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Surface Magnetism

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Science consists of two parts – experiment and theory – which are in constant interplay with each other. It is hardly possible to carry out a meaningful experiment, unless one has a specific idea or theory in mind, and a scientific theory is worthless unless it is based on experimental observations.

Per-Olov Löwdin (1916–2000)

7.1

Introduction

The topic of magnetic properties of surfaces, thin films, and thin film systems (such as multilayers and superlattices) is of tremendous scientific and economic importance, not only for well-known data storage devices but also for future electronics, which may utilize the electrons' spin in addition to their charge. Surfaces, interfaces, thin films, and nanostuctures often display magnetic properties fundamentally different from the properties of bulk crystals, which are thus important to understand principles of magnetism. Recent experiments probed local magnetic moments (and their temperature dependencies) of films and their surfaces/interfaces, small clusters, as well as nanowires, nanodots, and single atoms deposited on solid surfaces.

Surface magnetism is inseparably connected to the magnetism in ultrathin films, the reason being that even the surface of a paramagnet can become magnetic after growing a ferromagnetic thin film on top of it. Also, our initial knowledge of magnetic surfaces comes from the theoretical analysis of ultrathin film slabs, which are being used by theorists in band structure calculations, and also from experiments with ultrathin magnetic films.

When discussing surface magnetism (or, more generally, low-dimensional magnetism) several phenomena should be considered. First of all, any change in the electronic states’ occupation at the surface results in a change of the surface magnetic moment. Lower atomic coordination results in a band narrowing, leading to further changes of the surface moment. From an atomic perspective, one expects these moments to increase at the surface, which has dimensionality somewhere between bulk (nonmagnetic for most materials), monolayer, and isolated atoms.
(most of which possess a net spin). Second, from a statistical mechanics perspective, the average moment at nonzero temperature is expected to decrease. For surfaces, the loss of magnetic neighbors in a magnetic surface represents a weakening of the exchange interaction, which results in a stronger decrease of magnetic order with temperature, a changed Curie temperature, and a changed critical behavior if compared to that of a bulk material. Third, at the surface, the translational symmetry along the axis perpendicular to the sample surface is broken, thus the orbital moment is less quenched than in the sample volume. Consequently, the spin-orbit interaction becomes significant, leading to a large surface magnetic anisotropy that can dominate the system’s magnetic anisotropy and forces the easy magnetization axis to be oriented perpendicular to the sample in the case of ultrathin films.

However, before starting to discuss surface magnetism we should answer a fundamental question: what does “surface” mean and how “thick” is it? Per analogiam, if someone wants to carry out experiments on two-dimensional ferromagnets, the first and most important question is “how thin must the film be before its magnetic properties are two dimensional in nature?” A commonly accepted criterion of magnetic two dimensionality comes from the spin wave theory: the thermodynamic properties of a film are those of a two-dimensional ferromagnet only if the lowest spin wave branch is thermally populated. Following this argument, Mills [1] defined the “critical thickness” \( N_c \) and stated: “the monolayer is a true two-dimensional magnet, and one makes the transition to three-dimensional magnetism in only a few monolayers.” Following this criterion, the “two-and-a-half” dimensional surface should be restricted only to the topmost or a maximum of two to three top atomic layers. In our discussion, we limit ourselves to surface phenomena that correspond to only the very surface atomic layers.

The changes of magnetic properties at surfaces can be investigated by a variety of experimental and theoretical techniques. Comparing experiment with theory, however, is not an easy task. First, the local measurements of the magnetic quantities (like magnetic moment or magnetic anisotropy) are quite difficult, and very often the information cannot be obtained directly. Second, calculations usually refer to simple model systems and therefore differ from real structures that are obtained experimentally.

The chapter is organized as follows: after a short introduction to magnetism, there will be a discussion of how static magnetic properties (i.e., the magnetic moment in the ground state) change at surfaces (Section 7.2). In Section 7.3 we review the experimental techniques that we found particularly useful in surface magnetism. Magnetic properties of ferromagnetic surfaces are discussed in Section 7.4. Magnetic excitations at surfaces, including those that are thermally excited, are discussed in Section 7.5. Surface phenomena influencing the magnetic anisotropy of thin films, magnetization distribution at surfaces, and how to visualize it with atomic resolution are subjects of Section 7.6.

When discussing magnetic phenomena at surfaces we describe (in general) only those experimental methods and techniques that are from our perspective very powerful and provide spectacular findings concerning the phenomena discussed
in this chapter. In this short chapter we cannot present all techniques and phenomena related to the magnetism of surfaces. The selection of the material reflects the experience (and preferences) of the authors and is subjective in this sense.

7.2 Magnetism in Low Dimensions

7.2.1 Introduction to Magnetism

Magnetization is a quantity of prime interest in magnetism. It is defined as the magnetic moment per unit volume \( M = \frac{m}{V} \). The magnetic moment is created by exchange interaction between electrons of the same atom and between electrons of different atoms. The exchange interaction is a consequence of Coulomb interaction in the presence of Pauli’s exclusion principles. The intra-atomic exchange interaction results in the formation of the magnetic moment, the interatomic exchange interaction is responsible for the ordering of magnetic moments. By forming a solid state, most atoms lose their magnetic moment; only very few magnetic solids are formed. This is due to electron delocalization caused by overlapping of the wave functions of neighboring atoms. The delocalization results in the reduction of the electrons’ kinetic energy, which is thereby transformed into the binding energy of a crystal. This applies not only to s and p valence electrons, but to 3d electrons as well. The overlapping of orbitals initiates a correlation between electrons, resulting in an “interatomic” exchange interaction according to Pauli’s principle. The nature of this exchange interaction depends on the length scale on which the atoms interact and the type of atomic bonding (e.g., covalent or ionic).

Ferromagnetic and antiferromagnetic materials are characterized by magnetic moments, which show a magnetic order below a critical temperature. For ferromagnets, this critical ordering temperature is called Curie temperature \( T_C \); for antiferromagnets, Néel temperature \( T_N \). These orders are the lowest energy configurations resulting from magnetic coupling dominated by the exchange interactions.

The strongest interaction that defines the magnetic order is the exchange interaction. In the Heisenberg model [2], the Hamiltonian describing the exchange interaction between two localized magnetic moments (spins) can be expressed by

\[
H_{\text{ex}} = -J_{ij} \cdot S_i \cdot S_j
\]  

(7.1)

where \( S_{i(j)} \) is the spin of the atom at \( i(j) \) position and \( J_{ij} \) is the exchange coupling constant (integral) between the two atoms. The system’s total energy changes, depending on the varying symmetry for different spin configurations. This includes the sign, that is, the relative orientation that can change from parallel to antiparallel, depending among others on the orbital symmetry and the distance between atoms.
The overlapping wave functions from neighboring atoms (where electrons of the opposite spin are forced into similar spatial wave functions) can lead to the same correlation effect as found among electrons in the same atom: at the smallest distances, the spins have an antiparallel alignment since the Pauli principle does not allow two electrons of the same spin to occupy the same position. Within this simplified picture, a small interatomic distance results in antiferromagnetic coupling between atoms and a reduction of the magnetic moment. The coupling is expected to change its sign and become ferromagnetic when the distance increases and the wave functions have no strong overlap. Within the limit of a free atom, the spins of individual electrons are aligned parallel: the electrons have different wave functions to meet Pauli’s principle and thereby the moment increases. The magnetic coupling between spins on different atoms determines the magnetic order, that is, ferromagnetic or antiferromagnetic order is observed.

At larger distances, the exchange interaction between d electrons becomes indirect (mediated by conduction electrons). When the wave functions of electrons carrying a magnetic moment do not directly overlap (e.g., because of an increasing distance beyond a few atomic spacings), this is referred to as “indirect exchange coupling.” There are many types of indirect interactions: super exchange, double exchange, and so on. In 3d metals an important role is played by indirect RKKY interaction (the abbreviation stands for Ruderman, Kittel, Kasuga, and Yoshida, who introduced and enhanced this theory). Here, the exchange interaction could be mediated by the spin polarization of the s and p electrons of the surrounding medium. Since the spins of both atoms and the sp electrons interact (producing a parallel or antiparallel spin orientation between d and sp electrons), the parallel atom spin configuration (ferromagnetic coupling) is always produced at small distances independent of the s electron polarization. The indirect exchange interaction is known for its oscillatory behavior (i.e., the coupling changes the sign periodically with the distance). This behavior is caused by the polarization of sp electrons induced by exchange interaction between these electrons and d electrons of magnetic atoms. The coupling constant depends on the distance between two interacting spins:

\[
J_{ij[RKKY]}(R) \sim \frac{\cos(2k_F \cdot R)}{(2k_F \cdot R)^3} \sim \frac{1}{R^3}
\]  

where \(k_F\) is the Fermi wave vector. Here, the oscillations are averaged out because of integration over the coupling between atom pairs at various distances in all directions.

The same mechanism is responsible for the thickness-dependent interlayer coupling between thin ferromagnetic films separated by a nonmagnetic spacer only a few nanometers thick. Coupling exists as the conduction electrons of the nonmagnetic spacer material respond (i.e., become polarized) because of the magnetic layers.

As the distance increases, the magnetostatic dipole interaction takes over the exchange coupling. The classical dipole–dipole interaction between local magnetic
moments (spins)

\[ H_{\text{dip}} = \frac{1}{4\pi \varepsilon_0} \frac{1}{R_{ij}^3} \left[ S_i \cdot S_j - \frac{3}{R_{ij}^2} (S_i \cdot R_{ij}) (S_j \cdot R_{ij}) \right] \]  

(7.3)

where \( R_{ij} \) denotes the distance between \( S_i \) and \( S_j \) and is always present. However, it is too weak to result in an ordering of the moments – at least at finite temperatures (the situation can be different e.g. in the case of nanoparticles with large magnetic moments).

The dipole–dipole interaction is important for ultrathin films and plays a decisive role in the magnetic moment orientation, which can be either perpendicular or parallel to the film plane (Section 7.6). If there are two ferromagnetic layers at a large distance (neither directly nor indirectly exchange coupled), the magnetic dipole interaction orients the magnetic moments of the layers to be antiparallel. This agrees fully with the experimental observations from microscopic bar magnets.

In 3d metals, itinerant electrons are not localized, but arranged in bands. In metal ferromagnets such as Fe, Co, and Ni, these electrons carry magnetic moments caused mainly by the electron spin. The commonly used theoretical approach for itinerant electrons assumes that they are spread over the whole crystal (Stoner model). In the case of magnetism related to itinerant electrons, the exchange interaction is described by the electron band model. Pauli’s principle states that no two electrons with the same spin can be at the same place. Consequently, the density of electrons of the same spin around an electron decreases, and the so-called “exchange hole” is formed. This makes the Coulomb repulsion spin dependent and can lead to spin polarization in the system. A different number of filled states with spin-up and spin-down electrons decreases the energy contribution resulting from the Coulomb repulsion but increases the kinetic energy. The material becomes ferromagnetic if the energy gain due to a decreased Coulomb repulsion exceeds the increase in kinetic energy. In a ferromagnetic state, the energy states of spin-up and spin-down electrons are separated by the energy and the momentum-dependent exchange splitting \( \Delta E_{\text{ex}} \). Because of the exchange splitting, the minority spin bands become less filled than the majority bands. This creates a spin imbalance, producing the magnetic moment. In the band approximation, the magnetic moment is given by the difference between the filling of majority and minority spin bands, that is,

\[ m(T) \sim \int_{-\infty}^{E_F} (D^\uparrow(E) - D^\downarrow(E))dE \]  

(7.4)

where \( D^\uparrow \) (\( D^\downarrow \)) is the density of states (DOS) for spin-up (and spin-down) electrons. Figure 7.2 shows the spin-polarized DOS of bcc Fe, which arises from integration over all states having different wave vectors but the same energy. It clearly shows that the magnetic moment is related to the exchange splitting between the bands.

Antiferromagnets also exhibit magnetic exchange splitting. The momentum and the symmetry-averaged value of \( \Delta E_{\text{ex}} \) indicate empirically that the value of the local magnetic moment for 3d transition metals (both for ferromagnets and antiferromagnets) is of the order of 1 \( \mu_B \) per electron volt of \( \Delta E_{\text{ex}} \) [4]. For Fe, Co,
and Ni, the values of $\Delta E_{ex}$ are $1.8–2.4$, $0.93–1.05$, and $0.17–0.33$ eV, whereas the corresponding moments are $2.2$, $1.7$ and $0.6 \mu_B$, respectively. Most of the moment is carried by the 3d electrons (about 110%), whereas the s and p electrons are weakly polarized in the opposite direction, giving rise to $-10\%$ of the total moment. The ratio of $\Delta E_{ex}$ and the magnetic moment gives an estimation of the so-called Stoner parameter $I$, which is an important characteristic of the exchange interaction in itinerant electron systems.

If the energy gain from the decreased Coulomb repulsion exceeds the increase in kinetic energy, the metal will order ferromagnetically. This is the so-called Stoner criterion for the existence of ferromagnetism:

$$I \cdot D(E_F) > 1 \quad (7.5)$$

where $D(E_F)$ is the DOS at the Fermi level and $I$ is the Stoner parameter. If the Stoner criterion is satisfied, the bands of spin-up and spin-down electrons split. The Fermi energy for both spin directions must be the same, causing a difference in the occupation for spin up and spin down. The exchange splitting causes the number of majority and minority states close to the Fermi level to be different. This results in a spin polarization of the conduction electrons, which is measured to be approximately $44\%$ for Fe, $45\%$ for Co, and $33\%$ for Ni [5]). It should be noted, however, that the spin polarization $P$ is often defined as

$$P = \frac{D_{\uparrow} - D_{\downarrow}}{D_{\uparrow} + D_{\downarrow}} \quad (7.6)$$

where $D_{\uparrow}$ ($D_{\downarrow}$) is the DOS at the Fermi level. The $P$ value calculated in such a way usually does not agree with the experimental measurements. The reason is that the transport phenomena (which are measured, e.g., by spin-polarized photoemission) are not defined solely by the DOS [6]. This is particularly important for materials such as Ni, which have both d electrons and s electrons at Fermi level. The electric transport is primarily because of the s electrons, whereas the DOS is mostly defined by the d electrons.

The Stoner criterion provides some insight into the differences in magnetic properties that are expected to exist in thin films and surfaces. The Stoner parameter and the DOS at the Fermi level depend on the chemical elements and the system’s dimensionality and can thus be modified. The DOS at the Fermi level depends on the width of the d-band, which can be roughly described as

$$D(E_F) \sim \frac{1}{W_d} \quad (7.7)$$

with the width of the d-band given by

$$W_d = 2 \cdot \sqrt{N} \cdot h_d \quad (7.8)$$

where $N$ is the coordination number and $h_d$ the hopping matrix element of the d electrons’ nearest neighbors depending on the transition metal and it scales reciprocal with the localization of the wave function $h_{3d} < h_{4d} < h_{5d}$. Therefore, for equal coordination $W_{3d} < W_{4d} < W_{5d}$, and thus $D(E_F)_{3d} > D(E_F)_{4d} > D(E_F)_{5d}$. Thus, the Stoner criterion is easiest satisfied by 3d metals such as Fe, Co, and Ni.
According to Eq. (7.8), $W_d$ can be decreased by reducing the coordination number $N$, that is, the number of nearest neighbors. An example of an fcc 3d metal with characteristic values of $N$ is 12 in bulk, 8 at the (001) surface, and 4 for an isolated monolayer (ML). Consequently, the DOS at the Fermi level increases with a decreasing $N$ value, keeping the relation between them as

$$D(E_F)_{ML} : D(E_F)_{surface} : D(E_F)_{bulk} = \sqrt{12} : \sqrt{8} : 1 \quad (7.9)$$

Following the arguments discussed above, this can explain the magnetic moment increasing with a decreasing dimensionality in agreement with theoretical band structure calculations and experimental results. However, the magnetic moment and $D(E_F)$ are not proportional. Thus, the spin polarizations of the conduction electrons for Ni, Co, and Fe are similar, whereas their magnetic moments are very different.

### 7.2.2 Magnetic Moment (and Magnetic Hyperfine Field) at Surfaces and in Ultrathin Films

A reduced dimensionality affects the ground-state magnetization, resulting in an increased magnetic moment and an increased DOS near the Fermi level, $D(E_F)$ [7]. The increased DOS near the Fermi level in a reduced dimensionality can result in ferromagnetic behavior even for elements that are nonmagnetic in bulk. This concerns elements very close to satisfying the Stoner criterion, that is, what is required by the Stoner–Wohlfarth model for the existence of ferromagnetism.

