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Electronic and Magnetic Properties
of Impurities and Clusters on Metal Surfaces

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Chapter 1

Introduction

This thesis describes the electronic and magnetic properties of the diluted impurities of transition metal atoms deposited on the surface of different substrates. The localized character of the impurity states due to the reduced coordination strongly influences the magnetism and the magnetic anisotropy of the impurities.

The properties of lodestone powder are known from a deep past, although a first historical evidence of a magnetic device is often referred to have been reported by the Chinese author Wu Ching Tsung Yao in 1040 B.C. (see J. Needham [1]) who described a floating fish-shaped water suspended compass, see figure 1.1.

This has probably been the first magnetic device of the history of science

![Image of water floating fish-shaped Chinese compass](image-url)

*Figure 1.1: Water floating fish-shaped Chinese compass [1].*

and technology. It exploits the same magnetic properties of materials to be used in magnetic devices: the existence of magnetic moments, the fact
CHAPTER 1. INTRODUCTION

that they are coupled together by the exchange interaction, and the magnetic anisotropy of the material, that blocks the magnetic moments along a preferential direction. The effects of the reduction of the coordination and dimensionality on the magnetic properties are of scientific and technological interest and systems of reduced dimensions are studied. This path starts from bulk metals and ends at the level of single atoms.

Van Vleck was the first to point out, in his investigations on the microscopic origin of the magnetic anisotropy [2], that the magnetocrystalline anisotropy could be due to the spin-orbit coupling, paving the way to all recent theoretical and experimental studies. The role of reduced symmetry and dimensionality in enhancing orbital and spin moments, as well as the magnetic anisotropy was first suggested by Néel [3].

The electronic and magnetic properties, i.e. the magnetic moments and the magnetic anisotropy of transition metal (TM), single atoms and impurities (few atoms) on metal surfaces are the subject of this thesis. The interaction of the transition metal atoms with the substrate is crucial and it has been studied choosing systems with a different degree of interaction. The theoretical basis needed to explain the experimental evidences of peculiar electronic and magnetic properties of transition metal impurities in simple metals hosts were introduced by Friedel [4], Anderson [5] and Kondo [6].

From the experimental point of view, in the last 20 years, the preparation of clean surface systems became possible and the refinement of x-ray absorption and photoemission spectroscopies strongly enhanced the knowledge of systems of reduced dimensions, as thin films, surfaces and nanostructures. In particular, in the field of magnetism, the development of dichroic absorption spectroscopies like X-ray Magnetic Circular Dichroism (XMCD) and X-ray Magnetic Linear Dichroism (XMLD) gave the possibility to probe, with element selectivity, the orbital and the spin magnetism. These techniques have been used in the study of magnetic multilayers, thin films and surfaces. At the moment XMCD is the only experimental technique capable of measuring such extremely diluted impurities, probing the electronic structure locally with element selectivity and evaluating both spin and orbital magnetic moments. This technique is a recent experimental improvement that has been applied for the first time to extremely diluted surface impurity systems by Gambardella and co-workers [7].

Mn and V, impurities have weak interactions with alkali metals substrates like Na, K, Cs. An extensive research has been conducted, including comparisons with other substrates as the Cu(100) and Al(100) surfaces for which the impurities have more intense interactions. Co single atoms on Cu(100) and on Pt(111) have been studied as well as Fe single atoms on Cu(100) surface. In this thesis the electronic properties of these systems have been studied using X-ray Absorption Spectroscopy (XAS) while the the magnetic properties have been studied with X-ray Magnetic Circular Dichroism, and magnetization curves, in high magnetic fields and at liquid helium temper-
atures.
The XMCD and XMLD techniques are discussed by means of their application to the study of the angular distribution of magnetic moments in ultra thin films of manganese (approx. 1 ML) deposited on a Fe thick films. By a combined use of XMCD and XMLD, the Mn moments are found to align along a non collinear direction tilted by respect to the surface normal and perpendicular to the Fe magnetization direction.

For Mn impurities on alkali metals surface, both from the analysis of the spectral lineshape and the magnetization curves, it is found that the Mn has a clear d⁵ atomic-like configuration with a spin magnetic moment of about 5 μB. Increasing the electronic density of the host, i.e. going from Cs to Al(100) the manganese atoms undergo a progressive weakening of the atomic-like configuration and magnetic moment. On Al(100) Mn shows to have a small but not negligible magnetic moment, in contrast to the case of Mn impurities diluted in bulk Al.

Vanadium has a more complex electronic structure, with no simple atomic-like configuration even if the spectra show clear atomic-like multiplets. It has weak orbital moments, coupled antiparallelly to the spin, with decreasing size as the interaction with the substrate is increased. The data have been compared to theoretical multiplet structure calculations performed by S.S. Gupta and D.D. Sharma (unpublished results) simulating weak crystal field effects and an alternative mechanism for the reduction of the orbital moment is proposed. Configuration mixing as well as Van Vleck paramagnetism is also considered.

Mn, V, Fe, Co and Ni impurities on Cu(100) have been studied. Mn impurities due to its particularly stable electronic configuration show multiplet structures related to the d⁵ half filled shell atomic configuration, while the stronger hybridization with the substrate increases the width of the states and weakly reduces the magnetic moment. V instead undergoes much more intense hybridization effects that suppress almost all the multiplet structures that were present on alkali metals. The dichroism is very weak as a consequence of hybridization that strongly reduces the magnetic moments. Fe single atoms on Cu(100) have a rather small magnetic moment if compared to Fe on alkali metals, but strongly increased with respect to Fe thin films on Cu. Moreover they show a large magnetic anisotropy energy of 1.5 meV/atom. A completely different scenario is there for Co single atoms on the Cu(100) surface, in fact no magnetism and hence nonmagnetic anisotropy is found. This result, at first sight surprising, is consistent with a non magnetic Kondo state recently reported from Scanning Tunneling Spectroscopy measurements.

An important result of this thesis activity, is the evidence that Co single atoms deposited on the surface of Pt(111) have the highest magnetic anisotropy energy per atoms found up to now for any magnetic system: 9.2 meV/atom [8]. This large value, compared to bulk iron and thin films, is
explained as being due to a combined effect of the reduction of symmetry at the surface and the reduction of the coordination in the case of single Co atoms. This promotes the enhancement of orbital moment of Cobalt. Co adatoms polarize magnetically the Pt surface atoms, thus inducing a magnetic moment in the Pt. Through its large spin-orbit platinum contributes to the magnetic anisotropy of the system. The overall effect is the strong enhancement of the magnetic anisotropy energy.
Chapter 2

Magnetism of transition metal atoms and impurities

The aim of this chapter is to give a brief outline of basic concepts in magnetism of impurities and itinerant ferromagnets, needed to understand the experimental results presented in the thesis. The first section introduces the atomic magnetism and then the Anderson impurity model for the magnetism of localized moments. It further develops to include the Kondo system and the connection between Kondo physics and magnetism. Finally it introduces the Stoner-Hubbard model needed to describe the magnetism of itinerant ferromagnets. The second section gives an overview of the magnetic anisotropy, its origins and related properties.

2.1 Atomic Magnetism and solid state effects

The localized and the delocalized electron pictures of the magnetism are here introduced with the aim to provide the necessary framework to the subject.\(^1\)

The physical aspects to understand about the interaction between an impurity and the host are many: the level of localization of electronic valence states, the influence of the broken symmetry at the surface on the electronic properties and the strength of the interaction with the host. Moreover of interest are also the effects of crystal fields on the electronic configuration. The most important aspects that will be discussed in this thesis are the appearance of localized magnetic moment, their magnitude and the magnetic anisotropy. Another very important aspect is the effect of the change of atomic coordination on the magnetism. Moreover many materials properties change as a function of the coordination, starting from bulk systems, to

\(^1\)A more complete and detailed discussion can be found in classical books as [9], [10] and [11].
thin films systems, going to unidimensional chains systems and further on to trimer, dimers down to single atoms properties.

2.1.1 Atomic magnetism

The impurities systems that are the subject of the thesis can be described, thanks to the localized character of their electronic states, by atomic models. So it is natural to describe the physics of these systems starting from and atomic picture. The atomic Hamiltonian terms define the symmetry of the states and their energy splitting. Moreover also the description of the interaction between radiation and atoms is essentially based on atomic properties. The atomic Hamiltonian of an $N$-electron system, is described within the restriction of one-electron operators and can be thought as the sum of several term:

$$H = H_{\text{kin}} + H_{e-\text{nuclei}} + H_{e-e} + H_{\text{SO}} + (H_{\text{Zeeman}})$$

(2.1)
where:

\[ H_{\text{kin}} = \sum_i p_i^2/2m \]

\[ H_{\text{e-nuclei}} = -\sum_i \frac{Ze^2}{|\mathbf{R} - \mathbf{r}_i|} \]

\[ H_{\text{e-e}} = \sum_{i,j \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \]

\[ H_{\text{SO}} = \sum_i \xi(\mathbf{r}_i) \mathbf{l}_i \cdot \mathbf{s}_i \]

\[ H_{\text{Zeeman}} = -\sum_i \mu_i \cdot \mathbf{H} \]

\( H_{\text{Zeeman}} \) is inside brackets because it is considered as a perturbation of the Hamiltonian including previous terms. This is due to the fact that if the magnetic field is not too high (\( \beta H < \xi \)) and gives a small energy contribution compared to the spin-orbit term, and it does not mix states.

If the Hamiltonian up to the spin-orbit term is considered, the eigenstates are of the form \(|l s j m\rangle\). The effect of the Zeeman term is then to split the spin-orbit defined levels in \( m \) sublevels separated by \( E_m = \mu_B g_J H m \). Where \( \mu_B = e\hbar/2mc \) is the Bohr magneton, \( H \) is the magnetic field and \( g_J \) is the Landé factor:

\[ g_J = 1 + (g_e - 1) \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \] (2.2)

where \( g_e = 2.0023 \) is the gyromagnetic ratio and \( \mu = -\mu_B g_J J \) is the magnetic moment.

Each of the terms in the total Hamiltonian produce a change and/or splitting in the electronic energy levels. An example is given in figure 2.2 for the simple bielectronic system (3d)\(^2\). Of course the situation becomes more complicated increasing the number of electrons, since coupling the angular momenta of a n-electron system with \( n >> 2 \) can be quite difficult.

2.1.1.1 Magnetic moments in atoms with partially filled shells.

Let us consider an isolated atom with partially filled shells, for example a transition metal or a rare earth atom, and suppose that this shell has an angular moment \( l \), then the shell can contain \( 2(2l + 1) \) electrons with their spin-orbitals\(^2\). A completely filled shell has a total angular momentum equal

\(^2\)e.g. the d-shell (\( l=2 \)) can contain 10 electrons \((2(2 \cdot 2 + 1))\).
to zero and thus it is non magnetic.

In the case of LS coupling the electronic state can be described by coupling separately the \( l_i \) and \( s_i \) moments of electrons to get the total \( L \) and \( S \). The energy levels are then labeled by: \( 2S+1L \) (where the value of \( L \) is indicated by a letter S, P, D, F, G, ... for \( L=0, 1, 2, 3, 4, ... \)). The spin-orbit interaction splits the levels into sublevels of defined \( J \), while the Zeeman interaction produces a further splitting of \( (2J + 1) \) magnetic levels as can be seen in figure 2.2.

The problem is how these \( N \) electrons can arrange in a shell. The Pauli principle forbids the occupation of an orbital level by electrons with the same spin. The rule reduces the degeneracy and electrons with parallel spins tend to occupy the lowest available states. This effect produces the tendency to have the largest possible total spin value \( S \). Then the Coulomb repulsion forces the electrons to establish the maximum reciprocal distance allowed thus maximizing the total orbital moment \( L \). Finally the spin-orbit rules the coupling of \( S \) and \( L \) as the shell is filled by electrons switching from antiparallel coupling for less than half filled shells to parallel coupling for more than half filled shells. All these trends are summarized by empirical rules stated to determinate the ground state of an electronic configuration. These rules are called Hund’s Rules and can be stated as:

- **Hund’s First Rule** can be stated as: the ground state has maximum spin multiplicity \( (2S + 1) \) consistent with Pauli Exclusion Principle.
2.1 Atomic Magnetism and solid state effects

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
<th>J</th>
<th>L</th>
<th>S</th>
<th>gJ</th>
<th>gJ\sqrt{J(J+1)} (\mu_B)</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>[Ar]3d^14s^2</td>
<td>3/2</td>
<td>2</td>
<td>1/2</td>
<td>4/5</td>
<td>1.56</td>
<td>2D_{3/2}</td>
</tr>
<tr>
<td>Ti</td>
<td>[Ar]3d^24s^2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2/3</td>
<td>1.63</td>
<td>3F_2</td>
</tr>
<tr>
<td>V</td>
<td>[Ar]3d^34s^2</td>
<td>3/2</td>
<td>3</td>
<td>3/2</td>
<td>2/5</td>
<td>0.77</td>
<td>4F_{3/2}</td>
</tr>
<tr>
<td>Cr</td>
<td>[Ar]3d^34s^1</td>
<td>5/2</td>
<td>0</td>
<td>5/2</td>
<td>2</td>
<td>5.92</td>
<td>6S_{5/2}</td>
</tr>
<tr>
<td>Mn</td>
<td>[Ar]3d^34s^2</td>
<td>5/2</td>
<td>0</td>
<td>5/2</td>
<td>2</td>
<td>5.92</td>
<td>6S_{5/2}</td>
</tr>
<tr>
<td>Fe</td>
<td>[Ar]3d^64s^2</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>3/2</td>
<td>6.71</td>
<td>5D_4</td>
</tr>
<tr>
<td>Co</td>
<td>[Ar]3d^74s^2</td>
<td>9/2</td>
<td>3</td>
<td>3/2</td>
<td>4/3</td>
<td>6.63</td>
<td>4F_{9/2}</td>
</tr>
<tr>
<td>Ni</td>
<td>[Ar]3d^84s^2</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>5/4</td>
<td>5.59</td>
<td>3F_4</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar]3d^{10}4s^2</td>
<td>5/2</td>
<td>2</td>
<td>1/2</td>
<td>6/5</td>
<td>3.54</td>
<td>2D_{5/2}</td>
</tr>
<tr>
<td>Zn</td>
<td>[Ar]3d^{10}4s^2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1S_0</td>
</tr>
</tbody>
</table>

Table 2.1: 3d elements electronic configurations.

- **Hund’s Second Rule** can be stated as: the ground state has maximum orbital multiplicity \((2L + 1)\) consistent with **Hund’s First Rule**.

- **Hund’s Third Rule** can be stated as: on the basis of the two preceding rules:

  - if the shell is **less** than half-filled \(L\) and \(S\) couple antiparally and \(J = |L - S|\)
  - if the shell is **more** than half-filled \(L\) and \(S\) couple parallely and \(J = |L + S|\)

In table 2.1 we can see the values \(L, S, J, g_J\), for transition metal atoms together with their electronic configuration and ground state.

2.1.1.2 Paramagnetism of localized moments

Looking at the problem of atomic magnetism from a thermodynamical point of view, the classical magnetization for a system of \(N\) particles of magnetic moment \(\mu\) in a field \(H\) at a temperature \(T\) is proportional to a Langevin function:

\[
M = N\mu L(x)
\]

(2.3)

where \(x \equiv \mu H/k_B T\) and \(L(x)\) is the Langevin function defined as:

\[
L(x) = \coth x - \frac{1}{x}
\]

(2.4)

in the limit of \(x \ll 1\), then a series expansion of \(L(x)\) gives \(M = N\mu^2H/3k_B T\).

If instead of generic magnetic particles are considered \(N\) atoms all having
the same total angular moment $J$, spin moment $S$ and orbital moment $L$ in a volume $V$ at a temperature $T$, then we can calculate the magnetization $M = N/V\langle \mu_2 \rangle$ as:

$$M = \frac{N}{V} g_J \mu_B J B_J(x')$$

(2.5)

where $x' = \frac{g_J \mu_B J H}{k_B T}$:

$$B_J(x') = \frac{2J + 1}{2J} \coth\left(\frac{2J + 1}{2J} \frac{x'}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x'}{2J}\right)$$

(2.6)

is called the Brillouin function that for large $x$ tends to the saturation value of 1. In the limit of $x' \ll 1$, using a series expansion to first order of $\coth(x')$, the magnetization becomes:

$$M = \frac{N\mu_{eff}^2 H}{3k_B T}$$

(2.7)

where $\mu_{eff} = g_J\sqrt{(J(J + 1))}$ is an effective magnetic moment.

### 2.1.1.3 Orbital moment quenching

For the Iron Group impurities embedded in insulating crystals an important effect occurs: the orbital moment quenching. In fact, if we consider the effective number of Bohr magnetons $\mu_{eff} = g_J\sqrt{(J(J + 1))}$, this expression does not account for the experimental results unless a complete quenching of the orbital moment is considered and hence $\mu_{eff} = g_J\sqrt{(S(S + 1))}$ thus making evident that $L = 0$. This effect is explained taking in account the crystal field, i.e. the electric field produced by the crystalline structure of the host, depending on its crystal symmetry, and felt by the impurity.

As an example a single electron with $L=1$ is considered, forgetting the spin. In free space the ground state has a degeneracy equal to three since $m_l = 0, \pm 1$. In a crystal with orthorhombic symmetry then the electrostatic potential $V$ consistent with this symmetry and Laplace equation ($\nabla^2 V = 0$) has the form:

$$eV = Ax^2 + By^2 - (A + B)x^2$$

(2.8)

where $A$ and $B$ are constants. If we consider the wavefunctions of the unperturbed state as: $U_i = i\psi(r)$ with $i = x, y, z$, these functions are orthogonal and eigenfunctions of $L^2$ operator. In fact $L^2 U_i = L(L+1)U_i = 2U_i$, hence $L=1$ for $U_i$. It can be easily seen that the $U$ functions are diagonal by respect to the crystal field, this means that $\langle U_i | eV | U_j \rangle \neq 0$ only if $i = j$. This term splits the degenerate ground state of a quantity much bigger then magnetic field splitting, since the crystal field can be of the order of 1 eV while the magnetic field is usually much weaker (e.g. 7 Tesla correspond to 0.35 meV). The quenching of the orbital moment is then due to $\langle U_i | L_z | U_j \rangle = 0$ for $i=j$. Hence the total orbital moment is still there while the components
are averaged to zero.

The quenching of orbital moments is not present for all the impurities on metal surfaces. It depends strongly on the interaction between the impurity and the substrate. But if the interaction is weak enough as in the case of $3d$ impurities in an alkali metal host, there is also the possibility that the impurity has an atomic-like behavior with no sign of orbital quenching [7].

### 2.1.1.4 The Anderson model

The Anderson Model [13] is very useful in understanding the magnetism of impurities embedded in a simple metal and in general the interaction between the impurity and the metal host on which this impurity is deposited. This model shows how the magnetism of the impurity can be present depending on the interaction with the host. The physical description of Anderson also is the basis to understand the coupling of a localized moment to a Fermi gas of electrons thus leading to a correlated non-magnetic ground state as in Kondo systems. Moreover the exact correspondence between the two models has been demonstrated by Krishna-Murthy et al. [14].

An Anderson model Hamiltonian can be written, in second quantization, to account for the magnetism of a localized state as in equation 2.9.

$$H = \sum_{k\sigma} E_k n_{k\sigma} + E_d (n_{d\uparrow} + n_{d\downarrow}) + \frac{1}{\sqrt{N}} \sum_{k\sigma} \left[ V_{k_d} c_{k\sigma}^\dagger c_{d\sigma} + V_{k_d}^* c_{d\sigma}^\dagger c_{k\sigma} \right] + U n_{d\uparrow} n_{d\downarrow}$$

(2.9)

where the first term represent the host metal conduction band ($s$-band), with $E_k$ the energy of the electronic band state of wavevector $k$ and spin $\sigma$; $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ are the annihilation and creation operator of an electron in the conduction band, and $n_{k\sigma} = c_{k\sigma}^\dagger c_{k\sigma}$ is the electron numbering operator.

The second term represent the localized, non-degenerate state of the impurity, and $n_{d\sigma} = c_{d\sigma}^\dagger c_{d\sigma}$ is the numbering operator of the impurity orbital.

The third term is the $sd$ mixing term and represents the hybridization of the $s$-band of the host with the $d$-band of the impurity; $N$ is the number of unit cells of the metal; the interaction of the host Block state with the localized impurity state is $V_{kd}/\sqrt{N}$. The last term is the Coulomb repulsive interaction ($U > 0$) between electrons of opposite spin in the orbital.

The hybridization and the Coulomb term are in competition, the former trying to equalize opposite spins and the latter trying to create unbalance between opposite spins (and thus magnetism). The trend is quite clear with the Coulomb interaction driving toward a magnetic state and the hybridization driving toward a non-magnetic state.

If we neglect for a while the Coulomb term this situation gets simpler and leads to the formation of a resonance state and the local density of state at the impurity site can be written as:
Figure 2.3: Localized electronic states spin split by the exchange $U$ in two cases without hybridization (left) and resonances with hybridization (right). Adapted from [10].

$$n^0_d(E) = \frac{1}{\pi} \frac{\Gamma}{(E - E_d)^2 + \Gamma^2}$$

(2.10)

where $\Gamma$ is the width of the resonance centered at the impurity state energy $E_d$ and $\Gamma \propto |V_{sd}| n_0(E_F) = |V_{sd}|/W_F$ where $W_F$ is the energy width of the occupied part of the conduction band.

We now try to account also for the correlation term: $U n_{d\uparrow} n_{d\downarrow}$ considering the integrated density of state and in the unrestricted HF approximation to simplify $U n_{d\uparrow} n_{d\downarrow}$ with $U n_{d\uparrow} (n_{d\downarrow})$ and thus handling only one-particle operators, we can write two equations that must be solved self consistently.

$$\langle n_{d\uparrow} \rangle = \frac{1}{2} + \frac{1}{\pi} \arctan \frac{E_F - E_d - U \langle n_{d\downarrow} \rangle}{\Gamma}$$

(2.11)

$$\langle n_{d\downarrow} \rangle = \frac{1}{2} + \frac{1}{\pi} \arctan \frac{E_F - E_d - U \langle n_{d\uparrow} \rangle}{\Gamma}$$

(2.12)

This equation array has a nonmagnetic solution $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle$ but also magnetic solutions $\langle n_{d\uparrow} \rangle \neq \langle n_{d\downarrow} \rangle$. Figure 2.3 show an energy scheme for a localized system spin split by a Coulomb exchange with and without hybridization. In the case of zero hybridization there is one fully occupied spin-up state at an energy $E_d$ and an empty spin-down state at energy $E_d + U$. When the hybridization is turned on, two resonances appear in place of the localized state and the spin populations $\langle n_{d\uparrow} \rangle$ and $\langle n_{d\downarrow} \rangle$ influence the energy position of these two resonances.

Putting together these considerations it is clear that the main parameter to account for system to be, or not to be, magnetic are: $(E_F - E_d)/U$ and $\Gamma/U$, and they are coupled. This is precisely what is depicted in figure 2.4. The more the magnetism is suppressed, the more the resonance width is large.
with respect to the Coulomb interaction $U$ (larger $\Gamma/U$) and the more the $(E_F - E_d)/U$ is near to 0 and 1: when it is zero this means that the spin-up $d$ state is at the Fermi level, when it is 1 this means that the spin down state is at the Fermi energy. The best condition in this model for magnetism is when spin-up and spin-down states are placed symmetrically at $U/2$ below and above $E_F$.

### 2.1.2 Kondo systems

For some systems at low temperatures, the magnetic moment of the impurity is screened by the host, so to have a non magnetic collective state. These are the so-called Kondo systems.

The first experimental results about these systems reported the discovery of an anomalous behavior of the resistivity for diluted magnetic impurities in metal hosts as a function of the temperature with of a minimum at temperatures of tens of K, followed by an increase at lower temperatures [15]. This minimum is called Kondo minimum and the temperature of the minimum is called $T_K$, the Kondo temperature, after the name of J. Kondo who has interpreted this phenomenon as due to an increase in the spin scattering cross section of the host electrons related to the magnetic screening of the impurity [6], [16]. Kondo's explanation of this phenomenon is based on the model Hamiltonian defined in equation 2.13, which describes the spin interaction between a single impurity of spin $S$ and an electron in the conduction band with spin $s$.

$$H_K = -J \Omega S \cdot s \delta(r)$$  \hspace{1cm} (2.13)
where $\Omega$ is the volume of the unit cell, $J$ is a phenomenological parameter expressing the strength of the interaction. This kind of interaction is of contact type, and has antiferromagnetic character ($J < 0$).

