ni films or the (111) surface of bulk Ni measured at normal electron emission \([103, 104]\), confirming that at that coverage the bcc-fcc transition is completed. The measured band dispersion in the W [1\( \bar{T} 0 \)] direction is also in agreement with literature, where authors discuss the progressive approach of a sharp Ni peak (labeled H in Fig. 3.4a) to \( E_F \) for increasing polar angles up
Figure 3.3: a) ARPES and b) ARIPES spectra. The filled and empty electronic states of the Ni (7×1) phase (0.8 ML) sample are compared and plotted as a function of the polar angle Θ of rotation around the W[001] direction. The main spectroscopic features are labeled in the figure.

to 40° [104, 105]. The spectra from the empty states of the Ni thick film are reported in Fig. 3.4b as a function of Θ for a direct comparison with the PES results. Peak F, related to the Ni d-states, shows almost no dispersion while, starting from 20°, an additional shoulder (J) develops and shifts towards higher energies. This structure is related to the Ni sp-states, as reported in Ref. [106]. Interestingly, at Θ = 50° it is visible an additional feature (marked by an arrow) located at a BE of 200 meV (next to peak H). A similar double structure in bulk Ni(111), at normal emission and with a photon energy of 11.83 eV, was already observed in a pioneering work by Heimann and Neddermeyer [107]. There, the authors suggest that the double peak feature could be due to an exchange splitting of the bands of about 300 meV, even though they could not give a definitive proof of the spin polarized character of the states. Other authors studied in depth the exchange splitting effect for different Ni surfaces, as a
Figure 3.4: a) ARPES and b) ARIPES spectra. The filled and empty electronic states of the Ni fcc phase (8 ML) sample are compared and plotted as a function of the polar angle $\Theta$ relative to the [1 1 0] azimuth. The main spectroscopic features are labeled in the figure. The arrow marks a structure not clearly reported in previous studies in the literature.

function of the incident photon energy and sample temperature [104, 108–111].
Growth of thin Cr films on a passivated Fe substrate

This chapter describes the characterization of the Cr/Fe(001) interface performed by means of PES and LEED. Since this work was done to emphasize the differences in oxidations of Ni and Cr thin films on iron, some comments about the comparison will be given after reporting experimental data on Cr/Fe.*

4.1 Materials and methods

The experimental data shown in this section are related to 3 ML-thick Cr films, grown with the substrates kept at RT. The substrate was passivated by exposing it to a controlled flux of oxygen according to the procedure described in Chapter 2. The Cr/Fe-p(1×1)O samples were incrementally oxidized by flowing O$_2$ inside the chamber at a pressure of 10$^{-9}$ mbar for exposure up to 10 L and 10$^{-7}$ mbar for the highest exposures (up to 260 L). Since the crystal quality of the

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films was not good enough after these cycles of oxidation, samples were also annealed in-situ at increasing temperatures (up to 300° C) in steps of 50° C, for about 30 minutes each time. Samples were characterized by LEED, XPS and UPS, with the facilities described in Chapter 2. For what about the XPS, the Al anode was used and photoelectrons were collected at 25 eV pass energy, while for UPS electrons excited by He I line were collected at 0.5 eV pass energy. All the acquisitions were done with sample at RT. In the UPS section, some data about the sample work function are given. These were obtained by acquiring UPS spectra near the secondary electrons edge. A negative bias is needed in this case, as described in Ref. [113] so, during these measurements, a $-10$ V potential was applied to the sample.

### 4.2 X-ray photoemission analysis

XPS spectra corresponding to the Fe 2$p$ and Cr 2$p$ doublets were acquired at grazing emission with an angle of 60° from the surface normal. This arrangement allows for an enhancing of the surface sensitivity of the technique: in fact, being $\lambda$ the IMFP for the electrons traveling at a particular kinetic energy in a given material, the probing depth will be roughly equal to $\lambda$. If the sample is tilted with respect to the axis of the analyzer, according to the scheme in Fig. 4.1, photoelectrons that are collected are those emitted in a grazing direction. Since $\lambda$ does not depend on geometry, it will be the same for normal and grazing emission, but in the latter case the probed depth will result to be a projection of the electron path, namely $\lambda_{eq} = \lambda \cos \theta$.

In Fig. 4.2 Fe 2$p$ and Cr 2$p$ detailed scans are shown. Spectra labeled as A were measured on the as-grown 3 ML Cr/Fe(001)-p(1×1)O sample. Binding energy (BE) of the Cr 2$p_{3/2}$ peak lies at 574.5 eV, in agreement with what is found in previous works regarding metallic Cr [114, 115]. Spin-orbit splitting between the two Cr 2$p_{3/2}$ and Cr 2$p_{1/2}$ is 9.2 eV. Fe 2$p_{3/2}$ peak BE is found to be at 707.0 eV, as already reported in the literature for metallic Fe [116, 117]. Spin-orbit splitting is 13.1 eV, also in agreement with established values.

Spectra labeled as B and C (second and third rows in Fig. 4.2) were acquired respectively after O$_2$ exposure at RT and annealing at 300 °C. Finally, spectra labelled as D are those acquired after an additional annealing step at 300 °C in O$_2$ atmosphere.

In order to better understand the evolution of XPS signals, the line shape attributed to metallic components (as retrieved from spectra in A) has been subtracted to spectra B and C for Cr and D for Fe. The resulting difference spectra are attributed to oxidized species and are drawn as continuous lines in Fig. 4.2. The BE of the Cr 2$p_{3/2}$ peak in the difference spectra B and
4.2. X-ray photoemission analysis

Figure 4.1: Geometry of normal and grazing emission XPS experiments.