The ground-state magnetic properties can be modified by varying the DOS at the Fermi level. The lower atomic coordination associated with atoms at the surface (or in the monolayer films) can lead to a reduced overlap of d electron wave functions and to a resulting reduction in bandwidth. At the surface of 3d metals, the 3d band narrows, and the states are more localized than bulk ones. This leads to the increase in $D(E_F)$. Then the reduced overlap and relatively narrow bands can lead to an enhanced magnetic moment (Figure 7.1). The surface layer is expected to exhibit a weaker magnetic enhancement than a free-standing monolayer because of its less

![Figure 7.1](image-url)  

**Figure 7.1** Schematic representation of band narrowing and resulting increased magnetic moments at surfaces and in ultrathin films.
reduced atomic coordination number. The enhancement of the magnetic moment is related to the increase in the average exchange splitting $\Delta E_{\text{ex}}$. In contrast, early experiments reported magnetic dead layers at magnetic surfaces and at interfaces between magnetic (in their bulk form) and nonmagnetic materials. Recently, it was realized that not only the spin moment but also the orbital magnetic moment can be strongly enhanced with reduced dimensions, for example, at surfaces. In the presence of spin–orbit coupling, for reasons of symmetry, almost no orbital magnetic moment remains in the bulk ferromagnet. There are two qualitative arguments to explain the enhancement of the orbital moment at the surface. First, the spin–orbit interaction couples the orbit to the spin moment, so that the orbital magnetic moment increases with the increasing spin magnetic moment [8]. Second, the quenching of the orbital moment, which occurs in high lattice symmetries, can be removed by the symmetry reduction at the surface.

The magnetic hyperfine field is another magnetic quantity that can be calculated and measured. The dipole interaction between the nuclear spin moment and a magnetic field causes a so-called magnetic hyperfine splitting (also called Zeeman splitting). The effective magnetic field experienced by the nucleus is a combination of fields from the atom itself, from the lattice through crystal field effects, and from external applied fields. The magnetic field splits the nuclear levels. The measured effective hyperfine field, $B_{\text{hf}}$, in zero applied external magnetic field may be decomposed into four contributions:

$$B_{\text{hf,eff}} = B_{\text{hf,cp}} + B_{\text{hf,ce}} + B_{\text{hf,orb}} + B_{\text{hf,dip}}$$

(7.10)

$B_{\text{hf,cp}}$ is the Fermi contact field from polarization of the core s electrons, whose wave functions overlap the nucleus. In transition metals, this polarization is due to unpaired electrons in the d orbitals. $B_{\text{hf,ce}}$ is the field transferred to the $^{57}\text{Fe}$ nucleus by the spin of conduction electrons spin polarized via the RKKY interaction. This term represents a nonlocalized contribution that depends on the local environment and can therefore be different at the surface, in the ultrathin film, and in the bulk. $B_{\text{hf,orb}}$ is the dipolar contribution from the orbital magnetic moment. $B_{\text{hf,orb}}$ vanishes for bulk metallic Fe and its cubic alloys by interaction with the crystal field. $B_{\text{hf,dip}}$ is the sum of the dipolar fields from the spin magnetic moments. The summation is usually broken down into on-site and off-site contributions. The on-site contribution is small in cubic Fe by spherical symmetry of orbitals with $L = 0$. The off-site contribution includes the demagnetizing field $B_{\text{hf,d}}$ and the Lorentz field $B_{\text{hf,L}}$. In an infinitely large perfectly smooth thin plate with the magnetization parallel to the plane, $B_{\text{hf,d}} = 0$. $B_{\text{hf,L}} = 4\pi/3 M$ for cubic symmetry, where $M$ denotes the magnetization. At the boundary of a ferromagnet, however, $B_{\text{hf,L}}$ is not defined and the on-site contribution to $B_{\text{hf,dip}}$ does not vanish. If the surface is not perfectly smooth, local demagnetizing fields, $B_{\text{hf,d}}$, which increase with the surface roughness, are also expected to occur in the film. However, decomposition into $B_{\text{hf,d}}$ and $B_{\text{hf,L}}$ fails for the surfaces.

The magnetic hyperfine field is usually interpreted in terms of magnetization data, assuming proportionality between the magnetization and the magnetic hyperfine field. This is not always true, in particular in the case of uncoated
surfaces, interfaces, and ultrathin films, because the magnetic hyperfine field arises from the combination of the core and conduction electron contributions. Only the core electron contribution, $B_{hf,cp}$, scales with the magnetic moment at the surfaces; thus the total value of $B_{hf}$ is no longer proportional to the magnetization. Moreover, the $B_{hf,ce}$ contribution to $B_{hf}$ can be positive or negative in comparison to the always negative $B_{hf,cp}$. Thus, the absence of Zeeman magnetic splitting can be a result of zero balance of all the contributions and does not necessarily imply the absence of local magnetic moments. For the clean surface of Fe, this means that only an increase in the $B_{hf,cp}$ contribution to $B_{hf}$, which scales with the magnetic moment, should be expected. Since s electrons at the surface have a more atomlike character, one can expect a positive $B_{hf,ce}$ contribution to $B_{hf}$, compensating in part the dominating negative $B_{hf,cp}$ contribution of the core electrons.

Interpretation of the temperature dependence of the hyperfine magnetic field in terms of magnetization is possible if the effect of surface modification of the magnetic ground state can be eliminated. Even for the thinnest films we can assume proportionality between the reduced-to-0 K $B_{hf}$ value and the reduced magnetization using arguments pertaining to bulk Fe [9] (all contributions to $B_{hf}(T)$ are caused by $M(T)$ and therefore scale with it).

Magnetization can be calculated from first principles by band theory. Calculation methods are usually separated into (i) scalar-relativistic calculations and (ii) full-relativistic calculations. The scalar-relativistic calculations can predict the occurrence of ferromagnetism, the value of the spin moment, and several nonmagnetic properties. The full-relativistic calculations are additionally able to determine the magnetocrystalline anisotropy and the induced orbital moment. The most common approach uses the formalism of local density approximation (LDA) to the density functional theory (DFT) [10].

Historically, it has been difficult to perform first-principles LDA calculations of the electronic structure at the surfaces of ferromagnets. The difficulties arose from the loss of periodicity at surfaces perpendicular to the film plane. In regularly employed infinite slabs containing a few atomic layers to represent a surface, the lack of periodicity excludes the simple muffin-tin approximation. It is also difficult to exclude charge sloshing between the center and the surface of the film, which appears during iterations. Also, the problem of symmetry appears because the different atomic planes are not equivalent. The spin-dependent contribution to the total energy is approximated by the exchange-correlation potential, which depends only on the majority and minority spin densities. Many pioneering calculations of thin film- and surface magnetic moments were performed by the full-potential linearized augmented plane wave (FLAPW) [11]. Within this method, for thin films calculations, space is separated into muffin-tin spheres around the atoms and vacuum regions on both sides of the film. In each region, all quantities are expanded in basis functions which can be made progressively more complete. The magnetic configuration obtained by local density theory corresponds to the lowest energy state of the system.

From the calculated electronic structure the spin-dependent DOS can be extracted for each atomic layer separately. In particular, one can follow how the band
structure develops close to the surface. A number of theoretical studies on magnetic transition-metal films have predicted the enhancement of their surface magnetic moment with respect to their bulk values. Theoretical calculations are coherent with the simple picture that the properties of the atoms at surfaces are closer to the properties of isolated atoms compared to atoms in the bulk. Consequently, the magnetic moment is predicted to be a monotonic function of the dimensionality. The principles of magnetic hyperfine field ($B_{hf}$) calculation are basically the same, and the same methods can be applied.

7.3
Experiments Probing Magnetic Moment (and Magnetic Hyperfine Field) at Surfaces and in Ultrathin Films

7.3.1
Experimental Methods Probing Magnetization at Surfaces

There are several magnetometric methods applicable in situ under ultrahigh vacuum conditions (such as the torsion oscillation magnetometer (TOM) – or the superconducting quantum interference device (SQUID), which are sensitive enough to detect monolayer signals. Unfortunately, being integral and featuring no spatial resolution, these methods cannot be used for local (i.e., sensitive to the surface magnetization) investigations. An approach to measuring the total magnetic moment and extracting the surface magnetization by changing the film thickness cannot be applied. This would require the assumption that the magnetic properties at the surface/interface and in the film center are unchanged regardless of the film thickness, which cannot be justified. Thus, our knowledge of surface magnetism is based on techniques that are surface sensitive and that measure quantities that are not directly related to the magnetic moment. Thus, it is important to be sure how the signal measured with an occasionally complex method relates to the basic magnetic quantities such as the magnetic moment $m$ (or magnetization $M$), the Curie temperature $T_C$, or the anisotropy constants.

The methods that exhibit surface sensitivity are based on the scattering of electrons, photons, or ions from the magnetized surface. Below we review a few of them, showing basic principles and their particular applicability to the surface magnetism. We point out that the methods reviewed probe the quantities that are related to magnetic moment, but not the magnetic moment directly. In particular, there is no classic magnetometric method that features spatial resolution.

A powerful tool is the magnetization-induced second-harmonic generation (MSHG), which is intrinsically surface sensitive. Since the generation of the optical second harmonic is, for symmetry reasons, forbidden in cubic materials, all signal originates from the surface region (where the bulk translational symmetry is broken). The magnetization dependence of the second harmonic generation can be understood in a similar way as the linear magneto-optical Kerr effect, that is, as a combined effect of spin–orbit coupling and exchange interaction on the
polarization of the reflected light [12]. The electrons move in the current due to the electric field of the incident light (nonlinear contributions to this current causes second harmonic generation). Spin–orbit coupling acts like a magnetic field, and the corresponding “Lorentz force” rotates the direction of the electric field of the reflected second harmonic light. The effect is measured since the electric field rotates in opposite direction when the direction of magnetization is reversed (by an external magnetic field). In a ferromagnet, exchange interaction causes a different abundance of spins-up and spins-down and results in a preferred direction of the Lorentz force. As a consequence, there is no net effect on the polarization of the reflected second harmonic light [13, 14].

Spin-polarized low energy electron diffraction (SP-LEED) was an early method that was used for the investigation of surface magnetization [15]. The surface reflects an electron with a high probability when the electron cannot find an appropriate electronic state, that is, when its energy component perpendicular to the surface meets a gap in the electronic band structure. Experimentally, it is more efficient to use a polarized incident beam and measure intensity asymmetries. The asymmetry in the intensity of reflected electrons is large when the electrons with spin-up (-down) meet the gap, whereas the electrons with spin-down (-up) just find a state of high density (Figure 7.2). The asymmetry of the reflected intensity depends only on the atomic scattering amplitudes and not on the lattice periodicity, that is, intensity and asymmetry are decoupled. Within the kinematic approximation, the exchange asymmetry observed for scattering at a ferromagnetic surface should depend only on the effective magnetic moment per atom averaged over the information depth of the low-energy electrons. As a matter of fact, the spin asymmetry in the diffraction of spin-polarized electrons by solid surfaces is controlled by two effects: (i) spin–orbit coupling due to the coupling of the spin to the orbital momentum of the diffracted electrons and (ii) exchange coupling due to ferromagnetic long-range order and consequent exchange splitting of majority and minority electronic states. A special geometry is used for a separation

\[
A_0 = \frac{A^+ + A^-}{2}
\]

\[
A_{\text{ex}} = \frac{A^+ - A^-}{2}
\]

\[
A = \frac{1}{P_0} \frac{P_i - P_o}{P_i + P_o}
\]

Figure 7.2 Diffraction of spin-polarized low energy electrons (SP-LEED). (a) Schematic description of the experimental phenomenology. (b) Evaluation of the reflected intensities \(I_\sigma\) depending on the direction of spin polarization \(\sigma = +\) or \(-\) and magnetization \(\mu = +\) or \(-\) with respect to the normal of the scattering plane [3].
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of spin–orbit ($A_{so}$) and exchange ($A_{ex}$) effects. A quantitative evaluation of the exchange asymmetry in terms of magnetic moments is difficult and requires a dynamic LEED theory considering multiple scattering events. Nevertheless, some attempts were made to determine magnetic moments at surfaces. In addition, it is shown that $A_{ex}$ dependence on temperature is exactly the same as the temperature dependence of magnetization. This means that the SP-LEED method can be applied, for example, to analyze the critical behavior at the surface (Section 7.5).

SP-LEED is not the only example of probing magnetization by using the electron spin. The same electron spectroscopies that are so powerful for studying surfaces in general (probing the electronic structure as a function of binding energy, wave vector, and film thickness) can be made sensitive to magnetic properties when electron spin polarization is included as a parameter. The amount and origin of the electrons emitted from a surface depends on how electron emission is induced. This can be done by photons or primary electrons, which produce photoelectrons or secondary electrons, respectively [16].

Assuming that no spin flip occurs during emission, the sign and degree of electron polarization allow the relative amount of majority and minority spins in the solid to be determined for specific electron energy. However, the polarization of the emitted electrons ($P$) is not in average the same as the polarization in average of the volume electrons in equilibrium. The reason for this is that the probability of electron emission from the various electron states in the solid depends on the energy and polarization of the photons and also on the angle of incidence. In reality, the constant of proportionality depends on the sampled electron states and on the range of kinetic energies measured [17]. In general, the proportionality constant can be different for two different materials of different spin density distributions over energy. Thus, the polarization of secondary electrons can be taken to be proportional to the magnetization, but a quantitative deduction of the value of, for example, surface magnetic moment in general, is not possible. $P$ and $M$ are proportional when $M$ is small or only small changes of $M$ are considered.

In most cases, $P$ can be directly related to the magnetization $M$ within the surface layers. This is because of a very short escape depth of the electrons. Thus, the question of the existence of enhanced moments and exchange splitting in ultrathin films (rather than at surfaces) can be addressed by spin-polarized photoelectrons or secondary electrons. $P$ obtained in electron beam techniques accounts only for the spin magnetization. The orbital part does not contribute to $P$ because it disappears at the electron emission and beam formation. The most important advantages of the “magnetometry” with spin-polarized electrons are (i) element and electron state specificity, (ii) spatial and time resolution, and (iii) sensitivity to bands splitting in the exchange field. The most serious disadvantage/limitation of these techniques is that the depth from which the electrons emerge cannot be defined with single atomic layer accuracy, and thus the spatial layer-by-layer resolution cannot be obtained. The technique can be applied to probe occupied electronic surface states [18].

In photoemission spectroscopy (PES), electrons are optically excited from a state below $E_F$ to a final state above the vacuum level $E_V$ by absorption of a photon of
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Energy $h\nu$ (Figure 7.3a). The measured energy spectrum of the emitted electrons allows the band structure $E(k)$ to be determined. With additional spin polarization photoemission spectroscopic analysis (SP-PES), the spin character of the bands can also be determined. The PES measurements could be complemented with the analysis of the electron spin polarization regardless of the low efficiency of spin detectors. This is due to the availability of synchrotron radiation of high intensity. Most of the experiments probing surface magnetism were and still are performed by using this method.

Spin-polarized inverse photoelectron spectroscopy (SP-IPES) is shown to be a powerful new technique to study surface and near-surface electronic structure and magnetism. The process, the information obtained, and the apparatus required in a spin-polarized inverse photoemission measurement are compared to the complementary spin-polarized photoemission measurement. In the inverse photoemission, the empty states above $E_F$ are probed by injecting polarized electrons into these states. A beam of electrons is incident on a magnetic surface. After entering the sample, the electrons decay either radiatively or nonradiatively to states of lower energy. Radiative transitions between empty states are detected via the emitted photons (Figure 7.3b). The spectra are detected separately for the majority and minority spins by applying the spin-polarized incident electron beam. Polarization analysis is not needed in this case. The technique can be applied to probe unoccupied electronic surface states [20]. Both SP-PES and SP-IPES methods are suitable for measuring exchange splitting and its dependence on temperature.

The angular distribution of photoelectrons, which is governed by the scattering events of photoemitted electrons at surrounding atoms, is often employed for structural investigations in surface physics (photoelectron diffraction). Furthermore, the change of the spectral intensity distribution of photoelectrons on magnetization reversal yields information about the magnetic properties (magnetic dichroism). The magnetic order at surfaces can be probed with elemental resolution by photoemission dichroism from core levels [21]. Thus, by combining both photoelectron diffraction and magnetic dichroism, which implies recording the angular and spectral distribution of photoelectrons, one can study the structural and magnetic properties of surfaces at the same time. This effect is called magnetic dichroism in angular distribution (MDAD). The magnetic dichroism can be measured by performing photoemission experiments with circularly or linearly polarized soft X-rays of varying energy and collecting the electrons at a well-defined angle from the incoming beam direction (circular or linear magnetic dichroism in angular distribution MCDAD or MLDAD, respectively). The photoelectrons at intermediate kinetic energies (50–150 eV) corresponding to an average scattering length for the photoelectrons of the order of a few angstroms can be measured, thus yielding a high surface sensitivity. The photoemission asymmetry results from the two spectra measured after aligning the surface magnetization along two opposite directions parallel or perpendicular to the scattering plane. In particular, the MLDAD [23, 24, 41] asymmetry provides a probe of the long-range surface magnetic order. Within the atomic model approximation, the energy spread of the MLDAD signal measures the energy splitting of the 3p (or 2p) core hole interacting with the effective spin
Figure 7.3  (a) Phenomenology of (spin-polarized) photoemission (SP-PES). The incident photon with energy $\hbar \omega$ excites an electron from an initial state below the Fermi level $E_F$ to some final state above the vacuum level $E_{\text{vac}}$. The left panel shows the electron originating either from the valence band or the more localized core level. The right panel displays the excited electron energy distribution in the final state. In ferromagnetic systems, because of the spin polarization of the electronic structure, a spin dependence in the response of the system may be anticipated [19]. (b) Phenomenology of (spin-polarized) inverse photoemission spectroscopy (SP-IPES). If the incident electron energy $E$ is swept while holding $\hbar \omega$ constant (isochromat mode) the measured photon counting rate replicates the unoccupied density of states. The incident electrons may be spin polarized [20].
field determined by the spin-polarized valence band at the core hole site. Thus
the MLDAD energy width ($W_{\text{MLDAD}}$) is proportional to the local spin magnetic
moment. The magnetic dichroism has generally two contributions: (i) the atomlike
dichroism, which is constant in the angular dependence and determined mainly by
the magnetic moment of the atom, and (ii) the contribution from diffraction effects,
which causes the magnetic dichroism to vary strongly around each low-index axis
of a film.