The microscopic explanation of this phenomenon can be found by the Anderson theory. In fact if we consider a “two-orbital molecular model”, with a single localized impurity orbital $\psi_f$ that represents the impurity and one extended orbital $\psi_k$ that represents the Fermi sea, we can put two electrons with their spins in this molecule$^3$.

The two orbital molecule then gives rise to a bonding state and an antibonding state. The two spins can be allocated: antiparallel in the bonding state ($S=0$), antiparallel in the antibonding state ($S=0$), or one in the bonding and one in the antibonding state ($S=0,1$). The lowest energy state is a singlet ($S=0$) non magnetic state. If we now turn on the Coulomb interaction represented by the repulsion parameter $U$, and we consider the limit of $U \to \infty$, what happens is that the lowest state is always a singlet but with a small energy difference 10-100 meV from the triplet states to whom an electron can easily get excited by thermal fluctuations through a spin-flip process. This limit case shows the basic features of the Kondo effect, the lowest state is a singlet non-magnetic state, this is the situation for very low temperatures; at higher temperatures the thermal excitation induces a transition from single to triplet thus giving rise to magnetism.

More realistic Hamiltonians [10], can be used to better describe the situation and quantify the parameters connected to these properties for example producing an expression for the Kondo temperature, $T_K$.

$$T_K = \frac{W_F}{k_B} \exp \left( -\frac{|e_f|}{2V_s^2 f^2 n_0(E_F)} \right) \tag{2.14}$$

For $T \ll T_K$ the non-magnetic ground state is present, while for $T \gg T_K$ the thermal fluctuation promotes electrons to the triplet magnetic state. Moreover it is also possible to calculate the susceptibility for $T \ll T_K$ as:

$$\chi_K = \frac{N}{V} \frac{\mu_B^2}{k_B T_K} \tag{2.15}$$

which is higher of a factor of $\frac{3}{2} T_F/T_K$ by respect to the Pauli paramagnetic susceptibility $\chi_p$. It is also interesting to compare $\chi_K$ with the Curie susceptibility $\chi_c$:

$$\chi_c = \frac{N g^2 J(J+1)\mu_B^2}{3k_B T} \tag{2.16}$$

of a $N$ atoms systems with moments $g\mu_B J$. If we consider the atomic value for Co $J=9/2$ and $T_K = 80$ K at $T = 4K$ we thus have $\chi_K/\chi_c = \ldots$
3/g^2J(J + 1) × T/T_K = 0.03 × 0.05 = 0.0015. Therefore at low temperatures, the susceptibility of a Kondo system is much weaker than the one of a Curie paramagnet.

### 2.1.3 The Stoner-Hubbard model for magnetism

The magnetism of a delocalized electron system is the complementary approach to the localized moments magnetism. This approach is suitable to understand many aspects of the 3d magnetism of bulk ferromagnetic metals and thin films, that cannot be explained with a localized moments approach. The picture will start from electrons described by Block functions.

Let us consider a metal with a simple Bravais lattice, with N unit cells and a volume V = NΩ, described by a single conduction band partially filled. In a one-electron approximation the Hamiltonian known as Stoner-Hubbard Hamiltonian can be written as:

\[
H = \sum_k E(k) \left[ c_{k\uparrow}^\dagger c_{k\uparrow} + c_{k\downarrow}^\dagger c_{k\downarrow} \right] + U \sum_m c_{m\uparrow}^\dagger c_{m\downarrow}^\dagger c_{m\downarrow} c_{m\uparrow} \tag{2.17}
\]

where \( E(k) \) is the k-dependent energy of the band and \( c_{k\sigma}^\dagger, c_{k\sigma} \) are the annihilation and creation operators for an electron with wavevector \( k \) and spin \( \sigma \), \( U \) is the Coulomb repulsion parameter and \( c_{m\sigma}^\dagger c_{m\sigma} \) the annihilation and creation operator at the lattice site \( t_m \). It is clear that depending on the ratio between the Coulomb parameter and the width of the band, the bigger is \( U \) the more the system will tend to magnetism. In the case of a narrow band and \( U \) sufficiently large the band will split into a spin-up band fully occupied and an empty spin-down band.

If we consider the system at \( T = 0 \), and using the unrestricted Hartree-Fock approximation to simplify the Hamiltonian, we can replace \( c_{m\sigma}^\dagger c_{m\sigma} \) with their expectation values in the ground states and, also considering a magnetic field, then the spin bands take the simple form:

\[
E_{k\uparrow} = E_k + U n_\uparrow + \mu_B H \tag{2.18}
\]

for spin-up electrons and:

\[
E_{k\downarrow} = E_k + U n_\downarrow - \mu_B H \tag{2.19}
\]

where \( n_\sigma = N_\sigma / N \). We have considered the magnetic moment in Zeeman coupling as coming only from the spin with no orbital moment. It is thus possible to calculate the density of state using Fermi-Dirac distribution at \( T = 0 \) getting:

\[
N_\downarrow - N_\uparrow = \left[ U(n_\downarrow - n_\uparrow) + 2\mu_B H \right] \frac{1}{2} D(E_F) = \frac{\mu_B H D(E_F)}{1 - \frac{1}{2} \frac{D(E_F)}{N} U} \tag{2.20}
\]
Keeping in mind that the magnetization can be written as \( M = \mu_B (N_1 - N_t)/V \) it is possible to calculate the susceptibility as:

\[
\chi = \frac{1}{V} \frac{\mu_B^2 D(E_F)}{1 - \frac{1}{2} \frac{D(E_F)}{N} U}
\]  
(2.21)

From the denominator it is clear that, being \( U > 0 \), the susceptibility diverges, giving a transition toward ferromagnetism if:

\[
\frac{1}{2} \frac{D(E_F)}{N} U = 1
\]  
(2.22)

This is the so-called Stoner criterion for ferromagnetism. If \( U = 0 \) the criterion is never satisfied and \( \chi = \chi_p \), the paramagnetic susceptibility.

### 2.2 Magnetic anisotropy

Up to now the magnetism, its origins and the existence of magnetic moments have been discussed within the implicit assumption that the system is isotropic. This assumption contradicts the experience for which many magnetic systems display a preferential orientation with respect to some crystalline axis, or with respect to the external shape of the body. This preferential direction of the magnetization is called easy magnetization direction or easy axis. The anisotropy due to the existence of an easy axis is at the basis of all magnetic devices, in technology as well as in everyday life.

The easy axis reflects an orientation where the total energy is minimized, while along the hard axis the energy has a maximum. The energy required to rotate the magnetization from the easy direction to the hard direction is called: Magnetic Anisotropy Energy (MAE). This energy is usually found to be between \( 10^{-6} \text{ eV} \) per atom (for bulk ferromagnets) and \( 10^{-3} \text{ eV} \) (for systems with large magnetic anisotropy). It is small compared for example to the exchange energy (\( \approx 10 \text{ eV} \)), the crystal field (1 eV) or even the spin-orbit energy (0.1 eV). The anisotropy energy is thus a small contribution to the total energy that arises from relativistic corrections to the Hamiltonian (see Bruno [19]). This correction has two main sources: the dipole-dipole interaction and the spin-orbit coupling. The fundamental importance of these two interactions is strongly related to the existence of ferromagnetism in low dimensional systems. According to Mermin-Wagner theorem [20], two and one dimensional systems at non-zero temperature, with isotropic exchange interaction cannot be ferromagnetic without dipole-dipole interaction or spin-orbit coupling.

From a phenomenological point of view, for a general bulk magnetic object, two different kind of anisotropies can be introduced:
2.2 Magnetic anisotropy

Figure 2.5: Fe-Co alloy magnetization along different crystallographic axis, adapted from [18]

1. The Shape Anisotropy, that is related to the shape of the object and is due entirely to dipole-dipole interaction.

2. The Magneto Crystalline Anisotropy (MCA), that is related to the crystalline axes of the object and it is due mainly to the spin-orbit interaction as proposed by Van Vleck [2] and to a smaller extent to the dipole interaction.

Also other kind of anisotropies can be present in a magnetic system, such as magnetoelastic and magnetostrictive anisotropies that are related to the influence of the strain and stress on the magnetization. These anisotropies originate also from the spin-orbit interaction.

When the dimensionality is reduced, as in the case of thin films, the surface contribution cannot be neglected any more and its contribution can become more important than the one of the volume. The anisotropy energy density $K$ defined as MAE/atom can be written in the case of a thin film as $K = K_V + 2K_S/t$ where $K_V$ is the volume contribution, $K_S$ is the surface contribution and $t$ is the thickness of the film. The preferential in plane orientation of most magnetic thin film systems is due to the shape anisotropy energy.

Most recently the discovery of multilayer and thin films with Perpendicular Magnetic Anisotropy (PMA) has encountered great interest also from the technological point of view due to possible applications to magneto optical
and high density recording [21]. The preferential out of plane orientation of these system has been investigated in term of spin-orbit interaction on the path opened by Néel [3] who proposed that spin-orbit induced anisotropy is increased in low dimensional systems such as surfaces, thin films and interfaces. A general description of the MAE in terms of the crystallographic directions can be quite complicate. Fortunately in the cases of interest a uniaxial description can be used and the angular development of MAE reduces to:

\[ MAE = K_0 + K_2 \sin^2(\alpha) \]  

(2.23)

where \( \alpha \) is the angle between the easy axis direction \( \mathbf{E}_a \) and the magnetization (magnetic moments direction). The geometry of a magnetic system with uniaxial anisotropy is depicted in figure 2.6. Uniaxial systems, as 1D-chains Co chains grown on Pt(997), have been shown [22] to have an increased anisotropy (with respect to the bulk and to the monolayer). Moreover as discussed in chapter 5 this anisotropy is further increased in the case of 0D system: Co single atoms on Pt(111) at low temperatures [8].

In the case of an uniaxial anisotropic system the magnetic anisotropy energy \( MAE \) can be written as:

\[ MAE(N) = E_{tot}(\theta = 0; N) - E_{tot}(\theta = \pi/2; \phi_0; N) \]  

(2.24)

where \( E_{tot} \) is the total energy of a system with \( N \) (3d and 4s) electrons per atom, the magnetization direction is defined by \( \theta \) the out of plane angle and \( \phi \) the azimuthal angle with \( \phi_0 \) is the in-plane angle for which the \( |MAE| \) is maximum (see [23]).
2.2 Magnetic anisotropy

2.2.1 Bruno's model

In the approximation of only spin-orbit dependent contributions to the anisotropy, and neglecting dipolar spin-orbit contributions, the Magnetic Anisotropy Energy (MAE) coincides with the Magneto Crystalline Anisotropy energy (MCA). Useful relations between the quantities of interest: MAE, \( \langle L_z \rangle \), and \( (L \cdot S) \) have been established by Bruno [24], [19] within a tight binding calculation scheme. The magnetic anisotropy reflects in a small change in the orbital moments and depends on the spin-orbit expectation value. The spin-orbit interaction can be written in a one electron approximation as \( \xi \mathbf{L} \cdot \mathbf{S} \). The spin-orbit constant \( \xi \), for 3d elements, has a value of about 50-100 meV, which is quite small with respect to the d-band width (few eV). Thus the spin-orbit operator can be evaluated in second order perturbation theory, in a tight binding model. The first important result is about the expectation value of the orbital moment \( \mathbf{L} \), along the quantization axis \( z \), \( \langle L_z \rangle \):

\[
\langle L_z \rangle = \langle d_1 \sigma_1 | L_z | d_2 \sigma_2 \rangle = 2\delta_{\sigma_1, \sigma_2} \langle d_1 \downarrow | L \cdot S | d_2 \uparrow \rangle
\]  

(2.25)

where \( d_i \) are the 3d-subbands \((xy, yz, zx, x^2 - y^2, 3z^2 - r^2)\), \( z \) is the direction of the quantization axis, taken normal to the surface plane, \( \sigma \) are the spins. These results are particularly useful from the experimental point of view if they are written in the following way [19], [25], expressing the relation between the magnetic orbital moment \( \mu_l \) and the spin-orbit energy \( E_{SO} \):

\[
\mu_l = \mu_l^\perp + \left( \mu_l^\parallel - \mu_l^\perp \right) \sin^2 \theta
\]  

(2.26)

and

\[
E_{SO} = -\frac{\xi}{4\mu_B} \left[ \mu_l^\perp + \left( \mu_l^\parallel - \mu_l^\perp \right) \sin^2 \alpha \right]
\]  

(2.27)

The MAE is the difference of spin orbit energy between the normal direction \( \theta = 0^\circ \) (\( \perp \)) and \( \theta = 90^\circ \), the direction parallel to the surface (\( || \)):

\[
MAE = \Delta E_{SO} = -\frac{\xi}{4\mu_B} \left[ \mu_l^\perp - \mu_l^\parallel \right]
\]  

(2.28)

In this way an explicit relation is given between MAE and the magnetic orbital moment anisotropy \( \Delta \mu_l \). These relations have been compared to the XMCD experimental results by Weller et al. [26] for an Au/Co/Au layered structure and found to be in agreement within the order of magnitude. It is of note that the equation 2.29 is exact in the limit in which the exchange
Magnetism of transition metal atoms and impurities

spitting $\Delta_{ex}$ is much bigger than the bandwidth $W$. In the general case, it should be slightly modified:

$$MAE = \Delta E_{SO} = -\frac{G}{H} \frac{\xi}{4\mu_B} \left[ \mu_1^+ - \mu_1^\parallel \right]$$  \hspace{1cm} (2.29)

where $G$ and $H$ are defined in [24]. When $\Delta_{ex} >> W$ then $G/H = 1$ but for a transition metal $G/H < 1$ and estimated [26] to be approximately 0.2. Some things should be pointed out: in the calculation the $3d - 4s$ hybridization is taken in account and its main effect is to strongly change $K_2$ as a function of the number of $3d + 4s$ valence electrons. The second thing to consider is the crystal field and its effect in the reduction of symmetry of the system. The crystal field strength can be represented by $\Delta$, the energy difference between in-plane $xy$, $x^2 - y^2$ and out-of-plane $yz$, $zx$, $3z^2 - r^2$ orbitals. The value of $K_2$ is strongly dependent on the value of the crystal field; for example if it is high and positive it gives a high and negative value for $K_2$ thus expressing the out-of-plane anisotropy.

It is important to note that at surfaces and interfaces the MAE can be strongly enhanced compared to bulk materials due to an increase in the spin-orbit expectation value connected with a reduction of the coordination number which narrows the $d$-bands thus leading to an enhancement in the orbital moment.

Bruno's approach considers a majority band completely filled (hard ferromagnet) and a minority band empty. This assumption is not valid in general and the model has been extended to include partial filling of the bands [27]. Thus giving:

$$\Delta E_{SO} = -\frac{1}{4} C \xi \left\langle \mathbf{L} \cdot \hat{\mathbf{S}} \right\rangle$$  \hspace{1cm} (2.30)

$$\approx -\frac{1}{4} C \xi \hat{\mathbf{S}} \cdot \left[ \left\langle \mathbf{L} \downarrow \right\rangle - \left\langle \mathbf{L} \uparrow \right\rangle \right] = -\frac{1}{4} C \xi \hat{\mathbf{S}} \cdot \left[ \left\langle \mathbf{L} \right\rangle - 2 \left\langle \mathbf{L} \uparrow \right\rangle \right]$$  \hspace{1cm} (2.31)

the last expression reduces to Bruno's result when $\langle \mathbf{L} \uparrow \rangle = 0$ because a completely filled spin up band has zero orbital moment. The scheme has been applied to interpretation of XMLD measurements of vicinal Co films [28]. For a discussion about XMCD, XMLD, TMCXD and how they can be used to measure the MAE refer to [29].

2.2.2 Magnetization of paramagnets with uniaxial anisotropy

To measure the magnetic anisotropy energy of paramagnetic systems, we have to consider how the anisotropy energy enters in the magnetization. In the case of a paramagnetic system without anisotropy, the magnetization
curve, supposing our particle to be of defined dimension, can be expressed by a Langevin function.

If we consider an ensemble of paramagnetic particles with magnetic anisotropy, made by $n$ atoms, the magnetization can be calculated on the basis of the magnetic energy $E(\theta_0, \theta, \phi)$, where $\theta_0$ is the polar angle of the easy magnetization axis $\hat{E}_a$ by respect to the $z$ direction, (the magnetic field $H$ being parallel to $z$), while $\theta$ and $\phi$ are the polar and azimuthal angle of the total magnetic moment $\vec{n}\mu$ by respect to the axes $(x, y, z)$ as in picture 2.6. The magnetic energy is the sum of the Zeeman term plus the uniaxial anisotropy term:

$$E = -\vec{n}\mu H \cos(\theta) - nK \cos^2(\alpha)$$  \hspace{1cm} (2.32)

where $\alpha$ is the angle between the moment $\mu$ and the easy axis $\hat{E}_a$ and $K$ is the MAE per atom. This expression can be rewritten by means of direction cosines as:

$$E = -\vec{n}\mu H \cos(\theta) - nK(\sin \theta_0 \sin \theta \cos \phi + \cos \theta_0 \cos \theta)^2$$  \hspace{1cm} (2.33)

Then the magnetization is calculated as:

$$M = M_{sat} \frac{\int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta \cos \theta e^{-E(\theta_0, \theta, \phi)/k_BT}}{\int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta e^{-E(\theta_0, \theta, \phi)/k_BT}}$$  \hspace{1cm} (2.34)

where $M_{sat}$ is a proportionality constant to account for the experimental value of saturated magnetization. This expression for the magnetization is applied to analyze the magnetization curves of the paramagnetic impurities. By means of a fit procedure, it is possible to evaluate the anisotropy energy per atom of the impurity. Further details on procedure used to apply these concepts to experimental spectra will be given in those chapters devoted to the data presentation and discussion.
Chapter 3

Experimental techniques and instrumentation

This chapter gives a description of the instruments and the techniques used to study the electronic and magnetic properties of 3d impurities and clusters systems. The chapter is organized in the following way: first, a section will outline the synchrotron radiation source, its basic features and some experimental possibilities that it offers. The two beamlines used for the investigations presented in this thesis, the Circular Polarized beamline at Elettra (Trieste) and the Id8 Dragon beamline at ESRF (Grenoble, France), are described. The following section will describe the x-ray spectroscopies used in this research. The X-ray Absorption Spectroscopy (XAS), the X-ray Magnetic Circular Dichroism (XMCD) and the X-ray Magnetic Linear Dichroism (XMLD), will be briefly outlined starting from a description of the interaction between light and matter. Finally the results of an experiment regarding the determination of the magnetic moments distribution of Mn/Fe thin films will be discussed as an example of the combined application of the XMCD and XMLD techniques to the study of antiferromagnetic-ferromagnetic coupled systems.

3.1 Synchrotron Radiation

Synchrotron x-ray radiation based experimental techniques exploit the capability of synchrotron radiation sources to give intense photon beams over a broad range of energies suitable to study physical, chemical as well as biological systems.

X-ray absorption is a method particularly powerful because the electronic behavior of a specific element can be selectively probed by tuning the photon energy across one of its characteristic absorption energies. To study the magnetic properties of 3d transition metal impurities by absorption spectroscopy,
the most suitable energies are the ones corresponding to the $2p \rightarrow 3d$ transitions. The corresponding photon energies are element specific, and go from approximately 400 eV to 1000 eV (see figure 3.1). At the moment absorption studies in this energy range are possible only with synchrotron radiation sources.

To fully understand the importance of the properties of synchrotron radiation sources let us start by comparing them to the standard x-ray sources as helium lamps, mercury lamps, Al-$K$, Mn-$K$ x-ray tubes. All these sources work on the basis of a process of excitation/de-excitation of atoms, that produces one or more x-ray lines. This means that although these x-ray emissions are of non zero width they can be anyhow considered as discrete. Moreover, different sources have of course different photon energies depending on the electronic level excited. Synchrotron radiation instead:

- is intrinsically emitted in a continuous way, with a spectrum ranging from visible to hard x-rays
- has a much higher brilliance by respect with traditional sources
  \[
  [\text{brilliance}] = \frac{\text{photons}}{m^2 \cdot s \cdot \text{mmrad}^2 \cdot 0.1\% \text{ bandwidth}}
  \]
- can be produced with horizontal, vertical and circular polarization
- has an intrinsic temporal structure, thus being suitable for time resolved experiments

Synchrotron sources have improved the available brilliance of about 12 orders of magnitude from the discovery of x-rays, in 1895, by W. C. Röentgen.
3.1 Synchrotron Radiation

The basic principle to produce synchrotron radiation is that an electric charge that undergoes an acceleration emits light to conserve the energy. In a synchrotron electrons travel inside a vacuum “ring” at speeds near to the speed of light (c). This relativistic regime produces the emission of radiation in the energy range from UV to Hard x-rays; secondly it produces an anisotropic emission of radiation which is mainly emitted onwards i.e. toward the direction of movement of the electrons. This effect highly improves the source brilliance.

A synchrotron radiation light source conceptually consist of few simple units. In the electron injection system electrons are emitted by a hot cathode and accelerated before injection, then they are injected in the synchrotron ring and further accelerated to energies of the order of some GeV. Devices along the ring, such as radio frequencies, correction dipole and quadrupoles and bending magnets, control the electron beam trajectory and energy. Special ones, called Insertion Devices, such as wigglers and undulators, produce intense radiation. The light emitted by the insertion devices is collected, focused and monochromatized by the beamlines, which are complex systems of optical elements.

Experimental end-stations, needed to analyze and measure the samples, are connected at the end of the beamline optical path. The radiation is focused by the beamline on to the sample and the interaction is studied collecting the out coming electrons, photons, or ions as a function of energy, polarization and angle, depending on the experimental technique. The end-stations can be of course quite different depending on the kind of sample (e.g. solid, liquid, gas, protein, molecule) and/or the experimental environment (e.g. air, inert gas atmosphere, vacuum, ultra-high-vacuum) and the experimental technique used. In figure 3.2 the main elements composing a Synchrotron

![Figure 3.2: Structure of a synchrotron.](image-url)
are represented in a simple pictorial way.

3.2 Circular Polarized and Id8 beamlines

3.2.1 Circular Polarized beamline at Elettra

The aim of my research activity at the "Circular Polarized beamline" of CNR-ISM at Elettra Light Source Laboratory in Trieste, was to study the magnetism of transition metal impurities and clusters as well as thin films with dichroic photon absorption spectroscopies by means a new experimental end-station that has been developed during this thesis. This new end-station is now in use at Circular Polarized beamline will be described in subsection 3.2.1.1.

The insertion device of Circular Polarized beamline at Elettra is the Elliptical Electromagnetic Wiggler (EEW) [31]. It is an electromagnetic wiggler, which means that the magnetic field needed to wiggle the electrons is changed by tuning the currents passed through coils that surround the wiggler soft iron poles, without changing the distance between the poles. To be able to produce circular polarized light, there are not only 2-poles elements that produce a magnetic field in the vertical (i.e orthogonal to ring's plane) direction and thus horizontally polarized light. There are also 4-poles elements, which, by means of a particular magnetic design, provide a horizontal magnetic field able to cause vertical wiggling of the electrons, thus giving vertical polarized light. The 4-poles elements are alternated to the 2-poles elements in order to produce circular polarized light. The degree of polarization is approximately 80% over the 3d elements L2,3 edges spectral range. Moreover the electromagnetic wiggler is capable to switch from right circular polarization to left circular polarization with higher frequency and reliability than mechanical undulators. It is designed to operate with frequency up to 100 Hz, while standard frequencies presently are 0.1 and 1 Hz. Having the possibility to change the photon polarization in this way improves the reproducibility and the sensitivity to very low dichroic signals.

The EEW is able to produce horizontal, vertical as well as left or right polarized radiation in a range from 5 to 1500 eV. It emits a spectrum of harmonics in the low energy range < 50 eV that can be tuned changing the currents in the coils. The fundamental energy is at 4.5 eV when Elettra operates at 2 GeV. In the range of 50-150 eV the EEW can work in pure circular undulator mode. At higher energies the harmonics merge in a continuous spectrum.