C is 576.9 eV, which corresponds to that reported in the literature for Cr$_2$O$_3$ [118]. Moreover, photoemission from oxide cations is also characterized by the presence of satellites on the high BE side of the main peaks. However, only the satellite peak related to Cr 2p$_{1/2}$ is visible, since the satellite related to the Cr 2p$_{3/2}$ peak is partially hidden by the overlap with the 2p$_{1/2}$ peak, resulting in a three-peak spectrum [118]. Spectrum D has the same lineshape of the difference spectra B and C: this means that no metallic Cr is left on the sample after the oxidation at high temperature (HT). There is, however, a slight shift in BE of about 0.2 eV in the Cr 2p$_{3/2}$ peak of spectrum D: this is well within the range of variation found in the literature [118], and might be due to a different position of E$_F$ inside the bandgap, that depends on the conditions in which the oxide layer is prepared. The small increase in the oxide-to-metal intensity ratio for Cr after the UHV annealing (spectrum C) is likely due to the partial dissolution of Cr at the interface with Fe at HT [153]. Fe seems to remain always metallic (spectra from A to C), except for the last HT annealing step in O$_2$, after which the substrate starts to oxidize. In this last case, the Fe 2p doublet can be decomposed in a metallic contribution, similar to that of the previous steps, and an oxidized one, characterized by a 2p$_{3/2}$ peak located at 709.7 eV (feature $c$ in the right panel of Fig. 4.2) and its corresponding satellite (feature $d$), 6 eV above. These values are typical of Fe in its 2+ valence state [120], thus suggesting that a FeO layer is forming at the interface.
Figure 4.2: XPS scans of the Fe 2p and Cr 2p regions of 3 ML Cr/Fe(001). A) as grown, B) exposed to 160 L of O₂ at RT, C) annealed at 300 °C for 90 min. in UHV and D) exposed to 10 L of O₂ at 300 °C (partial pressure 3 × 10⁻⁶ mbar). Continuous lines are difference spectra obtained by subtracting the A spectra (dashed lines in spectra B and C) from the experimental data. Spectra are normalized to the intensity of photoemission from metallic species (when present). After Calloni et al., "Electron spectroscopy investigation of the oxidation of ultra-thin films of Ni and Cr on Fe(001)", Journal of Physics: Condensed Matter 26 445001 [112]. © 2014 by IOP Publishing Ltd.

4.2.1 XPS intensity ratios

It is possible to give an estimation of the evolution of oxidized species during the different oxidation steps by computing the area subtended to the corresponding peak (metal or oxide). This evolution is shown in the graph of Fig. 4.3.

XPS intensity coming from oxidized Cr reaches saturation quickly, at about 10 L exposure. After each treatment, the intensity from metallic Cr and Fe decreases (data not shown) because of the top oxide layer, which gets thicker with both oxidation and annealing. This result can exclude the thermal dewet-
4.2. X-ray photoemission analysis

Figure 4.3: XPS intensities from the 3 ML Cr/Fe sample, as a function of the oxygen exposure and of the annealing treatments. The size of the data points is approximately equal to the uncertainty associated with intensity estimation. Overlapping signals are shown as slightly shifted on the vertical axis (appearing as partially overlapped) in order to show them all. After Calloni et al., "Electron spectroscopy investigation of the oxidation of ultra-thin films of Ni and Cr on Fe(001)", Journal of Physics: Condensed Matter 26 445001 [112]. © 2014 by IOP Publishing Ltd.

According to row D of spectra in Fig. 4.2, no metallic Cr is left on the sample after the annealing step in O$_2$ atmosphere, and some part of the Fe substrate gets oxidized (2+ valence, see Sec. 4.2). If we combine this information
with the fact that, as observed from Fig. 4.3, the O-to-Fe oxide ratio is smaller at grazing than at normal emission, it is possible to conclude that Fe$^{2+}$ ions are accumulating in the oxide layer close to the surface, mixing up with Cr oxide. This might indicate the formation of a ternary spinel oxide phase dispersed into the Cr$_2$O$_3$ overlayer, such as chromite (FeCr$_2$O$_4$). This would also be consistent with the observation of both Fe$^{2+}$ and Cr$^{3+}$ ions.

An estimation of the oxide layer thickness after the RT oxidation can be obtained by applying Eq. 4.1

$$d_o = \lambda_o \cos(\vartheta) \ln \left( \frac{N_m \lambda_m}{N_o \lambda_o} \frac{I_o}{\alpha I_m} + 1 \right)$$

where $d_o$ is the thickness of the Cr oxide layer, $N_m$ and $N_o$ are the atomic densities of the Cr atoms in the metallic and in the oxide layer, respectively.$^\dagger$ $\lambda_m$ and $\lambda_o$ are the IMFPs of Fe 2$p$ photoelectrons in the substrate and in the oxide, respectively [122]. $\vartheta$ is the emission angle with respect to the surface normal (0° and 60° at normal and grazing emission, see also the scheme in Fig. 4.1). The intensity ratio between the metallic and the oxide component ($I_m/I_o$) is computed based on our quantitative XPS analysis, as shown above. The correction factor $\alpha$ is given by $\alpha = 1/\{1 - \exp[-d_m/(\cos(\vartheta) \lambda_m)]\}$ The oxide thickness $d_o$ is obtained iteratively, starting from a guess of the actual thickness $d_m$ of the metallic layer. After several iterations, a thickness $d_m = 2.5 \pm 0.6$ Å for the metal layer and $d_o = 3.6 \pm 1.0$ Å for the oxide one are retrieved, meaning that only little more than 1 ML of metallic Cr has been converted into Cr oxide before the annealing steps.

### 4.3 UV photoemission analysis

The analysis of the valence band of this sample was performed by UPS, acquired after each oxidation and annealing step, as described in the previous section. Together with the spectra of the Fermi edge region, some were also acquired near the secondary electron threshold in order to gather information about the work function and its changes with respect to the substrate.

In Fig. 4.4 UPS spectra are shown relative to the 3 ML Cr/Fe-\(p(1\times1)\)O sample. In the first spectrum, the main features are highlighted and labelled with letters from $a$ to $d$: $a$ and $b$ are characteristic of the Cr-\(p(1\times1)\)O surface and come from Cr 3$d$ orbitals, as well as peak $c$. On the other hand, peak labelled $d$ is due to photoemission from O 2$p$ orbitals [123]. When the sample undergoes an oxygen exposure higher than 10 L, the valence band spectrum

$^\dagger$The whole analysis was performed employing the atomic density for $\alpha$-Cr$_2$O$_3$, but the use of the density for $\gamma$-Cr$_2$O$_3$ gives slight modifications, all within the uncertainty of the estimation.
4.3. UV photoemission analysis

Figure 4.4: UPS valence band of 3 ML Cr/Fe-p(1×1)O. From the top: as-grown, incrementally oxidized at RT, annealed in UHV at 300 °C and exposed to 10 L of O₂ at 300 °C. Features at about 0.15 eV (a), 0.7 eV (b), 1.8 eV (c) and 5.7 eV (d) are highlighted in the as-grown spectrum. The Cr 3d (at 2.6 eV) and O 2p (at 5 eV) emission regions for Cr₂O₃ are indicated in the bottom spectrum. After Calloni et al., "Electron spectroscopy investigation of the oxidation of ultra-thin films of Ni and Cr on Fe(001)", Journal of Physics: Condensed Matter 26 445001 [112]. © 2014 by IOP Publishing Ltd.

lineshape evolves towards that of α-Cr₂O₃ as already found in Ref. [124]. Nevertheless, a closer inspection of Fig. 4.4 reveals that all the spectra shown there, except for the one relative to the annealing in O₂ atmosphere, present a non-zero density of states near the Fermi edge, which is typical of metals. This means that either the Cr oxide overlayer thickness is quite small, or that it is not homogeneously covering the Cr top layer surface. Density of states at E_F vanishes only after the O₂ annealing (last spectrum). As shown in the previous section, this treatment makes the Cr overlayer completely oxidized, beside converting also part of the iron in the substrate into Fe³⁺. The corresponding UPS spectrum, however, does not show any feature that can be attributed to FeO, so one might conclude that Cr oxide is lying on the surface, completely covering Fe even after this final step, and that the Fe oxide which is formed remains at the interface between the two chemical species.