From the experimental point of view, an intense source of linearly polarized
synchrotron radiation is required. The main experimental difficulty is to establish a
conversion factor between the core hole splitting energy and the local spin moment.
The only possibility is to calibrate the MLDAD signal by obtaining the experimental
$W_{\text{MLDAD}}$ value for bulk Fe-3p (or 2p), for which the spin magnetic moment is
well known. Then the surface Fe-3p (or 2p) $W_{\text{MLDAD}}$ value can be interpreted
quantitatively as the surface spin magnetic moment $m_{S,\text{surf}}$.

Finally, our review of the methods that can be used to study surface magnetism
(of a clear surface sensitivity) is completed by photon and electron spectroscopies
after scattering of (highly charged) ions from a magnetized surface at grazing
incidence. The technique allows detection of the spin polarization of electrons at
the surface by their capture into excited terms of scattered atoms. The excited
atomic terms decay via the emission of polarized light. Ion interactions with solid
surfaces can be studied by electron capture spectroscopy (ECS) using light emission
and by multiple electron capture spectroscopy (MECS) using electron emission. In
the case of ECS, the spin polarization $P$ of captured electrons can be deduced from
the circular polarization of the fluorescence light. $P$ is related to the magnetization
$M_s$ at the sample surface, although a quantitative description has not yet been
established. If the geometry is correct, slow ions impinging on a solid surface are
sensitive only to the topmost layer, which makes them an ideal tool for analyzing
surface magnetism [22].

All the methods reviewed above are sensitive to surface magnetism; however,
they cannot probe magnetization with a spatial resolution on a monolayer level
and selectively at the varying depth below the surface in any case. The methods
cannot be applied for buried interfaces, that is, after the surface is coated with a
nanometer-thick overlayer.

A more promising quantity to be measured in this aspect seems to be the
magnetic hyperfine field ($B_{\text{hf}}$), which can be probed layer by layer because of the
isotope specificity of the Mössbauer spectroscopy (MS) (at least in the case of Fe
films and surfaces). This is important in view of the expected oscillating character
of $B_{\text{hf}}$ close to the surface and its dependence on temperature, which exactly follows
the temperature dependence of magnetization.

7.3.2
Experimental Methods Probing Magnetic Dichroism in X-ray Absorption

One of the most powerful techniques to study magnetism, and orbital magnetism
in particular, is X-ray magnetic circular dichroism (XMCD) in absorption. It has
several capabilities that are not offered by other conventional magnetic techniques, such as quantitative determination of spin and orbital magnetic moments, element specificity, and submonolayer sensitivity [25, 26]. Magnetic dichroism from core level is produced by a combination of spin-orbit coupling in the core levels and exchange splitting of the valence bands. The absorption of circularly polarized X-rays at elemental absorption edges leads to the excitation of core electrons into the unoccupied valence states just above the Fermi level. The transitions are spin polarized because spin-polarized photons are absorbed. The spin-polarized photoelectrons are excited into an unoccupied valence state and the transition rate depends strongly on the number of available final states (holes) with the spin parallel to the spin of the photoelectrons. Owing to the magnetization of the investigated system, the spin-polarized DOS is different for both polarization states, and therefore the transition probability for spin-up and spin-down electrons is also different. This results in a difference in the absorption of left and right circularly polarized photons.

As previously mentioned, the magnetic properties of the 3d transition metals are determined by their d valence electrons. The properties of 3d electrons are best probed in an X-ray absorption experiment by excitation of 2p core electrons to the unfilled 3d states (Figure 7.4). L-edge X-ray absorption spectra contain contributions from both p to d and p to s transitions, but the p to d channel dominates by a factor of 20. The L-edge position varies strongly with atomic number (thus the incident photon energy can be tuned to the absorption edge of a specific element). The L-edge absorption spectra are characterized by strong and sharp absorption resonances (lines) near the L$_3$ and L$_2$ thresholds. The sum of the intensities of both lines corrected from the transition to continuum is directly proportional to the number of d holes. In order to measure the difference between the number of

Figure 7.4 Electronic transitions in conventional L-edge X-ray absorption. The transitions originate from the spin-orbit split 2p core shell to empty conduction band states above the Fermi level.
d holes with spin up and spin down, the X-ray absorption process needs to be spin dependent. Since spin-up (spin-down) electrons from the p shell can be excited only into spin-up (spin-down) d holes, the difference in the transition intensity between both processes reflects the difference in the number of spin-up and spin-down holes (which is proportional to the spin moment $m_S$). The measurements for two X-ray helicities at the fixed magnetization direction are equivalent to the fixed X-ray helicity and switching the magnetization direction. The spin of the excited electrons is detected by the valence shell, which is spin-split.

The quantitative nature of the XMCD technique is based on sum-rule analysis of measured spectra, which, however, can be applied for limited number of atoms (only those displaying a sufficient separation of the L$_3$ and L$_2$ edges such as Fe, Co, and Ni). The difference in the resonance line intensities recorded with right and left circularly polarized light for the L$_3$ and L$_2$ edge (being of opposite sign reflecting the opposite spin–orbit coupling of the p$_{3/2}$ and p$_{1/2}$ levels) is quantitatively linked (by the sum rule) to the spin moment, $m_S$ (Figure 7.5). Similarly, the orbital moment

![Figure 7.5 X-ray magnetic circular dichroism shown in a one-electron model. By use of circularly polarized X-rays, the spin moment (a) and orbital moment (b) can be determined from the dichroic difference intensities A and B, as explained in the text [26].](image_url)
of the excited electrons is detected by the d valence shell, which possesses also an orbital moment, \( m_l \). By summing over the \( L_3 \) and \( L_2 \) intensities, the spin \( s \) is eliminated and the orbital moment of the valence shell is measured. The existence of the orbital moment can be immediately seen qualitatively since the difference in line intensity detected with right and left circularly polarized light for the \( L_3 \) and \( L_2 \) edge is different.

The most reliable transmission technique is difficult to use because the \( L \) edges for Fe, Co, and Ni are in the soft X-ray range in which the transmission technique is difficult. Moreover, the sample should be in a form of free-standing film thinner than 1000 Å in the case of soft X-rays. Fluorescence yield measurements suggest that the measured values do not quantitatively follow the true absorption dichroic signal. In the case of a third possible technique, electron yield measurements, the switching of the external magnetic fields causes some problems with normalizing the data. Nevertheless, typically the XMCD spectra are recorded at the adsorption edges by measuring the total yield of the photoemitted electrons for parallel or antiparallel alignment of the applied magnetic field with the light helicity. In order to record the projection of magnetization along different crystal orientations, the sample can be rotated about its polar and azimuthal axes with respect to the incident light direction [25, 26].

The method is not suitable to separately probe magnetism at the surface atomic layer because the XMCD signal is averaged over the electron escape depth, which is typically of the order of 10 atomic layers. However, some attempt was made to obtain a depth information from XMCD. The idea is based on the fact that the number of the electrons counted taking the X-ray absorption spectra (in the total yield measurement mode) is proportional to the X-ray absorption intensity. The electron escape depth changes depending on the direction of emitted electrons. Therefore, the probing depth of XMCD signal can be controlled by changing the electron detection angle. A special fitting procedure (taking into account both self-absorption of the incident X-rays and the electron attenuation) is necessary to extract the layer-resolved spectra; nevertheless, to some extent, the method can be applicable for the study of surface magnetism [27].

A method that is inherently spatially resolved (and is thus very suitable for surface and interface magnetism analysis) is X-ray resonant magnetic scattering (XRMS). X-ray scattering from surfaces is a well-established technique for structural studies, which benefits from the intense synchrotron beams. This is extremely important here because the surface charge scattering is, by a few orders of magnitude, less intense than that from the bulk of the material. This is even more critical since the intensity of magnetic scattering from surfaces is about 10 orders of magnitude weaker than the normal bulk Bragg intensities. The reason why this type of experiment became realistic was the discovery of the resonance exchange scattering, which results in a relatively large increase of the magnetic signal when the photon energy is tuned to the absorption edge [28]. Then the scattering amplitude contains, among the others, a complex resonant magnetic term, whose imaginary part is linked to the XMCD. The quantity that can be obtained is linked to the difference in the transition probabilities of transitions (the most intense
effects are related to dipolar transitions) from the core level to the Fermi energy for left and right circular polarization states of incoming X-rays. Its nonzero value results from the spin–orbit splitting of the core level and from the spin splitting of the conduction band caused by the exchange interaction, and can be dealt with as being proportional to the magnetic moment of the resonant atom.

Beyond the resonant surface magnetic X-ray diffraction approach to probe the magnetism at surfaces [29, 30], a technique to examine thin films (overlayers and buried layers) and multilayer systems is conventional X-ray reflectivity. Here, the reflected intensity is measured as a function of the incident angle, which is equal to the exit angle in the specular condition. Combining the magnetic contrast from MCD and conventional specular X-ray reflectivity enables one, in principle, to observe the magnetic depth profile of thin films and multilayer systems. In an angular and energy-dependent reflectivity experiment, the scattered intensity is measured either for two opposite states of an applied magnetic field or for two opposite states of the X-ray polarization at a photon energy close to resonance. If a net ferromagnetic magnetization exists, the two intensities differ, and the difference can be related to a cross term mixing charge and magnetic reflectivity, while the sum represents the charge scattering. If the sensitivity of the topmost atomic plane of the ferromagnet is achieved, the numbers for the surface (or interfaces) values come from the fit of the experimental data.

Summarizing, the X-ray resonant magnetic reflectivity (XRMR) method, which received a lot of attention in the soft X-ray range [31, 32], where lie the relevant absorption edge for 3d metal, is element specific, applicable to interfaces buried underneath several nanometers, and to some extent allows a spatial resolution [33]. The application of the method is not limited to Fe and Fe-based compounds only. Another advantage of the method in comparison to the Mössbauer experiment (see Section 7.3.3) is that no replacement of the film material with a Mössbauer isotope is necessary (and there is no need to control whether a probe/isotope layer is a continuous layer placed at a well-defined position across the magnetic film).

7.3.3 Experimental Methods Probing Magnetic Hyperfine Field at Surfaces

In view of the local (layer-by-layer) probing of magnetic properties, the Mössbauer effect has provided the most efficient contribution to our knowledge on ferromagnetism of thin Fe films and surfaces in particular. The real local character of MS is unique and of great advantage since in a film consisting of only a few atomic layers of $^{56}\text{Fe}$, it is possible to replace exactly one atomic layer by the Mössbauer isotope $^{57}\text{Fe}$ (Figure 7.6). Then the measured spectrum is a strictly local analysis of the hyperfine interaction parameters. One of them, the magnetic hyperfine field, $B_{hf}$, becomes a local probe of magnetic order. The disadvantage of the method is that Mössbauer measurements on metallic ferromagnets are possible only on crystals that contain Mössbauer isotopes and thus are limited mostly to Fe and Fe-based compounds.
A critical problem for the $^{57}$Fe probe layer analysis is the exclusion of $^{57}$Fe–$^{56}$Fe interdiffusion, that is, one has to grow the film at a temperature low enough to ensure that the $^{57}$Fe atoms are placed exactly in the desired atomic layer. In opposite, a high growth temperature is usually required to improve the film quality. MS offers a unique possibility for confirming whether the $^{57}$Fe atoms are placed at the surface of the Fe film by measuring the quadrupole splitting parameter, $\varepsilon$. The quadrupole splitting parameter $\varepsilon$ results from the interaction between the quadrupole moment of the nucleus and the gradient of the electrical field at the nucleus position and is thus a measure of charge distribution. The quadrupole splitting should definitely differ for the first and second monolayers (counting from the surface) because of their different symmetries. The corresponding experiment was performed for a 20 ML thick Fe film grown on W(110) [34]. It was found that $\varepsilon$ disappears already at the second monolayer, indicating the rapid screening of electrical fields in metals. In addition, $\varepsilon$ remains unchanged in the first atomic layer, with an increasing annealing temperature up to $\sim$500 K and then, after further annealing, decreases, approaching zero value (typical for bulk). Thus, it can be concluded that most of the $^{57}$Fe atoms stay at the surface at a temperature below 500 K and start spreading over the film volume only above this temperature.

In the standard MS, absorption of $\gamma$-quanta versus their energy is measured. However, the most effective technique to measure Mössbauer spectra of ultrathin films is to detect conversion electrons emitted as a result of the proceeding excitation by absorption of $\gamma$-quanta (so-called conversion electron Mössbauer spectroscopy – CEMS). In the case of $^{57}$Fe, with a probability of about 90%, the released energy of the de-exciting Mössbauer nuclei is transferred to one of the atomic electrons orbiting around the nucleus. The electron is then ejected from the atom with an energy equal to the excitation energy (14.4 keV in the case of Fe) minus its binding energy (7.1 keV for innermost K-shell), that is, with a kinetic energy of 7.3 keV in the case of Fe (a process called “internal conversion”). Further, handling electrons, such as filtering their energy to improve the signal to noise ratio, is technically straightforward (Figure 7.7a). In order to apply the CEMS
7.3 Experiments Probing Magnetic Moment at Surfaces and in Ultrathin Films

Figure 7.7 (a) The standard method to measure Mössbauer spectrum is to use transmission geometry. The count rate decreases in resonance, because the radiation can be preferentially absorbed. In backscattering geometry one measures either the emitted $\gamma$- or X-ray radiation or the emitted electrons. As this radiation has to leave the sample to reach the detector, only a thin layer at the surface contributes to the backscattered spectrum. (b) Mössbauer spectrum reflects the hyperfine interactions of the sample. Several parameters such as isomer shift, quadrupole splitting, and magnetic hyperfine field can be extracted from the spectrum. These parameters can be used to identify the chemical and magnetic phases present in the sample like a fingerprint.

method to the analysis of surfaces (and thin films), a number of requirements must be met. In particular, the detection limit below a monolayer of Fe needs to be achieved. The detection limit is determined by the relationship between the number of electrons emitted in resonance (conversion and Auger electrons) and by the number of electrons emitted out of resonance (background) [35]. The only method for reducing the background is to eliminate all electrons with energies other than 7.3 keV by applying an electron analyzer as an energy filter.
There is a concept of the depth selectivity by analyzing the energy of the conversion electrons emerging from the surface. The spectra are accumulated separately for the electrons of different energies, assuming that the energy loss of electrons clearly correlates with the depth at which they originate [36].

If there is a magnetic field at the nucleus position, a six-line Mössbauer spectrum (Zeeman sextet) can be measured. The distance between the outer lines of the sextet is proportional to the effective value of the magnetic hyperfine field, \( B_{hf} \) (Figure 7.7b). Both the local structure of \( B_{hf} \) near surfaces (which can be different from that of the magnetic moment, \( m \)) and its temperature dependence (equal to that of \( m \)) can be measured for Fe films. Furthermore, information is obtained about the local magnetic structure and the composition of the solid by means of hyperfine interaction between \(^{57}\)Fe nuclei and electric and magnetic fields produced by their surroundings. The shape of Mössbauer spectra (relative intensities of the lines) depends on the angle between the direction of the magnetization and the incident \( \gamma \)-ray and can thus provide some insight into the magnetic anisotropy.

The knowledge of magnetic properties at interfaces between ferromagnetic films and nonmagnetic coating material is of crucial importance for magnetic thin film and multilayer devices. However, the experimental approach is again difficult because most of the experimental methods apply to clean external surfaces only and they have insufficient sensitivity to probe the single interface atomic layer only. MS is the experimental method that is applicable also to buried interfaces. The application of MS for the experimental analysis of variations in the local atomic structure, the atomic order, and the ground-state magnetic hyperfine field around surface/interface regions (in a monolayer scale) is widely used. The spatial resolution on the monolayer level is based on the unique capabilities of the \(^{57}\)Fe monolayer probe method (direct layer-by-layer analysis described above).