The figure 3.3 depicts the optical layout of the beamline. The radiation emitted by EEW is shaped by a pinhole at a distance of 10 m from the source, thus limiting the acceptance of the beamline to a maximum of (2 hor. × 1 vert.) mrad². The radiation is deflected in the vertical plane by a
3.2 Circular Polarized and \textit{Id}8 beamlines

plane mirror \(M_0\) and focused by a toroidal mirror \(M_1\) on to the entrance slit \(S_1\). Then it reaches the cylindrical \(M_2\) mirror of the monochromator that deflects it on to the gratings. Four gratings are available to cover an energy range from 50 eV to 1000 eV. After being monochromatized by the Variable Angle Spherical Grating Monochromator (VASGM) the beam passes through the exit slits \(S_2\) and finally it is focused on the sample by a toroidal mirror \(M_3\). A Normal Incidence Monochromator is available for the low energy range, from 7 eV to 50 eV.

At the sample position the beam has a flux of \(10^{10}\) ph/sec (200mA ring current, at 850 eV), a resolution of \((\Delta E/E) = 5 \times 10^{-4}\) at 850 eV (Ne-K1) and the spot has a width of 500 \(\mu m\) and an height equal to the exit slit aperture (typical 20-100 \(\mu m\)).

3.2.1.1 Experimental Chamber

In the course of the thesis, the experimental end-station depicted in figure 3.4 was built at the Circular Polarized beamline at Elettra. It is now the main experimental chamber available at the beamline. A top view of the end-station, is depicted in figure 3.4. It is a completely UHV system consisting of three chambers: preparation chamber, transfer chamber and magnet chamber. It is an easy movable system, designed to be interchanged with other experimental end-stations and to make possible research activity not only with synchrotron radiation.

The preparation chamber is equipped with several standard tools for surface science: an \(Ar^+\) ion-gun for the sputtering of the sample, an electron bombardment heating station for sample annealing up to 1000 °C, a LEED-Auger to check the structural and chemical composition, four electron bombardment evaporator for atom deposition growth, a microbalance, two gas sources for preparation or dose and fast entry lock to allow a quick change of samples without breaking UHV.

From the preparation chamber the samples are transferred to the horizontal liquid helium cryostat; this chamber is also equipped with a quartz microbalance and evaporators to do atom depositions at low temperatures. To
put the sample in the measurement position the cryostat is moved into the magnet chamber and then in the center of the magnet gap. The radiation is coaxial to the magnetic field. The magnet chamber is equipped with a bipolar 0.2 Tesla liquid nitrogen cooled electromagnet. The control of the magnet is computer based and it is connected to the beamline control software.

For out-of-beamline activity the chamber is equipped with a SMOKE (Surface Magneto Optical Kerr Effect) optical assembly, developed during this thesis. It is an optical assembly that permits to study the magnetism of thin films without the use of synchrotron radiation. The scheme of this assembly is presented in figure 3.5. It consists of two optical micro-mounting chas-sis that house all the optical elements and are locked onto a 1.5 cm thick aluminium plate, with an arrangement suitable for angular adjustments. The plate is welded to a cylindrical locking system designed to mount the SMOKE on a CF 150 view port of the electromagnet chamber.

As it can be seen in figure, the first micro-mounting array is made of the laser source (a solid state 15 mW red laser), a focusing lens and Polarizer (Glan Taylor type) that polarizes the radiation incoming on the sample. The beam reflected by the magnetic sample undergoes a small rotation of the polarization axis. This small rotation can be detected in may ways. In this system the analyzer (that is a Glan-Taylor polarizer) is initially set at the extinction angle (with the polarization axis at 90 degree by respect to the polarization plane set by the Polarizer). As the magnetization of the sample changes by effect of the magnetic field generated by the electromag-
net, a magnetic rotation of the polarization direction of the out-going beam occurs. This rotation is detected by the diode at the end of the optical path as a change in the intensity of the laser beam. The actual system has a sensitivity that permits to measure coverages down to about 5 ML of Fe.

3.2.2 Id8 beamline at ESRF

ESRF is a 6 GeV synchrotron light source mainly devoted to studies in the hard x-rays energy range. The Id8 beamline is dedicated to the study of magnetic systems in the soft x-rays, by means of several techniques, absorption spectroscopies as XAS, XMCD, XMLD; photoelectron spectroscopies also with spin polarization analysis; x-ray diffraction and emission.

To produce circularly polarized light Id8 uses two Apple II undulators with permanent magnetic arrays mounted at 90° to each other. With this design and appropriated phase matching the system is able to produce a radiation beam at the sample position, in a range of energy of 500 - 1600 eV, with a degree of circular polarization of 99% and with a spot dimensions of $< 1 \times 1 \text{mm}^2$ that can be reduced with post focusing optics to 40 μm vertical. The flux is of $10^{12}$ ph/sec (at 850 eV), with an energy resolution of $\Delta E/E = 5 \times 10^{-4}$ at 850 eV.

The optical layout of the beamline is depicted in figure 3.6. The radiation emitted by the undulator is partially selected by a pinhole. Then the light is deflected by two mirrors (DFM) that absorb the higher energy side of the photon distribution and deflect the photon beam toward a pair of spherical mirror in Kirkpatrick-Baez configuration. The mirror focus the beam on the
horizontal plane (HFM mirror) and on the vertical plane (VFM mirror) onto the entry slit. The monochromator is of the Dragon type [32] with spherical gratings. The compensation of the defocussing is done by moving the exit slits. The beam is refocused toward experimental end-stations by a Vertical Re-focusing mirror (VRM).

For the experiment described in the next chapters, it has been used an end-station equipped with a 7 Tesla superconducting liquid helium magnet, and with a liquid helium cryostat. The magnetic field can be ramped up relatively fast, (0–7 Tesla in 2 minutes, −4 → +4 Tesla in 1 minute). The field produced by the coils is along the light propagation direction. The sample is vacuum-mounted onto a 3 K sample cooler (VTI, variable temperature insert). This insert can be rotated over 180 degrees. The sample space is ultra-high vacuum, obtained by the cryo-pumping of the liquid helium. The end station, depicted in figure 3.7 is made of two UHV chambers. The top chamber houses the superconducting magnet, with its reservoirs of liquid nitrogen and liquid helium, needed to reach temperatures low enough to keep the magnet coils in the superconducting state. At the center of this chamber, along the vertical axis there is the cryostat. Once the sample is mounted on the cryostat it is possible to rotate it around this axis. By this rotation the angle between the normal to the surface of the sample and the direction of the magnetic field can be changed. In the bottom chamber the sample surface can be prepared by Ar ion sputtering, and temperature annealing. In the same chamber there are also two e-beam evaporators to grow thin films in situ. Alkali and transition metals evaporators can also be mounted in the measurement chamber to evaporate on the substrate kept at
3.2 Circular Polarized and Id8 beamlines

liquid helium temperature. The samples are transferred from the preparation chamber to the magnet chamber by means of a vertical transfer system.

3.2.3 Sample Preparation

All the samples measured in this thesis have been prepared in-situ in a UHV environment. In this process two phases can be considered, in the first the substrate, i.e. a single crystal surface is prepared, while in the second atoms of different elements are deposited on top of the clean substrate.

The preparation of the substrate is performed through cycles of Ar-ions sputtering and thermal annealing. The sputtering with a noble gas is needed to remove the contaminants from the surface, while the thermal annealing is needed to promote an ordering of the surface after the ion bombardment. Several cycles of sputtering and annealing are needed to acquire a clean and ordered surface. The details of these procedures depend strongly on the element that composes the single crystal. For what concerns the Ar ion sputtering, the Ar pressure in the chamber of the order of $1 \times 10^{-6} \text{mbar}$ and the cleanliness of the gas have been checked by means of a mass spectrometer. The ion current on the sample during the sputtering was of the order of $2 - 6 \times 10^{-6} \text{Ampère}$. The sputtering have been done in cycles of 30 minutes alternating with cycles of thermal annealing of the sample duration. The
ion energies range from 1500 eV to 600 eV, depending on the substrate with the higher energy used only for the first cycle.

Thermal annealing is more sample depending than the sputtering. It has been achieved with the same result by irradiation from tungsten filaments or from electron bombardment. This last option is needed to achieve temperature over 1000 K keeping the degassing of sample plate and surrounding elements at minimum since it allows a focused heating. Since all the experimental end-station involve sample transfer systems the temperature cannot be measured by a thermocouple, instead of it, optical pyrometers have been used to measure the surface temperature by means of its thermal emission of radiation. The annealing temperatures are summarized in table 3.1 for the different substrates. For platinum the preparation of the substrate involves

<table>
<thead>
<tr>
<th>Single crystal</th>
<th>Annealing temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(100)</td>
<td>900</td>
</tr>
<tr>
<td>Al(100)</td>
<td>730</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>920</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>900 - 1100</td>
</tr>
</tbody>
</table>

*Table 3.1: Annealing temperatures.*

heating in O₂ pressure 900 K at and further annealing at 1100 K (see ref. [33]). The cleanliness and ordering of the samples surface was checked by XAS spectra and by LEED.

The deposition of thin films and impurities have been performed by means of electron beam evaporator provided with water cooling systems, both custom built by our group and commercial ones like the EFM Omicron evaporator. For the alkali evaporation SEAS getter alkali source have been used. It is important to note, for the evaporation performed at liquid helium temperatures that molecules and atoms deriving from the outgassing of evaporators during operation can easily contaminate the sample due to the higher sticking coefficient by respect to RT. In particular since alkali metals are very reactive they can be contaminated very fast also during atoms deposition. For these reasons it is mandatory, in order to prevent these effects to do an extremely careful degassing of the 3d metal sources and of the alkali metals. Of course it is also mandatory to work with a local pressure not higher than 1 × 10⁻¹⁰ mbar.

The transition metals evaporations have been performed always with low evaporation rates, particularly low in the case of the deposition of transition metal impurities. For impurities typical rates are of 0.005 Å/min, while for Mn ultra thin films on Fe(100) the rate was of about 0.03 Å/min.

In the case of Mn/Fe the sample were not uniform but they have been grown as wedges. A pictorial view of a Mn/Fe sample grown as a wedge is presented in figure 3.8. In such a kind of sample the thickness is not uniform
but it is increasing from one side to the other of the sample along a specific direction. This scheme is very useful for thickness dependent measurement since it avoids to repeat several times a deposition to increase the thickness. In this way the measure becomes much less time consuming. Another advantage is that with a wedge the thickness can be varied continuously improving the sensitivity to those thickness dependent phenomena that occur only in a short range of thicknesses. From the experimental point of view to grow such wedges usually it is sufficient to use a shutter. The shutter is used to spatially cover (or discover) the sample in front of the operating evaporator. In this way it is possible deposit a different amount of material on different regions of the sample area. The local thickness depends on the evaporation rate and on the speed of movement of the shutter. These parameters are related to the thickness range and to the size of the sample. In the study of Mn/Fe presented at the end of this chapter the typical slopes of a wedge are of $0.5 \, \text{Å/mm}$, for a sample of 10 mm width. It should be noted that this kind of measurements are possible thanks to the reduced lateral dimensions of the incoming radiation beam.
3.3 X-ray Absorption Spectroscopy

In this section as well as in sections 3.4 and 3.5 the spectroscopic techniques used in the experiments are introduced. These are photon absorption spectroscopies. The absorption of photons by a material is measured as a function of the incident photon energy. Due to the continuum character of synchrotron radiation emission the technique can be applied in a wide range of photon energies.

When a monochromatic beam of photons is directed on a material of thickness \( d \), only a part of the photons will be absorbed by the material. If the initial intensity of the beam is \( I_0 \) then the intensity after passing through the material will be \( I = I_0 \exp(-\mu x) \), where \( \mu x \) is the absorption coefficient of the material. If the photon energy is scanned from an energy lower than the binding energy of the core electronic levels (as in figure 3.9) of the material to an higher energy, the absorption is dominated by strong features in correspondence of the binding energies of the core electrons.

In a simple single-particle picture, the absorption of the photon is ruled by energy conservation and produces the promotion of an electron in to an empty state. The excited state then can decay by Auger or fluorescence processes, with probability ratios depending on the specific material.

The photon absorption produces a small photoelectronic current from the sample that can be detected. This current is the product of several effects: the promotion of electrons to the empty states, the Auger emission of electrons and the decay of excitons. The electron yield \( Y(\omega) \) is proportional to the absorption coefficient \( \mu(\omega) \). The electron yield measurements have been shown [35] and to be closely similar to the standard measurements done in transmission, more recent investigation about electron yield measurements can be found in ref. [36]. An important advantage of electron yield measurements is that it avoids restrictions to sample thickness intrinsically present in transmission measurements. All the measurements presented in this the-
sis have been performed measuring the electron current from the sample.

3.3.1 Interaction between radiation and atoms

An introduction about interaction of radiation with atoms will be given in the following section. In this description atoms have been chosen instead of solid because this approach is particularly accurate for the impurity systems studied in this thesis since their electronic states have a strongly localized character.

In the framework of time-dependent perturbation theory the Fermi Golden rule for the absorption coefficient can be expressed as:

\[
\mu(\omega) = (4\pi e^2 \omega / c) \sum_f |\langle f | e \cdot r | i \rangle|^2 \delta(E_f - h\omega - E_i) \]  
(3.1)

\[
\mu(\omega) = (4\pi e^2 \omega / c) |\langle f | e \cdot r | i \rangle|^2 \rho(E_f) \]  
(3.2)

Here \( \omega \) is the frequency of x-ray radiation, and \( e \) is the polarization vector of the electromagnetic radiation. This expression is valid only under the constraint that the x-ray wavelength is larger than the dimension of the system (this requirement is generally fulfilled in soft x-rays). The term \( |\langle f | e \cdot r | i \rangle|^2 \) gives the selection rules that connect the symmetry of initial and final states, while \( \rho(E_f) \) is the density of state of the final states.

For an electromagnetic field\(^2\) \( \mathbf{E} \) and \( \mathbf{B} \) are perpendicular to each other and to the direction of propagation of the radiation \( \mathbf{k} \). The radiation field is described by the vector potential \( \mathbf{A} = \mathbf{A}(r,t) \) that can be expressed as a superposition of plane waves.

\[
\mathbf{A}(r,t) = \sum_{k\lambda} \hat{e}_{k\lambda} \{ A_{k\lambda} exp [i(k \cdot r - \omega_k t)] + A^*_{k\lambda} exp [-i(k \cdot r - \omega_k t)] \} \]  
(3.3)

where \( \hat{e}_{k\lambda} \) is a real vector of two components (\( \lambda = 1, 2 \)) that indicates the linear polarization of the radiation and satisfies the relation \( \hat{e}_{k\lambda} \cdot \hat{e}_{k\lambda'} = \delta_{\lambda\lambda'} \). In the Coulomb gauge (\( \nabla \cdot \mathbf{A} \)) we have that \( \hat{e}_{k\lambda} \cdot k = 0 \). The circular polarization vectors of the radiation can be defined on the basis of the linear

\[^1\]Some remarks have to be done about this expressions: the expression implicitly supposes that \( [r, \hat{H}] = (i\hbar / mp) \) where \( \hat{H} \) is the Hamiltonian of the system and \( \hat{p} \) is the momentum operator. This is true only if the same Hamiltonian is used for initial and final states. Moreover the \( \delta \)-function means that a infinite lifetime is supposed for the final state. If a final state with finite lifetime is considered, the \( \delta \)-function should be replaced by a Lorentzian [37].

\[^2\]For a detailed treatment see Weissbluth [37]
Experimental techniques and instrumentation

ones as:

\[ e_{k+1} = -\frac{1}{\sqrt{2}}(e_{k1} + ie_{k2}) \quad \text{right circ. polariz.} \]  
\[ e_{k-1} = \frac{1}{\sqrt{2}}(e_{k1} - ie_{k2}) \quad \text{left circ. polariz.} \]  

(3.4)  

(3.5)

The total Hamiltonian of an atom interacting with the electromagnetic radiation can be written as follow:

\[ H = H_{\text{atom}} + H_{\text{inter}} \]  

(3.6)

with

\[ H_{\text{atom}} = \sum_i \left( \frac{p_i^2}{2m} \right) + V \]  

(3.7)

where \( V \) contains all the Hamiltonian terms described in section 2.1.1 defining the atomic states e.g. the interaction with the nucleus, the Coulomb repulsion between electrons, the spin-orbit interaction, the crystal field and also external fields. The interaction Hamiltonian, \( H_{\text{int}} \), can be written as:

\[ H_{\text{int}} = \frac{e}{mc} p \cdot A + \frac{e^2}{2mc^2} A^2 + \frac{eh}{2mc} \sigma \cdot \nabla \times A \]  

(3.8)

where \( \sigma \) is the spin of the electron. If now we consider \( H_{\text{int}} \) as a perturbation of \( H_{\text{atom}} \), it is possible to calculate the effects of interaction of radiation with matter, on the basis of perturbation theory. Thus if we take into account only the first term in the interaction Hamiltonian, \( H_1 = (e/mc) p \cdot A \), writing it with \( A \) in the Schrödinger representation, and considering only an incoming wave with \( k \) and \( \lambda \) defined; we obtain:

\[ H_1 = (e/m) \sqrt{2\pi \hbar / \omega_k V} (\hat{\epsilon}_{k\lambda} \cdot p) e^{i(kr)} \]  

(3.9)

Where \( V \) is the volume of interaction. The element of matrix between an initial state \( i \) and a final state \( f \) is:

\[ \langle f | H_1 | i \rangle = (e/m) \sqrt{2\pi \hbar / \omega_k V} \left\langle f \left| \hat{\epsilon}_{k\lambda} \cdot p \right| e^{i(kr)} \right\rangle \]  

(3.10)

Furthermore, \( \langle f | (\hat{\epsilon}_{k\lambda} \cdot p) e^{i(kr)} | i \rangle \) = \( \hat{\epsilon}_{k\lambda} \cdot \langle f | p e^{i(kr)} | i \rangle \). If we then assume that the argument of the exponential is small (dipole approximation), and we do a series development of the exponential to the zero-th order i.e. \( e^{i(kr)} = 1 \), the matrix element can be written as follows:

\[ \langle f | p | i \rangle = \frac{m}{i\hbar} \langle f | [r, H_{\text{atom}}] | i \rangle \]  

(3.11)
and has an electrical dipole E1 character. If we go to the next order, $e^{i(k \cdot r)} = 1 + i k \cdot r + \ldots$, we will have two terms one symmetrical $O_S$ and the other antisymmetrical $O_A$:

$$\langle f | O_A | i \rangle = -i(m \omega_{\lambda}/c)(\hat{k} \times \mathbf{e}_{\hat{k} \lambda}) \cdot \mu_L$$

(3.12)

where $\mu_L$ is the magnetic orbital moment; this term has a magnetic dipole M1 character. Instead, if we consider the $O_S$ term in the expansion we have:

$$\langle f | O_S | i \rangle = -(m \omega_{\lambda}^2/2c)\mathbf{e}_{\hat{k} \lambda} \cdot \langle f | Q | i \rangle \cdot \hat{k}$$

(3.13)

where $Q$ is an electrical quadrupolar E2 operator defined as:

$$Q = \mathbf{r} \mathbf{r} - \frac{1}{3} r^2 \delta_{ij}$$

(3.14)

### 3.3.2 Selection rules

The atomic states are defined by their angular momentum quantum numbers: $J_i, M_i$ for initial states and $J_f, M_f$ for final states, i.e. $|i\rangle = |J_i, M_i\rangle$ and $|f\rangle = |J_f, M_f\rangle$. Then the matrix element can be written by means of 3J-symbols and with radial part separated from the angular part by means of Wigner-Eckart Theorem \[38\], \[39\]as in the following equation:

$$\langle J_f, M_f | \mathbf{e}_{\hat{k} \lambda} \cdot \mathbf{r} | J_i, M_i \rangle = (-1)^{J_f - M_f} \binom{J_f}{-M_f} \binom{1}{\lambda} \binom{J_i}{M_i} \langle J_f || \mathbf{e}_{\hat{k} \lambda} \cdot \mathbf{r}|| J_i \rangle$$

(3.15)

The selection rules come directly from the properties of these operators, since they are irreproducible tensors, from the condition for a 3-J symbol to be non-zero. For electric dipole transitions these conditions impose that:

$$\Delta J = 0, \pm 1, \Delta M = 0, \pm 1, J_f + J_i \geq 1$$

(3.16)

These selection rules are independent from the coupling scheme used. If we apply them to the LS coupling we get:

$$\Delta S = 0, \Delta L = 0, \pm 1, L_f + L_i \geq 1, \Delta M_L = 0, \pm 1$$

(3.17)

\[3\]This condition are for a general 3J-symbol $\binom{j_1}{-m_1} \binom{j_2}{m_2} \binom{j_3}{m_3}$: $m_1 + m_2 + m_3 = 0$

plus triangle relations $\Delta(j_1, j_2, j_3)$ see \[37\].
It is important to note that for right polarized light ($\lambda = +1$) we have that $\Delta M = +1$, for right polarized light ($\lambda = -1$) we have that $\Delta M = -1$, while for linear polarized light ($\lambda = 0$) we have that $\Delta M = 0$.

3.4 X-ray Magnetic Circular Dichroism

XMCD is the spectroscopic absorption technique that makes use of circular polarized radiation to study magnetic systems. It exploits the differences of the absorption coefficient of a magnetic material upon the parallel or antiparallel alignment of the helicity of circular radiation with respect to the magnetization. The sign “+” is used here for right circular helicity of the radiation, while “−” is used for left circular helicity.

From the theoretical point of view, dichroism studies in the x-ray regime started from the calculations of Erskine and Stern [40] proposing magneto optical effects to occur at $M_{32}$ edges of Ni. Thole et al. [41] predicted dichroic effects to be measurable for the rare earths. The first experimental studies have been done in late 80’s, showing dichroic effects for $M_{4,5}$ edges of rare earths [42], for K-edge of Fe in the hard x-ray regime [43] and in 1990 for $L_{3,2}$ of Nickel [44].

As an example of x-ray circular dichroism in a magnetic material, figure 3.10 shows two spectra, $\sigma_+$ and $\sigma_-$, acquired with right and left circular polarization of 3.4 ML of Fe on Cu(100) at room temperature in remanence from magnetic saturation, and their dichroism ($\sigma_- - \sigma_+$). In general, systems that can be studied with XMCD are ferromagnets, ferrimagnets and paramagnets. The first thing to understand is why a magnetic system should display dichroic effects (for a general overview about this subject see Stöhr [45]).

The magnetic properties of the transition metals are mainly due to $d$ valence electrons. In ferromagnets Fe, Co, Ni the d-shell is increasingly filled by electrons, resulting in a decreasing number of holes ($N_h$). The exchange interaction splits the band in spin up and spin down band. The spin moment is the proportional to the difference of the holes in spin up $N \uparrow$ and spin down bands $N \downarrow$: $\mu_s = -2 \langle S_z \rangle \mu_B / \hbar = (N \uparrow - N \downarrow) \mu_B$. The orbital moment $\mu_l = - \langle L_z \rangle \mu_B / \hbar$ arises from the spin-orbit interaction. The relative magnitude of these two moments can be qualitatively deduced from the fact that the exchange energy is around 1 eV in 3$d$ elements while spin-orbit is around 0.05 eV. The magnetic dipole moment is $\mu_D = -7 \langle T_z \rangle \mu_B / \hbar$, with $T_z = \sum_i s_i - 3 r_i \cdot (r_i \cdot s_i)$. Magnetic moment values for bulk 3d transition metals are given in table 3.2. From the spectroscopic point of view in bulk 3d metals the $2p \rightarrow 3d$ transitions show two main features that are called L$_3$ and L$_2$ edges. These two features are due to transitions from the spin-
3.4 X-ray Magnetic Circular Dichroism

Figure 3.10: Spectra of 3.4 ML of Fe/Cu(100) at room temperature. Right circular polarization ($\sigma_+$), left circular polarization ($\sigma_-$) and dichroism.