Fig. 4.5 is a graphical representation of the changes of the sample work
function after each treatment, with the Fe-\(p(1\times1)O\) substrate taken as a reference with \(\phi_{Fe-p(1\times1)O} = 4.46\) eV, as already shown by Cattoni et al. [125]. As a result of the deposition of 3 ML of Cr on this surface, the sample work function has a decrease of about \(\Delta\phi = -0.86\) eV. The first \(O_2\) exposure treatments set the \(\Delta\phi\) value very close to zero (0.04 eV), kept throughout the following oxidations, in agreement with the literature [126]. Finally, the two annealings in UHV and \(O_2\) respectively decrease the work function to \(\Delta\phi = -0.56\) eV value and subsequently increase it again due to oxygen absorption.

### 4.4 LEED analysis

A selection of LEED pictures is shown in Fig. 4.6 for the Cr/Fe sample. From left to right, the patterns are related to the 3 ML Cr/Fe-\(p(1\times1)O\) as grown surface, the same surface after exposure to 160 L \(O_2\) at RT, and the sample after the HT annealing in \(O_2\) controlled atmosphere, respectively. In all three of them, the pattern is square with a lattice parameter equal to that of the Fe substrate. The only observable difference is the lower contrast of the second and third images. Resuming what was said in Sec. 4.2, XPS results indicate the formation of a Cr oxide due to oxidation, namely \(Cr_2O_3\). The corundum \(\alpha-Cr_2O_3\) phase, however, is characterized by an \(hcp\) crystal structure, which would not match the LEED results. This might be explained if another arrangement of atoms in the Cr oxide is considered: the \(\gamma-Cr_2O_3\) defective spinel structure possesses the same stoichiometry of \(\alpha-Cr_2O_3\), and, moreover, was already shown to form during the very first stages of Cr(001) oxidation (as pointed out by Watari et al. [127]). It is then reasonable to expect to observe it also in the present study,
being their valence structures very similar to each other [128]. In the case of formation of a \( \gamma \)-Cr\(_2\)O\(_3\) overlayer, there would be no discrepancies with the LEED patterns reported in Fig. 4.6. Most important point of this LEED analysis is that a pattern, although less sharp than the first one, is always visible, even after the whole Cr layer oxidized. This is in contrast with previous works on the same topic [129], in which no pattern was present at all. The reason for this may be sought in the presence of the oxygen ordered monolayer on top of the Fe substrate acting as a surfactant and promoting the formation of an ordered Cr oxide phase.

4.5 Conclusions

The experiment just described highlights the peculiarity of thin Cr films to protect the underlying Fe substrate, which is highly reactive towards oxygen exposure. For example, in Ref. [112] a complete comparison is reported between Cr and Ni thin films, showing that, in the case of Ni, this protection does not take place and, as a consequence of oxygen exposure, Ni atoms tend to be buried, promoting Fe ions segregation towards the surface, so forming a Fe oxide overlayer on top of metallic Ni. The comparison is summarized in Fig. 4.7.

Even at very low (2 L) oxygen exposures, in the Ni/Fe sample both Ni and Fe oxide species formed, with Fe oxidation always preceding Ni one. This latter process is in agreement with the higher absolute value of the heat of formation for Fe-oxide than Ni-oxide \((-265\) kcal/mol for Fe\(_3\)O\(_4\) and \(-57\) kcal/mol).
Figure 4.7: Schematic representation of the layered structure formed. In the second picture of panel a), the presence of Ni atoms after the UHV annealing is represented by a thin layer with sharp interfaces, without considering a possible diffusion into the Fe substrate. After Calloni et al., "Electron spectroscopy investigation of the oxidation of ultra-thin films of Ni and Cr on Fe(001)", Journal of Physics: Condensed Matter 26 445001 [112]. © 2014 by IOP Publishing Ltd.

for NiO [130]). In the case of Fe-Ni alloys, the literature reports on Fe segregation, with Fe₃O₄ or a mixed NiFe spinel stabilized, depending on the Ni concentration [131]. Fig. 4.7a reports the schematic composition of the 3 ML Ni/Fe sample after a 300 °C annealing. At this temperature, the diffusion of Ni atoms towards the Fe substrate takes place, resulting in a stable 100% Fe-based oxide overlayer.

In the case of Cr described in this Chapter, the initial oxidation concludes with the formation of a ML-range oxide layer (Fig. 4.7b). It is possible to tune the thickness of the grown Cr oxide by changing the substrate temperature during exposure, obtaining a stable Cr₂O₃ overlayer. Nevertheless, after the final high-temperature oxidation step, the presence of a small quantity of Fe ions dispersed in the oxide layer was detected, as shown in the right part of Fig. 4.7b.

In the following Chapters, the magnetic properties of such Cr ultra-thin films are analyzed by means of absorption of circularly polarized light and photoemission with spin polarization.
CHAPTER 5

Magnetism of ultra-thin Cr films on Fe(001)-p(1×1)O

This chapter contains the magnetic characterization of Cr films deposited on Fe(001)-p(1×1)O with thicknesses in the monolayer regime. Namely, the magnetic coupling with the substrate is analyzed in detail by means of X-ray magnetic circular dichroism (XMCD) in absorption. When in the submonolayer regime, Cr atoms rearrange on the Fe-p(1×1)O surface showing different patterns depending on the coverage. This microscopy study [132], performed by scanning tunneling microscopy (STM), will be briefly resumed in the first part of this Chapter.*

5.1 Experimental methods

Fe(001)-p(1×1)O surfaces were prepared by depositing Fe on an MgO single crystal by MBE, and then by exposing to oxygen, as thoroughly described in Chapter 2. This served as a substrate for the experiment discussed hereafter.