### 7.4

**Magnetic Moments at Surfaces and in Ultrathin Films of Fe**

#### 7.4.1

**Magnetic Moment at Surfaces of Fe**

The calculation method described in Section 7.3.1 can be applied to calculate the magnetic moment at the surface of ferromagnets under the same restriction concerning the modified layer spacing close to the surface. The FLAPW calculations have been performed for fcc and bcc Fe of three principal crystallographic orientations: for bcc; fcc and hcp Co; and for fcc Ni (summarized in Ref. [37]). In particular, the magnetic moment was calculated near the free Fe(001) and Fe(110) surfaces of bcc Fe [38]. The surface layer DOS shows some narrowing of the d-band width and shifts of peak positions (Figure 7.8). \( E_F \) is found to lie in the valley of minority spin bulk DOS, which coincides with the maximum of the corresponding surface DOS. A simple result of this is the enhancement of DOS at \( E_F \) near the surface. The surface layer magnetization for bcc Fe(001) is predicted to be enhanced by
30% in comparison to the film center, that is, up to 2.96 \( \mu_B \). The enhancement is reduced to 19 and 17% only for closer packed surfaces of bcc Fe(110) and Fe(111), respectively. Although the Fe atom at both Fe(001) and Fe(111) surfaces has the same number of nearest neighbors (4), the surface magnetic enhancement for Fe(111) is only half of that for the Fe(001) surface. This indicates that the surface magnetism depends not only on the coordination number but also on details of the atomic arrangement.
The increasing surface magnetization of Fe(110) was experimentally confirmed by SP-LEED [40]. Clean Fe(ll0) surfaces were prepared by epitaxial growth of Fe(110) films on W(110) substrate. Exchange ($A_{ex}$) and spin-orbit ($A_{so}$) scattering asymmetries of spin-polarized low-energy electrons from Fe(110) were measured at room temperature for several beams at constant energies versus the polar angle of incidence (“rocking curves”). Corresponding calculations by means of a relativistic multiple scattering formalism gave results in good agreement with the experimental data. The sensitivity of parts of the calculated curves to changes in the layer magnetization implied an enhancement of the topmost layer magnetization by about 36–40% with respect to the bulk and a possible reduction in the second atomic layer. With regard to the quantitative validity of the results, it should be mentioned, however, that the analysis was based on rocking curves measured at only one particular energy. Moreover, the magnetization model taken for calculations assumes an average magnetic moment at each site, while reality is better described by a fluctuating local moment model (described in Section 7.5.2) [40].

The SP-PES experiments on the Fe(110) surface show a clear spin asymmetry of the excited electrons. This, however, is difficult to be quantified to the value of the magnetic moment. Moreover, the SP-PES method can be applied only to the uncoated surface of ferromagnets. Thus a comparison of the signal from the deeper part of the sample is impossible. Therefore, most of the SP-PES and SP-IPES experiments deal with the question of the temperature dependence of the exchange splitting $\Delta E_{ex}$ and surface magnetization. Nevertheless, the spin polarization of electrons at the Fe(110) surface was also detected. It was found that the circular polarization of light emitted by decaying in the SP-IPES experiment clearly depends on the sample’s direction of magnetization. The electron spin polarization was estimated to be of the order of 15–20% [22]. However, it was difficult to conclude the enhancement of surface magnetization.

In the MLDAD experiment on an Fe(001) surface, Fe-3p photoelectrons having a kinetic energy 50–150 eV were measured. The energy-resolved spectra of the photoelectrons were decomposed into two contributions, being attributed to the surface atoms and to the bulk Fe. The bulk Fe-3p MLDAD signal could be subtracted from all of the as-measured Fe-3p dichroic spectra, and the resulting difference represents the signal originating from the Fe surface. The width of the surface Fe-3p MLDAD signal was found to be 36% larger than that for bulk, which corresponds to a surface-enhanced spin moment of $2.84 \mu_B$ [41]. This value agrees rather well with the value of $2.96 \mu_B$ predicted theoretically for the Fe(001) surface atoms [38].

Both spin and orbital magnetic moments at the surface of Fe are difficult to measure using the XMCD method since the signal is averaged over the top several ML.

A reduction of 25% (i.e., by $\sim 7$ T) of the magnetic hyperfine field $B_{hf}$ was predicted in the surface atomic layer of Fe(001), connected with an enhancement of the same order of magnitude in the second one [42]. According to theoretical analysis, these oscillations come from the polarization of the conduction electrons contributing to $B_{hf}$ and reflecting an oscillation in the conduction electron polarization. As mentioned previously, such an oscillation is attributed to the simultaneous cut-off
of the electron gas in real space at the surface and in $k$-space at the Fermi level. The oscillations are predicted to disappear when the electron gas is restored by a metallic coating of the Fe surface.

The $B_{hf}$ oscillations near the Fe surface were experimentally confirmed by literal monolayer probe Mössbauer analysis near an uncoated Fe(110) surface (Figure 7.9). The values of $B_{hf}$ at room temperature were determined by extrapolation of the slowly drifting fields (due to a residual gas adsorption and relatively long time of the spectra acquisition) to the time immediately after preparation. To compare with band structure calculations, which refer to the ground state, it was necessary to obtain the $B_{hf}$ values at low temperature. Since it is always risky to measure the spectra at low temperature because of the enhanced residual gas adsorption, which influences the value of magnetic hyperfine field, the Mössbauer spectra were measured only at room temperature. All values of the ground-state magnetic hyperfine fields were deduced from extrapolations to 0 K of the results obtained at room temperature. The extrapolation was based on temperature-dependent measurements that were safely done for the Ag-coated surfaces (preventing residual gas adsorption) and fitted by the Bloch formula (Section 7.5.2). The thermally induced size effect measured for the Ag-coated surface is expected to be the same as for the free surface. Using this assumption, it was possible to determine the $B_{hf}(0)$ for the free Fe(110) surface by combining the $B_{hf}$ measured at room temperature for the free Fe surface and $B_{hf}(T)$ determined for the Fe surface coated with Ag. It was found that $B_{hf}(0)$ is reduced in the first monolayer of Fe(110) and enhanced in the second one almost by the same value of approximately 0.75 T [43]. Theoretically, a reduction of 2.6 T was predicted for the same (110) oriented slab. The reduced $B_{hf}$ value in the first monolayer of Fe is not contradictory to the enhanced value of the magnetic moment. This is a result of the atomlike character of $s$ electrons at the surface, which give a positive $B_{hf,ce}$ contribution, reducing the $B_{hf,cp}$, which is enhanced because of the enhanced magnetic moment. Without doubt, the
phenomenon of a spatial oscillation of $B_{hf}$ in the ground state at the Fe(110) surface is confirmed by the $^{57}$Fe probe monolayer Mössbauer experiment [43].

For comparison, the depth profile of $B_{hf}$ near the Fe/Ag interface was first discussed in a pioneering experiment for epitaxial Fe(110) films on Ag(111) [44]. As predicted for metal-covered surfaces, the spatial oscillation has been removed here. Nevertheless, an increase of the ground-state $B_{hf}$ at the interface was found and interpreted in terms of enhancement of the magnetic moment. A much more detailed monolayer resolution CEMS analysis of the Fe/Ag interface in films of well-defined structure was done a few years later [43]. The results of this analysis show that at the Fe/Ag interface (Ag was used as coating), a slightly increased value of $B_{hf}(0)$ (by about 1 T in comparison to the film center) is observed, which decreases monotonically to the bulk value over a few atomic layers (Figure 7.10). The increase in $B_{hf}$ at the surface is consistent with the enhanced magnetic moment. The $s$ electrons do not reduce the value of $B_{hf}$ at the Fe/Ag interface since they are more itinerant-like and thus give a negative contribution to $B_{hf}$ (in comparison to the positive one at the clean Fe surface). Note that at room temperature, $B_{hf}$ at the interface is smaller than that for the bulk because of the magnetization’s temperature dependence, which is at least two times stronger at the interface compared with the film center (Section 7.5.3) [45].

7.4.2 Spin-Polarized Surface Electronic States

The electronic structure is modified close to the metal surface because the surface layer and the inner atomic layers (bulklike) are not equivalent. Electronic surface states can be formed because of the sharp boundary between bulk material and vacuum. The surface states are usually classified into two groups according to the localization of their charge density with respect to the surface atomic layer. The intrinsic surface states are typically centered in the first atomic layer, whereas the
image potential surface states are centered outside the surface. Surface states can also be formed because of defects and adatoms. Historically, there are two types of intrinsic surface states: Shockley [46] and Tamm [47] states. The Shockley states are s- or p-band states placed in the energy gap of the bulk band structure. The Tamm states are those that are split off into a gap from a continuum of d (and f) bulk states in the weaker potential at the surface. The image potential states are generated by a potential well formed by the Coulomb-like attractive image potential and the repulsive bulk band gap. The binding energies $E_n$ of a Rydberg series of normally unoccupied states converging toward the vacuum level $E_{\text{vac}}$ follow the expression

$$E_n = E_{\text{vac}} - \frac{0.85\text{eV}}{(n + a)^2} \quad (7.11)$$

where $n = 1, 2, \ldots$, whereas “$a$” is the “quantum defect,” which takes into account the penetration of the image potential state wave function into the bulk. The $n = 0$ solution is allowed. This solution decays exponentially away from the surface, has no nodes, and can be identified with the conventional Shockley surface state.

The image surface states can be exchange split. The splitting $\Delta E_{\text{ex}}$ is, however, very small in comparison to the exchange splitting of the 3d band (or even the sp bands). For example, for the 3d transition metals and for an image potential state of $n = 1$, the reported values of spin splitting $\Delta E_{\text{ex}}$ are of the order of several tens of meV depending on the material.

Historically, the first experiments on the spin-polarized surface DOS were performed by the measurement of the spin polarization in field emission spectroscopy (SP-FES), at least within the limited energy range accessible to field emission (~0.5 eV below $E_F$). The electrons were extracted from the sample by field emission (based on the idea of the field emission microscope), which probes (in some approximation) the surface DOS directionally weighted perpendicular to the surface at the Fermi energy. In these experiments, the sign of the spin polarization was found to be positive for Fe and negative for Ni, as expected from the spin-polarized DOS at $E_F$. In all cases, the magnitude of the polarization was found to be below 10%, that is, much lower than the expected spin polarization of the 3d levels at $E_F$ [48]. As it was mentioned in Section 7.2, this is because the electrons emitted from the ferromagnetic metal originate from the highly polarized localized d-like states as well as from the low-polarized, delocalized sp-like states. The sp-like states contribute substantially to the emitted electrons despite the fact that their DOS is 1 order of magnitude smaller than that of the 3d-levels. Thus, the low polarization found in the SP-FES experiments is explained by the dominant sp contribution to the emitted electrons. Since the method probes the surface spin-dependent DOS, it was concluded, for example, that it is similar in the bulk and on the surface of Ni [49]. In this way the existence of magnetic “dead layers” (in particular, in the case of the clean surface of Ni) was experimentally excluded for the first time.

The spin distribution of the electrons thermally excited above the Fermi level has nothing to do with the spin distribution of the surface electronic states. An electron, which is thermally excited, undergoes a multitude of excitation events


(by collisions with other electrons, phonons, magnons, etc.), which cause the spin states to be randomized (i.e., the thermoemitted electrons are unpolarized) [50].

The surface electronic states are typically probed with PES and I-PES (photoemission measures occupied states; inverse photoemission, unoccupied states) described in Section 7.3.1, or for more accuracy with two-photon photoemission (2PPE), which is particularly suitable for analyzing the image potential states. In the 2PPE technique, a first laser light pulse (pump) excites an electron from its initial state below the Fermi level $E_F$ into an unoccupied intermediate state (of Shockley or image potential type). A second pulse (probe) lifts the electron to the final state above the vacuum level $E_{vac}$, so it can be detected as a photoelectron. One of the possible data acquisition modes is to record energy-resolved spectra at a particular delay between pump and probe pulses [51].

Consequently, to probe spin-resolved surface states by photoemission (while mainly d electrons are emitted), SP-PES, SP-I-PES, or spin-polarized (SP)-2PPE must be applied. In the case of the (SP)-2PPE method, the spin separation is based on the observed polarization dependence of the 2PPE signal (Figure 7.11). The polarization of the pump pulse can be changed from s to p for a fixed p-polarization of the probe pulse. Then the changes of the p-spectra can be interpreted, for example, as a contribution of two peaks attributed to the emission from the two image potential states with different spin orientations. This is exactly what was measured for the surface of 6 ML of Fe grown on Cu(001) [52]. In this case, the spin effect was observed without spin analysis of the electrons. However, more specific information can be obtained by measuring the spin-resolved spectra [53]. Moreover, the uniform

![Figure 7.11](Image)

**Figure 7.11** Schematic representation of bichromatic SP-2PPE. The electron is excited from the occupied initial state $|i\rangle$ to the intermediate state $|n\rangle$ and the final state $|f\rangle$ by the pump ($3\ h\nu$) and probe ($\hbar\nu$) laser pulses. (i) Electrons are detected as a function of kinetic energy for a fixed delay between pump and probe pulses or (ii) for a fixed kinetic energy as a function of the time delay between pump and probe pulses [51].
magnetization of the sample was not at all necessary. The results showed a very small (~70 meV) spin splitting $\Delta E_{ex}$ of the lowest image potential states.

Another technique that can be applied to probe surface electronic states around the Fermi level is scanning tunneling spectroscopy (STS). STS offers more in comparison to PES and I-PES: within the same experiment both occupied and unoccupied states can be probed. In STS measurements, the tip is scanned over the sample surface and at each scanning position the tip to sample distance is fixed for a short moment while the bias voltage is ramped. This allows one to measure the changes of the tunneling current as a function of the bias voltage at each spatial point. In order to conclude on the electronic structure one has to measure the differential conductivity $dI/dU$, which is directly proportional to the local density of states (LDOS) at the sample surface. $dI/dU$ can be measured by applying a small alternating voltage on top of the ramped bias voltage. By detecting variations of $dI/dU$ (in lock-in technique) versus the bias voltage, the local electronic properties can be observed. Typically, STS probes the LDOS, which contains both surface states and “bulk” states of energies close to $E_F$.

It was shown that the tunneling probability between two ferromagnetic electrodes separated by an insulating medium depends on the relative orientation of the magnetization of both electrodes [54]. In the case of spin-polarized STS (SP-STS), the electrodes are replaced by a nonmagnetic metal tip coated with ferromagnetic (or antiferromagnetic) material and a sample. Changes in the $dI/dU$ spectra with a changing relative orientation between tip and sample magnetization are due to the exchange splitting of the probed electronic states into majority and minority states [55]. It is impossible to measure STS-spectra separately for spin-up and spin-down electrons. Nevertheless, minority and majority states could be distinguished by their opposite reaction to the changing magnetization direction (Figure 7.12). With a 100% spin-polarized tip, one could, in principle, strictly separate majority and minority states. With a real tip, the spin polarization is lower. However, identifying the spin nature is still possible. The only needed information is the spin polarization of the tip (positive or negative). If it is positive, then for parallel orientation the minority LDOS of the sample becomes more intense in the spectrum. If it is negative, it is the minority LDOS of the sample. If two states change in an opposite way, they must be of opposite character. Clearly, the exchange splitting can be measured.

Scattering of surface state electrons from structural defects such as terrace edges and adsorbates results in standing wave patterns showing a lateral periodic modulation of the LDOS. These types of quantum interference phenomena were observed on densely packed noble metal surfaces by STM. Nanometer-scale Co islands on the Cu(111) surface is a particularly interesting system because both Co islands and Cu substrate exhibit their own standing wave pattern, which are expected to be spin polarized in Co but not in Cu. In the case of thin Co nanoislands on Cu(111), two surface-related electronic states were found: a strong localized peak below $E_F$ and a mainly unoccupied dispersive state giving rise to quantum interference patterns. \textit{Ab initio} calculations revealed that the electronic states are spin polarized, originating from d minority (spin-down) and sp majority (spin-up) bands, respectively. The standing waves were found to occur exclusively
Figure 7.12 The principle of SP-STS using a sample with an exchange split surface state and a magnetic tip with a constant spin polarization close to $E_F$. The tunneling current of the spin component parallel to the tip is enhanced at the expense of its spin counterpart. Thus, a reversal in the $dI/dU$ signal is observed upon switching the sample magnetization ([55] and U. Schlickum, PhD Thesis, figure 2.6).