Figure 3.11: $L_3$ and $L_2$ edges of a transition metal spectrum. The two step function drawn in the figure is a model for $2p \rightarrow 4s$ transitions. Adapted from [45].
Table 3.2: Magnetic moments (in \( \mu_B \)) of bulk 3d transition metals. \( \mu_{\text{Tot}} \) is the total magnetic moment, \( \mu_s \) is the spin magnetic moment, \( \mu_l \) is the orbital magnetic moment, in units of \( \mu_B \). From [45].

<table>
<thead>
<tr>
<th>Element</th>
<th>( \mu_{\text{Tot}} )</th>
<th>( \mu_s )</th>
<th>( \mu_l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.28</td>
<td>2.19</td>
<td>0.09</td>
</tr>
<tr>
<td>Co</td>
<td>1.71</td>
<td>1.57</td>
<td>0.14</td>
</tr>
<tr>
<td>Ni</td>
<td>0.69</td>
<td>0.62</td>
<td>0.07</td>
</tr>
</tbody>
</table>

orbit split 2p core levels. Transitions from 2p\(_{3/2}\) core states are related to the L\(_3\) edge while transitions from 2p\(_{1/2}\) are related to the L\(_2\) edge. It is to note that the L\(_{2,3}\) edges are not only due to 2p \( \rightarrow \) 3d transition. They also contain contributions due to 2p \( \rightarrow \) 4s transition also allowed by the dipole approximation, although these last are weaker by a factor of 20 then 2p \( \rightarrow \) 3d (see ref. [46]). Furthermore even smaller contributions to the edge can come from quadrupole transitions.

To make some quantitative prediction about XAS and XMCD some models can be considered for the transitions involved. The first to be proposed was the Erskine-Stern model [40] in 1975. The initial states 2p are considered relativistically, spin-orbit split in 2p\(_{1/2}\) and 2p\(_{3/2}\) while the final empty d states are considered non-relativistically as being only of spin-down character (addressing the case of Ni). Thus since for dipole transitions \( \Delta s = 0 \), only transitions from spin down states to spin down states are considered. The transition probabilities from the initial states to the final states have to be calculated. If the initial states and final states are written in the form \( |i\rangle = |l, m_i, s, m_s\rangle \) and \( |f\rangle = |l' + 1, m_i', s', m_{s}'\rangle \), making use of the result of equation 3.15 the transition probabilities can be written as:

\[
|\langle l + 1, m_i' | \mathbf{e}_{k\lambda} \cdot \mathbf{r} | l, m_i\rangle|^2 = \left( \begin{array}{cc} l + 1 & 1 \\ -m_i' & 1 \end{array} \right)^2 |\langle l + 1 | \mathbf{e}_{k\lambda} \cdot \mathbf{r} || l \rangle|^2
\]

(3.18)

Where \( J' = l + 1 \) and \( J = l \) since dipole transitions can be seen as involving the exchange of a quantum of angular momentum from an initial state with orbital momentum \( l \) to a final state with orbital momentum \( l + 1 \). While \( m_i' \) and \( m_i \) are the final and initial states magnetic numbers. For the case of 2p \( \rightarrow \) 3d transition \( l = 1 \) with circular polarized radiation (\( \lambda = \pm 1 \)) hence the transition probability can be written as:

\[
= \left( \begin{array}{cc} 2 & 1 \\ m_i + 1 & -m_i \end{array} \right)^2 R^2 = \frac{(3 \pm m_i)(2 \pm m_i)}{30} R^2
\]

(3.19)

In fact the initial state is a p-state, so \( l = 1 \) and \( l + 1 = 2 \). In this expression are explicitly considered only transitions due to circularly polarized radiation, as expressed by the polarization values \( \lambda = \mp 1 \). Hence also the
magnetic number of the final states $m_l'$ can be different only of ±1 unit by respect to the initial state one $m_l$. Finally $R = \int dr r^2 R_{m=3l=2}(r) R_{m=2l=1}(r)$ accounts for the integration over the radial part. The explicit calculation for the general case of the 3j-symbols is due to Bethe and Salpeter [47].

<table>
<thead>
<tr>
<th>Core level</th>
<th>$m_l'$</th>
<th>matrix element for right circ. pol. light</th>
<th>matrix element for left circ. pol. light</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p_{3/2}$</td>
<td>+1</td>
<td>$2/15R^2$</td>
<td>$1/45R^2$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$2/15R^2$</td>
<td>$2/15R^2$</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>$1/15R^2$</td>
<td>$2/15R^2$</td>
</tr>
<tr>
<td>$2p_{1/2}$</td>
<td>+1</td>
<td>$4/15R^2$</td>
<td>$2/45R^2$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$1/15R^2$</td>
<td>$1/15R^2$</td>
</tr>
</tbody>
</table>

Table 3.3: Dipole matrix elements for left and right circular polarized light from $2p_{3/2}$ and $2p_{1/2}$ core levels, within the Erskine Stern model, i.e. considering only spin-down states.

matrix elements have been calculated in table 3.3, and the transitions are shown in a simple scheme in figure 3.12, within the approximation that only spin down final states are available, as assumed by Erskine and Stern for Ni. A pictorial representation of the transition strength is given by arrows that are thicker the larger is the matrix element. From this model a calculation of the total line strength due to sum of all allowed transitions is possible. The sum spectrum of left an right circular polarization, $(\sigma_+ + \sigma_-)$ and the difference spectrum $(\sigma_+ - \sigma_-)$ intensities can be calculated at the $L_3$ and $L_2$ edges:

$$L_3(2p_{3/2} \rightarrow 3d \downarrow) = \begin{cases} 
(\sigma_+ + \sigma_-) = 8/9R^2 \\
(\sigma_+ - \sigma_-) = -2/9R^2 
\end{cases} \quad (3.20)$$

Figure 3.12: The $2p \rightarrow 3d$ transitions for the Erskine-Stern model.
Experimental techniques and instrumentation

Then $L_3/L_2$ ratio is found to be 2:1 for the total cross section and -1:1 for the difference cross section. These results do not properly account for the experimental results. The experimental data show a dichroism at $L_3$ edge more intense then the expected one from Erskine Stern model (see for example figure 3.10).

This discrepancy is due to the fact that in the model of Erskine and Stern the spin-orbit of the 3d valence states is neglected. In a fully relativistic model [49] the spin-orbit splitting is considered for both initial and final states. For the valence states this produces an imbalance in the number of empty states. The scheme of transitions for a fully relativistic model is presented in figure 3.13, for a general case. In the figure together with the transitions also their strength is plotted and for each state the orbital an spin moments are also shown as vertical bars. Since the spin-orbit is included

$$L_2(2p_{1/2} \rightarrow 3d_{5/2}) = \left\{ \begin{array}{l}
(\sigma_+ + \sigma_-) = 4/9R^2 \\
(\sigma_+ - \sigma_-) = 2/9R^2
\end{array} \right.$$
the 3d states are split in two sublevels, the 3d_{3/2} and the 3d_{5/2}, respectively with \( j = 3/2 \) and \( j = 5/2 \). The increased intensity at \( L_3 \) is a consequence of Hund’s third rule for more then half filled shell elements where the \( j = 5/2 \) sublevels are more populated than the \( j = 3/2 \) ones. This is reflected in the spectra at \( L_3 \) since the only dipole allowed transitions to the \( j = 5/2 \) states can be done from the sublevel \( p_{3/2} \).

A considerable improvement, in the possibility of extracting information about the relevant physical quantities involved in magnetism from XMCD spectra, has come with the introduction of sum rules. The sum rules are theoretical expressions that link spectral properties to \( \langle L_z \rangle \), \( \langle S_z \rangle \), \( \langle T_z \rangle \) the expectation values of \( L \), \( S \) and \( T \) operators, along the quantization axis \( z \), for a magnetic system in saturation. The spin magnetic moment, \( \mu_s \), the orbital magnetic moment, \( \mu_l \) and the spin dipole magnetic moment \( \mu_D \) are related to \( \langle L_z \rangle \), \( \langle S_z \rangle \), \( \langle T_z \rangle \) by the following relations.

\[
\begin{align*}
\mu_s &= -2\mu_B \langle S_z \rangle \quad (3.21) \\
\mu_l &= -\mu_B \langle L_z \rangle \quad (3.22) \\
\mu_D &= -7\mu_B \langle T_z \rangle \quad (3.23)
\end{align*}
\]

For the spin operator the spin-orbit of initial states have the effect of producing electrons with opposites spin by means of + or − circularly polarized photons this is seen in the dichroic spectrum \( (\sigma_+ − \sigma_-) \) as a different sign at \( L_3 \) and \( L_2 \) edges. In figure 3.14, the integrals of dichroism at \( L_3 \) and \( L_2 \) are defined as \( A_1 \) and \( A_2 \) respectively. From these qualitative considerations the spin magnetic moment will be proportional to the difference of the two intensities (\( A_1 - A_2 \)). On the opposite the orbital magnetic moment would be proportional to the sum of the intensity at the two edges (\( A_1 + A_2 \)). These

\[\text{Figure 3.14: Integrals at } L_3 \text{ and } L_2 \text{ edges of dichroism.}\]
ideas have been formalized to the general case of n-electron system and thus three major sum rules have been derived:

\[ N_h C = \int_{L_3+L_2} (\sigma_+ + \sigma_-) dE \]  

(3.24)

This is the charge sum rule [50], [51] where \( C \) is proportional to the square of the radial \( p \rightarrow d \) matrix element, \( \sigma_+ \) and \( \sigma_- \) are the right and left polarized spectra, and \( N_h \) is the total number of holes:\(^5\)

\[ \mu_l = -\frac{4}{3} \mu_B N_h \frac{\int_{L_3+L_2} (\sigma_+ - \sigma_-) dE}{\int_{L_3+L_2} (\sigma_+ + \sigma_-) dE} \]  

(3.25)

This is the orbital sum rule [52], by means of which it is possible to calculate \( \mu_l \). Moreover another sum rule has been stated that allows to determinate the spin magnetic moment:

\[ \mu_s + \mu_D = -2\mu_B N_h \frac{\int_{L_3} (\sigma_+ - \sigma_-) dE - 2 \int_{L_2} (\sigma_+ - \sigma_-) dE}{\int_{L_3+L_2} (\sigma_+ + \sigma_-) dE} \]  

(3.26)

This last one is the spin sum rule [53]. The integrals should be performed from 0 to \( +\infty \) for each edge contribution if the two contribution would have been completely separated. Unfortunately this is not possible and a suitable energy \( E_m \) in between \( L_3 \) and \( L_2 \) has to be chosen to separate the two edges. This approximation holds better the higher is the spin-orbit of the initial states and thus the energy separation of the two edges. In the 3d series, the problem of determining the integration interval becomes critical for lighter elements as Vanadium, due to the partial overlapping of the edges.

Several things should be noted for the practical use of sum rules. First the term \( \mu_D = 7 \langle T_2 \rangle \mu_B / h \), the magnetic dipole moment, does not allow to determine directly \( \mu_s \). This quantity is often smaller than \( \mu_s \) and for cubic systems this term can be approximated to zero. For systems of reduced symmetry, \( \mu_D \) contribution can not be neglected. Furthermore the system should be magnetically saturated. Lastly, to make direct use of sum rules one should be able to extract from the \( \sigma_0 = (\sigma_+ + \sigma_-) \) spectrum the contribution of transition to 4s states. This is often done by approximating it with a double-step function as in [54].

Other important remarks are that the intensity of dichroism depends on the degree of polarization of incident light and on the experimental angle between the magnetization axis in the following way: \( \sigma_0 \propto k \cdot M \propto k M \cos(\phi) \) where \( k \) is the photon helicity vector and \( M \) is the magnetization.

\(^5\)If the anisotropy of the charge is included another term, \( N_Q \), related to the electric quadrupole interaction, should be added to \( N_h \).
3.5 X-ray Magnetic Linear Dichroism

In the X-ray Magnetic Linear Dichroism (XMLD), instead of using circularly polarized radiation and thus measuring a quantity proportional to $k \cdot M$, linear polarized light is used. The measure of dichroism becomes proportional to the square of the magnetization, and to the angle between magnetization and electric field of the radiation $E$.

$$
\sigma_0 \propto E \cdot M^2 \propto \cos^2(E \cdot M^2)
$$

(3.27)

This can be derived from the expression of the matrix elements by $3j$-symbols for $T = 0$, when only the $M = -J$ i.e. the lowest energy level is occupied. To account for effects $T \neq 0 [41],[55]$ it is needed to sum all the contributions due to the different $(2J+1)$ $M$ levels opportually weighted as it is done in equation 3.29.

$$
|\langle J', M' | \hat{e} \cdot \hat{r} | J, M \rangle|^2 \propto A_{J,J'}^0(\Theta) |\langle J' || \hat{e} \cdot \hat{r} || J \rangle|^2
$$

(3.28)

where $\Theta = k_B T / g \mu_B H$ and,

$$
A_{J,J'}^0(\Theta) = \sum_{M=-J}^{J} \left( \begin{array}{cc} J' & 1 \\ -M' & \lambda \\ M & \end{array} \right)^2 e^{-M/\Theta} \sum_{M=-J}^{J} e^{-M/\Theta}
$$

(3.29)

This expression can be rewritten in terms of $\langle M \rangle$ and $\langle M^2 \rangle$ depending on $\delta J = -1, 0, +1$ and on $\lambda = 0, \pm 1$ depending on light polarization, since:

$$
\langle M \rangle = -J B_J(J/\Theta)
$$

(3.30)

and

$$
\langle M^2 \rangle = J(J + 1) + \langle M \rangle \coth(1/2\Theta)
$$

(3.31)

where $B_J$ is the Brillouin function. From this we see that $A_{J,J'}^0(\Theta)$ depend only on $J$ and $\Theta$. If we consider the case of linear polarized light ($\lambda = 0$) with the electric field $E$ laying in the synchrotron electrons plane and orthogonal to the radiation propagation direction, then it is possible to discriminate between: $(E||H)$ and $(E\perp H)$. It is possible to find these expressions:

$$
A_{J,J'}^\parallel(\Theta) = A_{J,J'}^0(\Theta)
$$

(3.32)

$$
A_{J,J'}^\perp(\Theta) = \frac{1}{2} \left( \frac{1}{2J+1} - A_{J,J'}^0(\Theta) \right)
$$

(3.33)

From these two equation we can clearly see how the contributions depend only on $A_{J,J'}^0(\Theta)$. At an intermediate angle $\gamma$ the temperature dependent
part of line strength is proportional to:

\[
(A_{J,J'}^{||}(\Theta) \cos^2 \gamma + A_{J,J'}^{\perp}(\Theta) \sin^2 \gamma)
\]

In reference [55] there are the explicit expressions of \(A_{J,J'}^{0}(\Theta)\) as a function of \(\langle M^2 \rangle\) furthermore also expressions for \(A_{J,J'}^{\pm 1}(\Theta)\) are given as a function of both \(\langle M \rangle\) and \(\langle M^2 \rangle\). From these equations it is clear that the magnetic dichroic signal due to the difference of circular polarization spectra i.e. \((A_{J,J'}^{||}(\Theta) - A_{J,J'}^{\perp}(\Theta))\) is proportional only to \(\langle M \rangle\). XMLD, being proportional to the square of magnetization, can be successfully applied to uncompensated system and antiferromagnets (for which circular magnetic dichroic signal is zero).

This technique was applied for the first time by van der Laan et al. [42] to the study of rare earth compounds but it has also been used in the study of FM/AFM magnetic coupling studies [57], [58] and in XPEEM studies of Co on LaFeO₃ by a combined use of XMCD and XMLD [59]. Moreover another important possibility is to use XMLD to probe the magnetocrystalline anisotropy as proposed by van der Laan [60] and applied to vicinal Co films [28].

Figure 3.15 shows the absorption spectra of \(L_2\) edge of a NiO film with linear polarized light acquired at different angles between the normal to the surface and the direction of the beam. The clear multiplet structure of the edge allows to see the branching ratio changes in the two main features, that can be associated with the spin-spin correlation function [56] of the antiferromagnetic NiO. From the angular dependence of the linear dichroism signal, the orientation of the Ni moments can be determined. In the case of NiO films in figure 3.15, grown on MgO, the moments are found to orient preferentially along the direction normal to the surface plane.
3.6 Mn on Fe, magnetic moments distribution

In this section a study of the distribution of the magnetic moments of Mn thin films grown on Fe(100), is presented. This experiment is discussed here not only for the interest of its results, but also because it is a very interesting case of the combined application of XMCD and XMLD techniques. Manganese on Fe is an interesting system, that has attracted interest because of the interplay of ferromagnetic and antiferromagnetic interactions at the interface formed by these two metals.

XMCD and XMLD measurements have been performed as a function of the polar and azimuthal angles. The results together with atomic multiplet calculations of the spectra, performed by S.S.Gupta and D.D. Sarma for the Mn$^{2+}$ ion configuration, made possible to understand the magnetic moment distribution. A non collinear structure is found to originate from frustrated interface exchange interactions. The Mn moments point perpendicular to the surface with a small in-plane component pointing at 90° to the Fe moments, hence the Mn moments are canted with respect to the normal to the surface.

3.6.1 Background

The magnetic coupling between Mn and Fe at the interface of Fe(100) surface is a particular case of AFM/FM exchange coupled systems. Before presenting the experimental results it is instructive to briefly introduce the physics of FM/AFM systems. In figure 3.16 typical hysteresis loops are depicted for a FM system, a FM/AFM coupled system for which the coercitivity is enhanced, and a FM/AFM system that shows an exchange bias, i.e. the hysteresis is not symmetric around zero but it is shifted of an amount $H_B$. The exchange bias has been discovered by Meiklejohn and Bean \[61\] and it is thought to be due to the exchange interaction at the interface, in FM/AFM systems. The subject is one of the more active in research today and many aspects of the physics involved are still poorly understood. From the technological point of view the most important applications of exchange bias are in the field of magnetoresistive sensors and spin valves multilayer devices used in spintronics.

The energetic and the exchange coupling of Mn atoms in Fe(100) surface have been studied theoretically by several authors. Nonas \textit{et al.} \[62\], \[63\] found that it is energetically favored for impurities of Mn on the surface of Fe(100) to be included in the surface layer, with an atom exchange process, coupling with Fe antiferromagnetically. Furthermore considering the interaction of two Mn impurities, they are found to preferably couple to each other ferromagnetically while they both couple antiferromagnetically with the substrate. The Mn seems to be a particularly metastable case for which
also the ferromagnetic coupling between Fe and Mn cannot be excluded.

For the Mn monolayer on Fe(100) the magnetic structure have been studied by Wu and Freeman [64] and by Piazzagalli et al. [65]. They found a c(2×2) antiferromagnetic configuration, depicted in figure 3.17. In the figure we see that there are two inequivalent kind of atoms atoms “1” and “2”, for this reconstruction. The antiferromagnetic coupling occurs between inequivalent Mn kind of atoms coupling, with the magnetic moment of atoms “1” pointing in the opposite direction of the moments of atoms “2”.

For the magnetic coupling of Mn monolayer with respect to Fe(100) sub-

\[ c2x2 \]

Figure 3.17: Monolayer of Mn on Fe, c(2×2) model structure. Adapted from [65].

strate controversial results have been found by authors. Walker et al. [66] found that the Mn surface couple ferromagnetically to the Fe substrate, while Roth et al. [67] found an antiparallel coupling. The c(2×2) antiferromagnetic structure was also suggested by Spišák et al. [68], with an
enhancement of magnetic moments for a non collinear arrangement of moments that allows to reduce the frustration. Another important example of non collinear rearrangement of moments is the in-plane $90^\circ$ angle between Mn and Fe magnetization found for NiFe/FeMn bilayers [69] that has been explained by Koon as due to "spin-flop" states in the AFM [70].

Several experiment have studied the atomic structure of Mn and atom exchange process in the submonolayer and the $c(2 \times 2)$ structure have been confirmed by STM and STS measurements, [71], [72] at room temperature, for submonolayer and ultrathin Mn films on Fe(100).

From the experimental point of view, the magnetism of Mn in the submonolayer regime has also been studied by XMCD. The Mn is found to be ferromagnetic with an orientation antiparallel to Fe(100) ferromagnetic substrate, as seen by Rader et al. [73] and Dresselhaus et al. [74].

As can be seen from figure 3.18 the ratio between asymmetries\(^6\) of Mn and Fe decreases with increasing Mn coverage thus indicating a transition from FM to AFM. At about 1 ML the Mn is almost completely AFM. Different experimental results have been given by Andrieu et al. [75], where a ferromagnetic coupling is found for coverage from 0-2 ML with parallel orientation of Mn and Fe moments, while above 2 ML the ferromagnetism disappears. They also found a structural transition for Mn films around 2-3 ML.

From Kerr Microscopy measurement on Fe/Mn/Fe wedge shaped sandwiches Yan et al. [76] found, five domain patterns, related to ferromagnetic coupling, antiferromagnetic coupling, $90^\circ$ degree coupling, no coupling and a novel non collinear canted coupling for Mn thickness in the range from 6 to 12 Å.

A non collinear structure can be explained in terms of a competition be-

\(^6\)The asymmetry is defined as $\frac{(\sigma_- - \sigma_+)}{(\sigma_+ + \sigma_-)}|L_3|$ and measures the intensity of the dichroism.
tween two interactions. The Mn-Mn antiferromagnetic coupling, in fact, can compete with the antiferromagnetic coupling with Fe substrate. The total result of these opposite tendencies can be a non collinear structure.

3.6.2 Experimental results and calculations

The experiments were conducted at Circular Polarized beamline at Elettra with the chamber described in subsection 3.2.1.1. Before introducing the experimental results it is useful to describe in more detail the geometries used for the measurements: the polar geometry and the azimuthal geometry. These are depicted in figure 3.19. The quantities in the picture are $\mathbf{E}$ the electrical field vector that is always parallel to the axis $y$, the axis $x$ corresponds to the radiation propagation direction and the $z$ axis is perpendicular to the synchrotron ring plane. The polar angle $\theta$ is defined as the angle between the normal to the surface $\hat{n}$ and the $x$ axis. The azimuthal angle $\phi$ is the angle between the Fe magnetization direction and the electric field vector $\mathbf{E}$, and is defined to be $\phi = 0$ when they are parallel. Moreover $\mathbf{\mu}_{Fe}$ is the magnetic moment vector of Fe and $\mathbf{\mu}_{Mn}$ is the magnetic moment vector of Mn. In the polar geometry measurements the angle $\theta$ between the surface normal and the light propagation direction is changed. In this way, as shown in the top view of figure 3.19, the angle

![Polar and azimuthal measurement geometries](image_url)
between $\mu_{Mn}$ and $E$ is changed and the linear dichroism of the out of plane component of the Mn magnetic moment is probed. In the azimuthal geometry, the sample normal is parallel to the x axis direction (normal incidence) and the rotation is around the x axis. As the $\varphi$ angle is changed, the in plane component of the moment is probed by XMLD, since in this case $E$ is parallel to the surface plane.

The Ag single crystal has been mounted at 45 degrees by respect to the z axis so that in measurement position the [100] direction of Fe was parallel to the z axis for $\varphi = 0$. In fact the easy magnetization axis of Fe films is along the [100] direction and Fe grows on Ag(100) with the [100] crystallographic direction rotated by 45° by respect to the Ag [100] axis. First a film of Fe of a thickness of about 30 ML has been grown on the clean Ag(100). The Fe film has been checked with XMCD. Then a wedge of Mn has been grown on the Fe thick film with a maximum coverage of 3 ML and with the growth direction parallel to the z axis.

XMCD has been used to check the magnetization of Mn and Fe. Iron, as expected, did not show any change after Mn deposition. Mn as in reference [73] showed antiparallel magnetization with respect to the iron. In figure 3.20 are plotted the spectra of 0.2 ML of Mn (upper inset) and substrate Fe (lower inset) taken with left and right circular polarized light. In figure 3.21, instead, are plotted the normalized dichroic signals of Mn (upper inset) and Fe (lower inset) taken in remanence after application of an external mag-

![Figure 3.20](image-url)
netic field of 0.1 Tesla. By measuring in different positions of the sample, i.e. at different coverages, it has been possible to confirm the behavior for the asymmetry ratio of Mn and Fe as a function of the coverage shown in figure 3.18.