Cr films were grown by MBE as well, at a typical rate of 0.1 ML per minute, as checked by a quartz microbalance. When not specified, growth of Cr was performed with the substrate kept at about 700 K. The samples were characterized, from the morphological point of view, by STM and LEED, while XMCD was used for the magnetic characterization. XAS and XMCD data were acquired at the beamline BACH of the Elettra synchrotron radiation facility [134]. XAS spectra were obtained in total electron yield mode (see Ch. 2) and were normalized to the incident photon flux. The energy resolution was set at about 80 meV at the Cr edges and 130 meV at the Fe edges, respectively. The samples were magnetized at RT, prior to the XAS/XMCD measurements, along one of the equivalent in plane Fe ⟨001⟩ easy axes, by means of a permanent magnet brought in close proximity to the sample. All spectra were acquired in magnetic remanence and at RT. The angle between the incoming photon beam and the sample surface was 20° in order to enhance the dichroic effects. Possible contaminations of the sample were ruled out by XPS, while LEED was used to control the surface crystal structure.

5.2 Self-organized Cr oxide monolayers

Low coverages (< 0.1 ML) At this initial stage of Cr growth, STM images just show a random distribution of protrusions [see left panel of Fig. 5.1]. It is known that the Fe(001)-p(1×1)O surface is very flat with very few defects [135], so these features must be attributed to the presence of Cr. At this step, LEED patterns [Fig. 5.1, right panel] are those typical of a p(1×1) superstructure. It is important to underline that usually, at RT, the adatoms are observed to be highly mobile, so, in this present case, a blocking mechanism inhibits Cr atoms diffusion on the top layer of the substrate, in a similar way to that mentioned in Ref. [153], where Cr was instead deposited on the oxygen-free Fe surface. However, a previous experiment performed by the group with the same technique [137] gave no evidence for oxygen to influence the Cr layer mass transport.

Intermediate coverages (0.4–0.75 ML) When reaching 0.4 ML coverage, some zones of the sample surface get covered with a c(4×2) reconstruction of Cr atoms. At this level, it is visible only on certain areas, and the diffraction pattern, as seen by LEED, is very faint. This kind of reconstruction is well visible when 0.75 ML of Cr are deposited: here the surface is completely covered by an ordered Cr layer with a c(4×2) periodicity [see left-hand side of Fig. 5.2]. This peculiar reconstruction, which is basically due to the ordering of the
5.2. Self-organized Cr oxide monolayers

Figure 5.1: Left: atomically resolved STM image after deposition of 0.1 ML of Cr on Fe(100)-p(1×1)O (I = 5 nA, V = 100 mV). Right: corresponding LEED pattern (electron beam energy E = 100 eV). Reprinted with permission from Picone et al., “Self-organized chromium oxide monolayers on Fe(001)”, Physical Review B 87 085403 [132]. © 2013 by The American Physical Society.

Cr vacancies in the Cr overlayer, is also seen with sharp spots in LEED pattern (Fig. 5.2, right panel).

Figure 5.2: Left: atomically resolved STM image after deposition of 0.75 ML of Cr on Fe(100)-p(1×1)O (I = 5 nA, V = 100 mV). Right: corresponding LEED pattern (electron beam energy E = 100 eV). Reprinted with permission from Picone et al., “Self-organized chromium oxide monolayers on Fe(001)”, Physical Review B 87 085403 [132]. © 2013 by The American Physical Society.

Higher coverages (> 0.75 ML)  If just 0.05 ML of Cr is added to the surface described above (so, reaching 0.8 ML in total), the structure undergoes a phase transition towards a ($\sqrt{5} \times \sqrt{5}$)R27° reconstruction, for which STM and LEED measurements are shown in Fig. 5.3. Both phases c(4×2) and ($\sqrt{5} \times \sqrt{5}$)R27° exist in long range order. Both are characterized by two equivalent domains oriented at 90° with respect to each other, due to the fourfold symmetry of the substrate.

It has been already proven in Ref. [136], that the ($\sqrt{5} \times \sqrt{5}$)R27° super-
Figure 5.3: Left: atomically resolved STM image after deposition of 0.8 ML of Cr on Fe(100)-p(1×1)O (I = 5 nA, V = 100 mV). Right: corresponding LEED pattern (electron beam energy E = 100 eV). Reprinted with permission from Picone et al., "Self-organized chromium oxide monolayers on Fe(001)", Physical Review B 87 085403 [132]. © 2013 by The American Physical Society.

The structure is stabilized on the oxygen covered Cr(001) surface even when exceeding 1 ML of Cr. However, it has also been shown in Ref. [137] that, for higher coverages, the growth proceeds with the formation of pyramid-shaped islands, so the surface is less flat, and LEED and STM gave no clear results. On the other hand, the c(4×2) phase was observed for the first time in Ref. [132] for Cr deposited on the oxygen-covered Fe surface.

These self-assembled monolayers are actually oxidized, since oxygen covering the Fe substrate floats on top of the surface, binding no more to Fe atoms, but to the Cr atoms in the overlayer. This was proven by Auger electron spectroscopy (AES, [132]): indeed, when comparing spectra related to the pristine Fe surface with the oxygen passivated one, a peak at a lower kinetic energy than the main one arises, attributed to oxidized species. After the deposition of Cr, the AES lineshape for Fe resembles that of the initial one (oxygen-free), while O intensity is unchanged before and after the growth (see Fig. 5.4). This proves that the tendency of oxygen atoms is to migrate towards the surface, breaking the bonds with Fe and creating a monolayer-thick Cr oxide with stoichiometry Cr₃O₄ and Cr₄O₅ for c(4×2) and (√5 × √5)R27°, respectively.

5.3 X-ray absorption and dichroism results on ultra-thin Cr films

Fig. 2.11 in Ch. 2 reports XAS profiles of the L₂,₃ Fe absorption edges for the Fe(001)-p(1×1)O substrate. There are shown two absorption spectra relative to opposite light polarizations. Considering the frame of reference of the incoming photon beam direction, σ⁺ represents positive and σ⁻ negative photon helicity, respectively. The XMCD signal is retrieved as the difference
between the two, as explained in Chapter 2. Both XAS and XMCD lineshapes are found to be in good agreement with literature results taken on magnetized oxygen-free Fe(001) samples [138, 139]. In particular, the $L_2$ peak is located at a photon energy of about 722.8 eV, while $L_3$ is at about 709.9 eV, with a spin-orbit separation of 12.9 eV. The corresponding XMCD profile shows a negative peak in correspondence with the $L_3$ edge and a positive one at the $L_2$ edge; this will be taken as a reference for retrieving information about the relative magnetization between the substrate and the Cr oxide on top of the surface.