Experimentally this can be probed only by SP-STS. Spin-polarized measurements allowed a separation of spectral contributions arising from different island stacking or from opposite magnetization states, respectively. The Co islands on a Cu(111) surface were identified as having a magnetization pointing out of the surface and being of strong coercivity [57]. Recently, it was evidenced by $ab$ $initio$ calculations that the size of the islands has a pronounced influence on the spatial distribution of the spin polarization of the Co islands. The expected spin polarization of surface state electrons for the islands of triangular shape and varying edge length is shown in Figure 7.13 [58]. The spin polarization corresponds to the structure of LDOS for majority electrons affected by the quantum confinement. This theoretical expectation was confirmed experimentally using SP-STS [59]. It was shown how the standing wave patterns of confined surface state electrons on top of nanometer-scale ferromagnetic Co islands on Cu(111) are affected by the spin character of the responsible state. The contrast inversion was obtained by different bias voltages, which is the result of contributions to the LDOS from states of opposite spin (their
relative weights depend on the applied bias voltage). In particular, it was shown that only delocalized sample majority electrons take part in the detected LDOS oscillations while localized minority d-like electrons do not.

7.4.3 Magnetic Moment in Ultrathin Films of Fe

There are three widely accepted models applied to magnetic systems with interacting atomic moments (Ising, XY and Heisenberg). Coming toward a true monolayer (i.e., the two-dimensional distribution of atoms), it is well known that in two dimensions, in contrast to other two models, the Ising model describes a spin system displaying a true long-range ferromagnetic order at finite temperature. The Hamiltonian in the Ising model is given by

\[ H_1 = - \sum_{<ij>} J S_i^z \cdot S_j^z \]  

(7.12)

where the sum runs only over next nearest neighbors, \( J \) is the exchange constant of the nearest-neighbor interaction, and \( S_i^z \) is the z-component of the spin at site \( i \). The Ising model in two dimensions was solved exactly [60].
In the XY model, the spins can freely rotate in the $xy$-plane. The Hamiltonian is given by

$$H_{XY} = -\sum_{\langle ij \rangle} J \left( S_i^x \cdot S_j^x + S_i^y \cdot S_j^y \right)$$

(7.13)

where $S_i^{x(y)}$ is the $x(y)$ component of the spin in site $i$. The two-dimensional XY-system (of an infinite area) does not show spontaneous magnetization at finite temperatures.

In a two-dimensional Heisenberg ferromagnet, with the Hamiltonian given by

$$H_{HS} = -\sum_{\langle ij \rangle} J \left( S_i \cdot S_j \right)$$

(7.14)

a long-range order cannot exist, except for systems displaying anisotropy. The long-wavelength (low frequency) spin fluctuations excited at any non-zero temperature break up the long-range order (Mermin–Wagner theorem [61]). However, a small external magnetic field can stabilize the magnetic order.

For two-dimensional magnetic systems without a uniaxial anisotropy, the driving force for the magnetic order is still uncertain. Nevertheless, the experiments performed during the past 10–20 years on various ultrathin films provided clear evidence that ferromagnetic order exists even in monolayer-thick films. The long-range ferromagnetic order is now understood to be stabilized by either magnetic uniaxial anisotropy or long-range dipolar interaction. It was also shown theoretically how effectively anisotropy can suppress those large amplitude fluctuations that break up the long-range order in the isotropic Heisenberg model.

In experiment, the lack of ferromagnetism for ultrathin films is often attributed to formation of isolated islands and resulting superparamagnetism. Thermal excitations are then responsible for random magnetization distribution between each island of the film actually possessing long-range ferromagnetic order. This is extremely important for the magnetic storage materials. It is well known that higher bit densities imply smaller clusters that may have larger or smaller magnetic moments and may not sustain order in the absence of an applied field. The “superparamagnetic limit” is then defined as the limit at which the inherent magnetic anisotropy of a small magnetic particle is no longer strong enough, compared to the thermal energies, to yield stable magnetization over the extended times needed in nonvolatile magnetic memory. Although detailed analytical [62] approaches are available to model the magnetization reversal of superparamagnetic particles, experimental verification was impossible because of the lack of adequately sensitive techniques. Only recently did spin-polarized scanning tunneling microscopy (SP-STM) close this gap, as it combines ultrahigh spatial resolution with spin sensitivity down to the atomic scale, allowing the direct imaging of single superparamagnetic particles [63] (a more extended discussion concerning SP-STM is included in Section 7.6).

For monolayers (or ultrathin films) on nonmagnetic substrates, the questions of spontaneous magnetization, exchange interaction, and anisotropy are similar to that of the surface. However, there is another fundamental question concerning
7.4 Magnetic Moments at Surfaces and in Ultrathin Films of Fe

the influence of the substrate’s crystallographic and electronic structure. Here, magnetic properties are a function of both substrate and film materials. For the monolayer, which exhibits a clear ferromagnetic order and is grown on a paramagnetic (or diamagnetic) substrate, two effects have to be considered: (i) reduction of band width due to reduced coordination (as for a free-standing monolayer) and (ii) hybridization with the bands of the substrate (similar to the situation of a nonmagnetic monolayer on a ferromagnetic substrate described in Section 7.4). The reduced coordination number in a monolayer configuration leads to band narrowing, enhanced DOS near the Fermi level, and a resulting enhanced magnetic moment. Hybridization usually causes band expansion, which decreases the DOS at the Fermi level. As a function of the film thickness, the electronic structure develops from the interface dominated to be bulklike.

Hybridization would not affect the electronic structure of a free-standing monolayer. This is a subject of interest from a fundamental magnetism point of view; however, no such structure can be produced experimentally. The magnetic moment of 3.1 $\mu_B$ was calculated for the free-standing monolayer of Fe, which is remarkably enhanced compared to the bulk Fe [64]. The magnetic moment of a monolayer of Fe on MgO was calculated to be 3.07 $\mu_B$, a value that is only slightly smaller than the moment of the free-standing monolayer. The virtual identity of the results of an Fe monolayer on MgO with the free monolayer has been attributed to the lack of electronic interaction with the MgO substrate. However, magnetic monolayers e.g. on Ag and Au behave similarly to isolated monolayers, and their magnetic moments are larger than in monolayers grown on transition-metal surfaces. This is because the hybridization of magnetic monolayers on noble metal substrates is rather weak since the d-band of the noble metals lies several eV below the Fermi level.

The best approach to measure magnetic moment would be to measure it directly with magnetometric methods. Methods in which a direct measurement of the magnetization is made yield the basic quantity of the ferromagnetic system without the difficulties connected to the interpretation of the more indirect methods, such as those based on spin polarization measurements. Standard magnetometric methods such as TOM can be applied in situ to study thickness-dependent quantities even in ultrathin films. However, they can be used only if sufficiently sensitive instrumentation is available. In TOM, the sample is suspended by a very thin torsion wire in a homogeneous external magnetic field $H$. The sample’s period of torsion oscillations around the equilibrium position is measured. The period depends on the torque constant, which is a sum of the mechanical component that is caused by the wire, and of the magnetic component. The components could be separated by a measurement at zero fields. The magnetic component measures the magnetic coupling of the sample to the external field, which is a combined coupling of the magnetization $M$ to the external field $H$ and of $M$ to the sample by the anisotropy energy. A measurement of the magnetic component as a function of $H$ provides both the magnetic moment and the anisotropy field independent from each other [3].
A realistic determination of the magnetic moment by using the standard magnetometric method is problematic for the thinnest films, at least if the magnetic moment is intended to be measured for films consisting of an integer number of completed atomic layers. The biggest limitation is the fact that any correlation between the measured magnetic moment and the actual film structure is seen in the experiment. Strictly speaking, only the mean value of the magnetic moment averaged over the actual film thickness is measured in this case. Therefore, magnetometric measurements (and not only these – this concerns all methods probing the magnetization of ultrathin films) should be combined with an analysis of the film topology done best by STM.

An integral MS can be applied to measure the magnetic hyperfine field in ultrathin films. For such studies, thin films are usually prepared from pure $^{57}$Fe. However, in some cases, the magnetic hyperfine field varies widely from one atomic layer to another, even in a film consisting of only a few atomic layers of $^{57}$Fe. This can be helpful to control the topology of the growing films. In the case of an ideal monolayer, only one component of the Mössbauer spectrum is expected since all atoms are exactly at the same atomic surroundings. The corresponding $B_{hf}$ is a specific property related to the specific substrate being chosen. Any other component detected in the spectrum should be interpreted as a deviation from the two-dimensional atomic arrangement that is expected for the perfect monolayer.

A number of monolayer/substrate combinations were investigated theoretically and experimentally. One of the first representative examples refers to the monolayer of Fe on W(110), which is thermodynamically stable. For this system, a ferromagnetic order in two dimensions was detected for the first time [65]. Before that, the two-dimensional ferromagnetic properties were never clearly related to the well-documented two-dimensional arrangement of atoms. The Fe/W(110) system displays a strong in-plane uniaxial magnetic anisotropy, supposedly triggering the long-range magnetic order. For the theoretical calculations, the system was approximated as a single slab consisting of five layers of W(110) covered with 1 ML of Fe on each side. The interatomic distances for Fe and W as well as the W–W interlayer distance were taken to be those of bulk W. Concerning the W–Fe interlayer spacing, it was found that the total energy went through a minimum at the Fe–W interlayer spacing, corresponding to a 9.5% downward relaxation compared to the average value of the bulk Fe–Fe and and W–W distances. The ground-state values of the magnetic hyperfine field and of the magnetic moment depend to a large extent on the interlayer spacing. The value taken for calculating $B_{hf}$ (or magnetic moment) should correspond to the minimum energy of the system.

The calculated Fermi contact hyperfine field, $B_{hf,c}$, calculated for 1 ML of Fe on W(110) was decomposed into core-$B_{hf,cp}$ and conduction-$B_{hf,ce}$ electron contributions. The core electrons contribute to $B_{hf,cp}$ with a large negative value of $-30.6$ T, which scales exactly with the magnetic moment. The conduction electrons contribute to $B_{hf,ce}$ with a positive value of 15.8 T (because of direct polarization) and greatly reduce the magnitude of the total Fermi contact term.
The contribution from 4s conduction electrons strongly depends on the environment of the Fe atoms. In the case of bulk Fe, the calculations result in a small negative $B_{hf,ce}$ value of $-4.7$ T. As a consequence, the Fermi contact contribution to $B_{hf}$ is more than two times larger for the bulk ($B_{hf,c} = -35.2$ T) than for the relaxed 1 ML of Fe on W(110) ($-14.8$ T). Consequently, the $B_{hf,ce}$ contribution to the monolayer is more atomlike than the one at the surface of a clean Fe(110) surface (4 T) because of the larger Fe–Fe atomic distance (the Fe monolayer is pseudomorphic with the W(110) substrate) [66]. For absolute values, only when the unquenched orbital moment and the dipolar contribution are included does the total hyperfine field value reduce to the one measured experimentally by MS [3]. Considering the various approximations made in the calculations, the agreement was rather good: $B_{hf}(0)$ is equal to 9.3 T compared with the experimental value of 10 T for the uncoated relaxed monolayer.

The value of the magnetic moment calculated for 1 ML of Fe on W(110) equals 2.18 $\mu_B$ and is related to the contribution of the core electrons through the scaling factor of about 14.6 T/$\mu_B$. The calculated value of the magnetic moment for the same thermodynamically stable Fe monolayer on W(110), but covered with Ag, differs only slightly from the one calculated for the uncoated monolayer and equals 2.17 $\mu_B$. In order to experimentally determine the ground-state values of the magnetic moment in the monolayer, magnetometry and Mössbauer analysis were combined (Figure 7.14). By applying CEMS, optimal conditions for monolayer film preparation were established. A single-component Mössbauer spectrum served as proof for the uniform (two-dimensional) character of the local atomic arrangements.

**Figure 7.14** Magnetic hyperfine field ($\circ$) and magnetic moment (+) of a pseudomorphic monolayer of Fe(110) on W(110), coated with Ag. The magnetic moment is extrapolated to $T = 0$ assuming that its temperature dependence is the same as for $B_{hf}$ [35].
over the entire film area. The experimental value of the magnetic moment was found to be $2.51 \mu_B$ after an extrapolation to 0 K [66]. The enhancement of the magnetic moment with respect to the bulk value cannot be reproduced by the FLAPW calculations, which predict a slight reduction.

The most general comment that can be made here is that the measured magnetic moment was increased, whereas the magnetic hyperfine field was one-third of the bulk value. This has to be compared to the theoretical calculation of a free-standing Fe single atomic layer (monolayer), revealing a moment of $3.1 \mu_B$. The difference between the results for the free-standing monolayer and the monolayer supported on W(110) is due to the electronic hybridization in the latter. Since the electronic hybridization between the film and substrate often counteracts with the reduced dimensionality, the best substrate is one the electronic structure of which is clearly separated from that of the film. MgO is a good candidate in this respect. Unfortunately, this result is difficult to confirm experimentally. The reason is that Fe does not grow layer by layer on an MgO substrate and a real monolayer is difficult to obtain.

7.5 Magnetic Excitations

Magnetic excitations can be classified into single- and many-electron excitations. The single-electron excitation is a transition between electronic bands with an opposite spin (spin flip). In strong ferromagnets, that is, those with a filled majority spin band (such as Co and Ni), the single-electron excitation requires a minimum energy $\Delta$, which is called the Stoner gap. At zero momentum transfer, the energy of the single-electron excitation corresponds to the exchange splitting $\Delta E_{\text{ex}}$ (Figure 7.15). The collective many-electron excitations are spin waves (magnons).

7.5.1 Spin Waves – General Description and Experiments

Spin waves in thin films have become a subject of increasing interest since the prediction of their excitation in the short-wavelength region [67, 68]. On the other hand, more studies have focused on the dynamics of the magnetization processes because of their importance in applications, mainly in spintronics. Smaller and faster devices in magnetic recording and storage require more knowledge on the dynamical motion of spins [69, 70]. For magnetization dynamics, the collective magnetic excitations (spin waves) are of major importance.

Thin films posses a spectrum of spin excitations that reflects their dynamic response. These excitations can be represented by quasiparticles that have a magnetic moment, a wave vector, and energy. The last two are linked by a dispersion relation. Depending on the wave vector, different magnetic interactions determine the spin wave energy. For wave vectors above $10^{-3} \text{Å}^{-1}$, the exchange
interaction is the only interaction that determines the spin wave energy. In the exchange dominated regime, two different approaches have been developed: the Heisenberg model, in which localized magnetic moments are assumed, and an itinerant electron model, where the moments are carried by delocalized electrons. In a simple picture, a spin wave can be considered a quantum of spin reversal spread coherently over the entire crystal [71], which can be imagined in a classical Heisenberg picture of localized moments. Each spin is slightly canted out of its equilibrium position and precesses around this position. Neighboring spins have a fixed phase relation in the precession, which is determined by the spin wave’s wave vector. For the physical description of spin waves of high energy and short wavelength, a spin density fluctuation model seems much more appropriate. The model considers local fluctuations of the magnetic moment not only in direction and magnitude but also in space and time. Generally, collective excitations existing in an itinerant electron system are identical to the well-defined spin waves in the localized model within the limit of low energies and small wave vectors.

Spin waves in thin ferromagnetic films can be studied by ferromagnetic resonance (FMR) [72]. In FMR, the sample is placed in a static magnetic field, holding the spins aligned. In addition, an alternating magnetic field in the microwave regime is applied, seeking to disturb them. This could result in a coherent precession of the magnetic moment. This resonant excitation leads to a drop in the reflected (or transmitted) microwave power, which is then measured. In this case, the spin waves are created by the coupling of the magnetic moments to the external field.

In all scattering techniques, regardless of whether photons, neutrons, or electrons are scattered, the same approach is applied for detecting spin waves. It is based on the measurement of the energy (and the wave vector) loss of the particles upon their scattering from magnetic surfaces. Spin waves in ultrathin films can be studied by...
Brillouin light scattering [73–75]. The electrical field of the photons couples to the spin wave via spin–orbit interaction in this case. The possible wave vector transfer parallel to the surface is, however, limited by the wave vector of the incident light, which is of the order of $10^{-3}$ Å$^{-1}$. Thus, in this method, only modes with a very long wavelength compared to the lattice constant are excited.

In general, high wave vector (short-wavelength) spin waves can be investigated by inelastic neutron scattering, which allows the observation of spin waves within the whole Brillouin zone. In this case, the coupling mechanism is the interaction of a neutron’s magnetic moment with a spin wave’s oscillating magnetic field. Neutron scattering, however, is not suitable for surfaces and ultrathin films, since the interaction of the neutrons with the spin waves is weak and the scattering cross section is extremely small. Thus, a large amount of material and sophisticated detectors are needed [76].