Then a sample of uniform coverage, with a thickness chosen to be the low-
est compatible with no Mn dichroism (i.e. approx. 1 ML), was grown. As discussed before the disappearance of Mn dichroic signal, suggests that its magnetic structure is changed from FM to AFM. It has to be noted that an alternative explanation of the absence of dichroism, even though this possibility would contradict theoretical predictions, is that the zero Mn dichroism is due to a strong suppression of the magnetic moment of Mn atoms.

A series of measurement as a function of the polar angle \( \theta \) where performed with linear polarized light with the \( E \) field horizontal (i.e. parallel to \( y \)). In figure 3.22 are shown the spectra of \( L_3 \) edge of Mn while in figure 3.23 the spectra of \( L_2 \) edge of Mn, in both cases as a function of the polar angle. The multiplet features in the spectra reflect the atomic multiplets of the \( d^5 \) electronic configuration of Mn, that are not completely suppressed by solid state effects. The sample has been magnetized along the \( x \) axis and then measured in remanence. The changes in the spectra are due to the changes of angle between the electric field of incident radiation and the direction of the Mn moments. To relate the spectral changes to information about magnetization direction requires evaluation of the XMLD effects through calculation. Mn is a favorable case since the spectra show \( d^5 \) multi-
plet configuration related features [74]. Therefore the spectral lineshape can be addressed by means of atomic multiplet spectra calculations. Atomic multiplets calculations for the case of d⁵ electronic configuration (Mn²⁺ ion) have been performed by S.S. Gupta and D.D. Sarma, by exact diagonalization of atomic many-body Hamiltonian, based on a fully coherent spectral function in the scheme proposed by Mahadevan and Sarma [77].

The parameters of calculation have been chosen as follows. The average Mn 3d – 3d multiplet interaction (U_{dd}) was chosen to be 4.0 eV, the Slater-Condon multiplet parameters were rescaled to 75% and the Mn 2p – 3d multiplet interaction (U_{pd}) was set to 4.4 eV. The final spectra are obtained by a gaussian broadening to account for experimental resolution (which at this energy is around 0.2 eV), while core hole lifetime was simulated by
Lorentzian broadening. For L_3 region γ₀ = 0.6 eV and α₀ = 0.1 eV, and for the L_2 region γ₀ = 0.55 eV and α₀ = 0.2 eV. Where γ₀ is the Lorentzian width at the lower energy end of each edge and α is the rate of increase of width with energy.

These calculations gave the lineshape dependence of spectra as a function of the angle between electric field and magnetic moment. The comparison of the experimental and theoretical results is presented in figure 3.24. In particular, at L_3 the experimental spectra at \( \theta = 0^\circ \) show a small intensity increase and a shift toward higher energies by respect to the spectra at \( \theta = 0^\circ \). The calculations account well for this trend. Also at L_2 a similar displacement occurs together with a branching ratio change for the two peaks as a function of the angle. Since these variations are accounted consistently by the theoretical calculation, it is possible to deduce the moment angular dependence by means of its relation to the theoretical geometry used. It is then possible to conclude that the Mn magnetic moment has a strong out of plane component.

The XMLD dichroism has been calculated from the spectra and compared to the experimental linear dichroism. This two signal are plotted in figure 3.25. At L_3 linear dichroism changes sign, being positive before edge and
negative immediately after the edge, the same happens at L₂. Both these features are accounted by the calculated XMLD. The overall lineshape agreement is good and only some details are not perfectly accounted.

With polar measurements only, it is not possible to determine whether there is also a preferential in-plane component of the magnetization and in which direction it points. To do this, azimuthal measurements are needed. After magnetization along x, the sample has been measured again with linear horizontally polarized light as a function of azimuthal angle φ. A very small change of the order of magnitude of 3% has been detected for the intensity ratio of the two L₂ peaks over an angular range of 360°. In figure 3.26 the behavior of the ratio of the L₂ peaks as a function of the azimuthal angle, is plotted. The behavior is similar to a sin²(φ) function. The maxima being approximately located at ±90°, with the zero of the angle set by the magnetization direction along y.

Making use of the same behavior of the L₂ peaks determined from calculations it is possible to say that when the branching ratio has a minimum the electric field vector and the magnetic moments are perpendicular. Moreover at φ = 0 we know that Fe magnetization is along y. Thus there is a component of the Mn moment in the plane and perpendicular to the iron magnetization direction. These components can be driven by “spin-flop” states in the AFM as shown by Koon [70]. The in-plane 90° angle between Mn and Fe magnetization is similar to the one found for NiFe/FeMn bilayers [69].

In summary, the combined use of XMCD and XMLD, in conjunction with atomic multiplet calculations has allowed the determination of the distribution of the magnetic moment for antiferromagnetic Mn at near ML coverage,
by respect to Fe moments. The main conclusion that can be deduced from these results is that 1 ML of Mn on Fe(100) form a non-collinear magnetic structure. The direction of the Mn moment point mainly perpendicular to the Fe surface and easy magnetization axis. A graphical representation of the geometry of Mn moments determined is presented in figure 3.27.

![Graphical representation of Mn and Fe moments.](image)
Chapter 4

3d metal impurities on alkali surfaces

The electronic and magnetic properties of manganese and vanadium impurities on alkali metals (Cs, K, Na) and for comparison on Cu(100) and Al(100) surfaces have been investigated, by XMCD and magnetization curves measured with circular polarized radiation. The weak interaction between the transition metal impurity and the substrates with low electronic density enhances the localized character of the impurity electronic states. As the electronic density of the substrate increases, from Cs to Al, the localization and the magnetism of these states is gradually weakened. No significant magnetic anisotropy is found for Mn and V impurities on all substrates. On the basis of the observed magnetic behavior a predominant $d^5$ atomic-like electronic configuration has been established for the Mn impurity on alkali metals. The case of V impurities on alkali metals is more complicate. A simple atomic configuration ($d^3$, $d^4$, $d^5$) does not fully account for the experimental results. The results are discussed considering crystal field effects, mixing of configuration, and for the case of $d^4$, Van Vleck paramagnetism. A mechanism is proposed to account for the small orbital moments measured.

4.1 TM impurities on alkali metals

Transition metals atoms diluted on a simple non metallic host can be considered a system in between the two extreme situations of atomic and itinerant magnetism. From the pioneering works of Friedel [4] and Anderson [5] the subject has always attracted great attention. The very basic questions is: how do the 3d transition metal states interact with the valence host states and how does this influences their magnetism? To answer this question a first step is to consider those cases where hybridization and the crystal field interactions between the transition metal impurity and the host are weak.
The alkali metal valence states are free-electron-like $s$ states, that have low density of states at $E_F$ thus they weakly hybridize with the $3d$ states of the transition metal atoms. Also crystal field effects are very weak for these systems with respect to bulk $3d$ systems. Riegel et al. [78] and Kowallik et al. [79] studied Fe and Ni isolated atoms choosing as hosts, the alkali metals. In the case of Fe in K, Rb, Cs, an atomic $d^6$ electronic configuration was established by Riegel. The magnetic moment for a $d^6$ system moment is $\mu_{at.}(d^6) = 6.7 \mu_B$ (see section 2.1.1.1). For the case of Ni in K, Rb, Cs the configuration of Ni was found to be $d^0$ by Kowallik, with a magnetic moment of $\mu_{at.}(d^0) = 3.5 \mu_B$. Moreover an host dependency was found, in fact the magnetic behavior of the impurity changes, with changing volume of the host (from K to Li), from an atomic magnetic configuration to a non magnetic state.

Recently, Beckmann et al. [80] renewed the interest on the subject, reporting "giant" magnetic moments for Fe, Co impurities deposited on the surface of Cs films. From anomalous Hall resistance measurements the authors reported magnetic moments of $8 \mu_B$ for the Co/Cs system and of $7 \mu_B$ for the Fe/Cs. These values are larger than the atomic value ($\mu_{at.}(Fe) = 6.7 \mu_B$, $\mu_{at.}(Co) = 6.63 \mu_B$). The authors explain this discrepancy as due to the magnetic polarization of the Cs host in similarity with the well known polarization effect (giant moments) in Pd and Pt, for (Fe, Co) on (Pt, Pd) alloy systems. This interpretation, apparently contrasting with previous measurements has been at the a center of a debate [81], [82], [83]. It was pointed out that the interpretation of data was biased by the assumption that the orbital moment was zero ($L = 0$) as if it was quenched by crystal field, while using atomic values for $g$, $L$, $S$ the data were in agreement with Riegel and Kowallik. Furthermore it is well known that the magnetic susceptibility of alkali metals is small, so an explanation based on large induced moment on the host appears to be unlikely.

Most recently Gambardella et al. [7] used XAS and XMCD to determine the electronic configuration and the magnetic moments of Fe, Co, Ni impurities on the surface of K and Na films. They found atomic-like spectra with strong multiplet structures that allowed them to determine the electronic configuration by comparison with multiplet structure calculation of atomic spectra from van der Laan and Thole [84]. Fe, Co, Ni electronic configurations on K were determined to be $d^7$, $d^8$, $d^6$ respectively. From these electronic configurations it is clear that there is a strong charge transfer from the host to the $3d$ shell of the impurity, that acquires an electronic configuration of the type: $d^{n+1}$. In line with the experimental results a Co $d^6$ configuration was obtained in the framework of Hubbard modified local spin density calculations from Kwon et al. [85] for Co on Cs. For the case of Ni the experimental observation of Gambardella et al. agrees with Kowallik results [79]. Moreover Ni on Na is found to be non magnetic, while Ni on K is $d^6$ and thus magnetic. This result is in qualitative agreement with...
4.1 TM impurities on alkali metals

calculations by Papanikolau et al. [86] for impurities in the volume. On the basis of Friedel's idea that the localized states of an impurity hybridize with substrate bands and form a resonant bound state, Anderson showed that appearance of local magnetic moment depends on two parameters. The intra-atomic exchange energy $U$ and the width $\Delta$ of the impurity bound state. A Stoner-like criterion for the appearance of magnetism in the case of impurities can be written as: $U n_{loc}(E_F) > 1$ where $n_{loc}$ is the local density of states at Fermi energy. The localized electronic states of the impurity are broadened by the interaction with an host of higher electronic density. Being less localized their magnetic character is suppressed. The spin polarized

\[ \begin{array}{c}
\text{Ti} \\
\hline
\text{Mn} \\
\hline
\text{V} \\
\hline
\text{Fe} \\
\hline
\text{Cr} \\
\hline
\text{Co}
\end{array} \]

\[ E - E_F (eV) \]

Figure 4.1: Spin polarized local densities of states for 3d metal impurities on K. Adapted from [86].

densities of states, calculated within KKR method, for 3d metal impurities (from Ti to Co) in K, are plotted in figure 4.1. This densities of states are characterized by the presence of a very narrow Friedel's virtual bound states. The width of these states is related to the hybridization with the substrate. The stronger the hybridization the larger the width. As an example, for the Mn impurity, the width of the bound state changes of a factor of 5 going
from K to Li. This is due to the fact that the hybridization between host and impurity is proportional to the electronic density of the host. For the alkali metals the electronic density increases decreasing the volume of the atom, thus it increase going from Cs to Li. The electronic density of alkali metals and of Al, Cu, Ag, Au metals is plotted as a function of the atomic number $Z$ in figure 4.2. A simple model used to describe the electronic properties of an alkali metal is the jellium model. In the jellium model [87] the alkali metal is described as a uniform charge background with an electronic density $\rho$ defined as: $\rho = -3e/4\pi r_s^3$, where $r_s$ is the Wigner-Seitz radius [88], [89]. The jellium critical density is plotted in figure 4.3 as a function of the impurity element for $3d$ and $4d$ series. The densities of several non-magnetic host are shown as horizontal lines. The impurity is magnetic when its critical density $\rho_c$ is bigger than the jellium density of the host. Song and Bergmann found enhanced magnetic moments for 0.01 ML of V impurities on K and Na [90]. The magnetic moment they estimate is of 7 $\mu_B$ for V/K and of 6.5 $\mu_B$ for V/Na. These values are strongly enhanced from the atomic value of 0.77 $\mu_B$ for the $d^3$ electronic configuration of V. Even assuming that the orbital moment is totally quenched the remaining spin magnetic moment is 3.87 $\mu_B$ does not explain the results. Also in this case, the authors propose that the V polarize the alkali and thus the total moment is due also to a significant contribution of the alkali moments. The authors pointed out that this result clearly rules out the possibility of atomic-like configuration for the V impurity. According to these results and to the proposed interpretation the alkali should have a very strong magnetic moment, of few $\mu_B$, which would be extremely surprising, since bulk alkali metals are diamagnetic with very small magnetic susceptibilities. In a more recent paper [91] the same authors found for V impurities on the
4.2 Co on K coverage and temperature dependence

Studies performed at the Circular Polarized beamline at Elettra, on Co impurities on alkali metals films are presented. Useful information have been obtained about the temperature and coverage dependence of the electronic properties of impurities. The importance of low temperature deposition of the 3d impurities on the alkali substrates is pointed out.

The growth of alkali metals on metal substrates have been reviewed recently by Diehl [93]. Changes in the growth mode are seen to happen depending on the specific substrate, its crystallographic surface and temperature. A most important fact is that lighter alkali metals can have a liquid phase at RT and structural transition can occur if the temperature is reduced. For the case of K and Na on Cu(100) at low temperatures the growth has been found to follow Straski-Krastanov mode with the formation of 3D islands, after the the first layer is completed.

surface of Rb and Cs films smaller magnetic moments (3.6 $\mu_B$ on Rb and 4.2 $\mu_B$ on Cs) than in Na and K. They attribute this to undefined changes in the electronic structure of the impurity changing the host. The problem is that the trend found by Bergmann and co-workers is the opposite to what is expected on the basis of theoretical calculations, which predict that the magnetic character should increase for decreasing electronic density, i.e. going from Na to Cs. Theoretical calculations by Sahu and Kleinman [92] found magnetic moments of 4.22 $\mu_B$ of V/Na or V/K, though they supposed this value to overestimate the V moment because they neglect orbital moment contributions. It has to be noted that by the same kind of calculation they strongly underestimate the magnetic moment of Fe and Co on K.

Figure 4.3: Critical densities for occurrence of magnetism for 3d and 4d metal impurities, [86].
The clean substrate was cooled down at 55 K. To grow a sufficiently thick alkali film the evaporation has to be done keeping the substrate cold. The growth of K was monitored by XAS spectra of $L_{23}$ edge of K and Cu. The coverage of K was estimated by measuring the Cu intensity decrease due to increased alkali absorption. Finally impurities of Co where deposited by e-beam evaporation. In figure 4.4 are depicted Co impurities deposited on an K film. Coverage dependence series of measurements were performed for Co impurities on K.

Co impurities on alkali metals have been found to have giant magnetic moments \cite{80} and their origin has been related \cite{7} to the atomic-like character of the electronic structure. At the basis of this atomic-like electronic structure there is the reduced coordination between Co atoms together with the very weak interaction of the impurity with the substrate \cite{94}, due to the low electronic density at Fermi level of alkali metals. Figure 4.5, shows the comparison between ESRF measurements performed at 10 K (on the left) and the measurements done at Elettra at 55 K (on the right). In the spectra taken at 10 K there are strong multiplet features for the lowest coverage (0.007 ML) that as the coverage is increased (from bottom to top) tend to became less and less evident and finally at approximately 0.1 ML eventually disappear. Measurements done at Circular Polarized beamline, on the right, do not show multiplet features even in the lowest coverage which is remarkably low ($1 \times 10^{-3}$ ML). The difference is due to the effects related to thermal diffusion \cite{95} since the deposition rate is the same: at 55 K the temperature is not low enough to inhibit the thermal diffusion of the Co monomers and the formation of clusters can take place even at low coverages. In a cluster the Co atoms coordination is increased and this strongly influences their electronic properties. Moreover with an increased temperature the Co impurities can also interdiffuse in the alkali substrate. In this
Figure 4.5: Comparison of spectra series for Co impurities on K, data at 10 K [7] on the left and data at 55 K on the right.
case the electronic structure of the impurity is different from the impurity on top of the surface because there is an higher number of host atoms with which the impurity electronic states can hybridized. Hence it is clear that the amount of material deposited and that we evaluate in ML does not uniquely define the distribution and thus the electronic properties of the impurities. In the case of deposition at 10 K where the diffusion is strongly reduced the impurities can be considered as isolated and the coordination is small thus the atomic character of the electronic structure is preserved. This atomic-like electronic structure is evident as atomic multiplet structures in the spectra. In the case of deposition at 55 K the thermal diffusion is present and thus the impurities have higher mobility and clusters are formed. The larger the size of this cluster is, the higher the coordination and the stronger the band character of the electronic structure and thus the more the spectra are similar to the ones of a thin film or bulk 3d metal with no evident multiplet features. The change in coordination and thus in the electronic configuration is expected to produce a variation in the branching ratio of the spectra due to the reduction of the orbital moment as a consequence of the increased coordination. From the first sum rule (equation 3.24) the total intensity of an isotropic spectrum is proportional to the number of the holes, this total intensity is due to the sum of the transition strengths over the two $j$ multiplets (i.e. $L_3$ and $L_2$ edges). The branching ratio is defined as the ratio between the strength of the transitions of one multiplet and the total strength. Thole and van der Laan [96] found that there is a linear relation between the branching ratio and the expectation.
value of the spin-orbit operator (and thus to the expectation value of the orbital moment). This relation can be written for $2p \rightarrow 3d$ transitions as:

$$B_j(\psi) = \frac{2j + 1}{6} \pm \frac{1}{3N_h} \langle \psi |(\mathbf{L} \cdot \mathbf{S})| \psi \rangle$$  \hspace{1cm} (4.1)

where $j=3/2$ for $L_3$ and $j=1/2$ for $L_2$ and $\psi$ is the initial state function. The ratio $B_{1/2}/B_{3/2}$ is then proportional to $I_{L_2}/I_{L_3}$ but,

$$\frac{B_{1/2}}{B_{3/2}} = \frac{N_h + \langle \mathbf{L} \cdot \mathbf{S} \rangle}{2N_h - \langle \mathbf{L} \cdot \mathbf{S} \rangle}$$  \hspace{1cm} (4.2)

Since the expectation value of the spin orbit $\langle \mathbf{L} \cdot \mathbf{S} \rangle \propto \langle \mathbf{L} \rangle$ is proportional to the expectation value of orbital moment if the spin moment is constant, and since $\mu_t = -\langle L_z \rangle \mu_B / h$ then if the $I_{L_2}/I_{L_3}$ ratio decrease the the orbital moment increase.

In figure 4.6 where is plotted the ratio $I_{L_2}/I_{L_3}$ as a function of the coverage for both set of measurement, the one at 10 K and the one at 55 K. We see that the two curves have the same behavior, but different dependence on the coverage. The ratio decreases with increasing coverage, this is due to the fact that an increased coordination strongly reduces the orbital moment. The double arrows in left inset of the figure shows that at the two different temperature, the same value of $I_{L_2}/I_{L_3}$ is achieved at different coverages. In the inset the spectra of the two coverages are compared.

In summary, the electronic structure of Co impurities on K films displays changes as a function of both coverage and temperature. Thermal diffusion effects and coverage increase produce clustering and modify the coordination. In both cases, the effects are evidenced by changes in the branching ratio of x-ray spectra. These results remark the need to perform measurements at low temperatures ($T < 10$ K) and low coverages ($\theta < 0.05$ ML) to study diluted impurities and isolated atoms.
4.3 Manganese on K

The electronic structure and the magnetism of Mn impurities on the surface of K films, Cu(100) surface and Al(100) surface have been studied by means of XMCD and x-ray magnetization curves.

In figure 4.7 are plotted $\sigma_+$ and $\sigma_-$ spectra respectively acquired with right and left polarized radiation, of an Mn impurity deposited on a K film. The spectra show noticeable multiplet structures that are a clear fingerprint of an atomic-like electronic configuration. The strong differences in the spectral shape between the two polarizations reflect the presence of localized magnetic moments of an atomic-like configuration. A comparison of experimental dichroism for the lowest coverage of Mn on K, with multiplet structure calculation is presented in figure 4.8 (left inset). The atomic multiplet calculations performed by S.S. Gupta and D.D. Sarma for the $d^5$ electronic configuration, within a cluster model scheme (see ref. [77]) and with a gaussian broadening to account for experimental resolution and a Lorentzian broadening ($\Gamma_0=0.2$ eV, $\alpha=0.1$ eV). The agreement between the experimental and calculated spectra is excellent and permits the attribution to Mn impurity on K of a $d^5$ atomic configuration. A $d^5$ impurity is expected to have an atomic magnetic moment of $5\mu_B$.

The lineshape comparison of spectra acquired with opposite circularly polarized photons and theoretical multiplet calculation by van der Laan and Thole [84] is presented in figure 4.8 (right inset). The comparison is done at L$_3$ edge after the subtraction of a linear background to the spectra in figure
4.3 Manganese on K

Figure 4.8: Dichroism of a Mn impurity on K film at T=5.5 K. Comparison with calculations of S.S. Gupta and D.D. Sarma, (left inset) and comparison of spectra acquired with + and - circular polarizations and atomic multiplet calculation from van der Laan and Thole for the $d^5$ atomic configuration of Mn [84].

4.7. The energy positions of the main structures are very well reproduced, while the small difference in the relative intensity of these structures are related to an incomplete magnetization. Magnetization measurements have

Figure 4.9: Comparison of a magnetization curve of Mn impurity on K, at 5.5 K and angle $\theta = 0^\circ$ with a Brillouin function with $d^5$ electronic configuration parameters: $L = 0$, $S = 5/2$, $J = 5/2$, $g = 2$, $\mu = 5\mu_B$ and $T = 5.5K$. 
been performed on Mn/K. In this kind of measurements the signal from the sample \( I(E, H) \) due to a fixed polarization is acquired, while the magnetic field is scanned from -7 to +7 Tesla, at two photon energies: \( E_1 \) before the \( L_3 \) edge and \( E_2 \) on the maximum of \( L_3 \) edge. The magnetization curve is operatively defined as: \( \bar{M}(H) = (I(E_2, H) - I(E_1, H))/I(E_1, H) \). In figure 4.9 is plotted the magnetization curve obtained with this procedure at a temperature of 5.5 K and the Brillouin function for the \( d^5 \) configuration at \( T=5.5 \) K. Note that as introduced in section 2.1.1.1 the magnetic moment is defined as: \( \mu = g(J, L, S)\mu_B \) but since for the \( d^5 \) the orbital moment \( L \) is zero (see table 2.1) the magnetic moment is entirely due to the spin. The agreement between the experimental data and the Brillouin function for the \( d^5 \) electronic configuration is very good and confirms the attribution of \( d^5 \) electronic configuration to the Mn impurity on a K film.

By means of x-ray magnetization curves it is possible to address also another question: whether the system displays a magnetic anisotropic or not. As it will be discussed in chapter 5, Co single atoms on Pt(111) and Fe single atoms on Cu(100) have a large magnetic anisotropy and this effect is related to the fact that their interaction with the substrate is quite strong. While in the case of Mn on K the interaction is much weaker and also the spin-orbit coupling is weaker than in Cu or Pt. The two magnetization curves depicted in figure 4.10, are measured for different values of the angle between the normal to the surface and the direction of the magnetization: \( \theta = 0^\circ \) and \( \theta = 60^\circ \), at a temperature of 5.5 K.

![Figure 4.10: Magnetization curves of Mn impurity on K, at two different angles \( \theta = 0^\circ \) and \( \theta = 60^\circ \), at a temperature of 5.5 K.](image-url)
ratio and temperature measurement accuracy, for these systems with this method, even though in general a better accuracy can be achieved. Hence in this case it is possible to conclude that MAE is $0 \pm 0.3 \text{meV}$.

The experimental geometry used in this experiment is depicted in figure 4.11, where $H$ is the magnetic field, co-axial with the radiation propagation direction $k$, $\sigma_\pm$ are the two circular polarizations, $\theta$ is the angle between the surface and the direction of the magnetic field. The field aligns the magnetic moment of the impurity $\mu_{\text{imp}}$. When the angle $\theta$ is changed, the magnetic moment is aligned along different crystallographic directions. In this way the magnetic anisotropy of the systems can be probed.