Figures 5.5, 5.6, and 5.7 present Cr $L_{2,3}$ XAS and XMCD spectra, for Cr films grown on Fe(001)-$p$(1×1)O at high temperature, for the coverages corresponding to the surface reconstructions shown in previous Section. Each of
them is labeled by the relative LEED pattern. In particular, Fig. 5.5 reports on a 0.25 ML Cr oxide layer showing the \( p(1 \times 1) \) pattern (see "Low coverages" above); Fig. 5.6 reports the 0.75 ML Cr oxide case, with a \( c(4 \times 2) \) surface reconstruction (see paragraph "Intermediate coverages"); Fig. 5.7, finally, shows the 0.8 ML Cr oxide case, which is characterized by a \( (\sqrt{5} \times \sqrt{5})R27^\circ \) symmetry (see "Higher coverages").

The center of gravity of the \( L_2 \) and \( L_3 \) Cr absorption edges are located at 587.3 eV and 578.8 eV photon energy for the 0.25 ML case, at 587.0 eV and 578.4 eV for the 0.75 ML case, and at 587.4 eV and 578.9 eV for the 0.80 ML case (with a spin-orbit separation of about 8.5 eV for all cases), as shown in Figs. 5.5–5.7, respectively. No particular difference is observed between these results and the literature \[140\], where, however, different Cr oxides are analyzed. On the other hand, a single Cr oxide layer with the stoichiometries relative to the reconstructions described above has never been reported before. All the peaks appear to be splitted, as expected from ligand field atomic multiplet calculations related to Cr compounds (see Sec. 5.3.1 below) \[140–142\]. Concerning the XMCD profiles, all three cases present a positive peak cor-

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**Figure 5.5:** XAS spectra and XMCD profile for the 0.25 ML Cr sample with LEED pattern \( p(1 \times 1) \). After Brambilla et al., "Magnetic properties of monolayer range chromium oxides on Fe(001)", Journal of Applied Physics 114 123905 [133]. © 2013 by AIP Publishing LLC.
Figure 5.6: XAS spectra and XMCD profile for the 0.75 ML Cr sample characterized by a c(4×2) surface reconstruction. After Brambilla et al., "Magnetic properties of monolayer range chromium oxides on Fe(001)", Journal of Applied Physics 114 123905 [133]. © 2013 by AIP Publishing LLC.

responding to the L₃ edge and a negative one at the L₂ edge. This indicates that a long-range ferromagnetic order is established and makes it clear that the Cr oxide overlayer is coupling antiferromagnetically to the underlying Fe(001) substrate, since its XMCD signal has opposite sign with respect to that of Fe. It is worth noticing that the XMCD intensity in the ( √ 5 × √ 5 )R27° case appears to be lower than in the c(4×2) one. An explanation for such a behavior could be sought in the examination of the intensity of the relative XMCD peaks at the Fe edges for each Cr oxide coverage. Indeed, such intensity was sensibly lower than that of the reference, a likely indication that the substrate broke into domains, perhaps as a consequence of the magnetization procedure, which was not easily reproducible.

5.3.1 Analysis of XAS and XMCD profiles

For what concerns the multiplet profiles of the XAS spectra, they contain information about the state of oxidation of metallic elements [140]. Fig. 5.8 makes a comparison between the lineshapes of L₃ Cr absorption edges (taken
Figure 5.7: XAS spectra and XMCD profile for the 0.80 ML Cr sample characterized by a $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface reconstruction. After Brambilla et al., "Magnetic properties of monolayer range chromium oxides on Fe(001)", Journal of Applied Physics 114 123905 [133]. © 2013 by AIP Publishing LLC.

as the sum of $\sigma^+$ and $\sigma^-$) for samples relative to the three different coverages discussed in this Chapter. In all of them, three features are visible, and are labeled with capital letters A, B, and C in Fig. 5.8. All the $L_3$ lineshapes nicely resemble that of Cr oxide, in particular CrO$_2$, as shown in Ref. [142]. Despite they look very similar to each other, the relative weight of all three features is different in each case.

It seems clear from Fig. 5.8 that, if the spectra are normalized to feature C, as in this case, a decreasing of the relative weight of peaks A and B is observed with increasing Cr coverage. Nevertheless, these changes cannot be ascribed to a modification in the valence state of Cr atoms going from Cr$^{2+}$ in the $p(1\times1)$ case, to Cr$^{2.5+}$ in the $(\sqrt{5} \times \sqrt{5})R27^\circ$ case (for which the stoichiometry should be Cr$_4$O$_5$), passing through the Cr$^{2.7+}$ state of $c(4\times2)$ reconstruction, with formal stoichiometry Cr$_3$O$_4$ [132]. Moreover, it is important to highlight that XMCD main peak positions, marked by dashed lines in Figs. 5.5, 5.6 and 5.7 lie in correspondence of feature A in the integrated XAS spectra of Fig. 5.8, at a photon energy of about 577.4 eV.
5.3. X-ray absorption and dichroism results on ultra-thin Cr films

Figure 5.8: XAS spectra at the $L_3$ edge of 0.25 ML, 0.75 ML, and 0.8 ML Cr films grown at 400°C. All spectra were normalized to feature C. The dashed vertical lines indicate the position of the XMCD main peak. After Brambilla et al., "Magnetic properties of monolayer range chromium oxides on Fe(001)", Journal of Applied Physics 114 123905 [133]. © 2013 by AIP Publishing LLC.

5.3.2 XMCD sum rules

It is possible to gain some quantitative information about the magnetic moments of the system by applying the so-called sum rules to XAS spectra and XMCD signals. Based on the subtended integral area, such rules give a useful tool to evaluate orbital and spin magnetic moments with sensitivity to the chemical element. The complete theoretical description is given in Ref. [143]; here we just refer to the rules for the orbital and spin magnetic moments, $m_O$ and $m_S$, respectively (given in units of Bohr magnetons, $\mu_B$)

$$\frac{m_O}{\mu_B} = -\frac{4q}{3r} N_{eff}$$

(5.1)

where $q$ is the integral of the XMCD signal over the $L_3 + L_2$ edges, while $r$ represents the integral over the same edges on the XAS spectrum (for $\sigma^+ + \pi$...
\( \sigma^- \). \( N_{\text{eff}} \) is the number of holes in the 3\( d \) orbitals, and is estimated depending on the formal stoichiometry of the system.