Because it is highly surface sensitive, short-wavelength spin waves in ultrathin magnetic films and at surfaces can be probed best by scattering low-energy electrons. For these low-energy electrons (≈10 eV), scattered from ferromagnetic surfaces, the mean free path is limited to a few atomic layers because of a strong interaction with the electrons in the solid. In particular, electron energy loss spectroscopy in its spin-polarized version (spin-polarized electron energy loss spectroscopy, SPEELS) has proved to be a useful method for this purpose. In this technique, the spin-polarized electron beam is scattered from the surface of a magnetic sample. A spin-polarized electron, with a spin antiparallel to the majority spin orientation, may create a magnon by exchanging with another electron in the surface, whose (majority) spin is parallel, and comes out with a somewhat smaller energy. The scattered electrons are analyzed with respect to their energy and the wave vector transfer during the scattering. The difference between the energy of the incoming and the outgoing electron equals the spin wave energy. SPEELS allows probing of those spin waves, the wavelength of which is on the scale of a lattice constant. The spin wave loss feature occurs because of angular momentum conservation [77]. The creation of a spin wave through a beam electron decreases a ferromagnet’s spin angular momentum by $\hbar$. To conserve the angular momentum, the beam electron of minority character is exchanged with an electron of majority character. Spin wave emission is thus forbidden for a spin-up beam electron. Therefore, spin waves are the only excitations in electron scattering that give a 100% spin-polarized loss peak. Consequently, a spin detector is not required for observing the spin wave loss. Only a polarized beam is needed to measure the loss spectrum in the spin wave region for two cases: the beam polarization is first antiparallel and then parallel to the sample magnetization. The difference between the two loss spectra (more precisely, the spin asymmetry $A$) contains the spin wave loss feature. If the spin wave loss is the only feature in this energy range, then the spin asymmetry is 100%. In practice, other losses are also present, reducing the spin asymmetry [77]. The broad loss bands originally observed with this technique are caused by the spin flip scattering off the sample [78] produced by Stoner excitations.
7.5 Magnetic Excitations

Figure 7.16 SPEELS intensity spectra $I^\uparrow (\circ)$ and $I^\downarrow (\bullet)$ for 8 ML thick Co film grown on Cu(001), normalized to the average intensity $(I^\uparrow + I^\downarrow)/2$ at 0 meV energy loss, for $E_0 = 6.7$ eV and $\Delta K = -0.87$ Å$^{-1}$. The dashed line indicates qualitatively the contribution of the Stoner excitations to $I^\downarrow$. The inset described the scattering geometry: $S^\uparrow(\uparrow)$ is the spin polarization of the incident beam, $M$ is the magnetization direction, $k_i, k_f$ are the wave vectors of the incident and scattered electron, $\theta$ is the incident angle, and $\theta_0 = 90^\circ$ is the angle between the monochromator and the detector [79].

The first experimental results for Co ultrathin films grown on Cu(001) were obtained by SPEELS with momentum-resolved scans including and extending out to the boundary of the surface Brillouin zone [79]. The results showed a pronounced spin wave loss feature (Figure 7.16). The obtained dispersion could be fitted using the Heisenberg model assuming nearest-neighbor interactions only. As a result of the fit, the $JS$ value ($J$ denotes the exchange coupling constant and $S$ is the magnitude of the spin per unit cell) of $15 \pm 0.1$ meV for the surface spin wave mode has been obtained, which is surprisingly very close to the bulk fcc Co value of $JS$ found from the neutron experiment. However, in general, the Heisenberg description has to be applied very cautiously because it can be inadequate for other systems (such as Fe thin films) because of their itinerant electron character. The spin wave dispersion curve agreed with the results of the dynamical theory [67, 68].

7.5.2 Thermally Excited Spin Waves at Surfaces

Temperature is a fundamental parameter in magnetism. The long-range magnetic order decreases with an increasing temperature up to a critical value (called Curie temperature in the case of ferromagnets), at which the order breaks down. Two
approaches can be used for explaining the change of magnetization with an increasing temperature. In the Heisenberg model, the magnetization vanishes by first orienting the moments less regularly and then at random in the paramagnetic phase. It is assumed that the magnetic moment on each atom persists unchanged, independent of temperature. In the Stoner model, however, the magnetic moment decreases gradually with increasing temperature and vanishes in the paramagnetic phase. This is because of the exchange splitting $\Delta E_{ex}$, defined as the energy difference between the majority spin bands and the minority spin bands, which decreases with an increasing temperature until the majority and minority spin bands merge at the Curie temperature $T_c$. It is assumed that ferromagnetism disappears by a single-electron spin flip process. However, this costs more energy than necessary for disordering magnetic moments and gives a Curie temperature much higher than the observed values. The Stoner theoretical approach is less suitable for itinerant ferromagnets such as Fe, Co, and Ni because d electrons form narrower bands and cannot be considered as quasi-free electrons. A better description comes from the “local-band theory,” permitting strong correlation effects that keep the local moments constant in value but fluctuating in direction with increasing temperature. Curie temperature, $T_c$, is the temperature at which long-range magnetic order disappears. A short-range spin order may persists (even) above $T_c$.

The model assuming a local (short-range) order in the small “domains,” whose orientations fluctuate with an increasing temperature can be considered as similar/equivalent to the description by spin wave excitations (magnons). In the localized magnetic moment description, the Heisenberg Hamiltonian allows low-energy (i.e., long-wavelength) collective excitations of spins, as described by Bloch in the low temperature limit [80] (the Heisenberg model is valuable due to its simplicity). Thermally induced spin waves of a long wavelength dominate at low temperatures, that is, they are low-energy excitations. Considering these collective excitations, Bloch was able to explain the well-known $T^{3/2}$ law of the variation of magnetization at low temperatures:

$$\frac{M(T)}{M(0)} = 1 - b \cdot T^{3/2}$$

where $b$ is a spin wave constant. Within the spin wave model, the exponent of $T$ depends on the system dimensionality $D$ and equals $D/2$. Thus, for bulk material (with $D = 3$), the magnetization follows a $T^{3/2}$ dependence (Figure 7.17). In two dimensions, that is, for ferromagnetic monolayers ($D = 2$), a linear decrease could be expected [81].

The concept of disordered magnetic moments assumes that atomic moments are basically independent of temperature. Hence the decrease of the net magnetization is a result of the deviation of the atomic moments from the magnetization axis. The average deviation increases with temperature, making the net magnetization smaller. Since the atomic moments remain unchanged, the fundamental intra-atomic spin splitting stays unchanged. This means that in the first approximation the total DOS of the system does not depend on temperature. This also means that since the atomic moments deviate from the axis of global magnetization, the
distribution of the total DOS between the spin-up and spin-down channels changes with temperature. Thus, the temperature dependence of the spin polarization, $P$, at Fermi level (measured, e.g., by SP-PES) can be related to the temperature dependence of the magnetization, $M$.

In low-dimensional systems the situation is different. Qualitatively, the stronger dependence of $M$ on $T$ at the surfaces compared to the respective bulk material can be understood as a result of the reduced coordination of surface spins (the same reduced coordination at the surfaces is responsible for the enhanced $M(0)$ compared to the bulk). A reduced exchange energy per spin lowers the energy of a spin wave, leading to enhanced spin wave excitations, which are equivalent to an increase of the spin wave parameter $b$ (Eq. 7.15). More quantitatively, it is suggested that each frequency component of the fluctuating magnetization arising from thermal spin waves possesses a vanishing normal derivative at the surface, and thus each standing spin wave should have an antinode at the surface. Under this assumption, the fractional deviation of the spontaneous magnetization at temperature $T$ from its value at 0 K was calculated as a function of the distance from the surface [83]. The surface spin deviation was found to be larger than in the bulk by a factor of 2, resulting in the characteristic profile of a local magnetization close to the surface [83]. However, the profile depends on the local value of the exchange constant. The spin wave parameter $b$ at the surface is two times larger than in the bulk, but only if $J$ at the surface ($J_S$) is identical to the bulk exchange constant.

The value of $M_S(T)/M_S(0)$ for the surface layer could be enhanced by a factor of more than 2 if the exchange coupling between the surface layer and the adjacent layers is reduced (surface exchange constants perpendicular to the film plane are
smaller than those in the bulk) [84]. The strengthening of the exchange coupling parallel to the surface can make it even smaller than the thermal decrease of the magnetization in the bulk. As mentioned in Section 7.2, the exchange interaction can be described by the exchange constant \( J \), which is defined by the exchange energy \( J S_i \cdot S_j \) between the magnetic moments of two atoms. The value of \( J \) can be altered at the surface (\( J_\text{S} > J \)), resulting, for example, in an increased Curie temperature of the surface. Dramatic changes of \( J_\text{S}/J \) can be obtained, for example, by depositing a fraction of another metal’s monolayer on the surface.

The Bloch (spin wave) parameter \( b \) in Eq. (7.15) reflects changes in the thermal decrease of \( M \), caused by all possible variations of exchange coupling. In particular, it is intuitively expected that \( b \) is reciprocally proportional to \( J \), that is, any reduction of the exchange coupling at the surface must result in an increase in \( b \). Although the \( T^{3/2} \)-like character of the temperature dependence of the magnetization is retained, the spin wave parameter \( b \) can change drastically. For instance, if \( J_\text{S,perp}/J = 0.1 \) and \( J_\text{S,paral}/J = 1 \), \( M_\text{S} \) decreases by as much as 20% at \( T/T_C = 0.3 \), whereas if \( J_\text{S,perp}/J = 1 \) and \( J_\text{S,paral}/J = 3 \), \( M_\text{S} \) decreases by only 4%, which is actually less than that for the bulk [18]. It is not easy to comment on the strengthening of the exchange at the surface, which is based on the experimentally found relation between \( M_\text{S}(T)/M_\text{S}(0) \) and \( M(T)/M(0) \) for bulk. Nevertheless, one can try to fit the data, with some restrictions concerning the strengthening of \( J_\text{S,paral} \) with respect to \( J_\text{S,perp} \), and thus conclude on the lowest bound of the surface exchange enhancement.

Vice versa, any decrease in \( b \) at the surface by less than 2 with reference to the bulk means that the exchange in the surface is strongly enhanced [85].

The problem is how to measure \( M_\text{S}(T) \) and how to correlate it to the exchange constant \( J_\text{S} \) at the surface (which determines the value of the \( b \) parameter). All experimental techniques described in Section 7.4 can be applied to probe \( M(T) \) at the surfaces (\( M_\text{S}(T) \)). In particular, the spin-polarized analysis of surface-emitted electrons can be applied. Magnetometry based on spin-polarized electrons of low energy offers an average magnetization \( M_\text{S} \) over a probing depth of a few surface layers (for transition metals), regardless of whether the film underneath is magnetic or not. One can determine the temperature dependence of \( M_\text{S} \) at the surface by measuring \( P_\text{S}(T) \) where the changes of \( M \) are small, that is, in the spin wave regime [18]. However, one must remember that for roughly 3 ML of probing depth, with an ideal surface with a bulk exchange at the surface \( J_\text{S}/J = 1 \), the value of \( P_\text{S}(T)/P_\text{S}(0) \) is expected to be enhanced only by a factor of 1.5 in comparison to the \( M(T)/M(0) \) for the bulk (because of the sensitivity not only to the surface layer). Also, the monolayer probe CEMS can be applied. This allows not only reaching the surface sensitivity but also the spatial resolution on the monolayer level. As an example, in Figure 7.18, spin wave parameters \( b_n \) are shown separately for each atomic layer (\( n \)) of a 21 layer thick Fe film on W(110) covered with Ag. The results were obtained from a \(^{57}\text{Fe} \) monolayer probe CEMS analysis. Temperature dependencies of \( B_\text{hf} \) were fitted to the Bloch formula (Eq. (7.15)) and \( b \) parameters were deduced. At both interfaces, \( b_{\text{W/Fe}} \) and \( b_{\text{Fe/Ag}} \) (at the W/Fe and the Fe/Ag interface, respectively) were found to be enhanced, compared to the central value,
by a factor of approximately 2. However, when compared to bulk $b$, the value of $b$ for the surface layers was enhanced by a factor of more than 2. This is most likely due to a reduced perpendicular exchange coupling between the surface layer and the adjacent layers.

### 7.5.3 Thermally Excited Spin Waves in Ultrathin Ferromagnetic Films

Both in theory and experiments, surface magnetism is mostly probed for surfaces of ultrathin ferromagnetic films (not for bulk materials). Therefore, it is not easy to separate surface effects from effects associated with reduced film thickness. Usually, the surface information is extracted from the thickness dependence of the quantity, which is analyzed. The surface anisotropy is a typical example for this approach (Section 7.6.1). Also, calculations are performed for slabs consisting of only a few atomic layers. Thus, it is important to remember that the surface magnetism quantities could be, in general, strongly dependent on the slab thickness.

Many experimental results confirm that the $T^{3/2}$ power law can be fitted to the temperature dependence of magnetization in ultrathin films. An extended application was made, for example, to Fe(110) films on W(110) with a different coverage down to the thermodynamically stable monolayer [86]. For a quantitative discussion of the thermal decrease of $M$, the Bloch law provides a good approximation in a surprisingly wide range of conditions – even down to monolayer, where a theoretical foundation is missing. The advantage of this description is that one single parameter only, given by the Bloch (spin wave) parameter $b$, is needed as a measure of the thermal decrease of $M$.

The above-defined average spin wave parameter $b$ can be used to describe the dependence of the average magnetization on the thickness at finite temperatures well below $T_c$. In a good approximation, $b$ is proportional to the reciprocal of the number of actual atomic layers, $N$. A possible explanation, based on a combined analysis of the average magnetization and its spatial distribution, can thus be proposed: the thermal reduction of the total magnetic moment of the film is independent of $N$. However, this is to be expected only if the spectrum of thermal
excitations is independent of \( N \) (so-called ultrathin film approximation). Within the range of ultrathin films (consisting of a few atomic layers) and at low temperatures, there are thermal excitations of spin waves with \( k_z = 0 \), only as imagined for a real two-dimensional system. The number of magnons, \( n_m \), does not depend on film thickness. The total magnetic moment of the film, \( m \), is then proportional to the film volume, \( V \), which is given as the interlayer spacing, \( A \), multiplied by the number of actual atomic layers, \( N \) [87]:

\[
m(T) = M(0) \cdot V - 2\mu_B \cdot n_m = M(0) \cdot N \cdot A \cdot S - 2\mu_B \cdot n_m
\]  

(7.16)

with \( M_0 \) denoting the magnetization at 0K and \( S \) the area of the film. The change of magnetization at finite temperature is given by

\[
\Delta M = M(0) - M(T) = \frac{m(T)}{V} = \frac{2\mu_B \cdot n_m}{A \cdot S \cdot N}
\]  

(7.17)

and is proportional to the reciprocal of the number of atomic layers, \( N \) (film thickness). If the temperature change of magnetization is parameterized by the spin wave parameter \( b \), an inverse proportionality between this parameter and the number of layers, \( N \), can be expected and was experimentally confirmed for ultrathin Fe films on W(110) (Figure 7.19). Physically this means that with an increase in \( N \), the energy density associated with a given spin wave mode spreads over a large number of spins. Since the energy stored in one mode is fixed, its contribution to the amplitude of thermal fluctuations of a particular spin decreases with an increasing film thickness. For thicker films, the linear \( b \)-average vs. \( 1/N \) dependence is a direct consequence of the decreasing surface/interface contribution to the magnetization with increasing film thickness, if dependence of surface magnetization on film thickness (thick film approximation) is assumed.

The character of the spatial distribution of \( b \) across a film is thickness dependent. As mentioned before, \( b_{\text{surf}}/b_{\text{center}} \) is around 2, assuming the exchange coupling at the surface and in the film center are the same. If the exchange interaction across a very thin film is the same as in the bulk \( (J_S = J) \), the size effect related to decreasing film thickness should override surface effects. This implies that a reduced magnetization \( M(T)/M(0) \) should become homogeneous across the film and the difference between the spin wave parameter \( b \) at the surface and in the film center should vanish. In other words, the ratio of \( b \) at the surface and in the film center should be strongly dependent on the total film thickness and should approach a constant value for each atomic layer with a decreasing total film thickness [88]. This is in agreement with the experimental observation.
showing that the surface enhancement of the thermally induced magnetization deviation vanishes with a decreasing film thickness. Yet simultaneously, a significant reduction in the film’s mean magnetization at a finite temperature can be noticed [86].

As an important consequence of the strong enhancement of the surface exchange, an increased Curie temperature in comparison to that of the bulk may become possible at surfaces. This is attributed to a higher DOS at the Fermi level at the surface. The local magnetization in the surface layer, $M_S$, can differ from the bulk magnetization $M$. As already mentioned above, typically $M_S < M$. However, it may also happen that the exchange in the surface is increased to a critical value, and then $M_S = M$ [18]. If the exchange interaction would further increase, it could be that $M_S > M$. This could mean that $M_S$ still exists at temperatures where $M = 0$. However, such a phenomenon is difficult to be observed experimentally.