Increasing the coverage, the formation of small clusters of Mn on the surface of K is promoted. By a series of measurement at increased coverage it has been possible to study the changes in the magnetism of these clusters as a function of the size of the cluster. The growth in the size of the cluster means an increased coordination of the Mn atoms and a decrease in the dichroic signal is expected, due to the decreased localized character of the impurity states and also due to the fact that as the coordination is increased, the Mn moments tend to align antiparallel. In figure 4.12 are plotted the spectra of Mn at zero magnetic field, acquired with right circular polarized radiation, for coverages of Mn from 0.012 ML to about 1 ML. The lineshape changes as the coverage is increased: the multiplet structures becoming broader and less defined until they almost disappear around 0.8 ML. This effect is related to the increased coordination of Mn during the transition from isolated impurity to thin film. The electronic structure undergoes a strong change due to the formation of bands that decrease the magnetic moment (that in bulk Mn is about $1\mu_B$) and to negative exchange between neighbors that favors antiferromagnetic coupling. The magnetic counterpart of this effect is a strong reduction in magnetism from the atom to the thin film. This idea is supported by the normalized dichroism plotted in figure 4.13 for Mn coverages going from 0.012 ML to about 0.8 ML. The normalized dichroism decreases as the coverage is increased, and is almost zero at 1 ML.
Figure 4.12: Spectra of Mn/K, for Mn coverage, from 0.012 ML to 1 ML (bottom to top), taken with H=0 and at T=5.5 K. The spectra have been normalized at pre-edge and then shifted in intensity.

Figure 4.13: Normalized dichroic signal of Mn on K, for increasing Mn coverage, from 0.012 ML to 0.8 ML, taken with H=0 and right polarized light at 5.5 K. In the inset is plotted the Mn asymmetry at L3, as a function of the coverage.
4.4 Manganese on Cu(100) and Al(100)

It is interesting, at this point, to study how the electronic configuration and the magnetic properties change if the Mn impurity is deposited on a different substrate. Since K has a very low electronic density we have chosen for comparison substrates with higher density as Cu(100) and Al(100) surfaces. Going from K to Cu the electronic density changes from $1.4 \times 10^{22} \text{cm}^{-3}$ to $8.47 \times 10^{22} \text{cm}^{-3}$, thus from a general point of view the magnetism of the impurity could be reduced and the electronic configuration could be changed. From the calculation of Papanikolau et al. [86] the higher is the substrate density, the smaller is the magnetic moment of the impurity. In the case of Mn a reduction of the magnetic moment is expected, while on Al the moment is expected to be zero.

A comparison of Mn spectra on Cu and on K, for similar coverages, is presented in figure 4.14. The spectra have been acquired in a magnetic field of 7 Tesla at the angle $\theta = 0^\circ$. The spectra show that the Mn impurity on Cu(100) surface retains the characteristic multiplet features of the atomic $d^5$ electronic configuration. However it has to be noted that the multiplet structures are larger and less pronounced. This is mainly due to the effect of the hybridization of Mn localized states with Cu delocalized valence
The dichroism of Mn/Cu(100) is compared to the one of Mn/K in figure 4.15. The d^5 spectroscopic features are still present, but the dichroism intensity is weaker. This effect is attributed to the increased hybridization with substrate. This is confirmed by the x-ray magnetization curves that are presented in figure 4.16. In this figure are plotted the magnetization curves acquire at θ = 0° and θ = 60° (as empty circles) and the Brillouin function calculated for an electronic configuration, with \( J = 2.1 \), \( S = 2.1 \), \( L = 0 \), \( g = 2 \) at a temperature of 5.5 K, hence the magnetic moment is \( \mu = 4.2 \mu_B \). Both experimental and calculated curves have been normalized at \( H = +7 \) T for better comparison, the two curves coincide within the sensitivity of the measurements. Thus we can conclude that the magnetic anisotropy of the system is below the sensitivity of this technique, i.e. below 0.2 meV/atom. This is in agreement with the fact that for a d^5 atomic configuration \( L = 0 \), hence no magnetocrystalline anisotropy is expected since as introduced in 2.2 the MAE is proportional to spin-orbit, but if \( L = 0 \), then also spin-orbit is zero.

To study the effect of coordination in this case, the growth of Mn has continued to a coverage of 1.4 ML. Figure 4.17 shows pair of spectra acquired with plus and minus circular polarization for increasing coverage of Mn on Cu(100).

At the lowest coverage the electronic structure and magnetism is the one of isolated atoms. As the coordination increases, the interaction with other atoms becomes more important. The decrease of the normalized dichroic signal, indicates a decrease in the magnetization that is due partially to the increased delocalization of the Mn electronic states, related to band formation, but it is mainly due to the antiferromagnetic coupling of the Mn magnetic moments. Also the lineshape undergoes strong changes, the atomic-like spectral features visible in the lowest coverages tend to be smoothed out in
Figure 4.16: Mn/Cu(100), comparison of experimental magnetization data with a Brillouin function with a magnetic moment due only to spin of 4.2 μB with a temperature of 5.5 K.

Figure 4.17: Mn/Cu(100) coverage dependence. Pair of σ± spectra for coverages from 0.005 ML to 1.4 ML.

the highest ones. At the limit of 1.4 ML the lineshape is completely changed, and has become similar the lineshape of bulk manganese. The absence of
dichroism at this coverage is most probably due to the antiferromagnetic coupling of the Mn magnetic moments more then to the disappearance of the magnetic moments of Mn, similarly to the case discussed for Mn/K and Mn/Fe.

Aluminium has an electronic density of $18.1 \times 10^{22} \, e \, cm^{-3}$ more than 10 times the electronic density of potassium. Papanikolaou and coworkers [86], found that at aluminum electronic density all TM impurities are expected to be magnetic apart Mn which is at the limit. In figure 4.18 are plotted the spectra of an Mn impurity on Al(100). The spectra show a very small dichroism, though non zero, and a complete absence of multiplet structures while the spectral width is strongly increased. All these effects can be explained at least qualitatively as the strong hybridization of electronic states of the impurity with the substrate due to its high electronic density. The experimental results are in excellent agreement with calculations. Papanikolaou et al. [86] found, within the jellium model, for Mn/K a magnetic moment of $\mu = 4.9 \, \mu_B$, while our results give $\mu = 5.0 \, \mu_B$. For Mn/Cu, they find $\mu = 3.4 \, \mu_B$, while our results give $\mu = 4.2 \, \mu_B$. The moment of Mn on Cu is better accounted by calculations of Cabria et al. [97] and Stepanyuk et al. [98] that found a magnetic moment very close to $4.2 \, \mu_B$.

![Figure 4.18: Spectra (\sigma_+, \sigma_-) of Mn on Al(100), acquired with H=-7 Tesla at 5.5 K.](image)

4.5 Vanadium on Cs

The debate about the magnetic properties of vanadium impurities on alkali metal host has been introduced in section 4.1. Many aspects are still unclear thus it is interesting to use XMCD and XAS to study both electronic and magnetic properties of vanadium. The experimental procedure is the same
used in the case of Mn on alkali in section 4.3. At first Cs has been chosen as the alkali substrate to permit a direct comparison with the experimental results from Song and Bergmann [91] and with theoretical calculations available [86], [87], [92]. Then the study has been extended to K, Na and Cu(100) surfaces. In figure 4.19 are plotted two pairs of \((\sigma_+, \sigma_-)\) spectra of a V impurity on a clean film of Cs. The lower pair has been acquired at an angle \(\theta = 0^\circ\) and the upper one has been acquired at the angle \(\theta = 70^\circ\), in a magnetic field of 7 Tesla. The spectra show both narrow multiplet features typical of an atomic-like electronic configuration character, and broad edge features suggesting the presence of strong hybridization. In this case, as will be discussed in detail a direct attribution of simple atomic character is not so straight forward. Moreover also sum rule analysis (see equations 3.25, 3.26) is not easily applicable. It is possible to calculate the expectation value of \(L_z\), since this involves the integration of the dichroic signal over the entire \(L_{2,3}\) energy range. Unfortunately it is not possible to calculate the expectation values of \(S_z\) because the separate calculation of integral over \(L_3\) and \(L_2\) edge should be performed (see [99]), and the \(L_3\) and \(L_2\) are not separable due to the low spin-orbit splitting of the 2p states of V.

From the dichroic signal plotted in figure 4.20 it is possible to say (already by visual inspection) that the integral of the signal over the whole \(L_{2,3}\) energy range is positive. Hence from the orbital sum rule it can be inferred that the orbital moment is \(L_z\) is negative thus being antiparallel to the spin, as expected from the second Hund's rule for less then filled shells.

**Figure 4.19:** Spectra \((\sigma_+, \sigma_-)\) of a V impurity on the surface of a Cs film, acquired with \(H=-7\) Tesla at \(T=5.5\) K, for angles \(\theta = 0^\circ\) and \(\theta = 70^\circ\).
Figure 4.20: Dichroic signals of V on a Cs film, at H=7 Tesla and T=5.5 K, for angles: $\theta = 0^\circ$ and $\theta = 70^\circ$.

Figure 4.21 describes the relative orientation of $L_z$, $S_z$, and $J_z$ for less than half filled d shell (inset A) and more than half filled shell (inset B).

Figure 4.21: Graphical representation of the relation between $S_z$, $L_z$ and $J_z$, due to Hund's second rule for less than half filled d shell (inset A) and more than half filled d-shell (inset B).

For less than half filled shells the orbital moment aligns opposite to the spin and thus contributes negatively to $J_z$, while for more than half filled d-shell the orbital moment align parallel to the spin and thus adds to $S_z$ to give $J_z$. Moreover the sign of vanadium at L3 is the same sign of the dichroism of the Fe and Co impurities on K. This is best understood with the help of figure 4.22. The sign of the dichroism depends on the Zeeman coupling of magnetic moment with the field, and as shown in the figure, even in the case of $L_z$ antiparallel to the spin it can change depending if $L_z < 2S_z$ or $L_z > 2S_z$. It is the same of Fe and Co if $L_z < 2S_z$. The dichroism measurements at the two angles are almost identical, apart for some details between L3 and L2 edges. This means that the magnetic anisotropy of the system is below the experimental sensitivity.

The orbital magnetic moment $\mu_l$ has been calculated applying the orbital
Figure 4.22: Graphical representation of the effect of the relative magnitude of $S_z$ and $L_z$ on the sign of the XMCD signal due to the Zeeman coupling. The case for $L_z < 2S_z$ is shown on the left (1) while the case for $L_z > 2S_z$ is shown on the right, (2). Spectral calculations by S.S. Gupta and D.D. Sarma (unpublished results).

sum rule to the dichroism signal. To calculate the integral of the isotropic spectrum, that is at denominator of the orbital sum rule equation 3.25, the average spectrum of $\sigma^\pm$ has been used, after subtraction of an exponential background, as shown in figure 4.23. This operation in needed since the Mn has a small signal imposed over the strongly decreasing background due to the absorption of the substrate. In the calculation, the background subtraction details are intrinsically somehow arbitrary but, the overall result remains unchanged. The orbital magnetic moment of V on Cs, rescaled for

the incomplete magnetization, is thus: $\mu_l = -0.3\mu_B$, considering a number of the holes, $N_h = 6$ i.e. a Vanadium with four electrons in the d shell. This value of the orbital magnetic moment is very small, and it is negative, i.e. antiparallelly coupled to the spin magnetic moment. This result is ex-
3d metal impurities on alkali surfaces

tremely important to understand what is the electronic configuration and magnetism of the V impurity, since the atomic configuration like d^3 and d^4, have large orbital moments that are not consistent with the value of the orbital moment just found.
To further understand the magnetism of V/Cs, the experimental magnetization curves have been fitted with Brillouin functions. The data are presented in figure 4.24. The experimental data have been tested with Brillouin func-

tions starting from an atomic d^3 configuration (L = 3, S = 1.5, J = 3/2) that has a too small magnetic moment of 0.6 µB. The quenching of the orbital moment has been checked varying the orbital moment from L=3 to L=0. None of these configurations gave good agreement with experimental data.
The purely atomic d^4 is non magnetic so it is immediately ruled out from this analysis. If instead a partial quenching of the orbital moment is considered starting from d^4 configuration, then a good agreement with experimental data is achieved. In figure 4.24 the experimental data are compared with a d^4 with S = 1.65, L = -0.3 and J = 1.35. The fit done at T=5.5 K is in good agreement with the data and consistent with the overall picture. The magnetic moment coming from the fit is then µ = 3.0µB.
Is is important to note that vanadium free atom has a d^3 atomic configuration, on the other side, for Fe, Co and Ni impurities on K, it has been seen to occur a charge transfer from the alkali to the impurity. The same is expected to happen for V/Cs although the electronegativity difference is smaller. Hence considering the charge transfer would lead to a d^4 electronic
configuration. The atomic $d^4$ has $L = 2$, $S = 2$, and most important $J = 0$, this means that pure $d^4$ configuration would not be magnetic, as previously stated. Even if a second order Zeeman term due to population of levels at higher energy with respect to the ground state is taken in account, this is not enough to explain the size of the observed moments. This second order effect is called Van Vleck paramagnetism [100] and is expected to be much weaker than the ionic Curie paramagnetism [88]. Including the Van Vleck second order term for $d^4$ configuration, the magnetic moment at 10 K is estimate to reach 1.6 $\mu_B$ [101], this would mean that at $T=5.5$ K the expected moment would be even less.

So a first conclusion is that V/Cs behaves as an atomic $d^4$ configuration with a strongly reduced orbital moment. It is still to explain what physical mechanism reduces the orbital moment, from the $L=2$ of the atomic configuration to the experimental value of $L = 0.3$. A possibility would be the presence of a strong crystal field able to quench the orbital moment. Unfortunately, as remarked by Riegel and Kowallik, [78], and Bergmann and coworkers [90], this possibility has to be ruled out because the crystal field is extremely weak for alkali metals, since their charge distribution is poorly directional and no effects of these kind have ever been reported for these systems. But if we consider the crystal field only as a conceptual tool to modify the size of the orbital moment it is instructive to consider the bonding effects in a formalism that includes crystal field effects. In this contest S.S. Gupta and D.D. Sarma, performed multiplet structure calculations within a second quantization cluster model, including explicitly the Zeeman coupling of magnetic field with both $L$ and $S$, changing the crystal field strength for different symmetries in the $d^3$ configuration in the attempt to simulate the dichroic signals of figure 4.20.

Including a mechanism that reduce $L$ by respect to $S$ is also needed to explain the sign of dichroism at $L_3$ that is be expected to be the opposite of Fe and Co, for purely atomic $d^3$ and $d^4$ configurations. the sign is due to the coupling of spin and orbital moment to the field. If one considers the Zeeman expression,

$$H_{Zeeman} \propto (L_z + 2S_z)H$$

It is clear that the sign flips if $L_z < 2S_z$, in less than half filled shell $L$ is usually bigger and opposite to $S$. The flipping of XMCD then can happen only if $L$ is partially or totally suppressed as in the case of crystal field. Once the crystal field is considered, the values of $J$, $I$, $S$ are no more constrained by the atomic structure and depend strongly on the crystal field strength, the 10Dq parameter (eV). These calculations for the $d^3$ configuration in octahedral geometry $O_h$ are plotted in figure 4.25. The values of $S_z$, $L_z$, $J_z$ and $T_z$ are plotted as a function of the crystal field strength 10Dq. The insets show the calculated dichroism for the specific values of crystal field strengths. As expected, it is possible to see that the orbital moment
decreases for increasing crystal field strength \((10D_q)\) thus leading to a bigger total magnetic moment. Furthermore the spectral shape of dichroism changes strongly with the crystal field also reversing the sign for very small values of \(10D_q\). Nevertheless a completely satisfactory agreement with experimental dichroism is not found. The best compromise would be a value for \(10D_q\) between 0.02 and 0.2 eV.

The calculations performed for the \(d^4\) configuration in octahedral geometry \(O_h\) are plotted in figure 4.26. In this case at zero crystal field \(S_z\) and \(L_z\) are opposite hence \(J_z = 0\), but as the crystal field is increased, \(S_z\) and \(J_z\) increase, while \(L_z\) decreases.

Since for alkali metal the crystal is usually weak, the cases of interest are expected to be the ones for lower crystal field, of the order of 0.1-0.01 eV. In both cases, figure 4.25 and 4.26 no perfect agreement is found at least as the one found for Mn \(d^5\) atomic configuration. So a direct comparison does not allow to determine the electronic configuration.

The physical mechanism behind the reduction of the orbital moments by respect to the atomic free atom electronic configuration is the same that produces small orbital moments for the early 3d elements on Ag(100) surface. For this system calculations, in SPR-KKR framework, have been performed by Nonas et al. [102] and Cabria et al. [97]. These authors find for the less than half filled elements of the 3d transition metals, small and negative (antiparallel to the spin) magnetic moments, as shown in figure 4.27, while for
4.5 Vanadium on Cs

Figure 4.26: Value of $S_z$, $L_z$, $J_z$ and $T_z$ as a function of the crystal field for the $d^4$ electronic configuration in octahedral symmetry $O_h$. And dichroic signal for different values of $10Dq$.

the second half of the series the orbital moments are large and positive. This effect is understood decomposing the orbital moment as due to major $L_z^{up}$ and minority $L_z^{down}$ contributions as shown in figure 4.28. The majority sublevels, as in a free atom, are populated from $m_l = -2, -1, 0...$ that give negative moment which vanish when the subshell is filled and then the reverse order $m_l = +2, +1, 0...$ of population start. The major difference

![Diagram of orbital moments](image-url)

Figure 4.27: Orbital ($L_z$) and spin moments ($M_z$) for the 3d metals adatoms on Ag(100) surface. Adapted from [102].
from the free atom is that in the case of the less than half filled shell elements the width of the Friedel's virtual bound state, due to the larger extension of the 3d states in lighter elements, is much larger then in the second half of the 3d series, while their spin-orbit slitting is smaller. The combination of these two effects gives small and negative orbital moment for Ti, V and Cr. At the end of the 3d series, the virtual bound state is strongly narrowed, while the spin-orbit interaction is slightly increased and hence the orbital moments are enhanced. This is clear from figure 4.1, considering the system in a tight binding model one obtains that \( \mathcal{L}_z \cong -\xi [n \uparrow (E_F) - n \downarrow (E_F)] \). Where \( n \uparrow \) and \( n \downarrow \) are the spin-up and down local density of states at the Fermi Energy. Hence the narrowing or broadening of the virtual bound state plays a central role in the formation of the orbital moment. This effect of different broadening of the virtual bound state for the lighter and for the heavier 3d impurities is observed also for alkali metals due to the similar free electron-like character of the sp bands of alkali and noble metals. The experimental results, evidence a small and negative orbital moment in agreement with the theory. The slightly enhanced with respect to the orbital moment calculated for Ag is probably due to the weaker interaction of V impurity with Cs, K with respect to Ag(100). The spin moment is found to be \( \mu_s = 3 \mu_B \) which is smaller then the one calculated on Ag and with respect to the one calculated with jellium model \( \mu_s = 4.5 \mu_B \) (see ref. [86]) for V on Cs. This difference can be due to the fact that the authors consider the polarization of the s-states, localized at the impurity site, that enhances the spin moment.

![Figure 4.28: Majority \( L_z^{up} \) and minority \( L_z^{down} \) contributions for the 3d metals adatoms on Ag(100) surface. Adapted from [97].](image-url)
4.6 Vanadium on K

It is interesting to study how the magnetism of V changes when the impurity interacts with substrates of different electronic density. Experiments have been performed depositing V impurities on the surface of K, Na films and on the Cu(100) surface. It should be noted that Cs is the heavier of the considered alkali metals and thus have the lowest electronic density that increases for K and then for Na and furthermore for Cu. It is reasonable to expect that the magnetism of Vanadium impurity will decrease while changing the substrate from Cs to Cu passing through K and Na. Figure 4.29 depicts the spectra for 0.011 ML of V impurity on K and their dichroism. The spectral shape is very similar to the one of V on Cs of figure 4.19 and the only differences are related to fine details of the dichroic signal between 514 eV and 518 eV. The orbital moment has been calculated with the same procedure introduced for V on Cs. An exponential background has been subtracted and from the average spectrum to make possible the calculation of the integral of the isotropic spectrum. The orbital moment, corrected for incomplete magnetic saturation, found by this procedure is small and negative: $\mu_1 = -0.2\mu_B$. In figure 4.30 is plotted the experimental magnetization curve acquired for the V impurity on K. A Brillouin function calculated for

![Image](image.png)

Figure 4.29: Vanadium impurity on K. Spectra taken with ± circular polarized radiation at T=5.5K, in normal incidence (upper panel). Dichroic signal (lower panel).
a system at a temperature of 5.5 K and with $S = 1.5$, $L = -0.2$, $J = 1.3$ and thus a magnetic moment of $2.8 \mu_B$, fits well the experimental results. It is interesting to compare the experimental values just found for the magnetic moment of a V impurity on Cs, $\mu = 3\mu_B$, and on K, $\mu = 2.8\mu_B$, to the ones found by Song and Bergmann [90], [91]. These authors find a magnetic moment of $4.2 \mu_B$ for V/Cs, of $7 \mu_B$ for V/K and of $6.5 \mu_B$ for V/Na. The results are very different especially for the case of K where they find a magnetic moment more than two times larger the the present one. Moreover our results show a decreasing magnetic moment for increasing substrate density, in line with theoretical calculations, while Song and Bergmann results do not. It is still an open question whether a polarization of the alkali substrate is present or there is an error in their very critical data analysis procedure.

A very instructive comparison, between impurities of different transition metals can be clone on potassium, in fact on this substrate there are available spectroscopical data for impurities of V, Mn, Fe, Co and Ni. The experimental data for the first two elements have been just introduced, while the data for Fe, Co and Ni from [7]. In figure 4.31 are plotted the spectra for Mn/K and V/K and the spectra for Fe, Co and Ni on K, adapted from Gambardella et al. [7]. The electronic configuration established for this impurities are the atomic like d$^5$ for Mn, d$^7$ for Fe, d$^8$ for Co and d$^9$ for Ni, while for V the electronic configuration is not simply atomic-like. All these elements show important multiplet features both in the spectra and in the dichroism, that are related to the localized character of the impurity d-states, due to the weak electronic interaction with the alkali film on which they are deposited. This atomic-like character is reduced, when the interaction with the host is increased, as in the case of substrates of higher electronic density, or when the coordination of the atoms in the impurity is increased. The impurities with more than half filled shell, i.e. Fe, Co and

Figure 4.30: Vanadium impurity on K, comparison between experimental magnetization data and the Brillouin function function for a moment of $\mu = 2.8\mu_B$ and $T=5.5$ K.

3d metal impurities on alkali surfaces
Figure 4.31: Spectra acquired with ± circular polarizations and dichroism of Mn and V impurities (on the left), compared with Fe, Co, Ni impurities on K (adapted from [7]) on the right.
3d metal impurities on alkali surfaces

Ni, show an electronic configuration due to a strong charge transfer from the alkali to the 3d impurity. Mn on the other side does not show strong charge transfer effects, this is due to the fact that the d⁵ spin-only configuration is favored because it permits to align all the spins parallel maximizing the Coulomb repulsion and is connected to the relatively reduced electronegativity of Mn by comparison to V, Fe, Co, Ni. For the case of less than half filled Vanadium element, the situation is far more complicate, but a charge transfer from the alkali to the V impurity is expected, thus leading to an impurity with a number of electrons in the d-shell between three and four. Due to the larger spatial extent of the orbitals for the less than half filled 3d shell elements, the width of the resonant virtual bound state is larger compared to the one of Fe, Co and the spin-orbit is smaller. These two facts leads to small orbital moment for V compared to the one of Fe and Co. In fact the atomic-like configuration of Fe and Co show larger orbital moment, as can be see immediately from the spectra, where the sign of the dichroim at L₂ edge is negative, the same of the L₃ edge and hence (see XMCD sum rules) both edges contribute to a very large orbital moment. This particular feature is consistent with the atomic configurations from which the orbital magnetic moment should be \( \mu_l = 3\mu_B \).
4.7 Vanadium on Na and Cu(100)

The change of substrate from Cs to K means, in terms of electron density to change the jellium density from 0.9 to $1.4 \times 10^{22} \text{e} \text{cm}^{-3}$. The density can be further increased if one deposit the V impurity on sodium film. Na has an electronic density of $2.65 \times 10^{22} \text{e} \text{cm}^{-3}$, almost twice the one of K, so a further decrease in the localized character of V states is expected.