The rule for the spin magnetic moment, \( m_S \), is (again in \( \mu_B \) units)

\[
\frac{m_S}{\mu_B} = -\frac{6p - 4q}{r} N_{\text{eff}}
\]

(5.2)

in which, beside the parameters described for the previous rule, \( p \) is the integral of the XMCD over the L\(_3\) edge alone. The three relevant parameters \( p, q, \) and \( r \) are graphically shown in Fig. 5.9.

Figure 5.9: Graphical representation of the \( p, q, \) and \( r \) parameters used when applying XMCD sum rules for the calculation of spin and orbital magnetic moments. Light grey lines represent XAS (left) and XMCD (right) spectra, while dark grey lines represent the integral of the corresponding signal.

It is well known that such rules are reliable for the estimation of spin and orbital magnetic moments in heavy transition metals such as Co, Ni, and Fe [143]. However, in the case of lighter transition metals, such as Cr, further caution needs to be addressed in their application. In particular, for what concerns \( m_S \), where the integral \( p \) is evaluated, the retrieved values must be treated carefully. Due to the relatively small spin-orbit coupling and to the fact that the absorption process at the L edge is characterized by a quantum mechanical superposition of excitations from the \( 2p_{1/2} \) and \( 2p_{3/2} \) spin-orbit split states [144–146], the L\(_2\) and L\(_3\) edges are consequently partially overlapped, and this number is usually an underestimation of the actual value, so affecting the calculated value of the magnetic moment.
Furthermore, the case of low-dimensional systems, such as this, is even more complicated due to the reduced symmetry, and the limit case of two-dimensional oxides has not yet been made all clear [147]. By taking into account these two reasons, the application of sum rules in the present case should hardly be considered, at least as far as no theoretical study is made to support the results. However, since the Cr/Fe system had been greatly studied in the past because of its model character as AF/F heterostructure, it is possible to find pieces of literature entirely devoted in the development of analysis approaches and correction factors to be applied in order to get quantitative information from sum rules even in this limit case of monolayer Cr oxides [148–151]. It must be noted, anyway, that a large variability in the reported results is found, so for the analysis of these results the work by Ghirri et al. [151] will be chosen as a reference, due to the greatest similarity with our one.

A series of measurements acquired after having deposited Cr with the substrate at RT (not shown here), gave the biggest value for $m_S$ (approximately equal to \(-1.7 \mu B\)) if a number of 3$d$ holes equal to 6 is considered (on account of the formal 2+ valence state of Cr observed in this situation), and a correction factor of 1.75 is applied to the calculated value. The orbital magnetic moment is substantially quenched. The value for $m_S$ is very similar to that reported in Ref. [149] of \(-1.8 \mu B\) obtained with SP-PES on monolayer-range oxygen-free Cr/Fe interfaces. The sample on which this value was retrieved did actually exceed 1 ML of Cr thickness, so it might be possible that the initial formation of the second Cr layer could decrease the absolute measured value due to the antiparallel alignment of spins. By considering also this possibility, the likely actual value of $m_S$ in this former case could be close to \(-3 \mu B\). Moving now to the HT grown samples, some previous theoretical calculations performed on the same system gave a similar value of about \(-3 \mu B\) [132]. However, as already mentioned in this Chapter (see Sec. 5.3), the samples grown at HT appeared to be broken into domains, and the application of sum rules gave values for the spin magnetic moments of at most 65% of that reported for the RT case discussed above.
IN THIS CHAPTER the oscillation of polarization values of thin Cr films on top of Fe(001)-p(1×1)O are analyzed. Samples were grown in a similar way as those described in the previous chapter, so that surface reconstructions could be visible at LEED during the first stages.*

As already shown before in this dissertation, spins in Cr(001) films arrange in a way as to form ferromagnetic sheets each aligned antiferromagnetically with respect to the layer below [133]. In an ideal situation with a non-defective and abrupt interface, this should happen starting from the very first layer. Furthermore, theoretical predictions suggest that the first Cr layer at the interface would lie with opposite magnetization with respect to the Fe substrate. However, what is usually reported in the literature is that this AF stacking begins with a certain delay of about 5 Cr ML, mainly due to the intermixing between Cr and Fe at the interface. This is mostly found when Cr growth is performed at high temperature on the pristine Fe surface [153].

What will be shown in this chapter is that, if the surface of the substrate gets previously oxygen-passivated, the oxygen monolayer promotes the formation of a sharp interface and, since it floats on the top surface the more Cr is deposited, it leaves the Cr/Fe interface oxygen-free. The experimental demonstration is given by means of spin integrated and spin polarized PES.

6.1 Experimental methods

After the preparation of the Fe(001)-p(1×1)O substrates on the MgO single crystal, the procedure followed for the growth of Cr films was similar to that described in Ch. 5, with incremental depositions performed with the substrate kept at high temperature to allow for atom reorganization. The samples were then cooled down and photoemission spectra were acquired at magnetic remanence and at RT.

6.2 Spin-integrated photoemission analysis

When inspecting valence band (VB) states, peaks related to features attributed to different chemical elements may not be enough separated from each other to allow for an element-dependent analysis. This is what happens in this case, in which Cr and Fe states are partially superimposed and a clear attribution to each chemical species is very hard [56, 154]. However, it is necessary to highlight the contribution coming from Cr atoms in order to extrapolate information about the magnetism of the overlayer. To this purpose, a first spin-integrated study was carried out on VB spectra for incremental Cr coverage, whose results are reported in Fig. 6.1. By analyzing such results, some features characteristic of either Cr or Fe are observed, and they are marked in the figure with letters from \( a \) to \( e \). Even though another element is present in the sample, namely oxygen, its contribution to VB spectra is known to lie at BE above 4 eV, and it is not comprised in Fig. 6.1. Peaks \( a \) and \( b \) represent the contribution of Fe(001)-p(1×1)O. The former, \( a \), is associated to bulk Fe 3\( d \) states with both majority and minority spin characters [57, 76]. The latter (\( b \)), instead, is attributed to surface states from the Fe substrate [76]. For what about Cr, features \( c \), \( d \), and \( e \) are visible in the spectra: peak \( c \) has its BE at 0.15 eV BE and, as already reported in the literature, comes from both metallic and oxidized Cr 3\( d \) states [123, 155]. On the other hand, the last ones, \( d \) (at about 0.6 eV BE) and \( e \) (at about 1.6 eV BE), are only characteristic of oxidized Cr surfaces [123, 156]. Both of them seem to depend on Cr thickness, as their intensity gets larger with increasing coverage. However, in the choice for a VB state derived from Cr for the spin-dependent analysis, it looks that \( e \) would be the best one, since it is
6.3. Spin-resolved photoemission analysis