The Curie temperature depends in general on the system dimensionality. In particular, the Curie temperature decreases with the thickness, because of a reduced number of neighboring magnetic atoms modifying spin dynamics at finite temperature. This can be qualitatively understood by a reduction in the average coordination number, causing a decrease in the orbital overlap between neighbouring atoms [90] (which is also responsible for the increase in the ground-state magnetic moment discussed earlier in Section 7.4). According to the Ising model $k_B T_c = NJ$, where $N$ is the coordination number and $J$ is the exchange integral. Thus, qualitatively, $T_{c,\text{monolayer}}/T_{c,\text{bulk}} = N_{\text{monolayer}}/N_{\text{bulk}}$, and one can expect $T_{c,\text{monolayer}}$ to be one-third of $T_{c,\text{bulk}}$ for fcc and half of $T_{c,\text{bulk}}$ for bcc metals. Quantitatively, the dependence of the Curie temperature on thickness was found to obey a phenomenological power law ("finite size scaling formula") described by

$$\frac{T_{c,\text{bulk}} - T_c(D)}{T_c(D)} = C_0 \cdot D^{-\lambda}$$

(7.18)

where $T_{c,\text{bulk}}$ characterizes the bulk transition temperature, $C_0$ is a constant, and $\lambda$ is a shift exponent ranging from 1.0 for free surface boundary conditions to 2.0 for periodic boundary conditions (predictions of $\lambda \approx 1.56$ and 1.49 were made from the three-dimensional Ising and XY models, respectively) [89]. To agree with the simple mean-field arguments, $T_c$ should be proportional to the number of nearest neighbors. In the case of an Fe(110) monolayer, the number of nearest neighbors is reduced from $z_1 = 8$ (for bulk Fe) to $z_1 = 4$. In this approximation, a decrease of $T_c$ to a value half of the one for bulk material can be expected. Experimentally, it equals to 280 K, see Figure 7.15.

The Curie temperature of monolayers varies from 0 to around 450 K. Note that only the most perfect monolayers (those exhibiting an ideal two-dimensional atom distribution) should be considered as two-dimensional ferromagnets since strongly increasing values of $T_c$ are reported with a minor increase in thickness in most ferromagnet/substrate combinations. Another factor strongly influencing the value of $T_c$ is film morphology, which is highly dependent on the temperature at which the monolayer was adsorbed at the surface of a nonmagnetic material.
The magnetization curve of a two-dimensional ferromagnet near $T_c$ falls off much more abruptly than the one of a three-dimensional ferromagnet. Considering the critical behavior of $M(T)$, the temperature is usually replaced by the reduced temperature $t = (T - T_c)/T_c$, and the critical exponent $\beta$ of the power law

$$M(T) \sim (-t)^\beta$$

(7.19)

is discussed. It was shown earlier that in a two-dimensional Heisenberg system an additional uniaxial anisotropy stabilizes the magnetic order [91]. The phase transition was expected to be Ising-like, that is, the critical behavior was expected to be the same as that of a two-dimensional Ising model. Experimental investigations of this subject showed that the $\beta$ values found for various systems were close to the exact Ising value of 1/8 for many of the films that have either a perpendicular easy axis or an in-plane easy axis with an in-plane uniaxial anisotropy. As mentioned above, a spontaneous magnetization was found experimentally also in ultrathin films without a uniaxial anisotropy (which is, however, theoretically not yet fully understood). Without a uniaxial anisotropy, the spontaneous magnetization $M$ lies in the film plane. In this case, for example, for an Fe monolayer grown on W(001) surface [92], the critical exponent $\beta$ is close to $\beta = 1/4$, twice as much as the value reported for films with a uniaxial anisotropy.

### 7.6 Magnetic Anisotropy and Magnetization Distribution

One of the most attractive features, both for fundamental physics and potential applications, is the existence of magnetic surface anisotropies induced by symmetry breaking at film surfaces. The importance of magnetic anisotropy for the ferromagnetic order in general can be shown by the fact that magnetic anisotropy decides about the existence or nonexistence of magnetism in two dimensions (i.e., for thin films). The long-range ferromagnetic order cannot exist at a finite temperature in the isotropic Heisenberg system – an additional term, resulting from the anisotropy energy, must be included in the Hamiltonian.

In general, the magnetization direction of ultrathin films (which are the usual objects on which surface magnetism is studied) tends to be parallel to the film plane. A simple explanation is that there are no exposed magnetic free poles in this case except at the very ends of the film, which is equivalent to the magnetostatic energy minimum for the system (if the moments would be aligned along any other direction, the number of magnetic free poles would increase – which corresponds to the increasing magnetostatic energy of the system). However, by varying the individual layer thickness and choice of the appropriate elements, it is possible to manipulate the magnetic anisotropy. A dramatic manifestation of the varying anisotropy is the change of the preferential direction of the magnetization from the commonly observed in-plane orientation to the perpendicular direction. This is due to spin–orbit coupling, which can force the magnetization at surfaces/interfaces to be oriented perpendicular to the film plane.
If more than two atomic layers of magnetic material are deposited as thin film, the layers not forming an interface (to the vacuum and the substrate) show more bulklike properties. Thus, it is common to separate the volumelike contributions to the effective anisotropy constants, \( K_V \), from the surface/interface term \( K_S \). If \( d \) is the thickness of the film, the relation

\[
K_{\text{eff}} = K_V + \frac{2 \cdot K_S}{d}
\]  

(7.20)

is used, assuming that no difference between surface and interface terms is made and they are summed up to \( 2K_S \). While for smaller thicknesses, \( K_S \) can dominate, for thick films \( K_V \) determines the easy axis of magnetization. If these terms have a different sign, a reorientation of the easy axis might occur. When \( K_{\text{eff}} \) is plotted versus \( 1/d \), the volumelike contribution, \( K_V \), given by the intersection with the ordinate, the surfacelike term, \( K_S \), can be deduced from the slope of the curve [93]. If \( K_{\text{eff}} \cdot d \) is plotted, it is just the opposite: \( K_S \) is given by the intersection with the ordinate, whereas \( K_V \) determines the slope of the curve (Figure 7.20). Here it is assumed that the volume term does not depend on thickness. However, this is not necessarily true because crystallographic distortion, strain, and alloying with the substrate may be thickness dependent. In particular, strain is often assumed to vary in proportion to \( d^{-1} \). In addition, the separation of surface and volume contribution can be criticized, taking into account the limit of small film thickness [94]. In particular, a separation of the sample into bulk and two surfaces/interfaces for a film consisting of only two or three atomic layers does not seem appropriate.

Anisotropy is temperature dependent. This is simply because the ferromagnetic order is temperature dependent. This problem is well known in magnetic recording technology. During the past 50 years, the enormous increase in the recording density in hard disk drives has been achieved mainly by decreasing the size of the

![Figure 7.20](image-url)

**Figure 7.20** The product of the effective magnetic anisotropy and the Fe thickness versus the Fe film thickness for Fe films grown on Ag(001) at room temperature and annealed at \( T_A \). The vertical axis intercept equals a sum of the Fe/Ag interface and the surface anisotropy of Fe, whereas the slope gives the volume contribution [95].
magnetic grains that record bits in the storage layer. The bit is recorded by orienting
the magnetization of the grain along a well-defined direction. However, the
recorded data can be erased by thermal fluctuations of the magnetization if the
grain volume is reduced to a point (so-called superparamagnetic limit) where
the magnetic anisotropy energy per grain becomes comparable with the thermal
energy. Therefore, hard disk drives have to be made out of materials with large
uniaxial magnetic anisotropic energy (MAE).

7.6.1
Dipolar/Shape Anisotropy; Magnetocrystalline Anisotropy

To estimate the thickness at which a reorientation of the film magnetization
occurs, shape anisotropy must be taken into account. Owing to the long-range
magnetostatic interaction between magnetic dipoles, the magnetic dipolar inter-
action results in a shape-dependent contribution to magnetic anisotropy, which
generally prefers the magnetization parallel to the surface of a film. In-plane shape
anisotropy arises from the fact that the dipole–dipole interaction (described in
Section 7.2) between the atomic magnetic moments is minimized if the moments
align themselves parallel to the largest spatial extent of the sample, which is in
plane (the energy cost of the stray field is at maximum for the magnetization
perpendicular to the film plane). Shape anisotropy contributes only to $K_V$ and is
usually calculated as

$$E_{dd} = \frac{1}{2} \cdot \mu_0 \cdot M_s^2$$  \hspace{1cm} (7.21)

where $M_s$ is the saturation magnetization, that is, for the continuous magnetization
of the sample, which is, however, only an approximation. It was shown that, in
the case of rough films, a stray field contribution to the magnetic anisotropy
must be considered also for in-plane magnetization [96–98]. As a consequence,
the difference between the stray field energy density for magnetization oriented
perpendicular and parallel to the film plane is reduced. Thus, the out-of-plane
magnetization could be energetically favourable. However, the roughness-induced
dipolar anisotropy is found to be insufficient for inducing a spin reorientation
transition (SRT) from in plane to out of plane for a continuous film.

In magnetic materials, the magnetization prefers to be oriented along a certain
crystallographic direction, the so-called easy axis of magnetization. This is caused
by magnetocrystalline anisotropy. The physical origin of the magnetocrystalline
anisotropy energy is attributed to spin-orbit coupling of electrons, which results
from a relativistic coupling between the spin of a moving electron, and the electric
field created by all nuclei and other electrons present in the system [99]. The spin
momentum $S$ of the electron at the position $r$ is coupled to the lattice via the electric
potential $V$ of the ions:

$$H_{LS} = \sum_i \lambda_i \cdot L_i \cdot S = -\frac{e}{2m^2c^2} \sum_i \left( \frac{1}{r'} \frac{dV(r')}{dr'} \right) L(r - R_i) \cdot S$$ (7.22)
7.6 Magnetic Anisotropy and Magnetization Distribution

where $L$ is the orbital momentum and $V(r') = V(|r - R_i|)$ is assumed to be spherically symmetric around each of the ions located at positions $R_i$. Thus the spin–orbit coupling is large in the neighbourhood of the nuclei so that it can be considered a localized interaction [100]. Assuming that in a solid the electron could be forced by a crystal field to move within a certain crystallographic plane, and had a finite orbital moment, the electron spin would be aligned by the spin–orbit interaction in a direction normal to this plane. However, the symmetry of the crystal potential in bulk solids and thin films quenches the electronic orbital moments, and it is only due to the spin–orbit interaction that finite net orbital moment preserves. The orbital moment induced by spin–orbit coupling is much smaller than the spin moment that constitutes the macroscopic magnetization of a ferromagnetic system. It has been shown that the spin–orbit coupling changes the total energy of a system and leads to its dependence on the direction of magnetization (in the second-order perturbation theory for thin films and in the fourth-order for bulk cubic crystals) [100, 101]. The magnetocrystalline anisotropy energy (MAE) results from the anisotropy of the spin–orbit interaction, that is, it is the difference of the total energies obtained from the Hamiltonian, including the spin–orbit coupling term with the magnetization pointing in two different directions. The spin–orbit interaction induces a small orbital moment, $m_l$, which couples the total magnetic moment to the crystal axes. This results in the dependence of the total energy on the orientation of the magnetization with respect to the crystalline axes reflecting the symmetry of the crystal. MAE is directly related to the anisotropy of $m_l$ [102]. More precisely, the MAE, which is the difference of the energy $\Delta E$ (due to the anisotropy of spin–orbit coupling) for two different magnetization directions, is approximately proportional to the difference in the corresponding orbital moments [100, 102]. Therefore, in transition-metal atoms with a more than half filled d electron shell, the easy axis is the direction where $m_l$ is at maximum. Orbital moments are most efficiently quenched in a bulklike environment, where the coordination is highest and high symmetry additionally reduces the magnetic anisotropy. They are quenched to a lesser extent at surfaces.

Angle-dependent XMCD spectroscopy offers a possibility to determine the anisotropy of the orbital magnetic moment [103]. With this technique, the spectra are measured in an external magnetic field parallel to the X-ray propagation direction at varying angles with respect to the surface normal. The experimental results show that large $m_l$ anisotropy, hence large magnetic anisotropy values, is observed only if $m_l$ itself is large. For those films showing a perpendicular magnetic anisotropy (PMA) at low thickness, it must be concluded that with a decreasing film thickness the orbital moment becomes more and more anisotropic with a larger component perpendicular to the film surface [104].

As shown above, lower dimensionality favors an increase in the spin moment. It also enables the formation of a large orbital moment (which, however, can be quenched by the hybridization with neighboring orbitals of the substrate). Nevertheless, in low dimensions, both spin and orbital moments increase, enhancing the magnetic anisotropy. The influence of the exchange interaction becomes smaller due to the reduced coordination. Finally, opposite to bulk systems in which
the exchange interaction dominates, much of the magnetic behavior in reduced dimensions is controlled by magnetic anisotropy.

The lowered symmetry at the surface modifies strongly – compared to bulk – the magnetocrystalline contribution. The values of surface anisotropy are high (generally, by 1–2 orders of magnitude larger than that of bulk) because of the broken symmetry at the surface and the reduced coordination of the surface atoms. This anisotropy was introduced by Néel and is known as the Néel-type anisotropy. The reduced coordination leads to relaxations and reconstructions of the atomic layers that influence the magnetic anisotropy. Normally, a surface layer relaxes toward the bulk to compensate for the loss of its nearest neighbors (by reducing the distance to its neighbors and thereby increasing the hybridization) and hence counteracts the mechanism leading to an increased orbital moment at the surface. The same applies to the spin moment that is normally larger at surfaces, but is then reduced by relaxation. The magnetocrystalline anisotropy is a quantity that is very sensitive to structural changes. This sensitivity is also reflected in experiments, where different substrate preparation or growth conditions can lead to different structural properties and therefore to seemingly identical thin films with different anisotropies.

The competition between surface magnetocrystalline energy, shape, and other anisotropy energies gives rise to a striking magnetic phenomenon called spin reorientation transition, that is, a $90^\circ$ rotation of the magnetization direction from in plane to perpendicular or vice versa. The SRT can be driven by film thickness, temperature, or chemical composition. With a decreasing sample thickness, the average symmetry of atoms becomes increasingly reduced. Thus, for those thin films where the orbital moment $m_1$ is larger for the magnetization perpendicular to the film surface than for the in-plane orientation, the anisotropy of the orbital moment can become so large that it has a strong preference for a perpendicular orientation. There are two opposing mechanisms influencing the spin moment: the presence of a dipolar field forces the magnetization toward the in-plane orientation, whereas the presence of spin–orbit coupling forces the magnetization to be parallel to the out-of-plane orbital moment. This affects the situation for films of low thickness because here the ratio of the surface atoms to the atoms underneath is large enough. The easy axis of magnetization is determined by the relative strength of these two mechanisms, that is, whether the anisotropy of the spin–orbit energy is smaller or larger than the dipolar energy. In other words, it may be the case that the small orbital moment (induced by the spin-orbit coupling) forces the larger spin moment into a perpendicular alignment [105]. Extensive work on magnetic surfaces, thin films and one-dimensional structures showed that a lowering of the symmetry results in an increase in the orbital magnetic moment $m_1$ if compared to bulk systems, where d-state hybridization and the crystal field effectively quench $m_1$ [106–108].

In most cases, magnetocrystalline volume anisotropy does not play any decisive role in determining whether the easy magnetization direction is in or out of plane in ultrathin films. The direction of magnetization is usually determined by a competition between perpendicular surface and in-plane shape anisotropies. Thus,
SRT typically occurs if the surface anisotropy contribution (forcing out-of-plane magnetization in the case of thinnest films) is overridden by the shape anisotropy, forcing the in-plane magnetization in the case of thicker films.

Nevertheless, the magnetocrystalline volume anisotropy can be positive, that is, enforcing out-of-plane magnetization, due to symmetry breaking by tetragonal distortion. Even then, the negative dipolar term dominates in most cases and the magnetization lies within the film plane. It may happen, however, that the positive volume magnetocrystalline anisotropy is strong enough to dominate over the negative dipolar term. Assuming that for the thinnest films the magnetic anisotropy is determined by a strong negative interface anisotropy (forcing in-plane magnetization), this would result in a so-called reversed SRT, that is, in the transition from in-plane to out-of-plane magnetization when the film thickness increases [109].

Magnetocrystalline anisotropy of thin films can also be affected by so-called quantum well states (QWS). The electrons in such thin films could be confined perpendicular to the films to form QWS. The formation of QWS results in oscillatory physical properties as a function of film thickness such as the oscillation of the interlayer exchange coupling [110], magneto-optic effect [111], and magnetic anisotropy [112, 113]. Since the magnetic anisotropy is caused by the spin–orbit coupling of the electrons, it is affected by an altered electronic band structure. The QWS inside the FM film itself can directly alternate its electronic structure and modulate the magnetic anisotropy strongly. Theory predicts such effect, for example, in Co films on Cu(001) [112, 113].