The effect of this increase of the electronic density on the lineshape of the V impurity is evident from the spectra plotted in figure 4.32 where the two circular polarized spectra of 0.0075 ML of V on Na are presented. In the lower inset of the same figure is plotted the dichroic signal. The small double peaked pre-edge spectral structure present for V/K is lost, for both circular polarization the spectra have less or none multiplet structures. The dichroic signal is also less structured, and the asymmetry at L_3 is smaller by comparison with the V/Cs and V/K. The orbital magnetic moment calculated from the sum rules analysis of the dichroism, as described for V on Cs and corrected for incomplete saturation, gives a very small and negative orbital magnetic moment: $\mu_\text{L} = -0.05 \mu_B$. This means that the coupling is still antiparallel to the spin but the size of the moment is strongly suppressed.

In figure 4.33 are depicted the experimental magnetization data and the
Brillouin function with parameter $T=5.5$ K and $S = 1.45$, $L = -0.05$, $J = 1.4$. Hence the magnetic moment is $\mu = 2.65\mu_B$, which is slightly decreased with respect to the case of $V/K$, while the orbital moment has suffered a more severe reduction.

Considering $V$ on Cs, K, and Na it is possible to say that the orbital moment is small and negative for all these alkali metals. It reduces as also do the total magnetic moment and the spin magnetic moment, going from Cs to Na. This can be understood in term of increasing hybridization and a broadening of the width of the Friedel’s virtual bound state. The orbital moment is strongly reduced ($\approx 85\%$), while the spin and the total magnetic moment are less reduced ($\approx 15\%$). The magnetic moment derived from this analysis is in between $2.65 \ (V/Na)$ and $3\mu_B \ (V/Cs)$ much smaller than the ones measured by Song and Bergmann [90], [91].

Finally V has been deposited on Cu(100) surface, that has a higher electronic density with respect to all alkali metals, $8.47 \times 10^{22} \text{cm}^{-3}$. Even though, the V impurity should still be magnetic on this substrate, according to Papanikolau and co-worker calculations [86]. In figure 4.34 are plotted the spectra acquired with ± circular polarizations for a vanadium impurity on the surface of Cu(100). The lineshape is completely changed from Von Cs. No multiplet structure is evident and the $L_3$ and $L_2$ edge are smoothed out completely. Furthermore also the dichroic signal is strongly reduced and its shape is completely different from the V on Cs, with much broader structures. This is due to the increased hybridization of the localized states of V impurity with the Cu(100) substrate.

Moreover the orbital sum rule (see equation 3.25) states the integral over
4.7 Vanadium on Na and Cu(100)

Figure 4.34: Vanadium impurity on the Cu(100) surface, spectra acquired with circular polarized radiation at T=5.5 K.

the dichroic signal is proportional to the expectation value of the orbital moment along the quantization direction, it should be noted that in the present case the integral is clearly negative while in the case of V on Cs, K, the integral was positive and almost zero for Na.

In summary the electronic and magnetic properties of Mn impurities deposited on K films and Cu(100) and Al(100) surfaces and V impurities deposited on Cs, K, Na and Cu(100) have been studied. For Mn on K a clearly atomic d⁵ configuration has been established, both by magnetization measurements and by comparison of the XMCD spectra with multiplet structure calculations. Mn on the Cu(100) surface shows spectral multiplet features similar to the one of Mn/K, but the structures are broadened and the magnetic moment is smaller. On Al(100) the Mn impurities undergo a strong hybridization, the dichroic signal is severely suppressed and the spectra have no more trace of atomic multiplets. The agreement with calculations for both Mn/K and Mn/Cu is excellent. Vanadium impurities on Cs have been studied in detail, both by XMCD and magnetization curves. The electronic configuration is not of purely atomic character, nor d⁵, nor
d⁴, since their atomic magnetic moments are too small compared to the measured ones. The XMCD spectra of vanadium show, the presence of an orbital moment antiparallelly aligned to the spin moment as expected for the less then half filled shell elements. The data suggest the presence of a physical mechanism that quenches the orbital moment of a d⁴ electronic configuration. This reduction of the orbital moment is confirmed by the total magnetic moment that is found to be of about 3μB, that cannot be attributed to a atomic d³ configuration. A possible mechanism could be a weak crystal field and its effect on the orbital and spin moment has been discussed comparing the experimental data with multiplet structure calculations, nevertheless this possibility has been ruled out because the alkali crystal field is very weak. The effect of hybridization of the impurity with the substrate as a function of the electronic density has been experimentally examined changing the substrate from Cs, to K, Na. The spectra undergo an increasing broadening for substrates of higher density, with the smoothing out of the multiplet features typical of atomic-like localized states. The orbital moment is found to be small and negative (antiparallel to the spin) on Cs, to decrease on K and on Na, while it is almost zero but positive on Cu(100). The size of the orbital moment as a function of the electronic density of the host is explained by the changes of the relative size of virtual bound state width and spin-orbit through out the 3d series. The size and sign of the orbital moment calculated from the spectra is consistent with these calculations.
Chapter 5

Co single atoms on Pt(111)

The magnetic anisotropy and magnetic moments of Co single atoms on the surface of Pt(111) are studied, at very low temperatures and in high magnetic fields, by means of XMCD and magnetization curves. A very large magnetic anisotropy is found with MAE of about 9 meV/atom. This anisotropy tends to align the Co moments along the preferential orientation axis which is perpendicular to the surface plane. The microscopic origin of this uniaxial anisotropy is identified to be the magnetocrystalline anisotropy due to the spin-orbit interaction, related to a strongly enhanced orbital moment of Co atoms. The Pt substrate contributes to the total magnetic moment and to the enhancement of the magnetic anisotropy energy as a consequence of the mixing of 3d-5d states of, respectively, Co and Pt.

5.1 Magnetic properties of Co/Pt systems

Co single atoms on the surface of Pt(111) are a particular case of 3d-5d systems. Co/Pt, and Fe/Pt bi-element systems as well as the analogous 3d-4d, Co/Pd, Fe/Pd, have been studied in a variety of cases, from alloys to bilayer to multilayer systems. Elements like Pt and Pd are not magnetic, but they are known to have high magnetic susceptibilities and they possess large spin-orbit parameter. When a 3d element as Fe or Co is deposited on a Pd or Pt substrate, it induces a magnetic moments in the Pd or Pt neighbors, this effect is due to a mixing of 3d and 5d electronic states. There are strong analogies with diluted alloys like Pt-Co, Pd-Co that show giant magnetic moments, due to the spin polarization of the host. Furthermore these compounds have magnetic anisotropy energies strongly enhanced with respect, for example, to the pure 3d systems. The orbital moment of the transition metals undergoes a strong enhancement [25], [103] as can be seen in figure 5.1 where are plotted the XMCD spectra (together with the dichroism) of a Co thin film and of a Co/Pd multilayer. Multilayer system like Co/Pd
or Co/Pt have been shown to have a Perpendicular Magnetic Anisotropy (PMA), that is mostly due to the fact that in multilayer systems the MCA (deriving mostly from spin-orbit interaction) is strong enough to overcome the shape anisotropy (that would force the easy axis to be in plane) and drive the easy magnetization axis out of plane. The source of this PMA has been recently attributed [104], for Pt/Co multilayer to interfacial polarization and to the enhancement of orbital moments. A Pt contribution to the magnetic anisotropy is related to the induced moment on the Pt atoms by Co atoms and to the large Pt spin-orbit coupling.

From the approach of Bruno, introduced in section 2.2.1, the MCA contribution to the magnetic anisotropy energy is connected to the anisotropy of the orbital moment. This prediction of Bruno’s model has been demonstrated by angular dependent XMCD measurement by Weller et al. [26]. XMCD angular dependent measurement at both Co and Pt edges have been used [105] to study the MCA of CoPt$_3$ films grown at different temperatures. They reported the direct observation of the angular dependence of Pt orbital moment, showing that also Pt has an out of plane MCA.

The importance of interfacial hybridization can be understood in term of spin-orbit energy anisotropy in a ligand field model, as described in figure 5.2 by Stöhr [45] on the basis of Bruno model [24], [19]. For a half-filled Co minority band the crystal field splits in energy the d-subbands in a different way depending of the fact that the orbital lay in plane ($d_{xy}$, $d_{x^2-y^2}$), or out
5.1 Magnetic properties of Co/Pt systems

\[ S \parallel z \begin{cases} \langle L_z \rangle \\ \Delta_{(00)z} \end{cases}, \quad S \parallel x / y \begin{cases} \langle L_y \rangle \\ \Delta_{(00)x,y} \end{cases} \]

\[ d_{xy} = \frac{1}{\sqrt{2}} (|2, -2\rangle - |2, +2\rangle) \]
\[ d_{xz} = \frac{1}{\sqrt{2}} (|2, -1\rangle - |2, +1\rangle) \]
\[ d_{yz} = \frac{1}{\sqrt{2}} (|2, +1\rangle + |2, -1\rangle) \]
\[ d_{x^2-y^2} = |2, 0\rangle \]
\[ d_{z^2-r^2} = \frac{1}{\sqrt{2}} (|2, +2\rangle + |2, -2\rangle) \]

\[ \Delta_{(00)z} \]
\[ \Delta_{(00)x,y} \]

\[ 2V_\perp \]
\[ 2V_\parallel \]

Figure 5.2: Spitting of the d-subbands, due to crystal field (exagonal or tetragonal symmetry) and spin-orbit in minority filled band model of the Co free monolayer showing the connection between in-plane \( d_{xy}, d_{x^2-y^2} \) subbands width, \( \langle L_z \rangle \) and MCA. Adapted from [45].

of plane \( (d_{xz}, d_{yz}, d_{z^2-r^2}) \). The two bands have different bandwidth \( 2V_\parallel \) for in plane and \( 2V_\perp \) for out of plane, with \( R = V_\perp / V_\parallel \). Now if the spin-orbit interaction is considered, following ref. [106] the MCA is:

\[ MCA = \frac{\xi}{4\mu_B} (\Delta\mu_I) = \frac{\xi^2}{8V_\parallel} \left( \frac{3}{R} + \frac{2}{R+1} - 4 \right) \tag{5.1} \]

In plane anisotropy corresponds to \( MCA > 0 \) this means \( R < 1 \) hence \( V_\perp < V_\parallel \) as in the case of the free standing monolayer. Out of plane anisotropy corresponds to \( MCA < 0 \) this means \( R > 1 \), hence \( V_\perp > V_\parallel \). \( R > 1 \) when the overlap is preferentially between out of plane d orbitals. The strength of the interaction between Co atoms and other elements \( (X = Au, Pt, Pd, Cu) \), with respect to the in-plane Co-Co interaction (set to 1) is 1.53, 1.60, 1.38, 0.83 respectively [107]. This is also the case of Co-Pd for which MCA was attributed to \( d_{xz}, d_{yz} \) out of plane interfacial hybridization between Co and Pd atoms, see Wang et al. [108].

Single Co atoms on the surface of Pt(111) have a decreased coordination and lower symmetry than the in Co thin films. Qualitatively what can be expected from this reduction of dimensionality is an increase of the MAE.
Furthermore the reduced atomic coordination and hence a the more localized electronic character, enhance the size of the orbital magnetic moment as a consequence of the narrowing of the bands. Hence the strongest anisotropy may be expected for the single atom and as the number of atoms in the cluster is increased the orbital moment and the anisotropy energy is expected to decrease. Theoretical calculations for single atoms and small clusters of cobalt on Pt(111) surface have been performed by I. Cabria, R. Zeller and P.H. Dederichs [8], where they have been compared with the experimental result that are going to be discussed in the following pages. In figure 5.3 are depicted Co cluster of 1 to 5 atoms, on the Pt(111) surface together with the orbital magnetic moment (in $\mu_B$) for differents sites. These calculations are performed in the spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) LSDA Green’s functional method [102]. The values for the orbital moment are calculate also within the Orbital Polarization scheme (OP) proposed by Brooks [109]. for this latter case they seem to better agree with the experiment. The results are presented in table 5.1. From the table it is seen that the spin moment $\mu_s$ is increased from the bulk value of 1.6$\mu_B$ (see table 3.2) but changes very little as the number of atoms in the clusters is increased (and thus the atomic coordination is increased) from 1 to 5 atoms. The orbital moment is strongly enhanced from the bulk value of 0.15$\mu_B$ and undergoes a stronger reduction (almost 60%) from the single atom to the cluster of four atom. The orbital moments in the parenthesis are the ones obtained including in the calculations the Orbital Polarization, that is neglected by LSDA that accounts only for spin orbit but not for orbital polarization of the bands. In this scheme the orbital moment is predicted to be larger than in LSDA. The MAE for the single atom is positive, indicating that the easy axis is out of plane, the value of MAE is predicted, including orbital polarization, to be extremely high, +18.45 meV/atom, that
5.1 Magnetic properties of Co/Pt systems

Table 5.1: Calculated values of spin moment, orbital moment, orbital moment anisotropy and magnetic anisotropy energy density, averaged over different sites. From ref. [8].

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>$\mu_s$ ($\mu_B$)</th>
<th>$\mu_l$ ($\mu_B$)</th>
<th>$\Delta \mu_l$ ($\mu_B$)</th>
<th>$K$ (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.14</td>
<td>0.60 (1.50)</td>
<td>-0.25</td>
<td>+18.45</td>
</tr>
<tr>
<td>2</td>
<td>2.11</td>
<td>0.38 (0.74)</td>
<td>-0.11</td>
<td>+4.11</td>
</tr>
<tr>
<td>3 chain</td>
<td>2.08</td>
<td>0.34 (0.67)</td>
<td>-0.06</td>
<td>+3.69</td>
</tr>
<tr>
<td>3 triangle</td>
<td>2.10</td>
<td>0.25 (0.43)</td>
<td>-0.05</td>
<td>+2.22</td>
</tr>
<tr>
<td>4</td>
<td>2.08</td>
<td>0.22 (0.33)</td>
<td>-0.01</td>
<td>+0.75</td>
</tr>
<tr>
<td>5</td>
<td>2.08</td>
<td>0.27 (0.45)</td>
<td>-0.09</td>
<td>+1.81</td>
</tr>
</tbody>
</table>

means almost 1000 times larger than for bulk hcp Co [110]. Furthermore the anisotropy energy decreases very quickly with the number of atoms in the cluster but is still quite large for five Co atoms. As proposed by Bruno the magnetic anisotropy energy is proportional to the anisotropy of the orbital moment $\Delta \mu_l$ which for the single atoms is very high, about $-0.25 \mu_B$. Figure 5.3 shows that the value of the orbital moment changes depending on the local coordination of the Co atom, for small clusters of Co on Pt(111) with a number of atoms from 1 to 5.

The Pt contribution to MAE has also been calculated and found to of about 15% of the total MAE (2.8 meV/Co atom) for the single atom case. As the size of the cluster is increased the Pt contribution is found to become more important with respect to that of Co.

Other calculations where performed by Lazarovits et al. [111] for chains of finite size (1 to 10 atoms), using embedded cluster technique, for Co atoms within multiple scattering theory using Dyson equation [112], while Pt atoms have been treated with SPR-KKR method. For Co single atoms on Pt(111) surface, they find $\mu_l(Co) = 0.77 \mu_B/atom$, $\mu_s(Co) = 2.21 \mu_B/atom$ and $\mu_l(Pt) = 0.02 - 0.04 \mu_B/atom$, $\mu_s(Pt) = 0.09 - 0.14 \mu_B/atom$, for a total magnetic moment of Pt of about 0.6 $\mu_B$. They also calculate the magnetic anisotropy energy of Co and they find it to be $K = 5.9$ meV/atom. Calculations by Lazarovits et al. do not take in account orbital polarization. The agreement is within 30% for the orbital for the orbital moment whilst it is much better (3%) for the spin moment.

In figure 5.4 is represented the polarization effect of the Co adatom on the surrounding Pt atoms, the numbers are the magnetic moment (in $\mu_B$) induced by the Co atom in the Pt atoms.
5.2 Co on Pt(111), low temperature deposition.

The experiment has been performed at Id8 beamline (ESRF) with the experimental chamber described in section 3.2.2. The preparation of the Pt(111) crystal was achieved by cycles of Ar ion sputtering and annealing. Co atoms were evaporated with the substrate cooled down at $T=5.5\text{ K}$. At this temperature the thermal diffusion of Co atoms on the Pt(111) surface is completely inhibited and thus for a sufficiently small deposition dose the atoms distribute on the surface in a random way as single atoms, well separated from each other.

In figure 5.5 it is possible to see an STM image (85x85Å) acquired at 6 K of 0.01 ML of Co atoms deposited by e-beam evaporation on the surface of Pt(111). The atoms are isolated on the surface and they do not diffuse. This is an extremely important point since we are mainly interested here in the properties of “single” atoms. The atoms on the surface are randomly distributed, since the surface diffusion is inhibited at this temperature. When the coverage is increased the size distribution of the clusters is changed with an increasing percentage of dimer, and trimer by respect to single atoms, thus the average size of the cluster increases. It has to be noted that up to coverages of 0.03 ML the isolated atoms are the 85% of the total distribution. If the coverage is further increased or the temperature is raised dimers, trimers and small clusters start to form. This change in coordination leads to a reduction of the orbital moment and anisotropy.

Figure 5.6 depicts the geometry of the experiment. The magnetic field produced by the two split superconducting coils is parallel to the light propagation direction (and helicity). By changing the angle $\theta$ it is possible to

\[1\text{ML of Co on Pt(111)} = 1.5 \times 10^{15}\text{atoms} \cdot \text{cm}^{-2}\]
5.2 Co on Pt(111), low temperature deposition.

change the angle between the normal to the sample surface and the direction of the magnetization. In this way the magnetization along different crystallographic directions is measured. From XMCD measurements, at different

values of angle $\theta$, it is possible to evaluate the orbital and spin moment of the Co atoms along different crystallographic directions and thus evaluate the anisotropy of the moments. From magnetization curves it is possible first to evaluate if the system reaches the magnetic saturation or not. Moreover from the analysis of the magnetization curves at two different angles it is possible to quantify the total magnetic moment and magnetic anisotropy.

Figure 5.5: STM image of Co atoms on the Pt(111) surface at 6 K. The coverage is 0.01 ML [8].

Figure 5.6: Experimental geometry: $\sigma_\pm$ are the radiation circular polarizations, H is the magnetic field and $\theta$ the angle between radiation propagation radiation and the surface normal.
energy, MAE (see section 2.2.2).

5.3 XMCD and x-ray magnetization curves measurements

Figure 5.7 (upper inset) shows the spectra, \((\sigma_+, \sigma_-)\), of single Co atoms on Pt(111) surface taken with right (+) and left (-) circular polarization, in a field of 7 Tesla at angles \(\theta = 0^\circ\) and \(\theta = 70^\circ\). From visual inspection many important things can already be noticed. First the signal of Co atoms is weak and it is overimposed on the tail of the Pt background. This is due to the very small quantity of material that has been deposited: 0.01 ML. The difference between the \(\pm\) pair of spectra changes quite remarkably from \(\theta = 0^\circ\) to \(\theta = 70^\circ\), this is an indication that the system is magnetically anisotropic. From the dichroic signals (figure 5.7 lower inset) and from the spectra it is even more clear that the \(L_3/L_2\) ratio changes with angle and has the maximum at \(\theta = 0^\circ\). This can be understood for a system with uniaxial anisotropy as the evidence that the easy axis is along \(\theta = 0^\circ\) direction, i.e. normal to the sample surface. The very weak intensity at \(L_2\) edge and also in the dichroism signal at \(L_2\) is a clear fingerprint of the enhancement of the cobalt orbital moment. The number of holes \(N_h(Co)\) for the case of Co single atoms on Pt(111) has been calculated in the LSDA scheme to be \(N_h(Co) = 2.40\). The "spin sum rule" (see equation 3.26), once \(N_h(Co)\) is known, permits to calculate: \(\mu_s(Co) + \mu_d(Co)\), in this case \(\mu_s(Co) + \mu_d(Co) = 1.8\mu_B\). The spin moment is also calculated reliably and is \(\mu_s(Co) = 2.14\mu_B\). From these considerations the dipole magnetic moment is found to be \(\mu_d(Co) = -0.34\mu_B\), which is a value between those of the bulk and the free atom.

From the "orbital sum rule" (see equation 3.25) it is possible to obtain directly that the cobalt orbital moment is \(\mu_l(Co) = 1.1\mu_B\) at \(\theta = 0^\circ\). This value is extremely high with respect to the bulk hcp cobalt (\(\mu_l = 0.15\mu_B\), ref [54]) and also with respect to atomic chains on Pt(997) (\(\mu_l = 0.68\mu_B\), ref [22]). This enhancement of the orbital moment from the bulk to the single atoms is due to the reduction of the atomic coordination that produces a narrowing of the bands. This value of the orbital moment is in good agreement with the theoretical calculations reported in table 5.1.

Magnetization curves have been acquired with left circular polarized radiation at the two angles \(\theta = 0^\circ\) and \(\theta = 70^\circ\). The operative procedure is the following: the magnetic field is scanned from -7 T to +7 T and at each value of the field the signal \(I(E)\) due to the polarized radiation is acquired at two different photon energies. The first photon energy \(E_1\) is chosen at the pre-edge, the second \(E_2\) at the \(L_3\) edge. The value \(\bar{M} = (I(E_2) - I(E_1))/I(E_1)\) is then proportional to the magnetization of the system.
To determine the moment $\mu$ and the anisotropy energy per atom $K$, the curves $\hat{M}(H,0^\circ)$ and $\hat{M}(H,70^\circ)$ are then fitted with an anisotropic Langevin functions (as defined in section 2.2.2), for a fixed number of atoms ($\bar{n} = 1$) and temperature ($T=5.5K$). The original data have been rescaled in the following way: $\hat{M}(+7T,0^\circ) = 1$ while the curve at $\theta = 70^\circ$ is rescaled of a factor equal to the ratio of asymmetry of the spectra taken at $+7T$, i.e. $\hat{M}(+7T,70^\circ) = Asym(70^\circ)/Asym(0^\circ)$, to properly evaluate the difference of magnetization between the two curves.

In figure 5.8 two magnetization curves acquired ($\theta = 0^\circ$ and $\theta = 70^\circ$) are plotted after rescaling. From the fitting procedure the values obtained are: $\mu = 5.0 \mu_B$ and $K = -9.3meV/atom$. Since $\mu$ is the total magnetic moment of the system, i.e. $\mu = \mu_s + \mu_t + \mu_{Pt}$, the contribution to the total magnetic moment of the Pt can be calculated: $\mu_{Pt} = 1.8 \mu_B$. These values are mainly affected by temperature uncertainties and are reliable within a $\pm 15\%$. 

---

**Figure 5.7:** XMCD spectra and dichroism at $\theta = 0$ and $\theta = 70$ of Co single atoms on Pt(111) [8].
The anisotropy energy per atom $K$ of $-9.3\text{meV/atom}$ is the highest measured so far for magnetic systems. It overcomes Sm-Co compounds (used in permanent magnets) $K_{SmCo} = 1.8\text{meV/atom}$ (see ref. [113]) and also 1D Co atomic chains $K_{1D_{chains}} = 2.0\text{meV/atom}$ [22].

The orbital moment enhancement of Co is due to the reduced coordination of single atoms and the symmetry breaking at the surface that produce a strong localization of orbitals. Moreover d-d mixing between 3d orbitals of Co and 5d orbitals of Pt contributes to the enhancement of orbital moments and to the orbital moment anisotropy. This big size of orbital moment is a key feature to have strong MAE, but other elements should be consider as the effect of spin-orbit of Pt and the contribution of Pt to the total magnetic anisotropy energy.