Figure 6.1: Spin-integrated VB spectra taken at a pass energy of 0.5 eV on the Fe(100)-p(1×1)O substrate and on the Cr/Fe(100)-p(1×1)O system for increasing Cr coverage. He I source satellites were subtracted in all cases. Lowercase letters and dashed vertical lines mark the position of relevant features. After Berti et al., "Oxygen-induced immediate onset of the antiferromagnetic stacking in thin Cr films on Fe(001)", Applied Physics Letters 106 162408 [152]. © 2015 by AIP Publishing LLC.

visible even for the lowest Cr coverages: see, for example, the 1 ML Cr spectrum of Fig. 6.1. This last peak will be then the reference one to investigate the spin polarization of the Cr layer.
Chapter 6. AF stacking in thin Cr films on Fe(001)-p(1×1)O

Figure 6.2: Spin-resolved VB spectra (Maj = majority; Min = minority spin channel) taken at a pass energy of 7 eV on (a) the Fe(100)-p(1×1)O substrate and on the Cr/Fe(100)-p(1×1)O system for (b) 1 ML and (c) 3.9 ML Cr thickness. He I source satellites were subtracted in all cases. The arrows mark the position of the Cr-derived feature at 1.6 eV BE (feature e in Fig.6.1). After Berti et al., "Oxygen-induced immediate onset of the antiferromagnetic stacking in thin Cr films on Fe(001)", Applied Physics Letters 106 162408 [152]. © 2015 by AIP Publishing LLC.
6.3 Spin-resolved photoemission analysis

After the inspection of spin-resolved spectra, the choice of feature as a reference is confirmed, since the spin polarization is well visible there. Fig. 6.2 reports three example of SP-PES spectra taken on the Fe(001)-p(1×1)O substrate (Fig. 6.2a), on the 1 ML Cr sample (Fig. 6.2b), and on the 3.9 ML Cr one (Fig. 6.2c). Spectra reported in the first panel relative to Fe(001)-p(1×1)O were already shown in Ch. 2 and serve as a reference for the determination of the majority or minority spin character of that particular state, depending on the direction of the applied magnetic field. The analysis of spin-resolved spectra in Figs. 6.2b and 6.2c reveals that the Cr-derived feature at 1.6 eV BE (ε in Fig. 6.1) lies entirely in the minority electron band in Fig. 6.2b (1 ML) and in the majority one in Fig. 6.2c (almost 4 ML). This is a confirmation that the chosen feature is spin-polarized, and its relative spin orientation is of minority kind for 1 ML Cr thickness and of majority kind for 3.9 ML Cr thickness. This indicates, as also observed in the previous chapter, that the Cr film is characterized by a long range magnetic order with the magnetization direction depending on its thickness. In particular, results shown in Fig. 6.2b prove that the first Cr layer (that is actually a monolayer Cr oxide because of the floating oxygen coming from the Fe(001)-p(1×1)O substrate) is magnetized along the surface plane, with direction of magnetization lying anti-parallel with respect to that of the Fe substrate (see Ch. 5 and Ref. [133]).

The parameter to rely on when estimating the average direction of the magnetic moments in the Cr layers is the polarization (P), which is retrieved in this case through the formula

\[ P(1.6 \text{ eV}) = \frac{I^+ - I^-}{I^+ + I^-} \]  

(6.1)

where \( I^+ \) and \( I^- \) are the intensities of the SP-PES spectra at 1.6 eV BE, for the majority and minority electrons, respectively. The measured values of \( P \) are plotted as a function of the Cr coverage in Fig. 6.3.

The polarization for the starting Fe(001)-p(1×1)O substrate is about 45%, then, after the deposition of the first sub-monolayer coverages, \( P \) decreases, until a minimum at 1 ML Cr. After this, an increasing is observed, up to a new maximum at about 2 ML; the expected oscillation is then established, with maxima and minima at each complete Cr ML. In the framework of ideal layer-by-layer growth and AF stacking, \( P \) values at each coverage are given by the combination of the contribution of the substrate (attenuated from the overlayer) and the deposited Cr layers. Based on this very simple model, one might expect that at 3 Cr ML \( P \) becomes negative and starts oscillating around zero.
In this case, at the completion of the first Cr layer, $P$ gets very close to 0%, meaning that the polarization of a single Cr layer gives a contribution which is enough to balance the attenuated one from the Fe below. At reaching the second complete Cr layer, the maximum in the polarization is observed to be at about 25%. However, the experimental points coming after that do not change sign, in contrast with the above described model for the layered AF stacking of bulk Cr(001). Beside this, the oscillations relative to Cr coverages greater than 2 ML, although having the correct phase and periodicity, appear to be much damped and not centered around 0%. Such differences can be ascribed, first of all, to the contribution coming from a spin-polarized inelastic background in the same energy region of the spectrum from which $P$ is extrapolated. In order to avoid taking into account the effect of such a background and to uncouple

Figure 6.3: Polarization $P$ at 1.6 eV BE, as a function of the Cr coverage. The line is a guide to the eye. Adapted from Berti et al., "Oxygen-induced immediate onset of the antiferromagnetic stacking in thin Cr films on Fe(001)", Applied Physics Letters 106 162408 [152]. © 2015 by AIP Publishing LLC.
the eventual AF stacking of the Cr layers alone, the expected value of the polarization at each integer \((i)\) ML coverage was estimated with the interpolating continuous red line in Fig. 6.3. In order to rule out the polarization contribution coming from the inelastic background, an estimation of the polarization given by each \(i\)-th Cr layer, defined as \(\Delta I^\pm(i)\), is given by the subtraction between each SP-PES majority and minority spectrum related to the \(i\) ML coverage, \(I^\pm(i)\), and that corresponding to the \((i - 1)\) ML coverage, \(I^\pm(i - 1)\), this latter attenuated by the exponential decay through the \(i\)-th layer. This gives:

\[
\Delta I^\pm(i) = I^\pm(i) - I^\pm(i - 1)e^{-d/\lambda}
\]

where \(d = 1.44\ \text{Å}\) is the thickness of one equivalent Cr ML and an inelastic mean free path (IMFP) \(\lambda = 4.5\ \text{Å}\) has been used, in analogy with Refs. [55,56].