MAE is – after magnetization – the second fundamental magnetic parameter that is related to the ground-state electronic structure. Magnetocrystalline anisotropy is a property not predicted within the nonrelativistic theory and a relativistic approach must be applied to describe it properly. This is because, in the nonrelativistic theory, the energy of a ferromagnet does not depend on the direction of spin quantization, and thus the easy magnetization axis does not exist. A satisfactory calculation can be performed within a relativistic electron dynamics approach based on the Dirac equation and an approximate treatment of a many-electron system [114]. Alternatively, a semi-relativistic theory, with the spin-orbit coupling interaction added to the non-relativistic Hamiltonian, can be applied [102, 115, 116]. The part of total energy that depends on the magnetization direction is typically approximated by the band energy $E_b$ that is the sum of eigenvalues of occupied one-electron states calculated by integrating the energy density over the $k$-space volume enclosed by the Fermi surface. The evaluation of the MAE is then based on the so-called force theorem [114]. In this case, two subsequent calculations are performed: one with the magnetic field perpendicular to the surface and one with the magnetic field in the film plane. The magnetocrystalline anisotropy is then expressed as the difference between the band energies corresponding to the two orientations, $\Delta E_b = E_b^\parallel - E_b^\perp$. The total MAE is given by the sum of $\Delta E_b$ and the magnetostatic dipole–dipole interaction energy $\Delta E_{dd}$. The anisotropy energy was successfully calculated for many systems, showing a reasonable agreement with the experimental observations [e.g., [117].
Magnetic anisotropy can be determined from magnetization measurements, for example, by TOM, performed along two orthogonal directions of the external magnetic field relative to the sample (e.g., in plane and perpendicular). The MAE is given by the area enclosed by in-plane and perpendicular loops since simple electromagnetic considerations show that the energy necessary to change the sample magnetization in an external field \( H \) by an amount \( \Delta M \) is given by \( \mu_0 \cdot H \cdot \Delta M \). The MAE can be obtained from those fields at which saturation occurs.

An ideal method for studying qualitatively magnetic anisotropy of thin films is provided by the magneto-optical Kerr effect (MOKE) method. This method can be easily applied in situ under ultrahigh vacuum conditions and thus performed on films not covered with any protective layer. The only technical problem that must be solved concerns the external magnetic field that has to be applied. Nevertheless, several ideas such as the movable unipole magnet inside the ultrahigh vacuum chamber (with the coil outside the chamber) or the MOKE chamber placed in between the poles of a classic electromagnet were successfully applied. A disadvantage of the method is that the Kerr effect does not measure the magnetization directly. Thus, to obtain the MAE, a value for the saturation magnetization must be assumed. Also, the MOKE method is not surface sensitive because of the light penetration length, which is of the order of 10–20 nm.

The MOKE occurs when the ferromagnetic behavior is manifested by changes in polarization and/or the intensity of light reflected from the magnetic material. Magneto-optical effects in ferromagnetic materials result from a combination of net spin polarization and spin–orbit coupling [118]. In general, all quantities measured with the Kerr effect are proportional to the magnetization \( M(T) \) and vanish at temperatures above the Curie temperature \( T_c \). Even though the MOKE can probe for the presence or absence of magnetism, it is not well suited for probing enhanced or reduced moments directly (i.e., quantitatively). Moreover, the magneto-optical response is determined not only by the magnetization of ferromagnetic material. It is important to consider which quantity is measured (rotation or ellipticity), what is the photon energy, the incidence angle of the polarized light, and the incidence polarization (s or p).

The MOKE method is frequently used for probing magnetization of thin films. The slope of the thickness-dependent Kerr rotation (which is mostly the measured Kerr angle) shows how important the system composition (the substrate and the magnetic film materials) is for the magneto-optical response. By assuming that the ferromagnetic film is ultrathin (which is usually well satisfied), one can use approximate expressions for the longitudinal MOKE in magnetic films grown on nonferromagnetic substrates (if the incident light is p-polarized in this particular case):

\[
\Theta_k^{[012]} = \Re \left[ \frac{2 \pi \cdot N_0^2 \cdot N_2 \cdot \sin(2\varphi_0) \cdot Q_1 \cdot I_1 \cdot m_1}{\lambda \cdot (N_0 \cdot \cos \varphi_0 + N_2 \cdot \cos \varphi_2)(N_2 \cdot \cos \varphi_0 - N_0 \cdot \cos \varphi_2)} \right] \tag{7.23}
\]
Here, $\Re$ indicates the real part, $N_0$ and $N_2$ are, respectively, refractive indices of the ambient (vacuum) and the substrate, $\phi_0$ is the optical beam’s angle of incidence with a wavelength $\lambda$, and $\phi_2$ is the complex angle of refraction in the substrate [119]. Then, $t_1$ and $Q_1$ are, respectively, the thickness and the Voigt magneto-optical parameter (i.e., a ratio of off-diagonal to diagonal permittivity tensor elements) of the ultrathin magnetic film. Finally, $m_1$ is the relative magnetization of the magnetic film with respect to a complete magnetic saturation in the longitudinal direction. Equation (7.23) shows that the Kerr rotation from the ferromagnetic film should be proportional to the film thickness. Even if we consider possible interface effects (e.g., an electronic hybridization or usually expected alloying), which can add some contribution to the Kerr signal from a certain film thickness at which the interface is already stable, the Kerr signal should be changing linearly with the thickness of the film. For a given magneto-optical geometry (i.e., the angle of incidence and the incident polarization), the difference between the slopes of the Kerr rotation signal measured for the ferromagnetic films grown on two different substrates originates in the optical permittivity of the substrates, that is, from the difference between the values of the refractive index $N_2$. For example, the different slopes of the linear dependence of the Kerr rotation on the Co thickness in the Co/Cu(001) and in the Co/Pd(001) systems have nothing to do with the different magnetization of the Co films and can be well explained by the dependence of the magneto-optical response on the substrate material (because the film material is the same) (Figure 7.21).

MOKE is sensitive to the modified ground and excited states. Thus it is not easy to separate magnetism from optical effects. In particular, the Kerr signal from the film/substrate interface does not necessarily scale with the magnetic moment in the same way as for a several monolayer-thick film. This is because the optical

![Figure 7.21](image-url)

**Figure 7.21** Longitudinal Kerr rotation in saturation versus Co film thickness when grown on Cu(001) and Pd(001) substrates. The ratio between the slopes of linear changes agrees with the value calculated from Eq. 7.23 [120].
permittivity tensors of the film and the film/substrate interface region in general are different. Thus, the extrapolation of the linear variation of the Kerr observables to zero thickness sometimes results in an offset signal that can be positive (i.e., of the same sign as the signal from thicker films) or negative (i.e., of opposite sign with respect to the signal from thicker films) [120, 121]. Positive offset means an additional contribution to the total Kerr signal from the film/substrate interface. Negative offset signal means either a – missing – contribution of magnetically dead interface layers or a negative magneto-optical contribution from the film/substrate interface. The interface effect results in positive or negative offset, depending on the local atomic arrangement and its influence on the local electronic structure [122]. Such interface effects were clearly demonstrated in multilayers with a considerable number of interfaces. A negative interface contribution to Kerr rotation was observed for several systems such as Pd/Co/Pd(111) [123] or Au/Co/Au sandwiches [124], and for Co films on Pd(110) [125].

It is of technological interest to grow films/multilayers that are spontaneously magnetized perpendicularly to the film plane. This could increase the density of data storage, which is important in magnetic recording. Perpendicular magnetization in thin films can be achieved because of a positive (i.e., perpendicular) interface or volume anisotropy.

Perpendicular magnetization was successfully detected for many combinations of ultrathin films grown on nonmagnetic substrates such as noble metals. Mainly surface/interface anisotropy and other processes related to the interface (such as alloying) were found responsible for this effect. An enhanced orbital moment in the interface, indispensably related to the perpendicular anisotropy, was also experimentally confirmed [107]. Perpendicular magnetization can be also achieved in ultrathin films because of volume magnetocrystalline anisotropy. The magnetocrystalline anisotropy can change if the spin–orbit coupling is varied because of a change of the crystal symmetry. In the presence of the electric field of the surrounding atoms the energetically degenerate 3d levels split. The separation energy between orbitals changes with the varying symmetry of the atomic arrangement, which leads to a change of the spin–orbit coupling [126]. The Fermi energy can be adjusted to the orbitals energy by tuning the number of valence electrons per unit cell (e.g., by mixing two elements). This idea can be applied for thin films in order to force their magnetization to be oriented perpendicular to the film plane [127].

7.6.3 Magnetization Distribution, Magnetic Domains, and Domain Walls at Surfaces

The magnetization distribution at the surfaces of thin film or bulk ferromagnets can be of different origin. In the case of thin films, the magnetic anisotropy should be considered first, since it affects the magnetization direction in the initial stages of growth already. The islands, which are always formed before the first atomic layer is completed, follow all magnetization directions that are energetically equivalent. Magnetic anisotropy can change with increasing film thickness. In a transition
thickness range this may result in the presence of perpendicular and in-plane magnetized areas of the sample.

For a noncoupled, structurally homogeneous continuous ferromagnetic film below a certain thickness, the magnetization is usually homogeneous (so-called single-domain approach). In the case of particles, thin films (thick enough), and bulk samples, magnetic domains can be formed. This is because magnetic particles with a net magnetization have magnetic poles producing surface charges. These charges result in a magnetic stray field that is energetically unfavorable. A reduction of the stray field energy is achieved by aligning the magnetic moments parallel to the particle boundary to obtain a magnetically closed flux. As a direct consequence of this, the magnetic order in a ferromagnetic particle may split up into domains. In the case of ultrathin films (the surfaces of which we consequently discuss in this chapter), domain formation depends strongly on the direction of the easy axis of magnetization. If the magnetization lays in plane, the lowest energy state is the one homogeneously magnetized, whereas for out-of-plane magnetization domains could be more favorable. Within the domains, all magnetic moments point in one direction. A continuous transition between adjacent domains is formed by domain walls. In general, two different kinds of domain walls exist: Bloch walls, where the magnetization rotates in the plane of the wall, and Néel walls, where the magnetization rotates perpendicular to the plane of the wall. The width of natural bulk domain walls is determined by the competition between anisotropy and exchange energy. The exchange alone would result in an infinitely wide wall (where the angle between neighboring magnetic moments is infinitely small), whereas the anisotropy would prefer an atomically sharp transition. For bulk crystals or in thick films, typically Bloch walls are formed as these walls are free of magnetic charges. At the surface, Bloch walls produce magnetic charges and thus create a stray field. Néel walls are not charge free in the interior of the wall; however, they produce no charges at the sample surface. Therefore, Néel walls are often energetically more favorable at surfaces and in thin films [128]. To minimize the energy of bulk walls, the rotational direction of the magnetization near the surface can turn from a rotation parallel to the plane of the domain wall to a rotation perpendicular to it (Figure 7.22). In other words, to reduce magnetic charges, a bulk Bloch wall can terminate in a Néel wall at the sample surface [129].

![Figure 7.22](image_url) (a) Bloch and (b) Néel domain walls between two perpendicularly magnetized domains (inside the wall the magnetization has an in-plane component in both cases).
Imaging of Magnetization Distribution and Magnetic Domains at Surfaces

There are several techniques of magnetic imaging that have been developed exploiting different physical effects. Some of these methods map the local magnetic field that emerges from the sample (local magnetic stray field). Others investigate internal properties determined by the local magnetization. In the first group one has to mention magnetic force microscopy [130], which is based on the magnetostatic interaction between a magnetic tip and the stray field of the sample, analyzed with respect to the lateral tip position. The easily achievable high lateral resolution is of the order of 20–100 nm [131]. In the second group there are

- magneto-optical Kerr microscopy (based on the MOKE) – the lateral resolution is limited by the wavelength of light (500–700 nm),
- near field microscopy – the resolution is enhanced to below 200 nm [132, 133],
- various types of electron microscopes that analyze electrons emitted, reflected, or passing through a magnetic sample (the spin reflects the local magnetization of the sample near the surface). A famous example is scanning electron microscopy with polarization analysis (SEMPA), which has been applied by a number of laboratories to image the magnetization distribution in the first few atomic layers at the surface [134, 135]. Here, a highly focused primary electron beam is scanned across the sample surface, producing cascades of low-energy electrons whose spin polarization \( P \) is related to \( M_S \) in the surface area from which the electrons originate. A lateral resolution better than 10 nm was achieved recently [136, 137],
- photoemission electron microscopy (PEEM), based on SP-PES [138] and combined with XMCD (XMCD-PEEM) [139],
- low energy electron microscopy (LEEM) by using spin-polarized electrons – a resolution of 10 nm was achieved [140],
- spin-polarized scanning tunnelling spectroscopy – a typical resolution is below 1 nm.

The most typical example of imaging the magnetization at the surface (more precisely, in the first few atomic layers) was provided by SEMPA. In particular, a magnetization profile across a domain wall at its intersection with a surface has been obtained. It was found that a Bloch wall does not terminate abruptly at the surface to avoid a large magnetostatic energy density. This would be indispensable if the magnetization in the center of the Bloch wall would point perpendicular to the surface. Thus, the magnetization turns and lies in the surface perpendicular to the Bloch wall. The resulting Néel-like wall minimizes the magnetostatic energy.

It is well known that scanning tunneling microscopy (STM) allows to image the topography of a sample surface with atomic resolution [141]. The idea to map magnetic structures on the atomic scale by using the tunneling magnetoresistance effect was first mentioned by D. Pierce [142], and the first pioneering SP-STM experiments were performed in 1990. In this experiment, effects of the spin-dependent tunneling current between a ferromagnetic tip and an antiferromagnetic sample were measured [143], but it was not possible to strictly separate the
topographic and the magnetic information. Recently, two successful experimental approaches were developed, which allow the separation of magnetic and topographic information. The first approach developed to image the magnetic structure of a sample surface is based on spin-polarized scanning tunneling spectroscopy (SP-STS) [144]. The SP-STS measurements result in the imaging of the spin polarization of the sample surface due to the exchange splitting of the electronic states (Section 7.2). Changes in the $dI/dU$ spectra are caused by changes of the relative orientation between tip and sample magnetization. Depending on the magnetic tip coating, magnetic sensitivity can be achieved for the in-plane or perpendicular magnetization component.

The second approach of an SP-STM utilizes changes of the tip magnetization due to the external magnetic field [145]. In SP-STM, the tip magnetization changes with a high frequency due to a small alternating current passing through a coil wound around the tip (Figure 7.23). The average tunneling current (averaged over the opposite alignment of the magnetization directions) is independent of the spin polarization and yields topographic information as if a nonmagnetic tip was used. However, the difference of the two spin-dependent tunneling currents is proportional to the spin polarization. If the magnetization of the tip is switched with a frequency much higher than that of the feedback mechanism (which adjusts vertical position of the tip to keep a constant value of the tunneling current), no changes of distance occur and the changes of the spin-polarized tunneling current are averaged out. Therefore, an average tunneling current (giving topographic information) can be separated from the modulated current $\Delta I$ resulting from the spin-polarized tunneling current, which yields the spin alignment information [146]. The advantage of SP-STM measurements is that changes in the electronic structure can be separated clearly from the magnetic signal, which allows the investigation of alloys and of systems having unknown electronic structures. In the case of SP-STS, only variations of the spin-dependent tunneling current as a function of the bias voltage are detected. This means that a constant spin polarization cannot be detected because it would be compensated by changes of
the tip to the sample distance. With a W-tip coated with an antiferromagnetic material, the magnetic stray field nearly vanishes and SP-STS measurements can be performed under an applied external magnetic field. When using SP-STM, the magnetization of the tip must be switched, thus measurements for high fields are impossible. Both techniques, SP-STS and SP-STM, allow an imaging of magnetic structures with a high lateral resolution of at least 1 nm [147].

For example, it is known that when Fe is grown on W(110) at an elevated temperature, the resulting film consists of alternating monolayer and double-layer

![Figure 7.24](image)

**Figure 7.24** (a) Topography of 1.5 ML of Fe on W(110) and its schematic representation. (b) Tunneling spectra of monolayer and double-layer stripes exhibiting peaks at $U = +0.40$ and $+0.68$ V, respectively. For double-layer stripes, two quantitatively different spectra were measured when the W-tip was coated with Gd. The spin origin of this difference as well as the tip sensitivity to the out-of-plane magnetization are illustrated. (c) A map of the $dI/dU$ signal ($U = +0.68$ V) reveals that the spectra alternate between adjacent Fe double-layer stripes being caused by an antiferromagnetic dipolar coupling [55].
stripes. The double-layer stripes are perpendicularly magnetized. To see the electronic states for the monolayer and double-layer stripes from photoemission two experiments are required: PES to see the occupied majority spin part (spin up) and I-PES to observe the unoccupied minority spin part (spin down). In the case of STS only one experiment is required since STS can measure the LDOS on both sides of the Fermi level (Figure 7.24) [55]. If the W-tip is covered with magnetic Gd, two qualitatively different spectra are measured for the double-layer structures. Since both the majority and minority components of Fe(110) are present in the tunneling spectra (above and below \( E_F \)), the spin of one component is always parallel to the majority spin of the tip while the other one is antiparallel. Consequently, the spin component of the surface state parallel to the majority spin of the tip is enhanced at the expense of the component that is antiparallel.

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