A comparison to the experiment shows that calculations from Cabria, Zeller and Dederichs, are in good agreement with the data and give the right order of magnitude for the magnetic anisotropy energy. For the orbital moment the calculation done with standard SPR-KKR method give an orbital moment smaller of 40%, while including the Orbital Polarization the situation is improved. If the coverage is increased $K$ is almost constant from 0.007 ML up to 0.03 ML this means that up to this coverage the atoms are still isolated from each other. Beyond this coverage the formation of dimers and trimers and thus the increase in coordination produce a decrease in the orbital moment and thus also in the MAE. Still, up to 8 atoms per cluster, the anisotropy energy is high ($1\text{meV/atom}$), and then it slowly further reduces when the coverage and thus the number of atoms in the clusters, is increased. Figure 5.9 shows STM images of Co cluster formation on Pt(111) surface for temperature controlled thermal aggregation. Depositing the same amount of material at different temperatures the different thermal mobility induces
5.3 XMCD and x-ray magnetization curves measurements

Figure 5.9: STM images of Co cluster formation on Pt(111) surface by temperature control assembly. Inset (a) show 0.1 ML deposited at 50 K, the average cluster size is 2.9 atoms. Inset (b) show 0.1 ML deposited at 83 K, the average cluster size is 7 atoms. Inset (c) shows SPR-KKR cluster configuration considered in calculation.

the formation of clusters with increasing size for higher temperature. The same effect can be obtained increasing the coverage.

As the size of the cluster is changed also its electronic structure and mag-

Figure 5.10: XMCD dichroism for increasing mean size of the Co cluster. The curves are normalized to the L₂ feature [8].

netism change as a consequence of the increased Co-Co coordination. This is evident from figure 5.10, the normalized dichroism decreases with increasing size of the cluster. Another consequence is that increasing the cluster mean size the MAE decreases following the decrease of the orbital moment. This is clearly depicted in picture 5.11 where, \( \mu_o \) is the orbital magnetic moment and \( K \), the anisotropy energy per atom, are plotted as a function of \( \bar{n} \), the average number of atoms in the cluster. In the inset the linear relation between \( K \) and \( \mu_o \) is shown. In picture 5.12 are presented two magnetization curves acquired at a temperature of 10 K, for small clusters of Co
Figure 5.11: $K$ and $L$ as a function of the number of atoms in the clusters [8]
calculation results summarized in table 5.1 and are explained by the fact that increasing the average size of the cluster also the coordination is increased. It should also pointed out that the magnetic anisotropy energy is particularly enhanced when the cluster average size is below 10 atoms.

In summary, the magnetic properties of Co single atoms on the Pt(111) surface have been studied at low temperatures and in high magnetic fields by means of XMCD and x-ray magnetization curves. A strong enhancement ($\mu_l = 1.1\mu_B$) is found for the orbital moment by respect to the Co monolayer and the bulk. The system shows an extraordinary magnetic anisotropy with the easy axis direction perpendicular to the surface plane. The magnetic anisotropy density is the highest measured until now for any material: $K = 9.2\, \text{meV/atom}$. This anisotropy is due to the combined effect of the reduced atomic coordination of the Co single atoms, together with surface symmetry breaking and the Pt magnetic contribution. As the mean size of the cluster is increased the anisotropy energy per atom and the orbital magnetic moment decrease rapidly.
Co single atoms on Pt(111)
Chapter 6

Fe and Co atoms on the Cu(100) surface

The electronic and magnetic properties of Fe and Co single atoms on the Cu(100) surface have been studied by XMCD. Fe and Co are found to behave in a different way from Mn, on the Cu(100) surface (see section 4.4). They do not show atomic-like multiplet features and atomic magnetism. Moreover Fe and Co have drastically different magnetic properties between themselves. Fe single atoms on Cu(100) show a magnetic moment increased from the value of bulk Fe. This enhancement is mainly due to the increased orbital moment. Related to the enhancement of the orbital moment, a huge magnetic anisotropy energy of 1.5 meV/atom, which is 1000 times larger than the one of bulk Fe, is found for Fe single atoms. Co single atoms on Cu(100), on the other hand, show no dichroic signal in the XMCD spectra and thus are non magnetic in a magnetic field of 7 Tesla and at a temperature of 5.5 K. This absence of magnetism is understandable in the picture of the non magnetic Kondo screened regime for these atoms, and is consistent with recent Scanning Tunneling Spectroscopy studies.

6.1 Background

The magnetic moments and magnetic anisotropy of Fe on Cu(100) have been of great interest in the last ten years, mainly for the connection between the structural and magnetic properties of ultrathin films. Recently the availability of low temperature microscopic and magnetic measurements has permitted to understand the temperature dependence of the surface anisotropy [114] and the reorientation effects due to adsorbates [115]. Changes in the initial growth of Fe on Cu(100) surface from bilayer island to flat layer were found as a function of the rate [116]. They have been explained with the same atom exchange process at the basis of a bimodal growth found for Co.
Fe and Co atoms on the Cu(100) surface

on Cu(100) [117]. Total-energy calculations [98], showed that the exchange atom process between 3d adatoms and Cu surface atoms is favorable even for metals immiscible in the bulk and influences the magnetism.

The present chapter is dedicated to the presentation and discussion of data concerning the magnetism of single atom of Fe and Co deposited and measured on the surface of Cu(100) at low temperatures. The thermal diffusion on the surface is inhibited already at a temperature of 80 K [118], transient mobility is also excluded for the flat clean surface of Cu(100) [119] below 100 K. Thus at 5.5 K, the experimental temperature, the atoms after reaching the surface, simply moves toward the nearest four fold site as in figure 6.1 where Co (Fe) adatoms are depicted on the Cu(100) surface.

From the theoretical point of view many calculations examined the orbital and spin moments, for the magnetic anisotropy of Fe/Cu and Co/Cu monolayer and for multilayers structures in different frameworks. The case of Fe adatoms on the surface of Cu(100) has been studied by Lazarovits et al. [120] as the limiting case for the magnetism of atomic chains. The system is calculated in multiple-scattering theory as a finite size cluster embedded into a host system. The copper host is treated within fully relativistic screened Korringa-Kohn-Rostoker method [121], [122]. These kind of calculations are performed at $T = 0$ and hence do not account for the experimental temperature or directly for temperature effects. Apart from the determination of numerical values for the magnetic moments some general interesting informations are given.

In figure 6.2 is depicted the trend for the orbital and spin magnetic moment of the single Fe impurity as a function of the position with respect to the surface, with $S$ being the surface, $S - 1$ is the first layer below the surface, etc. The largest moments are obtained for the atom sitting on top of the surface. The more the Fe single atom is placed inside the Cu, the stronger the reduction of the moments. It is to note that the orbital moment, more

Figure 6.1: Adatom deposition (Fe or Co) on clean Cu(100) surface at low temperature.
than the spin moment, suffers of a large reduction if the Fe atom is inside the surface or one layer below. The moments converge rapidly to those of the impurity inside the bulk host, as the atom is moved to deeper layers. These effects can be explained on the basis of the changes induced by the coordination on the density of states as depicted in figure 6.3. On top of the surface the adatom has a spin down density of states with a narrow structure, centered slightly above the Fermi energy $E_F$, while the spin up is almost completely filled. As the atom is placed in the surface, as a consequence of the increased coordination the spin down structure is broadened and thus a larger amount of states is pushed above $E_F$. As the atom is placed in the second layer below the surface the nearest neighbor coordination reached its maximum, thus explaining the similarities with the bulk. The difference in the coordination number of the Cu atoms $N_{Cu}$ explains also why the orbital and spin moments are smaller on Cu(100) by respect to Cu(111). On the Cu(100) surface the adatom has four Cu nearest neighbors, while they are three on Cu(111), hence the hybridization is stronger on Cu(100) than on Cu(111). The expected values for spin and orbital magnetic moments and anisotropy energies, are given in table 6.1 for the Fe single atom (on top
Fe and Co atoms on the Cu(100) surface

Figure 6.3: Fe adatom spin-projected DOS for (solid line) Cu(001) and (dashed line) Cu(111) surfaces. Adapted from [120].

and in the surface) [120], the Fe monolayer on Cu(100) [123]¹, and for bulk (fcc) Fe [110]. The orbital and spin moments are enhanced in the case of the adatom on top of the surface with respect to the monolayer and to the bulk. The orbital moment shows the larger effect, being about 20 times the one in the bulk. The magnetic anisotropy energy calculated for the atom on top of the surface is of 2.8 meV, and the easy axis is expected to be perpendicular to the surface. This value is very large, about a thousand times more than in the bulk and five times more than the monolayer (the value between parentheses includes dipolar interactions that would favor the easy axis to be in plane). In KKR framework the Co adatom magnetic moment is calculated on the Cu(100) together with the magnetic moment for the other 3d elements [124], [98]. The magnetic anisotropy energy has been calculated by Pick et al. [125] to be 1.7 meV. Figure 6.4 shows the calculated magnetic moment for adatom and dimer of the 3d metals on Cu(100) surface. The magnetic moment as a function of the element in transition metals mostly

¹The first value is MCA contribution to total MAE while the value in parenthesis is the total MAE including dipole-dipole interaction and favors an in-plane alignment of the moment.
Table 6.1: Calculated values of spin, orbital and total magnetic moment and magnetic anisotropy energy per atom (K) for the Fe single atom, the monolayer on Cu(100) and Fe bulk.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_s$ ($\mu_B$)</th>
<th>$\mu_l$ ($\mu_B$)</th>
<th>$\mu_{tot}$ ($\mu_B$)</th>
<th>K (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>single atom (on top)</td>
<td>3.19</td>
<td>0.47</td>
<td>3.66</td>
<td>2.86</td>
</tr>
<tr>
<td>single atom (in surface)</td>
<td>3.01</td>
<td>0.14</td>
<td>3.15</td>
<td>-0.1</td>
</tr>
<tr>
<td>monolayer</td>
<td>2.78</td>
<td>0.08</td>
<td>2.86</td>
<td>0.41 ($\approx -0.1$)</td>
</tr>
<tr>
<td>bulk Fe (bcc)</td>
<td>2.19</td>
<td>0.078</td>
<td>2.268</td>
<td>-0.0014</td>
</tr>
</tbody>
</table>

Figure 6.4: Magnetic moments of 3d transition metal small clusters on the Cu(100) surface. Adapted from [98].

mimics the behavior of spin moment for the atomic elements. From picture 6.4 a value of the magnetic moment for the Co single atom is expected to be $\mu(Co) = 1.8\mu_B$. This value has been obtained by different authors, see also Pick et al. [125].

6.2 Fe on Cu(100): a magnetically anisotropic system

In the study of this system a combined use of XMCD and magnetization curves have been employed to evaluate the magnetic moment and the magnetic anisotropy of the system. By means of an XMCD analysis of the spectra the orbital and spin moments of Fe are obtained. From the magnetization curve the total magnetic moment as well as the the MAE per atoms are established. The geometry of the experiment is the same as for Co single atoms depositied on Pt and it is schematically drawn in figure 6.5. The two geometries (normal incidence and more grazing incidence) are
depicted, together with the geometrical relations between the physical quantities involved. In figure 6.6 are plotted the spectra acquired in a magnetic field of 7 Tesla for $(\sigma_+, \sigma_-)$ circular polarizations at two different values of the angle ($\theta$) between the direction of the magnetic field and the normal to the surface. The value of the angle $\theta = 0^\circ$ corresponds to the normal incidence of radiation with respect to the sample surface. The pair of spectra at $\theta = 0^\circ$ show a bigger difference for the two polarizations than the ones at $\theta = 55^\circ$ this is interpreted as due to the magnetic anisotropy. To better appreciate the difference of $\sigma_\pm$ curves, the normalized dichroic signals for $(\sigma_+, \sigma_-)$ for $\theta = 0^\circ$ and $\theta = 55^\circ$, are plotted in figure 6.7 By measuring magnetization
curves it is possible to have an independent measure of the total magnetic moment and of the anisotropy energy per atom. In figure 6.8 are depicted the magnetization curves acquired with $\sigma_-$ polarization at two angles $\theta = 0^\circ$ and $\theta = 55^\circ$. The curves are fitted with two anisotropic Langevin functions, as described in section 2.2.2 on the basis of the different intensity of dichro-
ism at L_3. The fit has been performed for a temperature of 5.5 K, and for single atoms (i.e. \( n = 1 \)). The free parameters being \( \mu \) the total magnetic moment and \( K = MAE/atom \). The values obtained are \( \mu = 3.7\mu_B \) and \( K = 1.51 \text{ meV/atom} \).

From the fact that \( \mu = \mu_s + \mu_L \), using the theoretical value for the spin moment \( \mu_s = 3.19\mu_B \) it is possible to calculate the orbital moment: \( \mu_L = 0.51\mu_B \). That agrees very well with the one calculated by Lazarovits et al. [120], \( \mu_L = 0.47\mu_B \). The magnetic anisotropy energy per atom, calculated by Lazarovits et al. is 2.86 \( \text{meV/atom} \). It is in agreement within the order of magnitude but overestimate the anisotropy energy density found from the experimental magnetization data to be 1.51 \( \text{meV/atom} \).

In the present case the substrate polarization can be safely neglected in the evaluation of Fe magnetic moment and magnetic anisotropy energy. Calculations by Lazarovits et al. [120] support this idea. The author found a very weak polarization for the surface layer where the polarization effects should be the strongest. They found a spin moment of \( \mu_s(Cu) = 0.02\mu_B \) and an orbital moment \( \mu_L(Cu) < 10^{-3}\mu_B \).

### 6.3 Co atoms on Cu(100): a Kondo system

Co impurities deposited on Cu disordered films has been studied by Wei et al. [126] by weak localization technique and the system was found to be a Kondo system with \( T_K = 23 \text{ K} \). Recently Co adatoms on Cu(100) have been studied by Scanning Tunneling Spectroscopy (STS) at a temperature of 6 K, by Knorr et al. [127]. Figure 6.9 (left) depicts an STM image of Co adatoms on the Cu(100) surface and (on the right) STS spectra of Cu(100). They found that Co adatoms on Cu(100) (and Cu(111)) surfaces are Kondo systems. The \( T_K \) has been established to be of 88 K on Cu(100) (in bulk it is of 500 K [128]) while for Co on Cu(111) it is \( T_K = 54 \text{ K} \). In a recent paper Stepanyuk et al. [98] found from their calculations with LSDA and KKR Green's function method, localized moments for the ground state of Co adatom and dimer on the Cu(100) surface. The cobalt moment was found to be about \( \mu = 1.8\mu_B/atom \). With XMCD and magnetization measurements it is possible to add some informations to discuss the magnetism of Co single atoms.

The amount of material deposited has been estimated on the basis of a previous calibration done at room temperature. These measurements are reported in figure 6.10 where a series of spectra of different coverage is plotted (left inset). The coverage value has been linearly extrapolated from the calibration curve (left inset) that plots the relative edge jump defined as the average signal at L_3 minus the pre-edge background signal divided by pre-edge \( (\Delta L_3/pre - \text{edge}L_3) \). The lowest coverage studied is 0.0028 ML of Co. For lower coverages the signal was too weak with respect to the background
6.3 Co atoms on Cu(100): a Kondo system

Figure 6.9: STM image (left) and STS spectra (right) of Cu(100) and Cu(111), adapted from [127].

Figure 6.10: Average spectra $\frac{+0\pm0}{3}$ of Co on Cu(100) at room temperature for coverages up to 2 ML at $\theta = 0^\circ$.

and to the noise level. In figure 6.11 are plotted the spectra of 0.0028 ML of Co on Cu(100), acquired with right circularly polarized radiation, changing the field from +7 Tesla to -7 Tesla. At the bottom of the same figure the dichroic signal derived from the spectra, is shown, with the same intensity scale. No dichroic signal is found in these spectra for Co single atoms on the Cu(100) surface. Moreover it is interesting to note, from figure 6.11, that the lineshape of the spectra is different from the thin film Co lineshape, presented in figure 6.10, and from the atomic-like lineshape spectra of Co impurities on alkali metals [7]. In fact a broad structure is present at 3.5 eV above the L$_3$ edge maximum energy.
The absence of dichroism is not in contradiction with the magnetic moments predicted for Co atoms on Cu in the jellium model used by Papanikolau et al., of 0.89\( \mu_B \), [86], and within the scheme used by Stepanuk et al. in ref. [98] where the authors find the moment of Co to be 1.8 \( \mu_B \). The apparent discrepancy is due to the fact that these kind of calculations, strictly valid at \( T=0 \), cannot account for Kondo effects, while they work well for a non Kondo state, as for the Fe single atoms on Cu(100).

If the system is in a Kondo state, following the arguments introduced in section 2.1.2, it will have a small but non-zero susceptibility at \( T=5.5 \) K. Hence it is possible to give, an estimate of the expected dichroic signal due to the weak magnetism of Kondo impurity. The comparison is made by calculating the ratio of susceptibilities of a Co Curie paramagnet with a magnetic moment of \( \mu = 1.8\mu_B/\text{atom} \) and a Kondo system with \( T_K \), an the rescaling the dichroic signal (Asymmetry at \( L_3 \)) of the paramagnet to this ratio. Thus, since the Kondo temperature is 88 K, the measurement temperature is 5.5 K, we have that the ratio between the Kondo susceptibility is \( \chi_K/\chi_C = T/T_K\mu^2 = 0.022 \). Hence any magnetic effect of a Kondo system is expected to be a factor of 50 weaker than for a magnetic moment of 1.8\( \mu_B \). It is now possible to rescale this on the dichroism: for the bulk hcp Co, as measured by Chen et al. [54], the total magnetic moment is \( \mu = 1.70\mu_B \), and the corresponding asymmetry at \( L_3 \) is -0.27 (-27\%). Hence a reasonable estimate for the asymmetry of the magnetic signal of a Kondo impurity of \( T_K = 88K \) is approximately of 0.6\% of the edge intensity at \( L_3 \). From picture 6.11 it is clear that a dichroic signal level of the order of

Figure 6.11: Spectra (\( \sigma_+ , \sigma_- \)) and dichroism of 0.0028 ML of Co on Cu(100) at \( \theta = 0^\circ \). The arrows indicate the \( L_3 \) edge and a second structure at higher photon energy.
0.6% of L₃ edge intensity is weaker than the noise in the experimental data and thus not detectable. The present data are therefore consistent with the STM measurements of single Co atoms on the surface of Cu(100) [127], and its description as a Kondo system.

Why, then, the Fe single atoms are not a Kondo system at 5.5 K? This can be explained on the basis of a simple assumption. Co impurities in bulk Cu have an estimated Tₖ of 500 K [128] and single atoms have a Tₖ of 88 K. Fe impurities (0.01%) in bulk Cu have a Tₖ of 20 K [129]. Hence the single Fe atoms on Cu(100) are expected to have a Tₖ, lower (or comparable) than the experimental temperature of 5.5 K.

6.4 V, Mn, Fe, Co atoms on Cu(100): a comparison

Finally a comparison between impurities of different 3d transition metals for the lowest coverages is given in figure 6.12, for vanadium, manganese, iron and cobalt on the Cu(100) surface.

The vanadium show broad edge features on both edges with a small dichro-
sequence of the hybridization. Manganese instead, thank to its stable electronic configuration has a large dichroism. Iron has still an intense dichroism even if less then manganese. Cobalt shows no magnetic dichroism at all. This behavior along the transition metals series is expect for example from Stepanyuk et al. calculations for the magnetic moment of transition metals.

A comparison with theoretical calculations is given in figure 6.13, where

**Figure 6.13:** Comparison of experimental and theoretical [98] magnetic moments for V, Mn, Fe, Co on Cu(100).

the dichroism of V, Mn, Fe and Co is compared to the adatom calculated values of figure 6.4, with the scale factor fixed for the case manganese.

In summary, the magnetic properties of Fe and Co single atoms deposited on the Cu(100) surface have been studied at low temperatures by XMCD and magnetization curves. Fe single atoms behave paramagnetically with a total magnetic moment of $\mu = 3.73\mu_B$ with an strongly enhanced orbital magnetic moment. Furthermore Fe single atoms have an uniaxial out of plane magnetic anisotropy with a magnetic anisotropy energy of 1.51 meV/atom, which is almost 15 times more than the monolayer and about 1000 times the bulk bcc iron. XMCD spectra of Co single atoms show no dichroism at all, this is found to be consistent with STS measurements at low temperature that established that Co single atoms on Cu(100) are a Kondo system with $T_K = 88$ K. The dichroism due to the very weak magnetism expected of such a Kondo system has been estimated to be below the experimental sensitivity. Finally the magnetic behavior of V, Mn, Fe and Co impurities is compared with available theoretical calculations of adatom magnetism for the 3$d$ transition metal series. The overall behavior that favors a stronger magnetism in the middle of the series, for Mn and Fe and weaker mag-
netism for the earlier and later elements like V and Co, is respected. The size of these moments agree very well for Mn, the agreement is good for Fe. Theoretical predictions fail to estimate the Co moment due to the intrinsic uncapability to account for the Kondo screening. Also in the case of vanadium the magnetic moment is overestimated.
Fe and Co atoms on the Cu(100) surface
Summary

The electronic structure and the magnetism of transition metal single atoms and magnetic impurities on metal surfaces has been studied by means of x-ray absorption dichroic techniques (XMCD, and magnetization measurements) in high magnetic fields and at low temperatures. The unique capabilities of XMCD to probe the both spin and orbital magnetic moments with element selectivity have been applied to diluted systems with low surface concentration ($\approx 10^{12} \text{ atoms cm}^{-2}$) down to the limit of isolated atoms. This kind of measurements have been applied to surface impurity systems only in the last few year thanks to the availability of high flux and brilliance synchrotron radiation sources. At the present these measurements represent the state of the art in the study of surface impurities.

Results have been reported for three different classes of systems: Mn and V impurities on the surface of alkali metals (Cs, K, Na); Mn, V, Fe, Co single atoms on the Cu(100) surface and Co single atoms on the Pt(111) surface. Furthermore results have been presented, regarding the magnetic moment distribution of a Mn monolayer coupled to the Fe(100) surface.

Manganese on potassium has been shown to possess an atomic-like magnetic $d^5$ electronic configuration. This electronic configuration is particularly stable for small hybridization changes induced by alkali metals of increased electronic density. If the hybridization is further increased as on Al(100) the spectroscopic features related to atomic multiplets are suppressed together with magnetism. Vanadium impurities on alkali metal surfaces also show atomic multiplet features. The electronic configuration is not an atomic-like configuration as $d^3$ or $d^4$. The orbital moment is found to be small $< 0.5\mu_B$ with respect to the purely atomic configurations and to be antiparallel to the spin. It decreases along the alkali metals column (group 1A) of the periodic table, as the electronic density is increased, i.e. going from Cs to Li. This effect is related to an increased hybridization with the substrate due to the larger electronic density. The measured magnetic moments are of the order of $3\mu_B$, and cannot be explained with simple atomic parameters. Two possible mechanisms have been proposed to explain the partial quenching of the orbital moment, the effect of a weak crystal field and the effect of hybridization through the larger width of Friedel resonant bound state for the early elements of 3d transition metal series.
Fe single atoms on Cu(100) surface have a large out of plane magnetic anisotropy of 1.5 meV/atom and enhanced orbital magnetic moment with the respect to the bulk. The Cu substrate does not contribute considerably to the anisotropy as in the case of Co on Pt. At the opposite Co single atoms on Cu(100) surface do not show any dichroism and hence magnetism. This result can be explained on the basis of the Kondo effect, since Co single atoms have been found to be a Kondo system with $T_K = 88K$. A comparison of the experimental data for V, Mn, Fe, Co impurities on Cu(100) with the calculated magnetic behavior of adatoms along the 3d series, gives an overall reasonable agreement, with important deviations for V and Co impurities.

Co single atoms on the Pt(111) surface have an extraordinary large out of plane magnetic anisotropy of about 9.2 meV/atom [8] due to the interplay between an enhanced orbital moment, consequence reduced coordination of the single atom, at the surface, and the effect of Pt hybridization, consequence of a $d-d$ mixing between Co and Pt orbitals. This result is of particular relevance since this magnetic anisotropy is the highest measured, by now, for any system.
Bibliography


Papers

“Giant Magnetic Anisotropy of Cobalt Single Atoms and Nanoparticles.”

“Localized Electronic States interacting with Metal Host States, the Case of Transition Metal Impurities on Alkali Surfaces.”

“Transition Metal Single Atoms on Cu(100) Interaction with the Substrate and Magnetic Anisotropy”

“Non-collinear Magnetic Moments Distribution in the AFM/FM coupled Mn Monolayer on Fe(100).”
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