![Figure 6.4: \(P'\) at 1.6 eV BE for difference spectra \(\Delta I^\pm(i)\). Adapted from Berti et al., "Oxygen-induced immediate onset of the antiferromagnetic stacking in thin Cr films on Fe(001)", Applied Physics Letters 106 162408 [152]. © 2015 by AIP Publishing LLC.](image)

The open red dots in Fig. 6.4 represent the polarization \(P'\) obtained for each \(\Delta I^\pm(i)\), up to \(i = 6\) ML. In analogy with \(P\), this is defined as

\[
P'(1.6\ \text{eV}) = \frac{\Delta I^+ - \Delta I^-}{\Delta I^+ + \Delta I^-}
\]

The dashed red line shows, on the basis of the results obtained for integer coverages, the expected behavior of \(P'\) for non integer Cr coverages: for a fractional \((i + f)\) coverage \((0 < f < 1)\), the difference spectrum is given by
the linear combination†

\[
\Delta I^\pm (i + f)_{\text{retr}} = (1 - f) \Delta I^\pm (i) + f \Delta I^\pm (i + 1)
\]  (6.4)

This has to be put in comparison with the experimental determination of \(P'\) for \(\Delta I^\pm (i + f)_{\text{exp}}\), represented by black dots in the figure, obtained, for each \((i + f)\) ML data point of Fig. 6.3, by substituting the experimental majority and minority spectra \(I^\pm (i + f)\) to \((1 - f)I^\pm (i) + fI^\pm (i + 1)\) in the expression of \(\Delta I^\pm (i + f)_{\text{retr}}\).

Even if within this very simple model the influence of subsequent Cr layers is neglected when estimating the magnetization of a single layer, by looking at the result of this simplified analysis, Fig. 6.4 shows the alternating sign of \(P'\) as theoretically expected for the AF stacking in Cr, although the oscillations look asymmetric because of the shift towards positive values of \(P'\), which makes minima to be closer to zero than the corresponding maxima. This behavior could be explained considering that, apart from the first Cr oxide layer which grows in quite a flat and ordered fashion, pyramid-shaped islands appear in correspondence with screw dislocations in the substrate when exceeding 1 ML Cr, these becoming well visible at 5 ML Cr coverage and above [137]. On one side, these particular Cr islands let more than one layer to be exposed to vacuum, while, on the other, the underlying dislocations might cause some spin frustration within the Cr layers. Both considerations can be used to justify the experimentally observed damping in the AF oscillations. More deviations from the ideal behavior can be ascribed to the spin dependence of the IMFP [157, 158]. Despite all these phenomena that make the experimental results behave differently from what expected, Fig. 6.3 clearly shows the AF stacking to start from the first Cr layer grown on Fe(001)-\(p(1 \times 1)\)O.

In conclusion, what had been found with this experiment is that, when growing Cr on Fe(100)-\(p(1 \times 1)\)O substrates kept at 700 K, the chemical intermixing is avoided, since the oscillations in polarization are observed starting from the first Cr layer, while this does not happen when performing the high temperature growth on oxygen-free Fe(100) substrates. In this latter case, the chemical intermixing makes the first 2-3 Cr layers not to contribute to the magnetism of the system, which results in delayed AF stacking. In the oxygen-passivated case, instead, a sharp interface is stabilized between the two chemical species Cr and Fe and, by consequence, the magnetic contribution to the overall system starts from the first Cr layers. Finally, some attention should be

†The deviations from a linear behavior of \(P'\) between subsequent integer coverages are due to slight variations of the mean intensity \((I^+ + I^-)/2\) in the SP-PES profiles for different \(i\) values
paid to the possible role of oxygen in enhancing the strength of the AF ordering of the Cr film, which sums up to the clear effect just described.
Concluding remarks

The main topic of this dissertation is the study of transition metal and transition metal oxide surfaces by means of photoemission and absorption spectroscopies.

The apparatus for SP-PES and IPES described in Ch. 2 is an upgrade of a system in which it was possible to perform just IPES with spin polarization (and only at room temperature). With the addition of a Mott detector in the PES for the analysis of spin polarization even in occupied states, and of a liquid He cryostat, the apparatus makes it now possible to study full and empty electron states in-situ, also with spin resolution. A brand-new topic which is attracting much attention in the field of spintronics is spin transport and dynamics in heavy metals with large spin-orbit interaction. In particular, the structural inversion asymmetry causes large Rashba splittings in single layer heavy metals (such as Bi or Tl) grown at the top of semiconductor surfaces with the $C_{3v}$ symmetry (e.g. Si and Ge), thus giving the possibility of having spin-polarized surface electron bands without the application of magnetic fields. The system described in Ch. 2 ("Photoemission and absorption spectroscopies") had already been employed in some preliminary measurements of this kind, showing that the Rashba parameter, which governs the removal of the spin degeneracy
around the M point of the Bi Brillouin zone, is greatly enhanced with respect to the Bi(111) surface one, evidencing that the spin-orbit coupling of heavy metals may be strongly increased by the symmetry of the semiconductor surface.

After the description of the apparatus, two systems have been characterized, namely Ni/W(110) and, more extensively, Cr/Fe(100)-p(1×1)O.

Experimental results regarding the former revealed the presence of a martensitic transition from bcc to fcc, which Ni undergoes when its thickness is progressively increased. The transition has been mapped with LEED patterns [passing through the (7×1) reconstruction] and with PES and IPES spectra for different Ni coverages, highlighting the evolution of different features in valence and conduction bands, also with angle resolution.

The second system, Cr/Fe(100)-p(1×1)O, was analyzed more in detail by means of several techniques. After showing the effect of post oxidation, which basically does not affect the underlying Fe substrate, apart from when performed at very high temperatures and oxygen exposure, the main focus was set on the magnetic properties of this sample, given its great importance in the discovery of the giant magnetoresistance effect.

The submonolayer film morphology had previously been studied by scanning tunneling microscopy, and the peculiar surface reconstructions obtained for high temperature growth were reported here for completeness. It is found that between 0.4 and 0.75 Cr ML, surface atoms arrange in a c(4×2) symmetry, while for higher coverages the surface reconstruction is \((\sqrt{5} \times \sqrt{5})R27^\circ\). The same reconstructions were analyzed by means of XMCD, nicely evidencing the antiferromagnetic coupling of the first Cr layer on the Fe substrate.

When higher Cr coverages are achieved, the polarization analysis in photoemission spectra points out the AF stacking expected for such films starting right from the Cr/Fe interface, ruling out the possible presence of chemical intermixing, which, on the contrary, is known to happen for Cr films grown on the pristine Fe(100) surface at the same temperatures.
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